Erasmus+

TL-IRMP

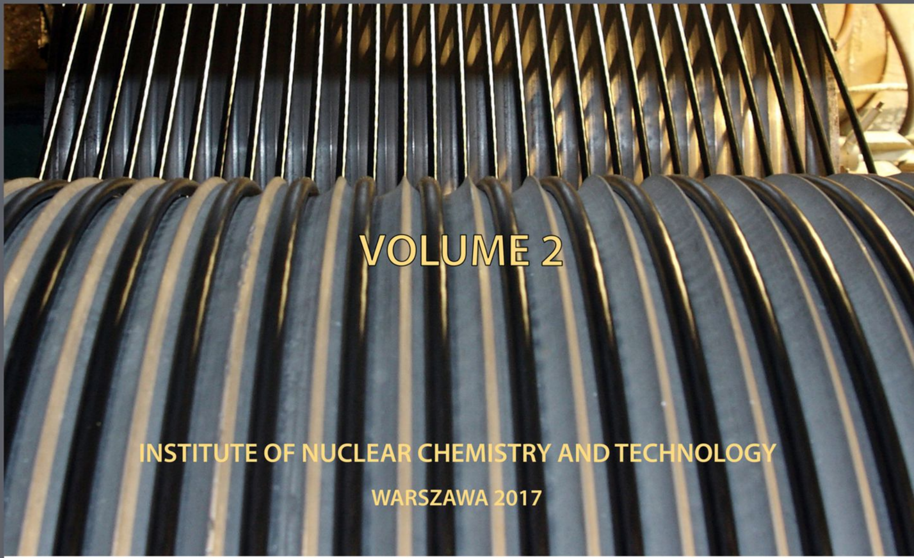
A book “Applications of ionizing radiation in materials processing” has been published within the Erasmus+ program on “Cooperation for innovation and the exchange of good practices – Strategic Partnerships for higher education”. It is a result of the Erasmus project (TL-IRMP) on the “Joint innovative training and teaching/learning program for enhancing the development and transfer of knowledge on the application of ionizing radiation in materials processing”. Seven institutions have participated in this program. This book was reviewed by Anthony Berejka, consultant to the IAEA on the effects of ionizing radiation on materials, reviewer for the US National Academies of its publication “Radiation source use and replacement” and for its operating arm, the National Research Council, of standards laboratories; co-founder and Past-President of the Council on Ionizing Radiation Standards and Measurements and of RadTech International North America, having over 42 years of industrial experience in radiation processing including conducting technology assessments for industrial companies.
This book is co-funded by the Polish Ministry of Science and Higher Education.

ISBN 978-83-933935-8-9
ISBN 978-83-946412-0-7 (Volume 2)

Erasmus+

APPLICATIONS OF IONIZING RADIATION IN MATERIALS PROCESSING

edited by
Yongxia Sun and Andrzej G. Chmielewski



VOLUME 2

INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY
WARSZAWA 2017

APPLICATIONS OF IONIZING RADIATION IN MATERIALS PROCESSING

edited by
Yongxia Sun and Andrzej G. Chmielewski

VOLUME 2

Institute of Nuclear Chemistry and Technology
Warszawa 2017

Editors
Assoc. Prof. Yongxia Sun, Ph.D., D.Sc.
Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.

Reviewer
Mr. Anthony J. Berejka, Owner/President IONICORP+

Technical editor
Ewa Godlewska-Para, M.Sc.

Cover designer
Sylwester Wojtas

“Joint innovative training and teaching/learning program in enhancing development and transfer knowledge of application of ionizing radiation in materials processing” – TL-IRMP (Agreement number 2014-1-PL01-KA203-003611).

Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche
Kaunas University of Technology
Institute of Nuclear Chemistry and Technology
Università degli Studi di Palermo
Hacettepe University
Université de Reims Champagne-Ardenne
“Petru Poni” Institute of Macromolecular Chemistry

ISBN 978-83-933935-8-9
ISBN 978-83-946412-0-7 (Volume 2)

Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warszawa, Poland
phone: +48 22 504 12 05, fax: +48 22 811 15 32
e-mail: sekdyrn@ichtj.waw.pl
www.ichtj.waw.pl

CONTENTS

VOLUME 1

VOLUME 2

Chapter 11

CROSSLINKING OF POLYMERS IN RADIATION PROCESSING

Grażyna Przybytniak
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

The first significant industrial use of radiation processing was implemented in the late 1950s, shortly after the discovery of the crosslinking of olefin polymers using ionizing radiation [1, 2]. The practical applications for radiation processing have since grown. Now this process technology is used to manufacture many articles, *e.g.* heat shrinkable tubing and tapes, encapsulations for industrial products, polyolefin foams, *etc*. [3]. The process is widely used in the wire and cable industry to crosslink the insulation and jacketing, with some formulations able to suppress flame propagation, and, being crosslinked, demonstrating increased abrasion resistance and resistance to fluids. Radiation crosslinking of polymeric pipes for water distribution is another product area. Controlled radiation partial crosslinking of the automobile tire plies enhances the dimensional stability of cord placement and reduces material consumption. In medical device area, radiation processing is used to manufacture hydrogels and to modify ultra-high molecular weight polyethylene (UHMWPE) for implants.

Radiation processing is supported by the continued progress in electron beam (EB) accelerator development [4, 5]. A variety of electron beam parameters, such as energy and power, scan width, *etc*., broadens the range of applications. High power accelerators, up to 700 kW, increase the output rate and make the radiation processing cost-effective and competitive with chemical processing [6, 7]. Additionally, irradiated products require neither extra additives nor thermal treatment. These benefits together with low power demand make radiation process a green technology [8, 9].

The practical aspects of radiation crosslinking demonstrate many product benefits [10-12]. The generation of intermolecular bonds between polymeric chains improves various product features, such as: mechanical properties, resistance to corrosive substances, thermal stability, processability, *etc*. Radiation processing can lead to an improvement in product quality and usefulness.

In the summary the innovative applications and trends in radiation technologies are discussed.

2. RADIATION PROCESSING IN INDUSTRY AND MEDICAL APPLICATIONS

2.1. ELECTRICAL WIRE AND CABLE

In January 1957, Paul Cook founded Raytherm Wire and Cable to take advantage of electron beam induced crosslinking of polyethylene (PE) [13]. Since then, the wire and cable industry has continued to adopt this type of production. The growing demand for crosslinked products stems from their higher quality compared to standard cables and their improved capability to withstand degrading environments [14, 15]. The uses of crosslinked wire and cable are found in various industries, such as: aerospace, automotive, railway, miniaturized electronic equipment and even solar panels.

A key challenge was the development of a non-toxic, low smoke, halogen free insulation and jacketing formulation [16, 17]. Radiation crosslinked wire and cable jacketing is thinner and lighter than competitive materials and, thus, occupies smaller space which is needed in cars, planes and other means of transport. Additionally, the crosslinked, three-dimensional polymer structure does not allow the polymer to melt at elevated temperatures which supports flame propagation resistance.

The composition of wire and cable jacketing varies and uses a wide range of polymers: polyolefins, as polyethylene (PE), blends of PE, ethylene-propylene rubber (EPR) or ethylene-propylene-diene modified elastomers (EPDM), ethylene-vinyl acetate copolymers (EVA), chlorosulfonated polyethylene (CSPE), poly(vinylidene fluoride) (PVDF), and ethylene tetrafluoroethylene (ETFE). The second major component is a flame retardant usually in the form of aluminum hydroxide ($Al(OH)_3$) or magnesium hydroxide ($Mg(OH)_2$). There are also many other additives: antioxidants, plasticizers, lubricants, colorants, stabilizers, inorganic fillers, zinc oxide, *etc*.

During irradiation, the interfacial effects between the conductor made of copper or aluminum and the insulation should be considered since:

- Irradiation is usually accompanied by some low molecular weight gaseous by-products, such as hydrogen in the case of polyethylene. If not diffused through the jacketing, the released molecules could disrupt the adhesion

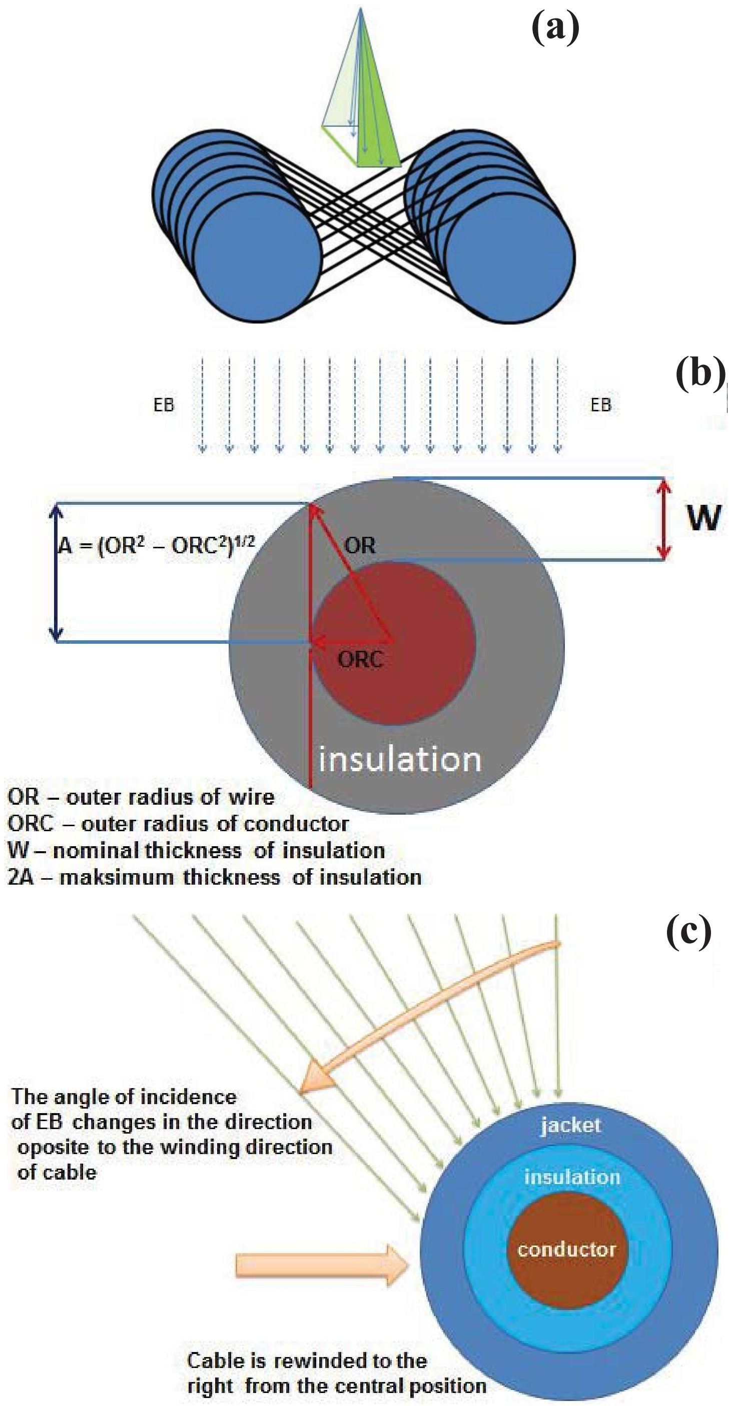


Fig.1. (a) Scheme of figure eight arrangement of under beam facility for radiation processing of cables. (b) Cross-section of wire illustrating penetration of EB by thickness of insulation varying in the range of W-2A. (c) Quasi multi-sided crosslinking during under beam cable transportation.

between the polymer and the conductor, thus impairing the functionality of the wire.

- Since the specific heat of metals is much lower than that of polymers, the heat generated as a result of radiation deposition is transferred from the metal conductor to the polymeric insulation what might undermine the integrity of the insulation.
- Some metals, particularly copper, are very efficient catalysts for redox reactions. In contact with polymeric insulation, such metals can prompt oxidative degradation by stimulating decomposition of peroxide structures and subsequent radical induced processes.

These adverse effects can be eliminated by controlling the parameters of the electron beam and by suitable cable under beam transport systems and, if needed, supplemented with a cooling system.

Important parameters in characterizing the appropriateness of the radiation crosslinking process are the dose and the homogeneity of dose distribution [18, 19]. The circumferential average dose distribution measured by gel fraction for multiple pass irradiation arranged in a figure eight configuration, as shown in Fig.1a, usually provides sufficient dose homogeneity. The uniform dose distribution results from the continuous change in the EB angle of incidence toward the wire or cable. Using an appropriate under beam handling system, as shown in Fig.1a, the wire or cable jacketing is exposed to EB from all sides as the angle of incidence varies continuously from a central to an extreme left/right side (Fig.1c). As shown in Fig.1b, for wire and cable, the electron beam voltage must be chosen such that the beam penetrates though half the cord length (A) of the maximum insulation cord thickness (2A), not just though the thickness of insulation (W). This and the gradual rotation of the wire or cable in an under beam system as shown in Fig.1a will assure uniform dose distribution.

Depending upon the cable thickness and stiffness, and on the EB voltage, under beam facilities can be arranged in one-, two-, or four-sided irradiation configurations [20]. The process technology is tailored to the cable geometry and its flexibility, the absorbed dose and its homogeneity, and electron beam parameters such as voltage.

2.2. SELF-REGULATING HEATERS

Another important application of radiation processing is its use in the manufacture of self-regulating or auto-therming cables which generate heat only if the temperature decreases below a specified level [21]. This is based on the positive temperature coefficient (PTC) of radiation crosslinked polymer compositions. If a semicrystalline polymer, such as polyethylene, is appropriately filled with a conductive carbon black (CB) and radiation crosslinked, it will conduct current and act as a resistor between two parallel conductors. As a resistor, the electrically conductive material will generate heat until it reaches the melt transition of the semicrystalline polymer. At that temperature, the crystalline structure "melts" but the material does not become mobile or fluid since it is crosslinked. However, the electrical connectivity amongst the conductive carbon black particles no longer exists and the softened polymer then becomes an insulator, stopping current flow between the parallel conductors. As the polymer cools, it recrystallizes enabling the conductive carbon particles to reestablish an electrical current flow between the conductors and again acts as a resistive heating element. The temperature at which this happens is controlled by the melt transition of the selected polymer, typically a polyethylene or ethylene copolymer. Because conductive carbon black can influence some mechanical properties of the composition, such as flexibility, it is desireable to minimize its concentration. This specific concentration is the percolation threshold, *i.e.* the minimum content of CB allowing for current flow [22]. Conductive nanoparticles, which can form micro-sized aggregates, could be used as the electrically conductive additive.

Self-regulating cables or pieces are often constructed from two parallel copper conductors covered with a semicrystalline polymer formulated with conductive carbon black at a concentration exceeding the percolation threshold. A rise in temperature above the melt transition (T_m) of the crystalline phase results in an increase in polymer volume due to the conversion of ordered domains into a disordered melted phase. This disrupts conductive pathways, which cause an increase in resistivity of several orders of magnitude, and results in the cessation of current flow and of resistive heating. These changes are then

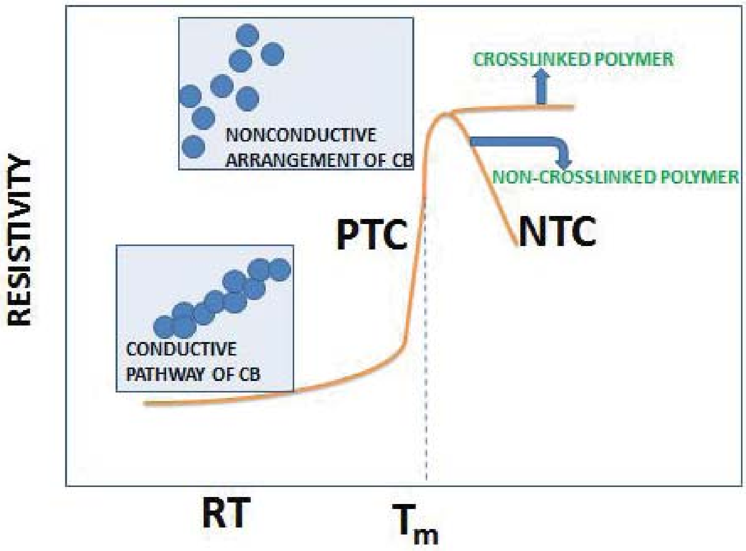


Fig.2. Resistivity as a function of temperature for semicrystalline polymer and CB composite.

followed by a negative temperature coefficient (NTC) when resistivity decreases with temperature increase. Above the polymer's melt transition, there is a CB discontinuity with no current being conducted through the formulated polymer.

The PTC materials require crosslinking. The intermolecular bonding between polymer segments enables the melt-crystallization melt-recrystallization cycles to be repeated. Additionally, the three dimensional polymer network enhances the PTC intensity and reduces the NTC effect, as shown in Fig.2.

PTC devices have to demonstrate the following features:

- Up to a specified temperature, the resistivity ought to be low enough to assure conductivity and consequently resistance heat generation at a desired level.
- High PTC intensity (at least three orders of magnitude) is needed in order to abruptly trigger sufficient resistivity at an elevated temperature (T_m).
- No NTC effect which can disrupt the turning on/off of resistive heating.
- Reproducibility and stability which are supported by radiation crosslinking.
- Low CB content at percolation threshold to assure adequate flexibility.

Under these conditions, at low temperature many conductive pathways correspond to the high power output, whereas at high temperature the termination of heat emission stems from a lack of the conductive pathways.

PTC heating products in the form of tapes or cables were patented from the mid-1970s (*e.g.* [23-25]). Wound around pipes they can be used as heating elements that protect transported fluid from solidification or decrease in viscosity of a fluid at low temperatures. PTC heaters might be also incorporated into shrinkable tapes or tubing (see Section 2.3) in order to induce heat shrinking and/or to activate a hot-melt adhesive [26].

The PTC effect is used in many applications, such as resettable fuses which protect electronic devices against overcurrent flow and overheating in computers, telecommunication equipment, rechargeable batteries, power supplies, *etc*. Other applications involve self-regulating heating cables for maintaining selected temperatures of floor heating systems, for the defrosting water pipes, for the snow clearance of roofs and gutters, for the temperature maintenance of hot water pipes.

Radiation crosslinked PTC cables are now being developed for a wide range of temperatures depending on user demand.

2.3. SHAPE MEMORY PRODUCTS

Heat shrinkable tubing and tapes are sometimes called shape memory products. Upon heating, they recover to an initial dimension. Heat shrinkable tubing protects connections and terminals in electrical systems against harsh environmental conditions. The tight sealing of the tubing around connectors and terminals keeps out humidity and dust. Heat shrinkable tubing is also used in medical devices, such as catheters or cardiovascular stents to reduce their diameter and minimize invasive surgery. Usually tubing contracts in diameter whereas shrinkable tapes contract in their length.

The manufacture of heat shrinkable products relies on the proper selection of raw materials and formulations to attain a desired set of properties. These formulations are then extruded and the extruded product is radiation crosslinked to create a three-dimensional network between macromolecules. The crosslinked, extruded products are then heated to a temperature above polymer melting transition and expanded. Tubing is expanded in diameter and tapes in length. In this form, the products are cooled to ambient temperature in order for the base polymer to recrystallize and to fix the marketed-shape. In such a state, heat will then be needed to decrystallize the polymer and allow elastic forces to shrink the product around an item [27, 28].

When heat shrinkable tubing or tape is used, reheating above the melt transition of the base polymer is needed to initiate shrinkage and recovery, *i.e.* to achieve the dimensions before expanding. The stages of the production processes are illustrated in Fig.3.

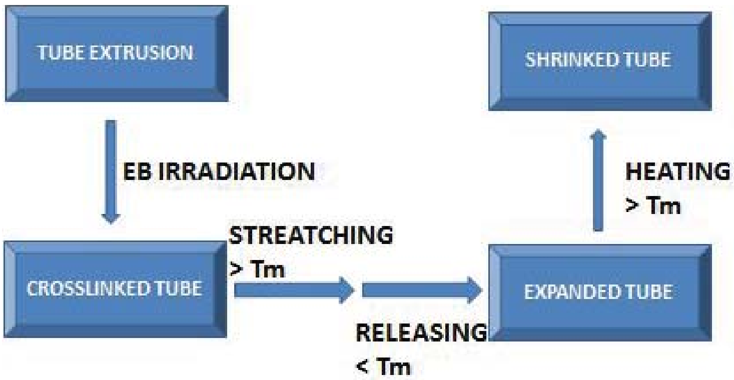


Fig.3. Production of heat shrinkable tubing. T_m – melt transition temperature of polymer.

In the shape memory cycle, shown in Fig.4, there are four distinctive stages [29]:

- heating to a temperature above the base polymer's melt transition,
- expanding or stretching under pressure or force to a shape at which the product will be marketed,
- cooling to room temperature (RT),
- shape recovery after heating above the T_m of the base polymer.

For heat shrinkable products, crosslinking is needed since expansion occurs above the melt transition of a thermoplastic and the product must maintain the stretched form for long period of time at ambient temperature. If polymers did have not intermolecular chemical bonds (crosslinks), they could not be ex-

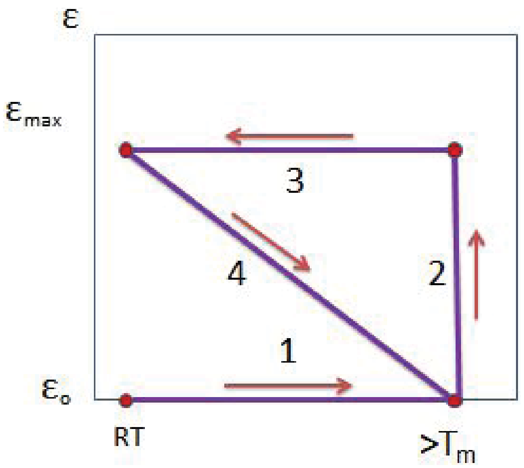


Fig.4. The shape memory cycle presented as a relationship between temperature and strain.

panded above their melt transitions. Shrinking stress increases with increased crosslinked density. The stretch ratio is defined as a ratio between the expanded and initial dimensions. To have maximum shrinkage recovery, the product heating temperature (4. stage in Fig.4) has to be above T_m, otherwise there will be only partially recovered.

Hot-melt adhesive coated heat shrinkable tapes can be applied to pre-insulated pipe systems, which upon heating melts the adhesive and shrinks the tape to form an impervious tight seal.

2.4. RADIATION LONG-CHAIN BRANCHING AND THE CROSSLINKING OF POLYMERIC FILMS

The processability of polymers is determined by their molecular structure. Linear, one-dimensional polymer backbones (Fig.5A) can exhibit poor processability. Highly crosslinked polymers will not melt and they cannot be extruded or molded (Fig.5C). Branched polymers (Fig.5B) and lightly crosslinked ones can be melt processed. When irradiated with small doses (10 kGy or less), the irradiation induces effects in polyolefins which cannot be estimated by gel fraction measurements since the polymer can be dissolved. This kind of modification is sometimes recognized as a long-chain branching (LCB) which can improve rheological properties, particularly melt strength, and the processability of the polymer. It must be then taken into account that upon branching, the melt strength increases and the crystallinity decreases. The side chains are considered as LCB if their chain length exceeds 40 carbon atoms.

The commercial applications of gel-free irradiated polypropylene (PP) was implemented in 1990s and of polyethylenes much earlier [30, 31]. Among

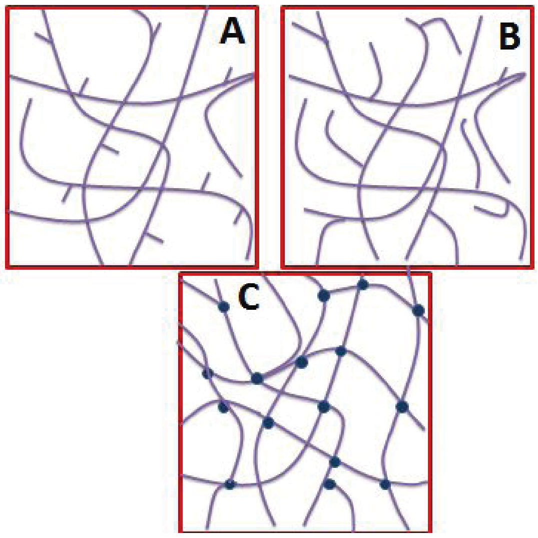


Fig.5. Various structures of polymers: (A) chains with many short branches, (B) long-chain branched polymer, (C) high density crosslinked polymer.

various types of polyethylenes, low density polyethylene (LDPE) itself demonstrates good melt strength resulting from the presence of long side chains. High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) do not have such branching. It was thought that low dose, gel free irradiation would enhance LCB and improve processability. Such low dose irradiation of polyethylenes and of polypropylenes to modify melt toughness has not been sustained in commercial practice.

The manufacture of irradiated blown films is one of the most common irradiation processes in use on a worldwide basis. Such films are manufactured by the extrusion of the molten polymers followed by irradiation and then blowing, cooling and winding of the finished film product [32]. In the first stage, the molten material is extruded by a circular die in the form of tube which is then irradiated. Subsequently the irradiated tube is expanded radially by introducing air to form a bubble up to several times larger in diameter than that of the extrusion die. The crosslinked bubble is also drawn by a pulling in the direction of extrusion. In the final stage of the production line, the stretched, crosslinked film is wound onto a drum. These films are heat recoverable as are tubings and tapes discussed above.

In many cases films are constructed from three to five layers and are produced by coextrusion. If the film layers do not bond together, they would delaminate. To overcome the problem, thin layers of polymers having adhesive properties, known as tie layers, are used in between the functional film layers. Thus, more than 5 layers are then required. Barrier films are produced with blown coextrusion technology where different resins are extruded and brought together through the die. The multi-layer extrudate is then irradiated and blown up into a bubble. When the bubble is cooled sufficiently, it is collapsed between rollers and collected on a roller.

The expanded bubble can be anisotropic and show two distinctly different axes as:

- the machine direction (MD),
- the transverse direction (TD).

Variations in tear resistance can be a consequence of the crystalline lamellar structure formed during film blowing. HDPE films have a row-nucleated fibrillar morphology, very loosely interconnected in the crosswise (TD) direction. In this case, MD tensile is greater than TD tensile, and the tendency to tear is opposite. On the other hand, for LDPE having long-chain branches, the preferential morphology is a lamellar structure interconnected by the separated bounds. This arrangement results in higher tear resistance in MD than in the TD direction. LLDPE tear properties are relatively balanced due to less oriented topology/morphology.

2.5. RADIATION USE IN THE PRODUCTION OF FOAMS

Foam technology has been developing since 1930s when blowing agents were used in the polymer processing. Polymer foams consist of two phases: a polymeric matrix and entrapped, well dispersed cells generated by blowing agents. Foams have several advantages: low density, insulating capability, energy absorption, *etc*. These make foams a desired product in many applications such as packaging, floating materials, paddings, shields for reducing noise, shoes, *etc*. [26]. Foam density varies across a wide range from several kg/m^3 to near thousands kg/m^3. The average size of the micelles determines their number in cm^3 which might reach 10^6 for conventional foams and above 10^9 for microcellular foams.

Various polymers are used in foam technology, among which the most widely used are polyurethanes, polystyrene, poly(vinyl chloride) and polyolefins [33]. The last group of materials, PE and PP, are low-cost polymers of well-balanced properties. When using radiation processing in foam manufacture, the production process consists of (i) compounding the polymer and blowing agent, (ii) extruding the compound into sheets, (iii) radiation crosslinking the sheet, and (iv) foaming the crosslinked sheet with heat provided by moving platens [34].

Foams can be crosslinked or non-crosslinked and can be open or closed cell [35]. In terms of mechanical properties, foams can be classified as hard (made from PP or PE) or soft (made from EVA copolymers). The amount of blowing agent and the crosslinked density determine the final foam structure. The advantage of using radiation processing is that one has a more robust process in that blowing agents will not be activated until after crosslinking which enables control of foam density and micelle size.

The structure of polyolefin foams is determined by the concentration of blowing agent mixed into the polymer. Micelle nucleation is trigged when the blowing agent thermally decomposes to release gases, such as nitrogen or carbon dioxide. Final foam density and morphology depends on the amount of gases released and on the crosslinked density of the polymer. The extrudate viscosity might be reduced since blowing agents can demonstrate a plasticizing effect.

Polymer crosslinked density is a factor influencing the growth of the foam structure by restricting cell coalescence under pressure of the expanded gas. Crosslinking of the polymer decreases the possibilities of cell wall rupture during expansion. The crosslinking density determines the micelle dimensions and controls their growth. During foaming the cell walls get thinner due to continuous stretching. Thus, the strength of crosslinked polymer must be sufficient to maintain bubbles inside the foaming material. It is well known that low and medium crosslinked density preserves some elastic features of polymer, whereas high crosslinked density can make a polymer more rigid.

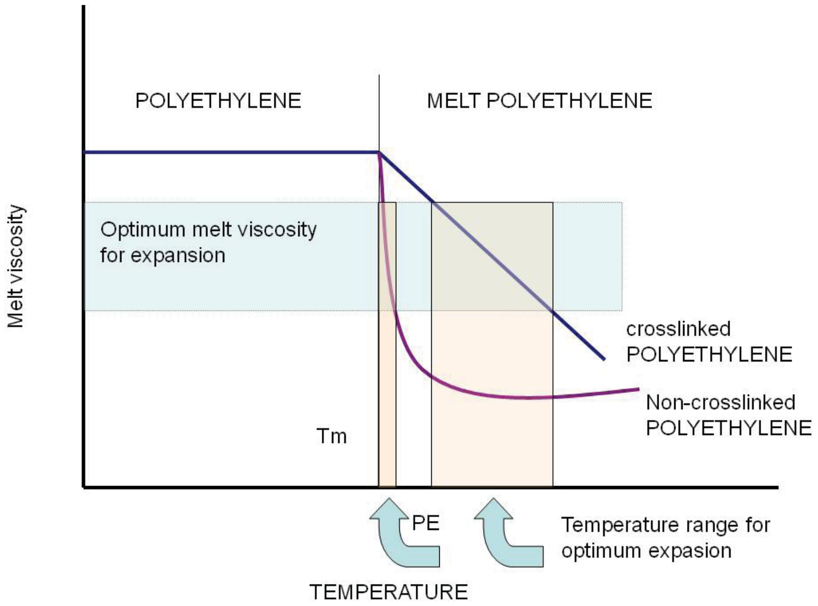


Fig.6. Influence of polyethylene crosslinking on the optimal range of processing temperature during foam production.

The modification of properties due to crosslinking extends the range of temperatures in which a foam might be formed. As seen in Fig.6, for a non--crosslinked polymer, the temperature range for foaming is very limited.

In polyolefin foam production, radiation processing permits a wider temperature range for expansion conditions. This results in the manufacture of low density foam with physical properties suitable for use in medical devices, automotive applications, sporting equipment, *etc*.

2.6. RADIAL TIRES

The manufacturers of radial tires use electron beam processing to partially crosslink plies that will be molded and cured into the final tire [36]. These radiation partially crosslinked rubbers allow tire cords to be positioned and held in place during the final molding process.

Rubber plies used in constructing a tire can deform during assembly if only a conventional vulcanization process is used. This can lead to an uneven distribution of the components and to reinforcing cords being dislocated. In order to avoid such undesired consequences in straight forward thermal curing, the rubber plies or belts are thickened. An alternative is to partially crosslink, usually in the range of 30-50 kGy, the rubber plies. This introduces dimensional stability, improves balance and allows the manufacturer to reduce the amount of material used in the tire (Fig.7). With EB processing, there are fewer defects in the tires and a lower consumption of rubber. Many tire companies, including all Japanese ones, routinely use EB crosslinking of tire plies as a high speed, tightly controlled pre-vulcanization process.

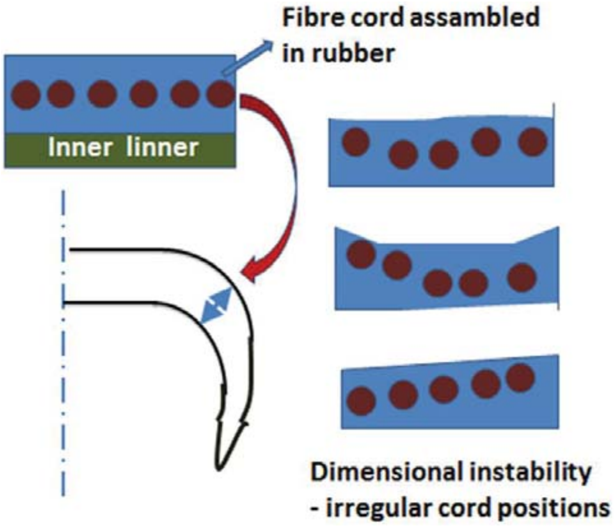


Fig.7. Dimensional instability of non-crosslinked tire plies.

2.7. RADIATION CROSSLINKING OF MEDICAL DEVICES

The acceptance of medical devices is a multistage complex process in which many factors have to be taken into account: clinical issues, structural requirements, material selection, processing aspects, *etc*. Such a strategy is also necessary in the development of implants. The acetabular cup for total hip replacements and the patellar components for total knee replacements are routinely manufactured from ultra-high molecular weight polyethylene (UHMWPE). Every year the forces of 4 to 7 times greater than body weight of patients are transferred millions times to the implant. Clinical experience indicates that in some cases 6 to 8 years after implantation the components fail due to oxidative degradation of polyethylene, facilitated by the surrounding body fluids. With time, small debris of the polymeric material is peeled away what is defined as progressive wearing. This wear process, together with implant fatigue, may cause pain and, ultimately, loosening of the prosthesis.

The wear resistance of UHMWPE might be enhanced by radiation crosslinking [37, 38]. This substantially improves material strength and prolongs implant lifetime. The final effects strongly depend on the initial UHMWPE structure. Alkyl radicals are generated by ionizing radiation in both phases, amorphous and crystalline, of the polymer during irradiation. In the disordered, amorphous domains, due to local conformational movements, the radicals recombine forming a three-dimensional crosslinked network. On the other hand, in the crystalline regions, radical centers are localized creating so-called residual radicals which are a relatively long-lived species. These radicals within the crystalline domains are stable and, in long term, are responsible for the oxidative degradation of the polymer [39, 40]. Several scenarios have been proposed to eliminate this drawback.

Heating UHMWPE at temperatures around its melting point is the most commonly used treatment to decay residual radicals [41, 42]. Thermally stimulated molecular movements promote the termination of radicals, leading to the interruption of chain sustaining radical formation. On the other hand, the thermal treatment decreases mechanical strength since upon cooling the crystalline phase of the crosslinked polymer diminishes.

In order to avoid reduction of crystallinity during post-irradiation heating, another approach has been proposed involving the doping of the radiation treated polyethylene with a biocompatible antioxidant in the form α-tocopherol (vitamin E) [43, 44]. The introduction of the vitamin significantly decreases the population of stable radicals but simultaneously increases the dose required to reach the assumed level of crosslinking.

Radical quenching under high pressure is another treatment that has been considered. At elevated temperature and high pressure, UHMWPE forms hexagonal crystals which have a tendency to form large ordered structures. Overall crystallinity increases presumably improving mechanical strength of the material.

Gradient crosslinking of UHMWPE using irradiation in molten state is a promising option that might overcome the drawbacks related to the residual radical effects. The liners are irradiated at temperatures of about 140°C with electron beam of energy below 2 MeV. The limited penetration of the accelerated electrons results in a considerable and gradual decrease in crosslinked density with the depth. Under such conditions, the implant interior remains unchanged, whereas the surface, which ought to withstand heavy tribological load, is protected by crosslinking.

Experimental results have shown inhomogeneous post-irradiation oxidation with severe subsurface embrittlement and cracking. The distribution of oxidation products is estimated by infrared determination of the oxidation index. This parameter is usually calculated as a ratio between the peak area of the carbonyl group (C=O) absorption band at 1717 cm^{-1} and the area of the methylene group reference band at 1370 cm^{-1}.

Generally, radiation crosslinking of the amorphous phase increases wear resistance of the implant. On the other hand, the enhanced interior crystallinity restrains the fatigue of the material [45]. Thus, a properly optimized microstructure is the key for providing UHMWPE materials with resistance to both wear and fatigue [46].

Recently, the following procedure has been proposed for manufacture UHMWPE implants: UHMWPE is blended with 0.1% α-tocopherol powder and then compression molded in the form of bars. The bars are radiation crosslinked with an elevated dose to overcome the scavenging ability of the vitamin. The irradiated polymer is then heated and compressed to promote free radical decay. The final implant product is machined from these irradiated bars, packed and sterilized with ethylene oxide.

3. EMERGING APPLICATIONS OF RADIATION PROCESSING

The development of cost-effective and diverse accelerators provides electron beams of various energies and powers, and stimulates progress in radiation processing that may offer a new generation of products with enhanced quality [47]. Radiation processing is of growing importance in medical devices, in aerospace applications, in the polymer industry and in agriculture. New trends for electron beam applications appear since EB processing substantially enhances the commercial value products.

There are many new areas that can in the near future generate a growing demand for electron accelerators.

Innovative high-performance carbon fiber composites

The manufacture of the carbon fiber reinforced polymer composites with exceptional resistance to harsh or aggressive environments might be performed through the use of ionizing radiation. Specifically oriented reinforcements in a form of carbon fiber layers allow for the production of materials with anisotropic features. Such carbon fiber composites can be made using radiation processing. These types of high-performance materials are recommended for use in space applications, communications or transportation areas.

Self-healing polymer composites

High energy electron beams may prove to be a convenient way to manufacture lightweight fiber reinforced composites which have high resistance to degrading factors and yet self-healing capacities. The EB technique might contribute to the construction of smart materials capable repairing damages caused by various stresses (elevated temperature, pressure, radiation, mechanical stress) over long periods of time.

A reversible correction of a composite might be performed if it includes a predetermined microencapsulated healing agent that would dispense upon damage (microcracks). Ionizing radiation is an appropriate source of energy both for synthesis of repair formulas and for their introduction into the polymeric matrix. The development of such work is targeted towards the automotive and aerospace industries.

Conducting nano- and microcomposites as sensors

Strain sensors using conductive polymer nanocomposites have recently been developed. These are promising materials for the construction of electromechanical sensors only if the conducting filler in a polymeric matrix reaches a percolation threshold. An innovative approach is needed to develop a reversible sensor using crosslinked flexible polymers of low hysteresis.

Strain sensing devices are being explored using EB crosslinking of conducting nanocomposites to improve their operation and durability. Radiation processing is also considered important for the production of current protection devices, shielding systems, sensors for security systems, *etc*.

Top-down and bottom-up synthesis of nanomaterials

EB processed nanotechnology opens up new possibilities for the fabrication of nanostructured materials. Ionizing irradiation permits the building of nano-sized structures with strictly defined and uniform geometry from the molecular level up or by a top-down approach when the material is ground or decomposed to the nano-scale.

This technique can be used for the formation of track nanoporous membranes (used also as a template for synthesis of inorganic nanoparticles) and for the generation of metal clusters in zeolites and solutions. Such nanoparticles with a desired functionality can find applications as biosensors or catalysts. Depending on chemical structure, these materials could be able to react or to change their size depending on external stimuli, such as ionic strength, heating, pH, light emission, reactant concentration.

Radiation technology in medically oriented applications

Nanogels are used in biomedical applications as drug delivery systems, as cell markers, as replacements for biopolymers, as structures for the immobilization of biologically active molecules, *etc*. An uncomplicated radiation process can initiate the synthesis and crosslinking of high-purity micro- or nanospheres.

The important advantage of this technique is that the resulting products can play a role as carriers for drugs, antibodies, enzymes, *etc*. In future the technology might be adapted for manufacturing biomedical microdevices, vectors for genes or other biologically active substances and their controlled release. The other attractive potential application involves scaffolds for tissue engineering, cartilages, artificial blood vessels, *etc*., or structures constructed from ligand binding nanoparticle as target receptors, which properties might be tailored by ionizing radiation treatment.

New crosslinkable polymers

The increase in heat resistance results in greater value added polymers. Thus, crosslinking in many cases expands the profit margins and the use of polymers. New substances might be developed which under selected conditions might be responsive to ionizing radiation and form intermolecular bonds or crosslinks. Radiation crosslinking of engineering polymers is difficult due to the presence of aromatic rings that disperse deposited energy. On the other hand, some polymers might be crosslinked only under specific conditions, *e.g.* poly(tetrafluoroethylene) (PTFE) is crosslinkable in near its melt transition. It has been found recently that radiation degraded polymers in paste-like form might be susceptible to radiation crosslinking.

REFERENCES

[1]. Machi, S. (2004). Role of radiation processing for sustainable development. In *Emerging applications of radiation processing* (pp. 5-13). Vienna: IAEA. (IAEA-TECDOC-1386).

[2]. Zimek, Z. (2004). Accelerator technology for radiation processing: Recent development. In *Emerging applications of radiation processing* (pp. 55-64). Vienna: IAEA. (IAEA-TECDOC-1386).

[3]. Cleland, M.R., Parks, L.A., & Cheng, S. (2003). Applications for radiation processing of materials. *Nucl. Instrum. Meth. Phys. Res. B*, *208*, 66-73. DOI: 10.1016/S0168-583X(03)00655-4.

[4]. Rouif, S. (2005). Radiation cross-linked polymers: Recent developments and new applications. *Nucl. Instrum. Meth. Phys. Res. B*, *236*, 68-72. DOI: 10.1016/j.nimb.2005.03.252

[5]. Becker, R.C., Bly, J.H., Cleland, M.R., & Farrell, J.P. (1979). Accelerator requirements for electron beam processing. *Radiat. Phys. Chem.*, *14*, 353-375.

[6]. Defrise, D., Abs, M., Genin, F., & Jongen, Y. (1995). Technical status of the first industrial unit of 10 MeV, 100 kW Rhodotron. *Radiat. Phys. Chem.*, *46*, (4-6) 473-476.

[7]. Lackner, M.V., Herer, A., Cleland, M.A., Jongen, Y., & Abs, M. (1999). The IBA Rhodotron: an industrial high-voltage high-powered electron beam accel-

erator for polymers radiation processing. *Nucl. Instrum. Meth. Phys. Res. B*, *151*, 242-246.

[8]. Woods, R.J., & Pikaev, A.K. (1994). *Applied radiation chemistry: Radiation processing*. New York: Wiley.

[9]. Clough, R., & Shalaby, S. (Eds.). (1996). *Irradiation of polymers: Fundamentals and technological applications*. Washington, DC: ACS Books.

[10]. Chapiro, A. (2002). Polymer irradiation: past–present and future. *Radiat. Phys. Chem.*, *63*(3-6), 207-209. DOI: 10.1016/j.radphyschem.2004.05.040.

[11]. Czvikovszky, T. (2003). Expected and unexpected achievements and trends in radiation processing of polymers. *Radiat. Phys. Chem.*, *67*(3-4), 437-440. DOI: 10.1016/S0969-806X(03)00081-1.

[12]. Zyball, A. (2004). Radiation processing of polymers. In *Emerging applications of radiation processing* (pp. 5-13). Vienna: IAEA. (IAEA-TECDOC-1386).

[13]. Drobny, J.G. (2010). *Radiation technology for polymers*. Boca Raton, London, New York: CRC Press.

[14]. Sasaki, T., Hosoi, F., Hagiwara, M., & Araki, K. (1979). Development of radiation crosslinking process for high voltage power cable. *Radiat. Phys. Chem.*, *14*, 821-830.

[15]. Peshkov, I.B., Meshchanov, G.I., Finkel, E.E., & Dikerman, D.N. (1983). Results and prospects of using radiation processing in electroinsulating and cable engineering. *Radiat. Phys. Chem.*, *22*, 379-385.

[16]. Studer, N. (1990). Electron beam crosslinking of insulated wire and cable: Process economics and comparison with other technologies. *Radiat. Phys. Chem.*, *35*, 680-686.

[17]. Chmielewski, A.G., Haji-Saeid, M., & Ahmed, S. (2005). Progress in radiation processing of polymers. *Nucl. Instrum. Meth. Phys. Res. B*, *236*, 44-54. DOI: 10.1016/j.nimb.2005.03.247.

[18]. Zimek, Z., Przybytniak, G., & Nowicki, A. (2012). Optimization of electron beam crosslinking of wire and cable insulation. *Radiat. Phys. Chem.*, *81*, 1398-1403. DOI: 10.1016/j.radphyschem.2012.01.028.

[19]. Zimek, Z., Przybytniak G., Nowicki, A., Mirkowski, K., & Roman, K. (2014). Optimization of electron beam crosslinking for cables. *Radiat. Phys. Chem.*, *94*, 161-165. DOI: 10.1016/j.radphyschem.2013.07.005.

[20]. Axamirsky, P.V., Kuksanov, N.K., Malini, A.B., Nemytov, P.I., & Salimov, R.A. (2001). 4-sided irradiation systems for electron treatment of cable and pipe-like products. *Vacuum*, *62*, 257-262. DOI: 10.1016/S0042-207X(01)00218-4.

[21]. Lee, M., & Nho, Y. (2001). Electrical resistivity of carbon black filled high--density polyethylene (HDPE) composite containing radiation crosslinked HDPE particles. *Radiat. Phys. Chem.*, *61*, 75-79. DOI: 10.1016/S0969-806X(00)00354-6.

[22]. Xie, H., Dong, L., & Sun, J. (2005). Influence of radiation structures on positive--temperature-coefficient and negative-temperature-coefficient effects of irradiated low-density polyethylene/carbon black composites. *J. Appl. Polym. Sci.*, *95*, 700-704. DOI: 10.1002/app.21220.

[23]. Smith-Johannsen, R. (1974). *Method of making self limiting heat elements*. US Patent No. 3,793,716.

[24]. Whitney, W., & Horsma, D.A. (1977). *Temperature overshoot heater*. US Patent No. 4,017,715.

[25]. Kampe, A.J. (1982). *PTC heaters*. US Patent No. 4,334,148.

[26]. Berejka, A.J. (2003). Electron beam curing of coil coatings. *The RadTech Report*, September/October 2003, 47-53.

[27]. Cook, P.M., & Muchmore, R.W. (1963). *Process and apparatus for producing materials having plastic memory*. US Patent No. 3,086,242.

[28]. Baird, W.G., Lindstrom, C.A., Besse, A.L., & d'Entremond, D.J. (1962). *Method of producing film having improved shrinking energy*. US Patent No. 3,022,543.

[29]. Berg, G.J., McBride, M.K., Wang, C., & Bowman, C.N. (2014). New directions in the chemistry of shape memory polymers. *Polymer*, *55*, 5849-5872. DOI: 10.1016/j.polymer.2014.07.052.

[30]. Scheve, B.J., Mayfield, J.W., & DeNicola, A.J. (1990). *High melt strength, propylene polymer, process for making it, and use thereof.* US Patent No. 4,916,198.

[31]. Kurtz, S.J., & Potts, J.E. (1985). *Low level irradiated linear low density ethylene/alpha-olefin copolymers and film extruded therefrom*. US Patent No. 4,525,257.

[32]. Zhang, Y. (2013). *Polyolefin formulations for improved foaming: effect of molecular structure and material properties*. Unpublished doctoral dissertation. Queen's University Kingston, Ontario, Canada.

[33]. Chen, N. (2012). *The effects of crosslinking on foaming of EVA*. Unpublished doctoral dissertation. University of Toronto, Canada.

[34]. Trageser, D.A. (1997). Crosslinked polyethylene foam processes. *Radiat. Phys. Chem.*, 9, 261-270.

[35]. Rodriguez-Perez, M.A., Lvarez-Lainez, M.A., & de Saja, J.A. (2009). Microstructure and physical properties of open-cell polyolefin foams. *J. Appl. Polym. Sci.*, *114*, 1176-1186. DOI: 10.1002/app.30283.

[36]. Karaağaç, B., Aytac, A., & Deniz, V. (2014). Application of radiation technology to rubber and tire industries. *J. Biol. Chem.*, *42*(1), 23-34.

[37]. Lewis, G. (2001). Properties of crosslinked ultra-high-molecular-weight polyethylene. *Biomaterials*, *22*, 371-401. DOI: 10.1016/S0142-9612(00)00195-2.

[38]. Herrera, L., Lee, R., Longaray, J., Essner, A., & Wang, A. (2007). Hip simulator evaluation of the effect of femoral head size on sequentially cross-linked acetabular liners. *Wear*, *263*, 1034-1037. DOI: 10.1016/j.wear.2007.02.010.

[39]. Costa, L., Jacobson, K., Bracco, P., & Brach del Prever, E.M. (2002). Oxidation of orthopedic UHMWPE. *Biomaterials*, *23,* 1613-1624. DOI: 10.1016/S0142-9612 (01)00288-5.

[40]. Costa, L., Bracco, P., Brach del Prever, E., Luda, M.P., & Trossarelli, L. (2001). Analysis of products diffused into UHMWPE prosthetic components in vivo. *Biomaterials*, *15*, 307-315. DOI: 10.1016/S0142-9612(00)00182-4.

[41]. Chiesa, R., Moscatelli, M., Giordano, C., Siccardi, F., & Cigada, A. (2004). Influence of heat treatment on structural, mechanical and wear properties of crosslinked UHMWPE. *J. Appl. Biomater. Biomech.*, *2*, 20-28.

[42]. Medel, F.J., Pena, P., Cegonino, J., Gomez-Barrena, E., & Puertolas, J.A. (2007). Comparative fatigue behaviour and toughness of remelted and annealed highly crosslinked polyethylenes. *J. Biomed. Mater. Res.: Appl. Biomater.*, *83B*, 380-390. DOI: 10.1002/jbm.b.30807.

[43]. Oral, E., Christensen, S., Malhi, A., Wannomae, K., & Muratoglu, O. (2006). Wear resistance and mechanical properties of highly crosslinked UHMWPE doped with vitamin E. *J. Arthroplasty*, *21*, 580-591. DOI: 10.1016/j.arth.2005.07.009.

[44]. Oral, E., & Muratoglu, O.K. (2009). Highly crosslinked UHMWPE doped with vitamin E. In *UHMWPE biomaterials handbook* (pp. 221-236). Amsterdam: Elsevier.

[45]. Galvin, A.L., Tipper, J.L., Ingham, E., & Fischer, J. (2005). Nanometre size wear debris generated from crosslinked and non-crosslinked ultra high molecular weight polyethylene in artificial joints. *Wear*, *259*, 977-983. DOI: 10.1016/j.wear.2005.02.035.

[46]. Brach del Prever, E., Bistolfi, A., Bracco, P., & Costa, L. (2009). UHMWPE for arthroplasty: past or future? *J. Orthop. Traumatol.*, *10*, 1-8. DOI: 10.1007/s10195-008-0038.

[47]. Makuuchi, K., & Cheng, S. (2012). *Radiation processing of polymer materials and its industrial applications*. Hoboken, New Jersey: A. John Wiley & Sons, Inc., Publication.

Chapter 12

RADIATION STERILIZATION

Andrzej Rafalski, Magdalena Rzepna, Urszula Gryczka,
Sylwester Bułka
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

1.1. A SHORT HISTORY OF RADIATION STERILIZATION

In a broad sense, sterilization is the complete destruction or removal of all forms of contaminating microorganisms from a material or product. Many medical devices, such as syringes, implants, cannulas (flexible tubes), catheters and intravenous sets are required to be sterile. Until the end of World War II, the only method of sterilization in common use was heat. This meant keeping medical devices, such as syringes or needles, in boiling water for several minutes just prior to use. This was simple, inexpensive and effective, but there were some exceptions, as the hepatitis viruses, which are resistant to temperatures of 100°C. A solution was found by using disposable syringes and other devices. However, the construction of syringes used then was too complex and hence were too expensive for only one time use only, as shown in Fig.1.

Fig.1. An old glass construction of a syringe.

A new, more simple construction for a syringe was developed using several types of polymers, first of all polyethylene and polypropylene. This construction, as shown in Fig.2, was less expensive, but not that resistant to high temperature.

Fig.2. Plastic syringe construction.

Because of this lack of temperature resistance, two new methods for sterilization were developed: gas sterilization and radiation sterilization. The first, the gas method, came into use in the middle 1940s. Gas sterilization is still in use today and is a frequently used method of sterilization.

Though the ability of ionizing radiation to kill bacteria had been observed at the end of nineteenth century and commercial radiation sterilization began in 1957 in the USA. Ethicon Inc., part of Johnson & Johnson, began electron beam (EB) sterilization of sutures using a 6 MeV, 4 kW linear accelerator. Since then this method of sterilization is being developed.

There are two different sources of radiation used in sterilization: radioactive gamma sources, mainly cobalt-60, and electrical sources based on accelerators that provide electron beams. In both cases ionizing radiation does the sterilizing and offers a number of advantages that make it an attractive choice in a number of situations:

- Radiation is a suitable means for sterilizing many materials, except for certain plastics, glass and, of course, living cells. At the sterilizing dose usually used, 25 kGy, radiation does not cause a significant rise in temperature, which permits the sterilization of heat-sensitive drugs and of articles made from low melt transition plastics. Radiation sterilization is often the only method for sterilizing biological tissues and preparations of biological origin.
- Due to its high penetration, radiation reaches all parts of an object to be sterilized. These items can be prepacked in hermetically sealed, durable packages, impermeable to microorganisms. The shelf-life of these prepacked and radiation sterilized items is practically indefinite. The convenience of packing and boxing prior to sterilization eliminates the need for aseptic areas and procedures. It also adds a psychological asset to the product in that the product is not touched after the sterilization procedure.
- The chemical reactivity of radiation is relatively low compared with the often highly reactive gases used in gas sterilization. Hence, the possibility of inducing a chemical reaction that may lead to undesirable changes in the product is very low. For the same reason, radiation offers greater freedom

than heat or gas sterilization in the selection of suitable packaging materials. Many thermoplastics can be used and the permeability factors associated with the steam or gas processes are not relevant. Although some plastic materials may be affected by radiation, such as polypropylene, poly(vinyl chloride) (PVC), *etc.*, radiation resistant grades of these polymers are available.

- Since there are no problems similar to the convection of heat or the diffusion of gas, the effect of radiation is instantaneous and simultaneous within the entire volume of the product. This also permits stopping the radiation at a desired time, or adding to any delivered dose, a precisely defined additional dose, if needed, to achieve a desired sterility level.
- Radiation can be easy adapted to continuous processing, as compared with the batch processing currently used with gas sterilization. In general, continuous operation requires less labour, but also presupposes large-scale production in order to be practical and economically viable.
- The radiation process is the most reliable of all of the competing sterilization methods because of the certainty that the radiation source emits radiation of a known energy and power. Therefore, time is the only variable that requires monitoring once the process parameters have been established. All the others methods of sterilization depend on simultaneous control of many factors, such as temperature, pressure, concentration, humidity, and others.

1.2. RADIATION MICROBIOLOGY

1.2.1. Direct and indirect action in biological systems

There are two distinct mechanisms by which a chemical change can be brought about by ionizing radiation [1]:

- by direct action, when the molecule undergoing change becomes ionized or excited by the passage of an electron or other charged particle through it;
- by indirect action, in which the molecule does not absorb the energy but receives it by transfer from another molecule.

This difference is particularly well defined when solutions are irradiated, as in the case of biological systems, where water is present as the solvent. Direct ionization of a water molecule leads to the formation of an ion. An ionized water molecule then dissociates into free radicals. These radicals have an unpaired electron which makes them extremely reactive. The lifetime of an ionized water molecule before it dissociates into a free radical is only on the order of 10 ps, and, in this time, the probability of an exchange of ionization with a substrate molecule of lower ionization potential is extremely small. For this reason, an indirect action in aqueous systems is believed to be produced entirely by the free radicals formed from water. The direct action (*i.e.* ionization) and indirect action by free radicals lead to cell damage and to the inactivation of enzymes and viruses. Ionization is more efficient than excitations in producing biologically significant changes.

1.2.2. Dose-response relationship in biological systems

The evaluation of irradiation effects can be obtained from survival curves of a microbial population in question. To prepare such curve, a known number of microorganisms of one kind is irradiated using gamma radiation or by an electron beam to a required dose and then the number of living cells is calculated [2]. The effect is described as a number of living cells in proportion to the number of microorganisms before irradiation. The procedure is repeated for several doses which generates the relationship between the surviving fraction of microorganisms and dose, as shown in Fig.3.

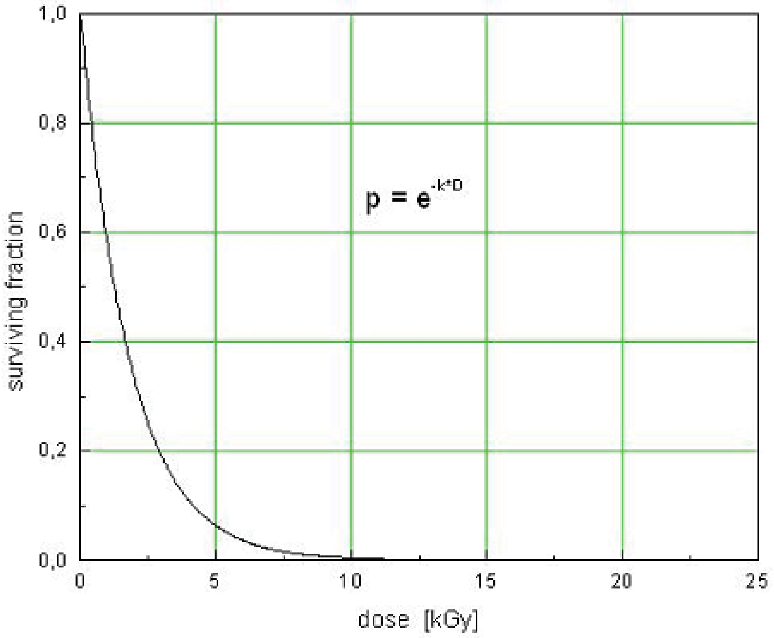


Fig.3. Surviving fraction of microorganisms as a function of dose (in linear coordinates).

In linear coordinates the most interesting region (*i.e.* for large doses where the surviving fraction is extremely low) is hardly visible. The much better way is to use the logarithmic scale for the surviving fraction, as shown in Fig.4.

From this logarithmic depiction, it is understood that the absolute sterility cannot be achieved. Sterility is about a partial inactivation or about the probability of finding a living microorganism on a medical device or a transplant.

The above relationship is very simplified. In practice the surviving fraction-dose relationship depends on many factors, such as the way the dose is delivered (divided or at once), the irradiation environment (presence of oxygen, humidity, *etc.*) and above all on the kind of the microorganism. In Fig.5, the

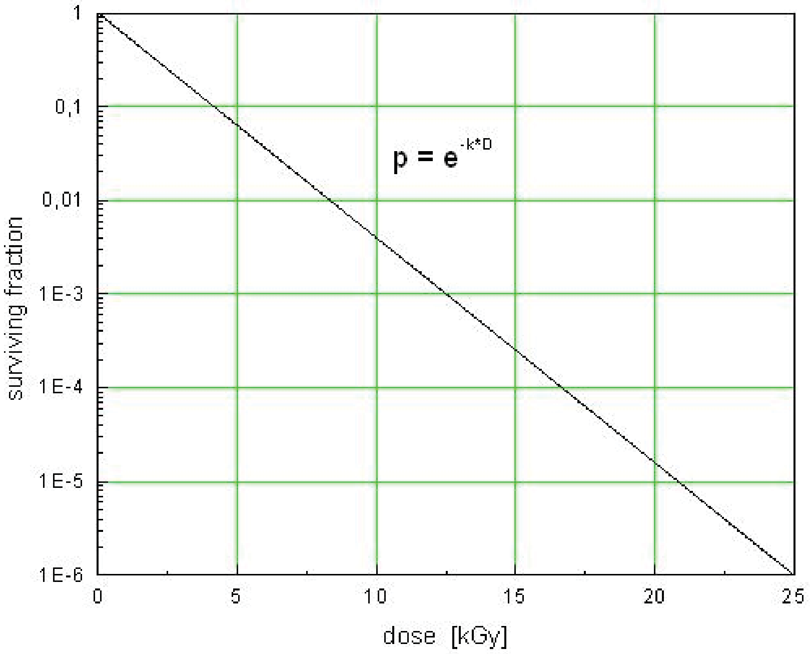


Fig.4. Surviving fraction of microorganisms as a function of dose (in linear-logarithmic coordinates).

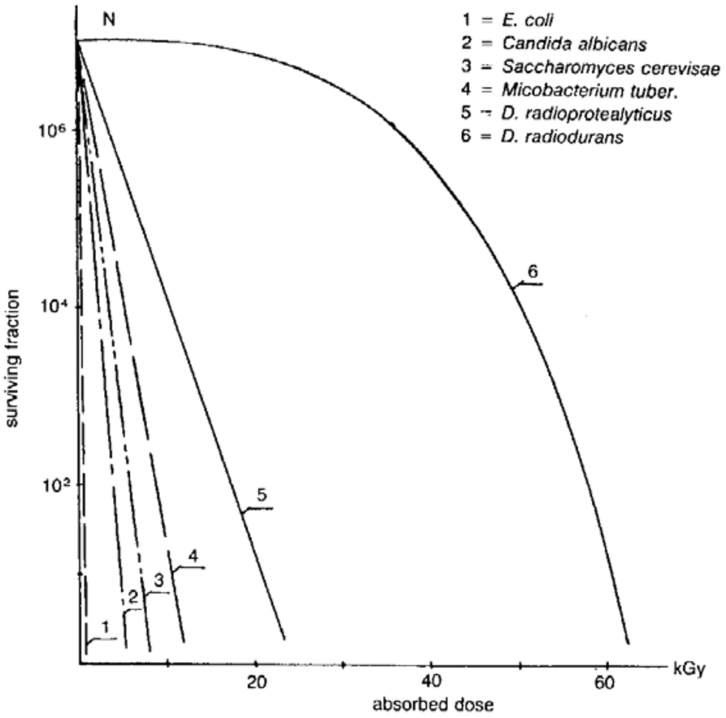


Fig.5. The surviving fraction-dose relationship for several kinds of microorganisms. (Reproduced from Ref. [2]).

real surviving fraction-dose relationships for several kinds of microorganisms are presented.

1.3. ESTABLISHING THE STERILIZATION DOSE

The main goal of sterilization is the sterility of a medical device or transplant, *i.e.* the state of being free from viable microorganisms. The level of sterility is described by the term SAL (sterility assurance level). The term takes a quantitative value, usually 10^{-6} or 10^{-3}. A SAL of 10^{-6} has a lower value and provides a greater assurance of sterility than a SAL of 10^{-3} [3].

There are several methods that may be used to establish the sterilization dose in accordance with one of the two approaches specified in ISO (International Organization for Standardization) standard 11137-2:2015 [3]. The methods used in these approaches are:

- dose setting to obtain a product-specific dose, and
- dose substantiation to verify a preselected dose of 25 kGy (or 15 kGy).

1.3.1. Methods based on the dose setting approach

Method 1

This method is used for products with an average bioburden equal to or greater than 1.0 cfu (colony forming units) for multiple batches. The method consists of six stages:

- 1st stage: Recording the SAL for the intended use of the product and selecting at least 10 product items from each of three independent production batches. The product items for establishing the sterilization dose should be representative of that subjected to routine processing procedures and conditions. Generally, each product item used for bioburden determination or in the performance of a sterility test should be taken from a separate primary package.
- 2nd stage: Determination the bioburden of at least 30 product items and calculating the average bioburden for each batch and the overall average bioburden.
- 3rd stage: Obtaining the verification dose from a proper table using the highest batch average bioburden or the overall average bioburden.
- 4th stage: Verification dose experiment: 100 product items should be selected from a single batch of product and irradiated at the verification dose obtained at the 3rd stage.
- 5th stage: Interpretation of results: verification is accepted if there are no more than two negative tests of sterility from the 100 tests carried out.
- 6th stage: Establishing sterilization dose: if the verification is accepted, the sterilization dose is obtained from the same table and for the same average bioburden as at the 3rd stage.

Method 2

There are two variants of method 2: method 2A is the method that has been generally used and method 2B which has been developed for products with a consistent and very low bioburden.

Method 2A consists of four stages:

- 1st stage: Recording the SAL for the intended use of the product and selecting at least 280 product items from each of three independent production batches. The same conditions should be followed as at the 1st stage of method 1.
- 2nd stage: Incremental dose experiment: 20 product items from each of three production batches should be irradiated as a series with not less than nine doses, increasing in nominal increment of 2 kGy. The dose may vary from the nominal incremental dose by 1.0 kGy or 10%, whichever is greater. For each of three production batches, the lowest dose from the incremental dose series should be determined where at least one of the 20 tests for sterility is negative. Using this value, a proper table and an equation, the sterilization dose can be derived.
- 3rd stage: Verification dose experiment: 100 product items should be selected from a single batch of product and irradiated at the verification dose derived at the 2nd stage.
- 4th stage: Establishing sterilization dose: using the results of the tests for sterility after the verification dose experiment and use of several equations, the final sterilization dose can be calculated.

Method 2B consists of four stages:

- 1st stage: Recording the SAL for the intended use of the product and selecting at least 260 product items from each of three independent production batches. The same conditions should be followed as at the 1st stage of method 1.
- 2nd stage: Incremental dose experiment: 20 product items from each of three production batches should be irradiated to form a series of not less than eight doses, increasing in nominal increment of 1 kGy. The dose may vary from the nominal incremental dose by 0.5 kGy or 10%, whichever is greater, with the exception that the allowed variation for the 1 kGy nominal dose is 0.2 kGy. For each of three production batches, the lowest dose from the incremental dose series should be determined where at least one of the 20 tests for sterility is negative. Using this value, a proper table and an equation, the sterilization dose can be determined.

The 3rd and 4th stages are the same as in method 2A.

1.3.2. Method based on the second approach: VD_{max} method

VD_{max} method for substantiation of a selected sterilization dose is similar to dose setting method 1. It also requires a determination of bioburden and the performance of a verification dose experiment.

In carrying out substantiation, the method verifies that the bioburden present on a product prior to sterilization is less resistant to radiation than a microbial population of maximum resistance consistent with the attainment of SAL of 10^{-6} at the selected sterilization dose. Verification is conducted at SAL of 10^{-1} with 10 product items irradiated in the performance of the verification dose experiment. The dose corresponding to this SAL is characteristic of both the bioburden level and the associated maximum resistance. In establishing the maximum resistance for a particular bioburden level, account has been taken of the various resistance components of the standard distribution of resistance (SDR), the latter being the basis of method 1. Components of the SDR of high resistance that have significant effect on the attainment of SAL of 10^{-6} have defined the maximum resistances on which this substantiation method is based. In this way, the level of conservativeness of the SDR, and thus of method 1, is preserved.

In practice, a determination is made of the average bioburden. The dose corresponding to this bioburden is read from a proper table. This dose is designated VD_{max} and it is the dose at which the verification dose experiment is carried out. Ten product items are irradiated to the VD_{max} dose and each item is subjected individually to a test for sterility. If there is no more than one negative test of sterility in the 10 tests, the preselected sterilization dose is substantiated.

This method is for selected sterilization doses of 25 and 15 kGy. The method for 25 kGy is applicable to products having an average bioburden in the range from 0.1 to 1000 cfu, whereas that for 15 kGy applies to a limited range of bioburden extending from 0.1 to 1.5 cfu only.

The VD_{max} method consists of five stages:

- 1st stage: Selecting at least 10 product items from each of three independent production batches. The same conditions should be followed as at the 1st stage of method 1.
- 2nd stage: Determination the bioburden of at least 30 product items and calculating the average bioburden for each batch and the overall average bioburden.
- 3rd stage: Obtaining the verification dose from a proper table using the highest batch average bioburden or the overall bioburden average.
- 4th stage: Verification dose experiment: 10 product items should be selected from a single batch of product and irradiated at the verification dose obtained at the 3rd stage.
- 5th stage: Interpretation of results: verification is accepted if there are no more than one negative tests for sterility from the 10 tests carried out and thereby substantiation of 25 kGy (or 15 kGy) is confirmed. If there are two negative tests for sterility in the 10 tests carried out, a confirmatory verification dose experiment should be performed. If there are more than two negative tests of sterility, the verification is not accepted and the verification

dose experiment may be repeated following the implementation of corrective action.

2. VALIDATION OF RADIATION STERILIZATION PROCESS

The definition of validation is a documented procedure for generating, recording and interpreting the results required to establish that a process will consistently yield product complying with predetermined specifications. Sterilization processes require periodic validation to demonstrate that they are working correctly and functioning within established norms. Such validation entails detailed measurement of various physical parameters throughout the sterilization process and assessing and comparing these results to relevant international standards. A validation for medical devices sterilized by radiation is governed by ISO 11137-1:2015 [4], ISO 11137-2:2015 [3] and ISO 11137-3:2015 [5].

For any irradiation use, there are two parties involved: the customer (the primary manufacturer) and the irradiation plant – although they may both be within the same organization. The responsibilities of each party shall be clearly specified.

Irradiation plant responsibilities are the following:

- installation qualification,
- operational qualification,
- controlling the irradiation process,
- change control of the irradiator,
- certification of the radiation dose.

Primary manufacturer responsibilities are the following:

- establishing the sterilization dose;
- developing product families;
- establishing the maximum acceptable dose;
- performance qualification;
- controlling the manufacturing process including the specifications for products that are submitted to the irradiator operator, *i.e.* product density, orientation, dimensions;
- revision of specifications submitted to the irradiator operator;
- change control of the product to include a review of product-related variables that impact processing categories;
- product release.

2.1. INSTALLATION QUALIFICATION

Installation qualification (IQ) is undertaken to demonstrate that the sterilization equipment and any ancillary items have been supplied and installed in accordance with their specifications. Operating procedures for the irradiator and associated conveyor system shall be specified. Process and ancillary equipment, including associated software, shall be tested to verify that they operate to design specifications. The test method(s) shall be documented and the results shall be recorded. Any modifications made to the irradiator during installation shall be documented. One of the requirements in Section 9.1.5 of ISO 11137-1:2015 [4] is to describe the properties of the electron beam. Depending on the design of the irradiator, this includes the position (in directions where the electron beam is not dispersed by the irradiator) and the shape of the beam spot, the electron energy, the beam current, the scan width (*i.e.* beam width: the dispersion of the electron beam by the irradiator to ensure product is irradiated over its full width) and the scan uniformity (*i.e.* the uniformity of the beam over its width).

Documentation of an installation qualification program shall be retained for the life of the irradiator, and shall include:

- the accelerator specification and properties;
- a description of the construction and the operation of any associated material handling equipment;
- a description of the process control system and of personnel safety systems;
- a description of the location of the irradiator within the operator's premises in relation to the means provided for the segregation of non-irradiated products from irradiated products, if required;
- a description of the materials and the construction dimensions of the containers used to hold products during irradiation;
- a description of the manner of operating the irradiator;
- any modification made during and after installation.

2.2. OPERATIONAL QUALIFICATION

Operational qualification (OQ) is carried out either with unloaded equipment or using an appropriate test material to demonstrate the capability of the equipment to deliver the sterilization process that has been defined.

Prior to operational qualification, the calibration of all instrumentation, including test instrumentation used for monitoring, controlling, indicating or recording, shall be confirmed. OQ carried out by irradiating an appropriate test material of homogeneous density to demonstrate the capability of the equipment to deliver appropriate doses, *i.e.* the irradiation process that has been defined. OQ provides baseline data to show consistent operation of the irradiation facility (*i.e.* within established and defined limits). OQ should be repeated to show consistent operation, *i.e.* the results obtained are within established and defined limits.

Dose mapping for OQ is carried out to characterize the irradiator with respect to the distribution and reproducibility of dose and to establish the effect of process interruption on dose. Dose mapping should be performed by placing dosimeters in an irradiator container filled to its design limits with material of homogeneous density. The density should be within the density range for which the irradiator is to be used. At least two dose mapping exercises should be carried out, one with material close to the lower limit of the density range for which the irradiator is intended to be used and another with material close to the upper limit of this range.

A sufficient number of irradiation containers (at least 3) should be dose mapped at each choice of density to allow for the determination of dose variability and dose distribution between containers. The detail and number of replicate dose mappings required will be influenced by the amount of knowledge gained from previous OQ dose mapping exercises using the same irradiator. This means that a greater number of replicate dose mappings may be required for a new installation than for requalification by dose mapping after reloading a source in the case of a gamma irradiator or at defined intervals for electron beams.

Individual dosimeters, dosimeter strips or dosimeter sheets should be placed in a three-dimensional array sufficient to determine and resolve the dose distribution throughout the entire volume of the irradiation container. The number of dosimeters will depend upon the size of the container and the design of the irradiation facility. For requalification dose mapping, data from previous exercises may be used to optimize the positioning of the dosimeters.

The response of some dosimeters is known to be influenced by the period of time between irradiation and measurement, and the magnitude of this effect can also depend on temperature during this period. These factors should be taken into account when interpreting measurements from dosimeters that have been subjected to process interruptions.

Separate dose determinations should be carried out in order to assess the effect of process interruption.

The irradiation container is irradiated under normal process conditions, and the process is interrupted when the container is under the beam. When an EB process is restarted, the effect of the interruption is evaluated by measuring the dose variation that occurs during the time of the interruption.

2.3. PERFORMANCE QUALIFICATION

Performance qualification (PQ) is the stage of validation that uses product to demonstrate that equipment consistently operates in accordance with predetermined criteria and the process yields product that is sterile and meets specified requirements.

Dose mapping shall be carried out using product loaded in irradiation containers in accordance with a specified loading pattern in order to:
- identify the location and magnitude of the minimum and maximum dose,
- determine the relationships between the minimum and maximum dose and the dose(s) at the routine monitoring position(s).

The manner of presenting product for sterilization shall be specified. This shall include:
- the dimensions and density of the packaged product,
- the orientation of product within the package,
- a description of the irradiation container (if multiple types of irradiation containers are used within the irradiator),
- a description of the conveyor path (if multiple conveyor paths are used within the irradiator).

Dose mapping documentation is part of the agreement between the manufacturer and sterilizer and hence part of a contract. This includes, for example, the documentation of:
- details of the dosimetry system (dosimeter type, readout system used),
- dosimeter batch,
- calibration including traceability of calibration,
- illustration showing the exact dosimeter placement,
- statistical analysis of dosimeter readings.

3. RADIATION DISINFECTION AND MICROBIOLOGICAL DECONTAMINATION

The most common methods used for disinfection and microbiological decontamination are processes in which heat, steam or chemical reagents, like ethylene oxide (ETO), are used. Because ETO is toxic to humans and has harmful environmental properties, radiation processing can be used as an alternative.

The biological effects of ionizing radiation on insects or microorganisms are directly related to the dose used, which also depends on type of organism and its storage conditions. To select a dose needed to achieve a desired effect of irradiation, the sensitivity to irradiation of a selected insect or microorganism must be known. Insects are less sensitive to ionizing radiation. The International Database on Insect Disinfestation and Sterilization (IDIDAS) is the website where all of the information on radiation doses for disinfestation and sterilization for more than 300 species of arthropods has been collected. This database was developed based on literature reviews and analysis of about 3000 references published during the past five decades [6]. Biological factors are destructive to infected material as shown in Fig.6 and are dangerous to humans. Radiation disinfection can be used to eliminate insects from fresh food [7], from packaging, paper or cultural heritage artefacts [8].

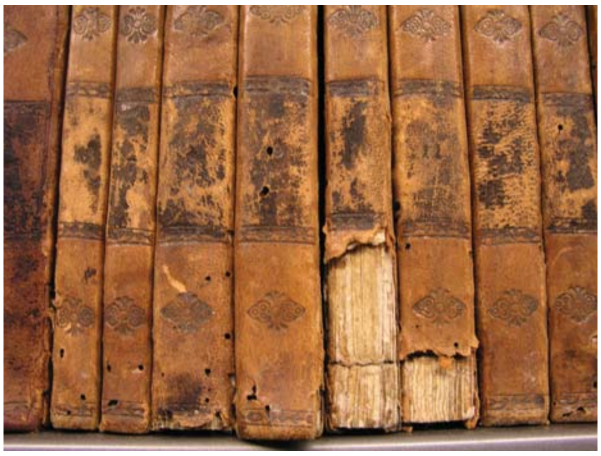


Fig.6. Damage of books caused by biological factors.

The elimination of insects with ionizing radiation requires doses below 1 kGy. There are two methods for pest treatment with ionizing radiation. The first method is known as the sterile insect technique (SIT). This method of insect eradication relies on sterilization and lethal mutations resulting from low doses. Insect males are sterilized with low doses of ionizing radiation and are released into native populations. A decline in the reproductive rate for the wild population is observed and it immediately results in decline in population number beginning from the next generation.

The second method is rapid insect death caused by higher doses of ionizing irradiation. Such approach cannot be used for the preservation of cultural artefacts, because in this case the rapid disinfection of valuable objects is needed. This method requires higher doses of ionizing radiation which leads to the rapid death of the irradiated insects [8].

More resistant to radiation than insects are fungi and bacteria. Fungal colonies can develop in books, where there is a large amount of natural adhesives and where water and dust can easily penetrate. Microscopic fungi colonies develop from spores frequently present in air, dust and dirt with just a slight amount of water. Fungi can live on paper books, leather, parchment or cloth. These materials are suitable for helping of microorganisms grow which can then degrade the material.

The resistance of every microorganism can be characterized using D_{10} values which describe the ability of radiation to reduce an exposed microbial population by 90% (one log 10) using a standard dose. In general, viruses are the most resistant to radiation. Examples of different microorganism D_{10} values are presented in the Table 1.

Table 1. The D_{10} values for selected microorganisms [9].

Organism	D_{10} [kGy]
Escherichia coli	0.30
Salmonella spp.	0.70
Listeria monocytogenes	0.45
Staphylococcus aureus	0.46
Clostridium botulinum	3.56
Bacillus anthracis	5.50

Radiation microbiological disinfection process can be used to eliminate the most harmful microorganisms such as *Bacillus anthracis* which has been and can be used as a bioterrorism agent. Elimination of such biohazards with ionizing radiation has been used for mail disinfection in the United States [9].

4. RISK ANALYSIS FOR RADIATION STERILIZATION PROCESS

Risk management should be an important element of each company's strategic management. It is a methodical process by which enterprises solve problems associated with the risk that may affect their activities. This means that a company is constantly and continuously monitoring changing situations and their impact on all activities, and is consciously monitoring any changes introduced, while remaining within established criteria. The use of preventive measures should be also economically justified in order to avoid hazards as much as possible and/or appropriately modify the level of risk.

4.1. RISK DEFINITION

Risk can be defined as a combination of the probability of an event and its consequences. According to PN-EN ISO 14971:2009 [10] concerning the use

of risk management to medical devices it is assumed that the risk concept includes the following elements:
- the probability of injury/damage;
- the level of difficulty it can be detected;
- the consequences of the damage, that is, how severe it might be.

4.2. RISK MANAGEMENT

The subject of proper risk management is the identification of potential hazards and suitable actions. Risk management conducted in an appropriate way provides benefits to all areas of a company. This includes understanding the potential positive and negative effects of factors that may affect the company. The faster the corrective or preventive actions can be undertaken, the lower costs will be incurred by the company by eliminating potential losses. This is possible only by introducing a correct risk management process [11].

The risk for a company and its operation can result from both internal and external factors which should be taken into consideration during hazard source identification. In the case of radiation sterilization services, a very important element is to ensure the quality and continuity of the service.

The risk management process should include:
- the risk analysis,
- the assessment of risk acceptability,
- risk control measures,
- oroduction and post-production information processing.

The risk management plan, which was established at the Institute for Nuclear Chemistry and Technology (INCT, Poland), includes all activities on the premises of the Radiation Sterilization Plant connected with the irradiation of medical devices, medicinal products and cosmetics provided by different manufacturers. The identification of kinds of hazards which can occur was done by answering questions like:
- What can happen at the Radiation Sterilization Plant that may have influence on the dose which was agreed with customer?
- Who can perform the process incorrectly?
- How can it happen?
- When may hazards occur?

4.3. RISK ASSESSMENT METHODOLOGY

The methodology used for risk analysis was failure mode and effects analysis (FMEA), which is a suitable tool for minimizing risk by focusing on failure modes and their effects [12]. FMEA is a methodology that can be used to evaluate a system and/or the design of a process or service for possible ways in which failures may occur (problems, errors, risk concerns). There are four main orientations of FMEA: design, system, process and service. The FMEA selection was made for an existing facility and for an already implemented quality system, so the analysis was limited to service and to process FMEA.

4.3.1. Service FMEA

Service FMEA is used to analyse services before they reach the customer. A service FMEA focuses on failure modes (tasks, errors, mistakes) caused by system or process deficiencies.

The output of a service FMEA is:

- a potential list of errors ranked,
- a potential list of critical or significant tasks or processes,
- a potential list of bottlenecks in processes or tasks,
- a potential list to eliminate errors,
- a potential list of monitoring system/process functions.

The benefits of a service FMEA are that it:

- assists in the analysis of facility flow,
- assists in the analysis of the system and/or process,
- identifies task deficiencies,
- identifies critical or significant tasks and helps in the development of control plans,
- establishes a priority for the improvement of actions,
- documents the justification for changes.

4.3.2. Process FMEA

Process FMEA is used to analyse manufacturing and assembly processes. A process FMEA focuses on failure modes caused by process or assembly deficiencies.

The output of a process FMEA is:

- a potential list of failure modes ranked,
- a potential list of critical and/or significant process properties,
- a potential list of recommended actions to address the critical and significant process properties.

The benefits of a process FMEA are that it:

- identifies process deficiencies and offers a corrective action plan,
- identifies the critical and/or significant process properties and helps in developing control plans,
- establishes a priority for corrective actions,
- assists in the analysis of the manufacturing or assembly process.

4.4. RISK EVALUATION IN THE INCT RADIATION STERILIZATION PLANT

Risk assessment levels and criteria that were taken into consideration. The risk assessment for the radiation sterilization process was based on the scale given in Table 2.

Table 2. Qualitative severity levels.

Importance of hazard	Frequency or occurrence	Detection ability	Risk level	Corrective action
Low	Very rarely	High	Low 1÷8	Not necessary
Significant	Rarely	Significant	Significant 9÷16	Advisable
High	Often	Low	High 17÷32	Necessary
Catastrophic	Very often	Unrecognizable	Catastrophic > 32	Critical state. Process must be stopped

The criteria for risk assessment which were taken into account are given in Table 3.

Table 3. Relationship between hazards and foreseeable sequences of events.

Importance of hazard	Consequences of hazard
Low (only single items of product may be damaged)	These is no effect on equipment status; the routine maintenance of equipment is sufficient
Significant (part of the batch has been damaged)	The equipment must be serviced and damage must be repaired
High (entire batch of products has been damaged)	Failure of equipment; complete repair is required
Catastrophic (large amount of the product has been damaged)	Significant financial losses; the equipment has been irreversibly damaged

The hazards identified and associated risk evaluations in the INCT Radiation Sterilization Plant are described below.

The risk assessment performed at the INCT Radiation Sterilization Plant is based on 1129 days (just over 3 years) during which a linear electron accelerator, Elektronika 10/10, had been used for radiation sterilization. Ways to minimize the level of risk had been proposed. From the collected data, the most hazardous process was irradiation of the product itself, particularly when certain product receives too low or an inhomogeneous dose, which can consequently result in a non-sterile product or when a product receives too high a dose, which can cause deterioration of product's material and physical and/or mechanical properties.

Table 4. Risk analysis.

No.	Hazard	Kind of records	P[a]	S[b]	D[c]	PN[d]	Proposal of diminishing the hazard level	Way of control
Packaging damage								
1	During transportation	Records in Internal Batch Report	1	1	1	1	Review of delivery company procedures concerning product handling	System documentation, legislation documents
2	Loading and unloading (fork-lift truck)		2	1	1	2	Personnel training. knowledge proved by control test	
3	Handling before and after irradiation		1	1	1	1	Review of place and qualification of warehouse safe method	
4	Storage (damage by rodents)		1	1	1	1	Review of procedure related with control against rodents	
5	Items translocation within package caused by transportation		2	2	1	4	Personnel training, knowledge proved by control test, conveyor maintenance instruction review control of cleanliness of conveyor	
6	Related with loading and unloading products into irradiation containers		2	2	1	4	Personnel training, knowledge proved by control test	
Measurement errors								
7	Accelerator parameters	Legislation and calibration certificates, records of personnel qualifications	2	3	2	12	Calibration of measuring devices, replacement of devices	System documentation, legislation documents
8	Conveyor parameters		2	1	2	4	Control of conveyor speed, maintenance	
9	Dosimetry systems		2	4	1	8	Calibration of measuring devices	
10	Product weight and calculations of area density		1	1	2	2	Scale legislation, calibration of weight standard	
11	Errors caused by personnel		2	3	2	12	Personnel training, knowledge proved by control test	

Table 4. Contd.

No.	Hazard	Kind of records	P^a	S^b	D^c	PN^d	Proposal of diminishing the hazard level	Way of control
Accelerator failures								
12	Irradiation interruption (magnetron EB scanning generator, vacuum pump HV power sources)	Operational Qualification Reports	1	2	1	6	Verification of procedures related with accelerator maintenance, training of personnel	System documentation, legislation document
13	Fluctuation of mains voltage, outage of mains power		2	3	1	6		
14	Gun modulator, gun HV control		2	2	2	8	Verification of instruction related with accelerator maintenance, training of personnel	
15	Conveyor, pulser		2	4	1	8	Verification of procedures related with accelerator maintenance, training of personnel	
16	Cooling system (magnetron section, scanning horn)		1	1	1	1	Water refill in cooling system, leak-tightness control and lock emergency system	
17	Computer system		2	3	1	6	Validation of computer system, review of archive data	
18	Irradiation container jam without EB shutdown		1	4	1	4	Control of interlocks accelerator-conveyer	
19	Electrical breakdown in magnetron modulator		1	3	2	6	Verification of instruction related with accelerator maintenance control of cleanliness of HV joints	
20	Waveguide ceramic separation window damage		1	5	1	5	Control of compressed nitrogen in waveguide, check and correction of magnetron alignment	
21	EB extraction window titanium foil damage		1	5	1	5	Titanium foil replacement, maintenance of scanning magnet power supply, control of interlock: generator-magnetron-modulator	

Table 4. Contd.

No.	Hazard	Kind of records	P[a]	S[b]	D[c]	PN[d]	Proposal of diminishing the hazard level	Way of control
Irradiation								
22	Too low dose: non-sterile product	Records in Internal Batch Report, other records, certificate	2	4	2	16	Additional dose control	System documentation, legislation document
23	Too high dose: potential damage to the product		2	4	2	16	Additional dose control	
24	Non-homogeneous dose distribution, partially non-sterile product		2	3	2	12	Experimental checking of irradiation continuity during accelerator failure	
25	Two times irradiation of the same product		1	4	1	4	Review and verification of loading system. Personnel training, knowledge proved by control test	

[a] P – probability.

[b] S – severity.

[c] D – detectability.

[d] PN – priority number.

The risk level of this hazard is within the range 8÷16. Therefore, this hazard is recommended for corrective actions. The risk assessment and actions to be taken as a result of this assessment are shown in Table 4.

Since the start of the sterilization service at the INCT, now for 45 years, with properly implemented control measures, no medical incidents caused by an incorrectly performed radiation sterilization process have been reported.

The documentation related to the risk management in Radiation Sterilization Plant is reviewed every two years. Conclusions drawn from audits, corrective and remedial actions are analysed and included in subsequent editions of the risk analysis.

REFERENCES

[1]. Bacq, Z.M., & Alexander, P. (1961). *Fundamentals of radiobiology*. London: Pergamon Press.
[2]. Zagórski, Z.P. (2007). *Sterylizacja radiacyjna*. Warszawa: Instytut Chemii i Techniki Jądrowej.
[3]. ISO. (2015). *Sterilization of health care products – Radiation sterilization – Part 2: Establishing the sterilization dose*. ISO 11137-2:2015.
[4]. ISO. (2015). *Sterilization of health care products – Radiation sterilization – Part 1: Requirements for development, validation and routine control of a sterilization process for medical device*s. ISO 11137-1:2015.
[5]. ISO. (2015). *Sterilization of health care products – Radiation sterilization – Part 3: Guidance on dosimetric aspects*. ISO 11137-3:2015.
[6]. FAO/IAEA (2012). *International Database on Insect Disinfestation and Sterilization or IDIDAS*. Retrieved February 4, 2016, from http://nucleus.iaea.org/ididas.
[7]. Bustos-Griffin, E., Hallman, G.J., & Griffin, R.L. (2015). Phytosanitary irradiation in ports of entry: a practical solution for developing countries. *Int. J. Food Sci. Technol.*, *50*, 249-255.
[8]. Chmielewska, D., Gryczka, U., Migdal, W., & Ignatowicz, S. (2011). Application of radiation methods to preservation of cultural heritage. *J. Ent. Acarol. Res. Ser. II*, *43* (2), 237-244.
[9]. Desrosiers, M.F., Coursey, B., Seltzer, S., Hudson, L., Puhl, J., Bergstrom, P., Bateman, F., Cooper, S., Alderson, D., Knudson, G., Elliott, T., Shoemaker, M., Lowy, J., Miller, S., & Dunlop, J. (2005). Irradiation decontamination of postal mail and high-risk luggage. In L.G. Gazso & C.C. Ponta (Eds.), *Irradiation decontamination. Radiation inactivation of bioterrorism agents* (pp. 115-126). IOS Press. (NATO Science Series, I: Life and Behavioural Sciences, Vol. 365).
[10]. ISO. (2009). *Risk management for medical devices*. PN-EN ISO 14971:2009.
[11]. ISO/IEC. (2002). *Risk management – Vocabulary – Guidelines for use in standards*. ISO/IEC Guide 73:2002.
[12]. Stamatis, D.H. (2003). *Failure mode and effect analysis: FMEA from theory to execution* (2nd ed.). ASQ Quality Press.

Chapter 13

RADIATION PROCESSING OF POLYMERS IN AQUEOUS MEDIA

Clelia Dispenza, Sabina Alessi, Giuseppe Spadaro
Università degli Studi di Palermo, Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Edificio 6, Viale delle Scienze, 90128 Palermo, Italy

1. INTRODUCTION

The focus here is on radiation-initiated processes that synthetize or modify polymers using water as a reaction medium. The motives for using water as the medium for polymerization reactions are reviewed. An historical perspective gives an outlook on the opportunities that radiation processing of polymers in water offers, especially in the emerging fields of bio- and nanotechnology. Some basic concepts of radiation-initiated polymerization and water radiolysis are noted. A distinction is made between homogeneous and heterogeneous polymerization processes in aqueous media. The radiation-initiated crosslinking of polymers is covered. This is an approach to the synthesis of hydrogels and their nanoscale analogues, nanogels (NGs), which represent two of the most successful uses of radiation-initiated synthesis of functional materials for biomedical applications. Finally, there is a brief discussion of the possible use of water radiolysis products to control the molecular weight of biopolymers and to produce nanoparticles.

1.1. WATER AS REACTION MEDIUM

The reasons for using water as a reaction medium are numerous. Generally, water-based processes are more environmentally friendly than those that make use of organic solvents. Using water as the reaction medium, whenever is possible, is one of the paradigms of “green chemistry”. More specifically, the advantage of using water as the reaction medium in radiation processing is that the radiation chemistry of water is a well-established field. The nature and yields of radiolytic species are known and can be tuned by changing the irradiation conditions and/or by adding co-solutes to suit the purpose of initiating chemical reactions. Water radiolysis products can be exploited to initiate polymerization reactions, the grafting of monomers onto polymers or substrates, and to initiate crosslinking, without requiring the addition of initiators and catalysts. As a result, purer products are obtained, containing no residues of the components that are inevitably present when polymerization is carried out by conventional processes, such as thermally initiated or photoactivated processes. This aspect is of particular importance for uses in medicine or electronics where high purity product yield is a requirement.

Polymerization, grafting or crosslinking can be regarded as additive processes, where the level of organization and complexity increases, along with the functionality; the system evolves from monomers to polymers, from monomers/polymers to graft-copolymers, from polymers to crosslinked networks. Subtractive processes can also be of interest. The oxidizing radicals, generated by the radiolytic decomposition of water, can be effective in promoting polymer degradation and in controlling polymer molecular weight.

Water can be present at the surface of materials exposed to ionizing radiation in various environments. Water can also be saturated with oxygen from the air or by other gases. Varnishes and encapsulation compounds, matrices of reinforced structural composites, adhesive and sealant compounds for nuclear reactors, polymers used in aerospace vehicles, satellites and resins used for the encapsulation of radioactive wastes are some examples of where water radiolysis products can promote the modification of the chemical structure of some polymers and consequent degradation of their properties. Even when polymerization or crosslinking is the desired process, molecular degradation of the formed chains or networks can occur. An understanding of the reaction mechanisms by which polymers exposed to water are produced and/or modified is important to the selection of the process conditions that can minimize adverse secondary processes and unwanted by-products.

1.2. HISTORICAL OUTLINE OF RADIATION PROCESSING OF POLYMERS IN AQUEOUS MEDIA AND OUTLOOK

The radiation processing of polymers in aqueous media has an almost century-long history, but with a somewhat discontinuous development. The pioneering studies of Hopwood and Phillips in 1939 [1] and, a few years later, of Joliot [2] provided the scientific community with the evidence that monomers, such as methyl methacrylate (MMA) or styrene, could be polymerized in solution (or in bulk) by either gamma rays or fast neutrons. The optical clarity and mechanical properties of radiation-polymerized poly(methyl methacrylate) (PMMA) was superior to its thermally polymerized analogue because of a lack of internal stresses.

After the Second World War, when the nuclear fission reactors provided relatively inexpensive, powerful gamma radiation sources, large-scale development of radiation-initiated polymerizations took place. In particular, waterborne polymers and latexes were produced from methyl methacrylate (MMA), styrene (St), and vinyl acetate (VAc) monomers, amongst others. Fundamental studies were carried out by eminent scientists in the United Kingdom, France, the United States, the former Soviet Union, the Czech Republic, Italy, Japan, and Poland in the 1960s and 1970s. In the following years, material scientists working in industry were renowned for their ability to engineer materials into products, processes and devices, and dominated the field. Radiation-initiated processes and products thereof, as well as the technology behind the electron beam accelerators then and now in use, were developed almost exclusively by private companies. The result was that some processes became commercially relevant. The radiation vulcanization of natural rubber latex, the degradation of polysaccharides dissolved in water and the radiation crosslinking of water--soluble polymers to produce hydrogels are some examples. These programmes were not always supported by studies on reaction kinetics and mechanisms. The lack of a systematic organization of the knowledge base has somehow limited the possibility of new developments in the field. At the turn of the twenty-first century, the emergence of nanoscience and nanotechnology and the rising expectations for better performing and multifunctional materials are forcing scientists and technologists to cross the boundaries between disciplines and to invent new ways of manufacturing materials. Designing polymeric materials at the nanoscale joins the world of chemistry and macromolecules with the world of nanomaterials and nanotechologies, since "manipulation" of materials at the nanoscale, *i.e.* at the molecular level, is often required to achieve nano-enhanced performance. This is facilitated by using focused energy sources, such as energetic photons or electron beams. Radiation chemistry and radiation processing have a role in this field. To this aim, any research and development activities must progress along two parallel tracks: (i) the synthesis of new nanomaterials which clearly demonstrate the benefits, either in the manufacturing process or in their properties, stemming from the use of ionizing radiation and radiation chemistry; and (ii) the study of the mechanisms of reactions that are at the basis of the formation of nanostructures.

A clear understanding of the reasons behind the success or failure of past endeavours is a necessary tool for any future developments.

2. POLYMERIZATION IN AQUEOUS MEDIA

2.1. GENERAL CONSIDERATIONS

Before examining more in detail the different possible strategies to either synthetize or modify polymers in aqueous media by high energy irradiation, some basic concepts will be briefly recalled.

Radiation-initiated polymerizations can occur *via* either neutral free-radical or ionic-radical mechanisms. In aqueous systems, the neutral free-radical mechanism is ubiquitous since water is a universal ionic inhibitor. Ionizing radiation can initiate the polymerization by producing primary radicals in the solvent and in the monomer.

At a given time, the concentration of propagating radicals is the net result of the reactions that form them, such as the non-thermal initiation and radical transfer toward the monomer or polymer, and the reactions that consume them, such as termination by combination or disproportionation. Since termination depends on the probability that two radicals meet, it is governed by the concentration of radicals and then on the instantaneous concentration of primary radicals formed, hence on the dose rate. Moreover since there is a competition between primary radical propagation and mutual recombination, termination markedly depends on the concentration of the organic substrate.

The availability of different type of irradiation sources (gamma cells, electron accelerators) and irradiation conditions can give rise to a wide range of accessible dose rates. This, together with the possibility of choosing either diluted or concentrated solutions of monomer and/or polymers, leads to a great variety of polymerization rates and final products.

A distinction between reactions occurring in dilute systems and in concentrated systems is made. Relatively low dose rates processes, such as those carried out with gamma sources, and high dose rate processes from electron beam accelerators will also be looked at for their impact on the reaction mechanisms and product properties.

2.2. THE ROLE OF WATER RADIOLYSIS IN INITIATING POLYMERIZATION

In dilute aqueous solutions, water absorbs ionizing radiation. In concentrated solutions or mixtures, the radiation energy is absorbed by both the solvent and the solutes, leading to both “direct” and “indirect” effects. Direct effects are related to the energy directly absorbed by the solute, while indirect effects, mainly when dealing with dilute solutions, are the consequences of reactions between aqueous radiolysis products and solutes.

Understanding water radiolysis and knowing the G-values for the radiolysis products of water are of importance for a proper process design. Even small changes in the composition of water, such as those responsible for changes in pH, or the presence of dissolved molecular oxygen, can significantly affect the G-values. For instance, solvated electrons, e^-_{aq}, are protonated at low pH, thus increasing the yield of hydrogen atoms, while at very high pH, the hydroxyl radical ($^\bullet OH$) can undergo deprotonation to produce the less reactive $O^{\bullet -}$. Different oxidizing species are produced in aerated or O_2-saturated solutions, such as hydroperoxyl radicals ($HO_2^\bullet$) from hydrogen and a superoxide radical anion ($O_2^{\bullet -}$) from the solvated electron, the latter being the deprotonated form of the hydroperoxyl radical [3]. These two formed species are considerably weaker oxidants than hydroxyl radicals. Hence, depending on the material, the final yield of oxidized products may not be significantly altered by the presence of O_2.

Oxygen can also react with propagating radicals leading to a reaction pathway, which involves the formation of peroxides and their possible evolution towards the formation of aldehydes, ketones and carboxyl groups. To avoid the influence of O_2, solutions can be purged with inert gas such as N_2 or Ar.

Elevated solute concentrations can also induce a change in G-values if a competition takes place between the reactions involving solutes and the primary radiation chemical reactions [4-6].

Hydroxyl radicals under deaerated conditions and hydroperoxyl radicals, in the presence of oxygen from air, are the main species generating polymer radicals. The reactions between unsaturated and saturated carbons, as in vinyl and acrylic monomers or polymers and $^\bullet OH$ or $HO_2^\bullet$ radicals are much faster than those with solvated electrons so that their effects in free radical polymerization can often be ignored [7]. Hydroxyl and hydroperoxyl radicals are neutral, so their initiation can be efficient without the need of electrolytes and buffers which are often required for most chemical systems.

When a higher concentration of initiating radicals is needed, solutions are saturated with nitrous oxide. Under these conditions solvated electrons give rise to hydroxyl radicals, thus doubling their yield. However, since a hydroxyl radical is not very selective in its reactions, it can react with many organic materials and functional groups *via* addition, hydrogen abstraction and/or electron transfer, resulting in a multitude of products and reducing the process selectivity.

In order to improve selectivity, the hydroxyl radical can be converted to a more selective one-electron oxidant by the addition of N_3^- or HCO_3^-, which will react with the hydroxyl radical according to reactions (1) and (2) [8, 9]:

$$^\bullet OH + N_3^- \rightarrow HO^- + N_3^\bullet \qquad (1)$$

$$^\bullet OH + HCO_3^- \rightarrow H_2O + CO_3^{\bullet -} \qquad (2)$$

Strong oxidizing conditions can be produced by adding $S_2O_8^{2-}$ to convert the solvated electron to $SO_4^{\bullet -}$ according to reaction (3):

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet -} \qquad (3)$$

2.3. THE REACTION OF INITIATING RADICALS WITH ORGANIC SOLUTES

Organic solutes react with the radiolysis products of water predominantly *via* abstraction or addition reactions. Table 1 gives an overview of the reactivity of primary radicals toward low molecular weight molecules which have some specific functional groups. A very concise description of the reactivity of hydroxyl radicals with a variety of materials is given.

Hydroxyl radicals are strongly electrophilic; as a consequence, the rates of hydrogen abstraction reactions from aliphatic and aromatic carbons are generally very high. They become lower when electron-withdrawing groups, such as carboxyls, carbonyls, nitriles, nitro, esters, amides, are present in aliphatic compounds. The aromatic analogues have comparatively higher reaction rates. Electron repelling groups, such as the amino group in organic amines, increase the reactivity.

Electrophilicity is also responsible for the addition of hydroxyl radicals to unsaturated bonds, both in alkenes and arenes, which often takes place in competition with hydrogen abstraction. As an example, with propylene as the material, the formation of the OH adduct (the addition of hydroxyl radicals to double bonds) is prevalent rather than the formation of the allyl radicals through hydrogen abstraction [11]. With alkenes containing more labile, secondary and tertiary allylic C–H bonds, having higher free radical stability, hydrogen abstraction can become the dominating reaction [12]. With aromatic compounds, the dominant reaction is the addition to the aromatic ring leading to intermediate cyclohexadienyl type radicals. For example, with toluene the cyclohexadienyl intermediates, cresol or the benzyl radicals are formed, depending on the pH of the solution [13]. Polarity is not the only factor affecting the reactivity of $^{\bullet}$OH radicals. The resonance stabilization energy of the radical products and their bond enthalpy changes contribute to introducing further selectivity. For instance, the reactivity for the hydrogen abstraction from alkanes is reported to increase in the order: primary < secondary < tertiary 1:5.4:9.9 (for gas phase reactions) [14].

The organic radicals formed will further evolve toward stable products by addition or abstraction reactions (that change the properties of the radical) and by combination or disproportionation reactions, which give rise to molecular or ionic compounds which do not carry an unpaired electron. In the presence of molecular oxygen, oxygen readily adds to free carbon-centred radicals giving rise to relatively stable peroxyl radicals, depending on the structure of the original alkyl radical. This will further evolve towards the formation of oxidation products. Disproportionation is an alternative to or competitive with combination, giving rise to two stable molecules, one of which is unsaturated. These reactions are briefly presented in Table 2.

Table 1. Reactivity of primary radicals towards low molecular weight molecules bearing specific functional groups. The symbols used to represent rate constant ranges ($dm^3 \cdot mol^{-1} \cdot s^{-1}$) are: +++ $k > 10^9$, ++ $k = 10^7$-10^9, + $k = 10^5$-10^7, – $k < 10^5$ [3, 10].

Molecule bearing a specific functional group	Rate constant range		
	e^-_{aq}	$H^\bullet$	$^\bullet OH$
H_3O^+	+++	–	–
O_2	+++	+++	–
Saturated hydrocarbon	–	++	+++
Unsaturated hydrocarbon	–	+++	+++
Aromatic hydrocarbon	+	+++	+++
Pyrimidine	+++	++	+++
Nitrile	++[a]	++	++[b]
Carbonyl	+++	+	++[b]
Carboxyl	++[a]	++	++[b]
Ester	++	+	++[b]
Amide	++	++	++
Amine	+	++	+++
Nitro	+++	++	–
Alcohol	–	++	+++
Ether	–	++	++
Chloride	++[c]	++	–
Bromide	+++	++	–
Iodide	+++	+++	–
Thiol[d]	+++	++	+++
Disulfide	+++	++	+++

[a] Range valid for low molecular weight aliphatic compounds; rate constants may exceed 10^9 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ for the aromatic analogues (7.1 × 10^9 for benzoic acid, 1.9 × 10^9 for benzonitrile).

[b] Range valid for low molecular weight aliphatic compounds; rate constants may exceed 10^9 $dm^3 \cdot mol^{-1} \cdot s^{-1}$ for the aromatic analogues (4.5 × 10^9 for benzoic acid; 4.4 × 10^9 for benzonitrile).

[c] The rate constant may exceed the range assigned with increasing the number of chlorine substituents.

[d] pH-dependent.

Table 2. Generic reactions describing the development of organic radicals in aqueous solutions. (Adapted from Ref. [3]).

Reaction	Description
$2RH^{\bullet} \rightarrow RH{-}RH$	Combination to give dimeric product
$2RH^{\bullet} \rightarrow RH_2 + R$	Disproportionation to give an insaturated product
$RH^{\bullet} + O_2 \rightarrow RHO_2^{\bullet}$	Reaction with molecular oxygen
$2RHO_2^{\bullet} \rightarrow RO + RHOH + O_2$	Formation of stable oxygenated products, *e.g.* carbonyl compounds, alcohols
$2RHO_2^{\bullet} \rightarrow RH{-}O{-}O{-}RH + O_2$	Formation of organic peroxide

2.4. POLYMERIZATIONS IN HOMOGENEOUS AND HETEROGENEOUS AQUEOUS SYSTEMS

Polymerizations can rely on a solvent and be carried out in solution, when both monomers and polymers are soluble in the reaction medium, or, in heterogeneous systems, such as emulsions or dispersions. The advantages of making use of a solvent are several: (i) the heat of reaction is efficiently absorbed by the solvent, therefore the reaction rate and polymer molecular weight can be better controlled as opposed to broadening of the molecular weight distribution, and thermally labile substances (as monomers or additives) can be incorporated directly into the solution; and (ii) the viscosity of the reaction mixture is reduced, which may prevent autocatalytic polymerization and gel effects at high conversion rates (the Trommsdorf effect). There are limits to water-soluble monomers and the possible contamination of the products from surfactants or other solutes which can be the drawbacks with respect to bulk polymerization.

Water is a very good solvent: it is inexpensive and non-toxic, it dissolves more substances than any other solvent and it has a very important role in radiation-initiated reactions. On the other hand, its relatively high heat of vaporization and high normal boiling point are responsible for significant costs for its removal by evaporation and/or by degradation of the product properties. Furthermore, water purification for recycling or before disposal can be expensive. Polymerizations in aqueous media are definitely preferred in applications where the water can be considered part of the product (*e.g.* hydrogels, water-based paints, polymeric nanoparticles for biomedical applications, *etc*.). High conversion rates, in order to avoid undesired lengthy purification processes, are also highly desirable.

The physicochemical properties of the monomer and its polymer as well as the target physical form and use of the product dictate whether the reaction system should be homogeneous or heterogeneous.

Solution polymerization is possible for water-soluble monomers and polymers, such as vinyl pyrrolidone, acrylonitrile, vinyl acetate, acrylic acid and esters of acrylic acids.

Partially soluble or insoluble monomers can be polymerized in the emulsion state. In the conventional approach, direct emulsion polymerization is a free radical polymerization process which involves emulsification of a relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by thermal initiation with either a water insoluble initiator (*e.g.* sodium persulphate (NaPS)) or an oil soluble initiator (*e.g.* azobisisobutyronitrile (AIBN)). The surfactant used for stabilizing the monomer droplets (one type of molecule or, more often, a mixture) is generally also effective in stabilizing the final polymer particles. This has been the predominant emulsion polymerization process for vinyl acetate, chloroprene, butadiene/styrene/acrylonitrile copolymers and several acrylates. It has also been used for producing methyl methacrylate, vinyl chloride, vinylidene chloride and styrene emulsion polymers [15].

The finely divided, stable latexes and dispersions find a wide range of uses such as for synthetic rubbers and thermoplastics, coatings, adhesives, rheological modifiers, plastic pigments, standards for the calibration of instruments, immunodiagnosis tests, polymeric supports for the purification of proteins and drug delivery systems, *etc*. Conventional thermal activation cannot be used for polymers whose glass transition temperature is lower than the polymerization temperature, otherwise aggregation will occur. It requires separation and purification of the polymer from the surfactant, or a contaminated product must be acceptable for the end-use.

Dispersion polymerization is carried out by suspending relatively large droplets (10-1000 μm) of insoluble monomers along with the catalyst in water. The water to monomer weight ratio varies from 1:1 to 4:1 in most polymerizations. The monomer droplets are prevented from coalescing by stirring in the presence of stabilizers. Suspension stabilizers are typically used in less than 0.1 wt% of the aqueous phase. Two types of stabilizers are used: (i) water soluble polymers such as poly(vinyl alcohol), sodium polystyrene sulphonate, hydroxypropyl cellulose, *etc*., or (ii) water insoluble inorganic compounds such as talc, barium sulphate, kaolin, calcium phosphate, *etc*.

3. POLYMERIZATIONS IN HOMOGENEOUS AQUEOUS SYSTEMS

3.1. RADIATION POLYMERIZATION OF DILUTE AQUEOUS SOLUTIONS OF VINYL MONOMERS

The polymerization of dilute monomer solutions are of little practical importance in the production of many vinyl polymers. Most of these polymers are commodity plastics with high volume production of different grades to suit various end-use applications. The use of dilute monomer solutions is not a viable option for mass production. Yet, such solutions have been of fundamental importance in understanding the radiolysis of water and in demonstrating that free radicals were produced from water (the monomers then act as free radical scavengers) [16]. Indeed, the presence of hydroxyl groups in the polymer, and of deuterium or tritium when using heavy water or radioactive water, was used to support the formation of $^{\bullet}$OH radicals and H from water radiolysis.

Experiments with monomers have been used to determine the G-values of radical products from water radiolysis. If all the initiating radicals derive from water radiolysis (at a low monomer concentration) and the mechanism of chain termination is known (in terms of the ratio between combination and disproportionation and relative importance of termination by primary radicals), the average number of polymer chains formed for a given dose can be used to determine the number of primary radicals and thereby their G-values.

Another reason for doing radiation-initiated polymerization of dilute aqueous solutions of vinyl monomers has been to study the kinetics of their polymerization reactions. The most instructive studies have been carried out using monomer/polymer systems that are water soluble, *e.g.* acrylamide, where the system is homogeneous throughout the polymerization process. The dependence of the polymerization reaction rate on monomer concentration and dose rate have been investigated. Radiation-initiated polymerization of polyacrylamide presented some expected and some anomalous results. The most common observations were:

- The polymerization rate as function of the time showed an induction (or inhibition) period followed by an acceleration period, up to a maximum value that remained constant until all of the monomer was depleted.
- Post-irradiation effects were observed: after irradiation, the reaction continued, yet at slow rate.
- The reaction order with respect to the monomer was equal to one or slightly higher than one (depending on the experimental conditions).
- The square-root law for the dependence on dose rate was generally observed but exponents higher than 0.5 were found for low dose rates.

The reaction mechanism that was proposed is the following:

$$H_2O + \gamma\text{-rays} \rightarrow R^{\bullet};\;\; R_i \tag{4}$$

$$R^{\bullet} + M \rightarrow RM^{\bullet};\;\; k[R^{\bullet}][M] \tag{5}$$

$$RM_n^{\bullet} + M \rightarrow RM_{n+1}^{\bullet};\;\; k_p[RM^{\bullet}][M] \tag{6}$$

$$RM_n^{\bullet} + RM_m^{\bullet} \rightarrow P_{n+m} \text{ or } P_n + P_m;\;\; k_\tau[RM^{\bullet}]^2 \tag{7}$$

The following assumptions have been made: (i) the initiation is caused only by the free radicals generated by water radiolysis and (ii) the primary radicals do not compete with the monomer in the propagation reaction or in growing the polymer chains to termination.

The general rate equation that can be derived, assuming steady-state conditions (chains are initiated at the same rate as they are terminated) and that the combination of primary radicals is negligible, is

$$R = k_p k_\tau^{-1/2} R_i^{1/2}[M] \tag{8}$$

Deviation from the above equation has been observed on several occasions. In some circumstances, polymer-water interactions were taken into account. If water is not a good solvent for propagating polymer chains, the polymer chains may take a coiled conformation, especially at low dose rates when higher molecular weights can be achieved. Therefore, radicals may not be available for chain termination. Other researchers have proposed that the formation of more stable radicals than the acetamide one, which will not easily react with either the double bond of the monomer or with another free radical (buried amongst the polymer radicals), was at the basis of the deviations [16]. None of the two hypotheses were supported by experimental data.

Ferric salts (*e.g.* ferric perchlorate) can be added to aqueous solutions to facilitate chain propagation and to efficiently terminate polymerization, according to the equation:

$$RM_n^{\bullet} + Fe^{3+} + H_2O \rightarrow P_n + Fe^{2+} + H_2O^{+};\;\; k_\tau'[RM_n^{\bullet}][Fe^{3+}] \tag{9}$$

Assuming stationary state conditions, the overall polymerization rate and average number molecular weight become:

$$R = \frac{k_p R_i [M]}{k_\tau '[Fe^{3+}]};\;\; \overline{P}_n = \frac{k_p[M]}{k_\tau '[Fe^{3+}]} \tag{10}$$

The overall rate of polymerization and the average molecular weight decrease with an increasing concentration of ferric salts.

3.2. RADIATION-INDUCED POLYMERIZATION OF CONCENTRATED MONOMER SOLUTIONS

With concentrated monomer solutions, initiation is more complex and generally a less understood process. Hydroxyl radicals and hydrogen can be still involved in the initiation, but a direct effect of radiation on the monomer cannot be ruled out. Furthermore, “energy transfer” effects are also important.

Therefore, it cannot be assumed that free radicals are being formed independently from monomer and water. The relation

$$G(R^{\bullet}) = G(OH^{\bullet}) + G(H^{\bullet}) + G(M^{\bullet}) \qquad (11)$$

may or may not be true.

Figure 1 illustrates a typical experimental curve for reaction rate as function of monomer concentration for the gamma-induced polymerization of aqueous acrylamide solutions from dilute to concentrated. This reaction shows an increase in reaction rate with monomer for concentrations below around 2 M and a drop in reaction rate as the concentration further increased. Acceleration and post-irradiation effects were also observed. At high concentrations, the solutions were very viscous and a "gel effect" could happen, reducing the efficiency of the termination reactions. White spots were also reported for conversions above 10%, which further grew to fill the entire volume for higher conversion values. Under these conditions, the polymerization resulted in a white, opaque polymer that looked like "popcorn". Above 6 M, the monomer is no longer soluble, so the curve is truncated.

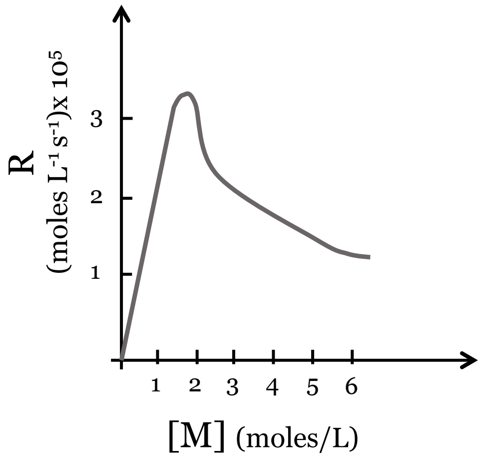


Fig.1. Influence of monomer concentration on the rate of gamma polymerization of acrylamide in aqueous solutions at a dose rate of 0.036 rad/s (= 0.36 mGy/s). (Adapted from Ref. [17]).

As for the dependence of polymerization rate on dose rate, at low dose rates, the rate of polymerization is proportional to the square root of the dose rate if the polymer remains in solution. When the dose rate is high and the monomer concentration low, the concentration of initiating radicals rises and termination starts to occur by a reaction between the growing polymer chains and the initiating radicals. The greater this effect, the lower the exponent that expresses the dependence on dose rate. If the polymer precipitates out from solution, there is a marked increase in the reaction rate (autoacceleration). The rate of polymerization increases above that expected from the (dose rate)$^{0.5}$ law. There are also significant post-irradiation effects, due to the formation of "buried" radicals. If the dose rates are very high (*e.g.* 10 000 rad/s), termination proceeds very rapidly and much of the product consists of a water-soluble material containing only one or two monomer units.

Although these different situations can be qualitatively understood, a detailed mechanism of these processes has not yet been developed [18].

4. POLYMERIZATIONS IN HETEROGENEOUS AQUEOUS SYSTEMS

4.1. RADIATION-INDUCED FREE RADICAL POLYMERIZATION IN OIL IN WATER EMULSIONS

Water-born polymer colloids have long been the focus of academic and industrial research [19-23]. In particular, ^{60}Co gamma ray-initiated emulsion polymerization has been discussed in the literature since the 1960s [24]. Radiation-induced free radical polymerization in microemulsions has been reported in the more recent years [25-29]. Focus will be on only oil in water (o/w) emulsions and on microemulsions. Inverse emulsions (water in oil, w/o), where the continuous phase is an organic solvent, are not an option for radiation-induced polymerizations, because of the interference of the organic solvent radiolysis products with the polymerization reaction.

Emulsion polymerization is a rather complex process where the steps of particle nucleation, growth and stabilization are affected by both the polymerization kinetics and by the various colloidal phenomena that occur simultaneously. Chemical reactions and colloidal phenomena are interlaced and mutually interfering.

The starting condition for emulsion polymerization is an oil-in-water emulsion, which consists of the monomer or a mixture of monomers, representing the dispersed oil phase, an aqueous solution as continuous water phase, and surfactant molecules in the form micellar aggregates or located at the oil/water interface (surface of the monomer droplets). The role of the surfactant is to reduce the surface tension of the oil phase and to prevent coalescence of the polymer particles being formed during their nucleation and growth, as well as to provide stability to the resulting latex.

The monomer can be completely water insoluble or partially soluble. In this latter case, it is partitioned in the continuous and dispersed phase. In general, monomer-swollen micelles are the principal loci for the initiation (micellar or "heterogeneous nucleation"). Polymerization does not likely take place inside the monomer droplets because of their relatively smaller surface area with respect to the micelles and the low capturing ability of the initiating free radicals. Homogeneous nucleation becomes significant only for systems with low surfactant concentration and/or for the polymerization of partially hydrophilic monomers. The radical-visited micelles grow over time being refurbished by monomer and surfactant from the other micelles. The particle nucleation stage generally ends with the disappearance of the micelles. The number of growing particles is then fixed and polymerization proceeds in the polymer particles at a constant rate (and homogeneously). The monomer concentration in the particles is maintained at a constant concentration by diffusion of the monomer from the monomer droplets through the solvent. When the monomer droplets disappear in the system, the particle growth stage ends, the reaction rate decreases and the conversion reaches a plateau.

During polymerization, processing conditions must be carefully controlled, since an external input in the form of mechanical energy (stirring, sonication, *etc*.) is required to disperse the oil phase in the water. The generation of particle nuclei during the early stage of the polymerization plays a crucial role in determining the final latex particle size, particle size distribution and the overall quality of the latex product.

The control of the particle nucleation process is a very challenging task. It requires an efficient transport of the initiating radicals, monomers and surfactant molecules to the growing polymer chains through the continuous medium and across the surfactant layer. Prolonged nucleation may result in products with a very broad particle size distribution and broad molecular weight distribution. The supply of monomer and of surfactant by the emulsified monomer droplets (acting as a reservoir) to the monomer-swollen polymer particles (primary reaction loci) is a key factor that governs particle growth stage. The distribution of growing chains among the discrete monomer-swollen polymer particles can greatly reduce the probability of their bimolecular termination and results in faster polymerization rates (with respect to solution polymerization) and in polymers with higher molecular weight. This last feature is often sought in emulsion polymerization.

One main advantage of using irradiation to initiate polymerization is that initiation is temperature independent and can be carried out at relatively low temperatures, below the T_g of the polymer particles (thus reducing the risk of their aggregation), and with limited or no risk of runaway reactions caused by the exothermic heat released by the polymerization reaction. Propagation, that is addition of monomer to the growing chain, is less affected by temperature than termination. Therefore polymers with higher molecular weight can be produced by keeping the reaction temperature relatively low.

Radiation can generate a virtually unlimited range of radical fluxes, which can be easily monitored during the course of the polymerization reaction. The ability to control the initiating radical concentration enables a better control of the increase in molecular weight and particle size distribution.

There are also some drawbacks. Irradiation can induce chemical changes in the formed polymer and in the surfactant. The polymer can undergo branching, crosslinking or changes in chemical functionality. The surfactant can be partially grafted onto the polymer, thus changing its structure and properties.

Water soluble initiators generate radicals only in the aqueous phase, whereas irradiation can generate radicals in both phases. So, it is important to know and compare the G-values of the radicals in the two phases: for monomers like styrene, G(radicals) in the monomer phase are almost one order of magnitude lower than in the aqueous phase, whereas for vinyl acetate these values are comparable. This last situation complicates the modelling of these reaction systems.

Finally, difficulties can be encountered in ensuring a homogeneous dose rate within a stirred tank on an industrial scale. For this reason, microemulsions are easier to handle, since stirring is not crucial to controlling latex particle size.

4.2. RADIATION-INDUCED FREE RADICAL POLYMERIZATION IN OIL IN WATER MICROEMULSIONS

Microemulsions are thermodynamically stable and optically transparent systems, which consist of monomer droplets (varying from 10 to 100 nm) dispersed in water or alcohol/water solutions or mixtures with the aid of an emulsifier at a concentration that exceeds its critical micelle concentration. Their classification as a heterogeneous system may not be correct. Nonetheless, polymerization of a microemulsion leads to a phase separated, solid polymer with submicron-sized particles and is more analogous with emulsion polymerization than with solution polymerization. Also for their end-use applications, emulsion polymerizates are similar to those of their micron-scale analogues [30].

Monomers become distributed between the continuous aqueous phase and the micelles, depending on their solubility. Hydrophobic monomers, such as styrene or butyl acrylate, mostly distribute inside the micelles. More hydrophilic monomers, such as methyl methacrylate, can be present in both phases.

For monomers with low radical yield, water radiolysis products initiate the polymerization. When the nucleation of polymer particles inside the micelles predominates, the monomer-swollen micelles interacting with the initiating radicals act as nano-reactors and polymer chains propagate over time. The other micelles act as reservoirs of monomer and surfactant.

The polymerization rate *vs.* irradiation time (dose) has a typical bell-shape, as shown in Fig.2A. After an induction time, the rate increases, then reaches a maximum and finally decreases when the monomer is depleted. The induction period depends on the O_2 content and other impurities (*e.g.* polymerization

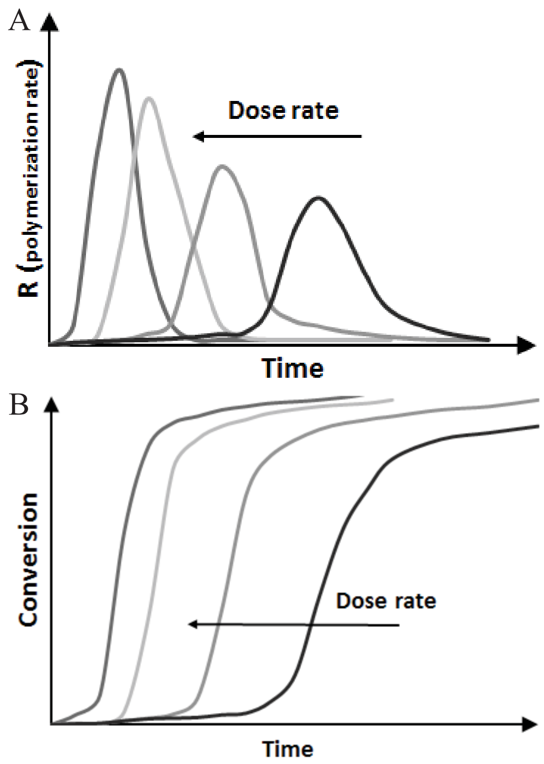


Fig.2. A – Polymerization rate as function of time at various dose rates, B – conversion as function of time at various dose rates.

retardants) present in the emulsion. Higher dose rate results in higher initiating radical concentrations, which results in faster particle nucleation (shorter incubation period) and an increased initial polymerization rate. The typical monomer conversion *vs.* irradiation time (dose) curve is S-shaped, as shown in Fig.2B. Monomer conversion reaches higher values at higher dose rates and generally higher than those attained by the use of chemical radical initiators.

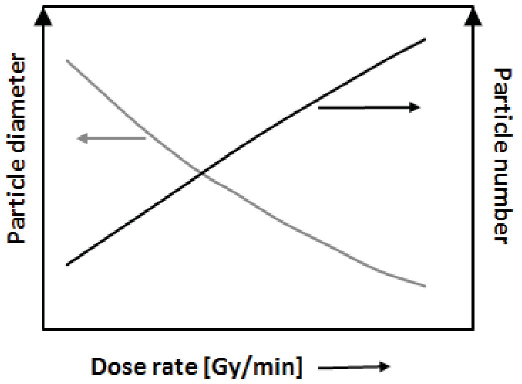


Fig.3. Effect of dose rate on the diameter and number of particles formed per unit of volume.

This is mainly due to a more homogeneous production of initiating radicals in the system [31].

Five to ten times higher molecular weight latexes are obtained by radiation-induced polymerization than for common microemulsion polymerization, since reactions are generally carried out at lower temperatures which favour propagation over termination [19].

The dose rate governs the rate of nucleation, *i.e.* the instantaneous concentration of "active" micelles. Therefore, an increase in dose rate generally leads to a decrease in the latex particle size and a relative increase in the number of particles, since dose rate increases the number of "active" polymer nuclei, as shown in Fig.3.

Only a few studies describe the variation of particle size and size distribution with absorbed dose or, in other terms, with monomer conversion [26-27]. At the very early stage of polymerization (low monomer conversion, < 10%), polymer nuclei are rapidly swollen by the monomer and they have their largest size (around 100 nm). When the polymerization further progresses, the size of the particles decrease as more growing particles are formed and the monomer is redistributed in the system. The larger swollen particles, that act as monomer reservoirs, decrease in size and the newly formed particles progressively develop. Newly nucleated particles can also form, especially when homogeneous nucleation is possible. When the system becomes depleted of monomer, there is no longer any further nucleation. This condition often leads to a reduced polydispersity. At very high conversions, there may be a slight increase in dimensions due to particle aggregation and bridging. Nanoparticles with size in the range of a few tens to a few hundred of nanometers can be produced.

4.3. RADIATION-INDUCED DISPERSION POLYMERIZATION

In dispersion polymerization, the starting system is a clear homogeneous phase that becomes turbid and heterogeneous at the early stage of polymerization, due to the reduced solubility of the growing polymer chains in the aqueous medium, where the monomer is still soluble. Stabilizers, monomer initiators, solvents and their concentrations, all play important roles in determining the ultimate particle size and the molecular weight of the product [32-34]. The solvent must be a good solvent for both the stabilizer and the monomer used, but a poor solvent for the formed polymer. Alcohols (ethanol or isopropanol) are often added to increase the solubility of the monomer and are involved in chain transfer reactions that can reduce the polymerization rate and help to control the growth of polymer molecular weight.

The typical monomer conversion *vs.* irradiation time curve in dispersion polymerization is also S-shaped. After a short initial period, the polymerization rate generally increases, almost linearly, up to a maximum, and then it decreases [35-38]. At an early polymerization stage, the system is homogeneous since polymerization occurs mainly in the continuous phase. When chains have grown to a length that makes them insoluble, then particle nucleation takes place. This situation is attained at relatively low monomer conversions, generally lower than 10%, for radiation-induced polymerization, which is higher than for thermal processes, which are generally only 2-5%. Indeed, the induction period and the nucleation phase are both quite short, since high energy irradiation can produce free radicals homogeneously in the system and at a very high rate, producing a metastable "supersaturated" solution and "delaying" the onset of phase separation. A rapid initiation and short nucleation phase are beneficial in order to obtain monodispersed systems: the particle number is soon fixed, and the particles grow independently and simultaneously [39]. As the monomer conversion increases, the locus of the reaction becomes the particle through the capture of oligomeric radicals from the continuous phase. Because of the higher viscosity within the particle, the rate of propagation becomes higher than the rate of termination, with termination being a diffusion controlled process, and the polymer molecular weight increases. This phenomenon is known as the "gel effect", similar to what happens in "bulk" polymerization.

For radiation-induced dispersion polymerization differs from conventional chemical polymerization in that stirring during irradiation is often not beneficial. The contact between two particles containing active propagating sites may lead to irreversible agglomeration. Therefore, it is essential to keep the solution stationary during irradiation, to ensure the maximum average distance between the particles. Some graft-copolymerization of the stabilizer may occur due to the low selectivity of primary radicals. The highest yields for grafting are expected on those polymer-monomer combinations in which the free radical yield of the polymer ($G(P^\circ)$) is much larger than that of the monomer M ($G(M^\circ)$) [23]. Therefore, by choosing a proper stabilized polymer-monomer combination, chemical grafting can be favoured over physical adsorption. Furthermore, since initiation is a continuous process during irradiation, by prolonging the irradiation, polymeric surfactant grafting, that was not initially favoured over monomer homopolymerization, may compete as a reaction product. This approach is particularly appealing if the polymeric dispersant can have a role in generating nanoparticles.

5. POLYMER CROSSLINKING IN AQUEOUS MEDIA

5.1. RADIATION PROCESSING FOR THE PRODUCTION OF HYDROGELS FOR BIOMEDICAL APPLICATIONS

Hydrogels are polymeric materials that can absorb significant amounts of water, because of their hydrophilic functional groups, without dissolving in water, since there are intermolecular bonds that link the different chains together. When in contact with aqueous solutions, hydrogels can swell up to a characteristic "equilibrium swelling" value, that corresponds to a balance between the osmotic pressure that drives water inside the network and the retroactive elastic forces that arise from the stretched polymeric segments between the crosslinks on swelling. Crosslinking is "chemical" when there are covalent bonds formed. Thus, the intermolecular bonds in hydrogels are called "chemical" or "permanent". The bonds between hydrogel molecules can also be "physical" or "non-permanent". These are due to electrostatic forces, hydrogen bonds, hydrophobic interactions or chain entanglements and the corresponding systems are called "physical" hydrogels or simply "gels". These interactions can be weakened by a modification of the physical and/or chemical properties of the environment (temperature, pH, salts, solvents), or by application of an external field (mechanical, electric, *etc.*), thus leading to partial or complete dissolution of the gel. Depending on their specific structure chemical (covalent) crosslinks can also be broken, *e.g.* through hydrolytic or enzymatic reactions. That is the case, for example, of ester bonds and amide bonds, the former being both hydrolytically and enzymatically labile, the latter degradable by the action of proteases.

Because of their general biocompatibility, and their soft consistency resembling many natural constituents of the human body, hydrogels, when in contact with body fluids and tissues, have been successfully used in several biomedical applications, as soft contact lenses, wound dressings, drug-delivery systems, super-absorbents, *etc*. More recent developments in the field deal with the design and synthesis of "smart" or "responsive" hydrogels capable of reacting to various environmental stimuli, such as temperature, pH, ionic strength, solute concentration, electric field, light, sound, *etc*. These materials can change their shape or volume as a response of a stimulus (by swelling or contracting), or undergo a specific, measurable change of a physical property (optical, electrical, *etc*.). For this ability, these "smart" hydrogels have been proposed as the actuators in drug delivery devices, in artificial muscles, in valves, *etc*. or as active materials used in sensing devices.

The interest in the use of radiation processing to produce hydrogels for biomedical applications began in the late 1960s as noted in the papers and patents published by Japanese and American scientists, among others Sakurada and Ikada, Kaetsu, and Hoffman [40-43]. Professor Janusz M. Rosiak and co-workers in Poland in the 1980s made a substantial contribution to this field by strengthening the underlying radiation chemistry and supporting the development of a commercial product in 1992 [44-46]. The simplicity of the process, the possibility of combining sterilization and crosslinking in a simultaneous operation, and the support of the International Atomic Energy Agency (IAEA) in promoting the technology transfer of the radiation production of hydrogel dressings and other hydrogels from the laboratory of Prof. Rosiak to many other laboratories around the world boosted the use of this technology in other countries.

Hydrogels can be synthetized by irradiating the solid polymer, the monomers (in bulk or in solution) or starting from aqueous solutions of a polymer. The irradiation of hydrophilic polymers in the dry form requires a pre-moulding step and much higher doses of ionizing radiation compared to irradiation in solution. Similar to other fields where radiation-inducing crosslinking is performed (coatings, adhesives and matrices of fiber-reinforced composites), difficulties may be encountered in obtaining homogeneous macroscopic networks when irradiation is performed in the solid state. It may be difficult to fully remove the oxygen that can promote unwanted side reactions.

Irradiation of some monomers in aqueous solutions can lead to polymerization and simultaneous crosslinking. Multifunctional monomers are often used to increase the degree of crosslinking. Particular attention must be given to purify the product of unreacted monomers, should the monomers be harmful or toxic. During irradiation many consecutive and parallel reactions occur, making the system rather complicated and difficult to describe even qualitatively.

There are clear advantages to initiating crosslinking in already formed polymers in the form of aqueous solutions. Indirect effects can help reducing the gel dose. Hydrogels can be produced starting from non-toxic and chemically stable polymers which lead to very pure products.

5.2. RADIATION-INDUCED POLYMER CROSSLINKING IN CONCENTRATED AQUEOUS SOLUTIONS

Since the demonstration by Charlesby and Alexander in the late 1950s [47, 48], it has been known that aqueous solutions of several crosslinking type polymers transform into macroscopic gels under high energy irradiation, especially if irradiated under deaerated conditions. It was also known that no gel was observed if the polymer concentration was lower than a certain value, which depends on factors such as the type of polymer, its degree of polymerization and the composition of the solvent. When the concentration is above this threshold value, gelation occurs suddenly and the irradiation dose required for incipient gelation (gel dose, Dg) decreases rapidly with increasing concentration. After reaching a minimum, Dg increases again, yet slowly. The gelation dose is generally determined from the sudden changes in viscosity, the degree of swelling (weight of a swollen sample compared to the weight of a dry sample) or the amount of sol fraction (the weight of the dry soluble fraction compared to the weight of the initial dry polymer), which occur at gel point. This critical concentration corresponds to the concentration at which polymer chains in solution start to intertwine.

Free radicals (hydroxyl radicals and hydrogen atoms) can be formed by water radiolysis. They can be transferred to the polymer by hydrogen abstraction, if the polymer is a fully saturated and/or by addition to double bonds present as the unsaturation in the polymer. Because of the high reactivity of primary radicals, hydrogen abstraction is a non-selective process; therefore, different kinds of macroradicals may form. The position of radicals in the polymer may also change due to intramolecular hydrogen abstraction and/or addition reactions [49, 50]. Direct effects such as the radiolysis of polymer, have to be taken into account at high polymer concentrations.

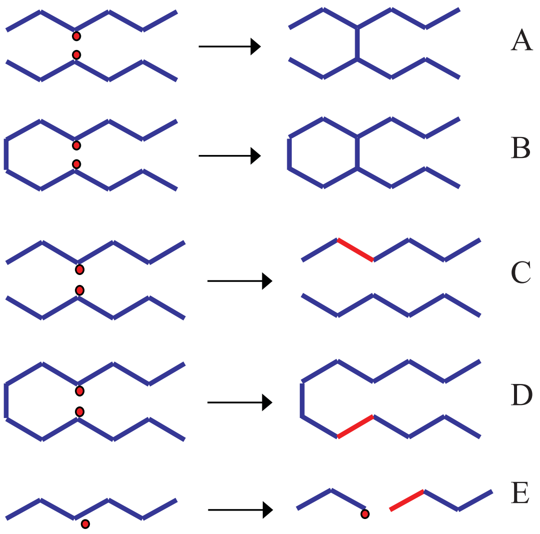


Fig.4. Schematic representation of all possible reactions producing macroradicals: A – intermolecular combination; B – intramolecular combination; C – intermolecular disproportionation; D – intramolecular disproportionation; E – chain scission. The segments in blue represent saturated bonds, the segments in red represent unsaturation.

Macroradicals are mainly involved in termination reactions (inter and/or intramolecular crosslinking and disproportionation), or propagation reactions (hydrogen transfer and chain scission). Hydrogen transfer reactions will only change the position of the radical centre and its reactivity, but will not affect the molecular weight of the polymer. Figure 4 is a schematic of all of the possible reactions that can produce macroradicals (excluding hydrogen transfer reactions).

Intermolecular termination reactions are diffusion controlled reactions that are without an activation barrier and involve two separated entities. They are bimolecular processes following second order kinetics with a reaction rate that can be expressed as:

$$-d[P\bullet]/dt = 2k_2[P\bullet]^2 \tag{12}$$

where P• is the instantaneous macroradical concentration and k_2 is the second order rate constant.

Compared to the starting linear polymer, intermolecular crosslinking gives rise to a three-dimensional molecular structure, with an increase of molecular weight to infinity. Intramolecular crosslinking causes changes in the polymer conformation and reduces segmental mobility. Disproportionation reactions do not affect the polymer molecular weight, but change the polymer chemical structure by introducing unsaturation that can further react with radicals generated upon irradiation. Chain scission results in a reduction of molecular weight of the polymer, leading to degradation. Scission reaction rates generally follow first order kinetics [50].

The progression of macroradical towards crosslinking or chain scissioning essentially depends on the chemical structure of the polymer even if these two processes compete. Polyvinylpyrrolidone (PVP) and poly(ethylene oxide) (PEO) mainly undergo crosslinking, while polysaccharides mainly undergo chain scissioning. The relatively long lifetime of the formed radicals in polysaccharides and the limited flexibility of the polymer chains in solution make termination *via* chain scissioning favoured over crosslinking [51, 52]. Nevertheless, also for the crosslinking-type polymers the relative contribution of degradation with respect to crosslinking can significantly change during irradiation, due to structural modifications of the irradiated material, such as an increase in rigidity, functionalization due to oxidation, *etc*.

When the starting polymer is a polyelectrolyte (*e.g.* poly(acrylic acid) (PAA)), electrostatic repulsions establish between the ionized groups on the polymer chain, belonging to the same chain or to different chains. These repulsions can affect crosslinking in two opposite ways, by preventing the combination of polymer radicals and by favouring a chain extended conformation of the polymer chains, thus increasing the probability that the polymer segments of different chains can be in contact with each other.

The extent of repulsive forces can be controlled by pH (changes of ionization level) and by the presence of salts (charge screening effects). In Fig.5A, the gel dose as function of polymer concentration is plotted for an aqueous poly(acrylic acid) solution irradiated to varying degrees of ionization, α, achieved by adding different amounts of sodium hydroxide. When the degree of ionization increases, the repulsions increase as does the critical polymer concentration for incipient gelation, as shown in Fig.5B. Figures 5C and D show the influence of NaCl in the solution. Salt is beneficial to gelation up to a maximum value then it becomes detrimental. There is a minimum in curve

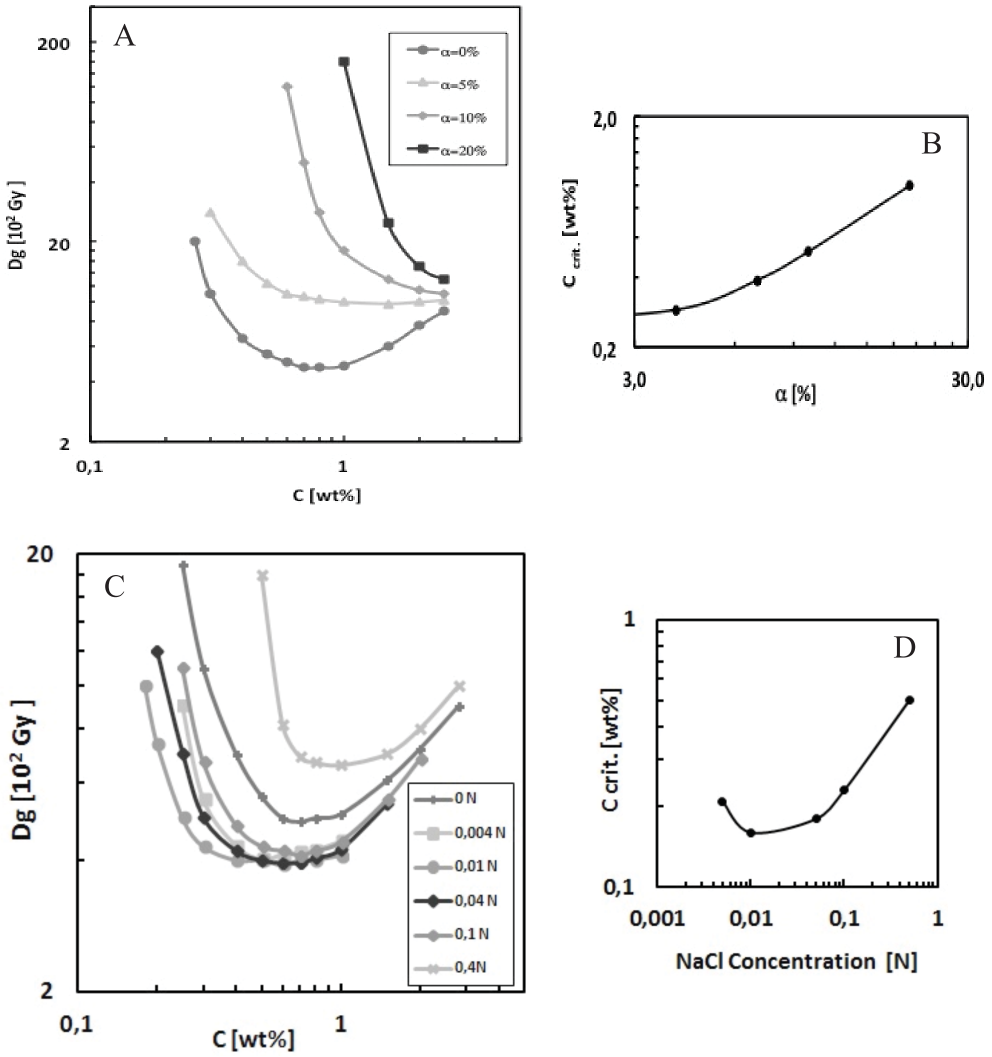


Fig.5. Irradiation of deaerated polyacrylic acid solutions with a ^{60}Co irradiator at 1.5 kGy/h: A – gelation dose, Dg, as function of polymer concentration for polyacrylic acid with various degrees of neutralization, α, and PAA irradiated in salt-free conditions; B – critical concentration for gel formation as function of the ionization degree and PAA irradiated in salt-free conditions; C – relation between gelation dose and polymer concentration for PAA in acid form with various amounts of NaCl; D – critical concentration for gel formation of PAA in acid form with various amounts of NaCl. (Adapted from Ref. [40]).

of critical concentration as function of salt concentration, as shown in Fig.5D. This is the result of the above described competing effects coming from repulsions between the ionized groups. At low salt concentration, the repulsion of fixed charges in the polymer prevents radical combination that then decreases so that gelation can occur more readily. If the NaCl concentration becomes too high, the polymer coils shrink and repulsion from groups on the same chain is screened so that macroscopic gelation by intermolecular crosslinking is no longer favoured.

If the radical recombination is prevented, the over-all extent of degradation will become larger. So, polyelectrolytes may undergo degradation more effectively when their charge density increases.

The relations between absorbed dose, sol fraction and gel fraction, gelation dose, the radiation dose at which the first "insoluble" fraction is formed, and the radiation yields for scissioning (Gs) and crosslinking (Gx) can be quantitatively described by the Charlesby-Pinner equation. This model relies on "sol-gel analysis" data and requires a number of simplifying assumptions for the description of the polymer system (random molecular weight distribution) and the reactions that occur (radiation crosslinking and scissioning occur at random and they are independent and only dependent on dose). The agreement between model and data is not always satisfactory for flexible polymers of the crosslinking type and several modifications of this equation have been proposed.

The Charlesby-Pinner equation and its consequences can be used only for the early stages of crosslinking. There is a point in the crosslinking process of a polymer when further crosslinking does not manifest itself in an increase of the degree of crosslinking (gel fraction) but in modifications of crosslinked density (reduction of the mesh size of the network, increase or decrease of the homogeneity in crosslinking points distribution). Other techniques than sol-gel analysis can be used for the calculation of Gx, *e.g.* by estimating the mesh size of the gel network through equilibrium swelling studies and/or by rheological measurements, or by assessing the homogeneity of the network by NMR techniques based on the measurements of the spin-spin relaxation time [44].

Typical examples of synthetic polymers used for macroscopic hydrogel formation by this method are poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO), poly(N-isopropylacrylamide) (PNIPAM), poly(acrylic acid) (PAA) and poly(vinyl methyl ether) (PVME), and their blends for producing interpenetrated networks. Gels obtained from PAA are responsive to pH and ionic strength, while gels from PNIPAM and PVME are temperature responsive. Variants of polyhydroxyethyl aspartamide (PHEA), a biodegradable synthetic polyamino acid, with side chains bearing both double bonds and carboxyl groups, have been transformed by irradiation into pH/electric field responsive hydrogels suitable for use with the stimuli triggered release of proteins [53, 54].

5.3. NANOPARTICLE FORMATION *VIA* INTRAMOLECULAR CROSSLINKING IN DILUTE AQUEOUS SOLUTIONS

Some of the possible approaches to the synthesis of hydrogel nanoparticles or nanogels (NGs), using radiation processing are covered. Indeed, the lack of inexpensive and well-established preparation techniques for such nanoparticles *via* conventional methods has been a main limitation to their development and use, despite of the great potential nanogels have as delivery devices for therapy and diagnosis.

The processes for the preparation of nanogels are either "top down", microfabrication techniques, such as photolithography, microfluidic, micro-molding, or "bottom up" self-assembly approaches, which rely on ionic or hydrophobic interactions [55, 56]. The former techniques require expensive equipment; the latter generally make recourse to nanocolloids as templates. Polymerization and crosslinking occur in the aqueous phase of an inverse nano/microemulsion. Surfactants and organic solvents are used to make a soft template, initiators and catalysts are required to drive the chemical reactions. These components can have a detrimental effect on the toxicological profile of the nanogels if they are not completely removed after synthesis. Product purification can, indeed, be time consuming, expensive and not particularly environmentally friendly.

Nanogels can be made by irradiating semi-diluted polymer aqueous solutions with pulsed electron beams without the use of surfactants as templates [57-59]. Polymers that mainly undergo crosslinking upon irradiation should be selected for this purpose [60-62]. The formation of nanogels with tailored particle size at the nanoscale is favoured by the prevalence of intramolecular crosslinking reactions over all the possible termination reactions that may occur during irradiation. This condition can be achieved at low polymer concentration

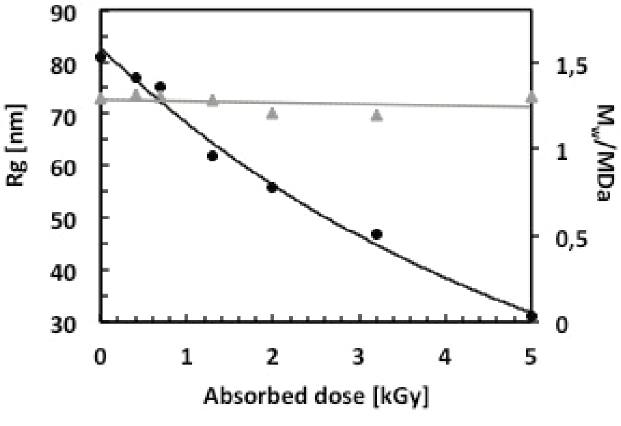


Fig.6. Molecular properties of electron beam irradiated PVP in aqueous solution as a function of an average absorbed dose; M_w of PVP = 1.3×10^6 g·mol^{-1}, dose/pulse = 320 Gy, pulse frequency = 0.5 Hz, pulse duration (width) = 2 μs. (Adapted from Ref. [60]).

(intermolecular termination is not favoured) and by the simultaneously formation of more than one radical on the same chain. For this reason, traditional nanogels are produced by carrying out irradiation under N_2O-saturated conditions, at high dose per pulse (high dose rates). These conditions ensure the simultaneous formation of many radicals per chain. The assumption is made that all the radicals formed in water (by water radiolysis) are efficiently scavenged by the polymer. For example, the irradiation of PVP at high dose per pulse (320 Gy/pulse) and low integrated doses (< 5 kGy) leads to nanogels with smaller radius of gyration (R_{gyr}) but the same weight average molecular weight (M_w) as the non-irradiated polymer. Intramolecular crosslinking explains the observed progressive contraction of the polymer coils at an increase of dose, as shown in Fig.6.

Interestingly, macroradical decay due to intramolecular crosslinking does not follow the homogeneous second order kinetics that is characteristic of intermolecular termination reactions. Since the reactive entities belong to the same polymer chain, the kinetics are governed by the mobility of the segments on which radicals are located, with a timescale and energy barrier depending on both their mutual distance and relative positions on the chain [63]. Since the formation of bonds within the polymer segments reduces their mobility and affects the kinetics of further reactions, the process cannot be described by a single activation energy or rate constant, but by their distributions. For this reason intramolecular crosslinking has been described as using a dispersive kinetics model, *i.e.* by recourse of "time-dependent" kinetic constants (non--homogeneous kinetic model) [64-66]. Intramolecular crosslinking is expected to become less effective with an increase of dose.

Recent studies [67-69] indicate that the final structure and properties of radiation-initiated crosslinked polymer nanogels are affected by several experimental parameters. They can be either related to the material system properties, such as polymer concentration, dynamics and diffusion kinetics of polymeric segments (affected, in turn, by temperature, nature of the solvent, polymer molecular weight distribution, *etc.*), type and half-life of formed macroradicals, or to irradiation process parameters, such as duration of each single pulse (*i.e.* pulse width), pulse repetition rate (or frequency), total dose delivered. In particular, polymer concentration has to be significantly lower than the critical chain overlap concentration, C* for dilute or semi-dilute systems. Dilute polymer conditions should ensure there is a sufficient distance between polymer chains so that a radical formed on a chain terminates by reaction with another radical formed on the same chain, before any encounter with radicals on different chains can occur during their random Brownian motion [66]. Concentration regimes depend on polymer molecular weight and chain conformation in solution. They can be experimentally determined, *e.g.* by measurements of zero-shear viscosity *vs.* polymer concentration. A log-log plot of zero-shear viscosity, $\eta°$, *vs.* polymer concentration is shown in Fig.7. For

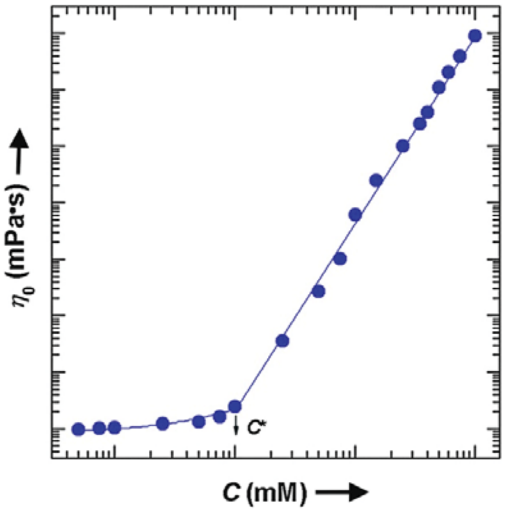


Fig.7. A typical concentration dependence of zero-shear viscosity for a polymer solution in a double logarithmic plot.

C << C*, the zero-shear viscosity is almost a constant (“dilute regime”) and the chains are isolated. For C >> C* (“concentrated regime”), the zero-shear viscosity generally follows a power law and coils are overlapping and strongly entangled. In the vicinity of C* (C < C*), in the “semi-dilute regime”, the viscosity rises more or less steeply with the concentration. Semi-dilute conditions are a characteristic feature of polymers and do not have analogies in solutions for low molecular weight materials where such regime does not exist.

All of the conditions that lead to a coiled conformation of polymer chains also favour intramolecular crosslinking. For example, in the case of PVP, the increase of the reaction temperature above 60°C gives rise to nanogels with lower molecular weight [69]. This effect is due to the break of the PVP–water hydrogen bonds, which are responsible for a chain extension conformation at lower temperatures. “Pure” intramolecular crosslinking leads to nanogel particles whose size and molecular weight are mainly controlled by the size and molecular weight of the starting polymer.

The effect of pulse frequency on the physicochemical properties of nanogels is such that if the time between two successive pulses is longer than the average lifetime of the macroradicals, radicals disappear in intra-pulse reactions and each pulse can be considered independent from the others. If polymer radicals have longer lives (they are more stable or too few), they can survive to the successive pulse. In the case of dilute PVP aqueous solutions, a pulse frequency effect has been observed on both the molar mass and on the hydrodynamic diameters of the nanogels even when the time between two successive pulses was considerably longer than the measured half-life of the carbon-centred macroradicals based on pulse radiolysis experiments. In particular, nanogels with higher molar mass and higher hydrodynamic size have been made at the lowest pulse frequency. It has been postulated that slower decaying radicals, which are not detected by the UV analysis of pulse radiolysis experiments, may form and become involved in interparticle reactions occurring in the "dark time" between pulses [69].

5.4. NANOPARTICLE ENGINEERING *VIA* MIXED INTRA/INTERMOLECULAR RADIATION CROSSLINKING IN SEMI-DILUTE AQUEOUS SOLUTIONS

A greater variety of nanogels, different in particle size, molecular weight and functionality, can be produced by the use of irradiation doses within the sterilization dose range 20-80 kGy with semi-dilute polymer solutions [68, 70-72].

When the polymer concentration is approaching C*, the two modes of crosslinking, intra- and intermolecular, concur in the initial phase of the process, at lower doses. The combined effect of these two reactions is that intramolecular combination progressively increases the crosslinked density of the nanogel, which reduces the macroradical segmental mobility; intermolecular combination reduces the number of independent polymer chains in the system and the probability of further reacting as well as the ability of the polymer to scavenge the primary radicals formed in water. Therefore, with an increase of dose both intra- and intermolecular crosslinking become less and less favoured, and the initiating radicals continuously produced by water radiolysis can mutually react, producing H_2 and H_2O_2. The radiolytic decomposition of hydrogen peroxide will become a source of molecular oxygen in the system which, after the gel nanoparticles are formed, starts to compete with intra/intermolecular termination to react with the newly forming macroradicals, thus leading to functionalized nanogels. Research activities carried out by Dispenza and collaborators have shown that carboxyl groups and amino groups can form on PVP nanogels, made by the irradiation of pure aqueous solutions of PVP at doses in the 20-80 kGy range [68, 73].

The presence of carboxyl groups and primary amino groups transforms the otherwise "chemically inert" PVP nanogels into multifunctional nanocolloids, amenable to modification with (bio)molecules and cell receptor-specific ligands of therapeutic and/or diagnostic relevance.

For the same purpose, the same and other research groups have pursued crosslinking and simultaneous grafting of functional acrylic monomers or polymers [71, 72, 74-77].

These strategies were successful in demonstrating the possibility of making nanogels with controlled particle size and functional groups that could be used for the incorporation and triggered release of molecular drugs [78], or in conjugation with oligonucleotides and proteins to be protected by enzymatic degradation and carried then to their targets [79, 80].

6. POLYMER NANOPARTICLE FORMATION FROM RADIATION-DEGRADABLE POLYMERS

Ionizing radiation is a well-known method that reduces the molecular weight of radiation-degradable polymers by controlled degradation. This approach is often used to improve the solubility of polysaccharides for a large variety of applications, including health care and personal care products, plant growth adjuvants, viscosity modifiers in the food industry, and in the textile industry. The mechanism of nanoparticle formation of polysaccharides consists in the irradiation leading to the breakdown of the ordered system of intermolecular as well as intramolecular hydrogen bonds. As a consequence, chain mobility increases, as well as the permeability by oxygen or water radiolysis products, and acetal linkages may also break [49, 81].

In 2010, Pasanphan *et al.* [82] have studied the possibility of making nanoscale-particle chitosan by exposing chitosan to γ-rays at room temperature in different physical forms (as solid flakes or in aqueous colloidal form) to achieve a fairly good control over particle size distribution. Both particle size and particle polydispersity decrease progressively with an increase in dose. Although the reaction pathway of radiation-initiated degradation of polysaccharides is well described in the literature [82-85], the mechanism that leads to the narrowing of particle size distribution has not yet been fully clarified.

7. CONCLUSIONS

Polymerization initiated by ionizing radiation in water is a process that leads to a large variety of functional polymeric materials for the many diverse applications.

A proper choice of the irradiation conditions, in particular the dose rate (continuous irradiation from radioisotopes) or the dose per pulse and pulse frequency (pulsed electron beam sources), produces initiating radicals from water radiolysis products at controlled rates and independent of reaction temperature. These radicals can react with the material or with themselves, triggering or sustaining chemical reactions that follow and that will then involve other solutes present in the system, such as monomers and polymers.

Because of the high penetration of ionizing irradiation, the primary reactive species are formed homogeneously within the system and throughout the process, both in the solvent and in the solutes or dispersed phases, including formed polymers. These reactants can be used not only to initiate polymerization but also to resize micro/nanoparticles, to induce a progressive change of their composition and surface functionality (*e.g.* by crosslinking, grafting of functional monomers onto already formed polymers, by oxidation, *etc*.).

The non-thermal activation of the main process permits an independent control of the rate of the eventual concurrent or competitive reactions (primarily by controlling dose rate, material concentration, pH and temperature). This can be used to increase the yield, or to fine-tune the composition, the topology, the morphology and, in turn, the properties of the desired product.

Material optimization, both in terms of properties and production process, relies on the fundamental knowledge about the mechanisms of the reactions from their precursors and the kinetics of the elementary steps involved. This knowledge is quite developed for some material systems while considerable research is called for in other cases.

Acknowledgements

The authors wish to acknowledge with appreciation the very careful review by Prof. A. Faucitano on the chapter, and comments and suggestions from Prof. K. Bobrowski and Prof. M. Jonsson on specific important points.

REFERENCES

[1]. Hopwood, F.L., & Phillips, J.T. (1939). Polymerization of liquids by irradiation with neutrons and other rays. *Nature*, *143*, 640-640.

[2]. Chapiro A. (1987). Historical outline of radiation effects in polymers. In M.J. Bowden & S.R. Turner (Eds.), *Polymers for high technology: Electronics and photonics* (pp. 31-36). Washington, DC: American Chemical Society. (ACS Symposium Series, Vol. 346). DOI: 10.1021/bk-1987-0346.ch003.

[3]. Spinks, J.W.T., & Woods, R.J. (1990). *An introduction to radiation chemistry*. New York: Wiley Interscience.

[4]. Pastina, B., & La Verne, J.A. (1999). Scavenging of the precursor to the hydrated electron by the selenate ion. *J. Phys. Chem. A*, *103*, 209-212. DOI: 10.1021/jp983865w.

[5]. Pastina, B., La Verne, J.A., & Pimblott, S.M. (1999). Dependence of molecular hydrogen formation in water on scavengers of the precursor to the hydrated electron. *J. Phys. Chem. A*, *103*, 5841-5846. DOI: 10.1021/jp991222q.

[6]. Stefanic, I., & La Verne, J.A. (2002). temperature dependence of the hydrogen peroxide production in the gamma-radiolysis of water. *J. Phys. Chem. A*, *106*, 447-452. DOI: 10.1021/jp0131830.

[7]. Lacroix-Desmazes, P., & Guyot, A. (1996). reactive surfactants in heterophase polymerization. 2. Maleate based poly(ethylene oxide) macromonomers as steric stabilizer precursors in the dispersion polymerization of styrene in ethanol--water media. *Macromolecules*, *29*, 4508-4515. DOI: 10.1021/ma951849g.

[8]. Buxton, V. (2008). An overview of the radiation chemistry of liquids. In M. Spotheim-Maurizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basic to application in material and life science* (pp. 3-16). France: EDP Sciences.

[9]. Wardman, P. (1989). Reduction potentials of one-electron couples involving free radicals in aqueous solution. *J. Phys. Chem. Ref. Data*, *18*, 1637-1755. DOI: 10.1063/1.555843.

[10]. Buxton, G.V., Greenstock, C.L., Helman, W.P., & Ross, A.B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O^- in aqueous solution. *J. Phys. Chem. Ref. Data*, *17*, 513-886. DOI: 10.1063/1.555805.

[11]. Morris, E.D., Stedman, D.H., & Niki, H. (1971). Mass-spectrometric study of the reactions of the hydroxyl radical with ethylene, propylene, and acetaldehyde in a discharge-flow system. *J. Am. Chem. Soc.*, *93*, 3570-3572. DOI: 10.1021/ja00744a004.

[12]. Hefter, H.J., Hecht, T.A., & Hammond, G.S. (1972). Radical attack on propylene as studied by electron spin resonance. *J. Am. Chem. Soc.*, *94*, 2793-2797. DOI: 10.1021/ja00763a043.

[13]. Jefcoate, C.R.E., Lindsay-Smith, J.R., & Norman, R.O.C. (1969). Hydroxylation. Part IV. Oxidation of some benzenoid compounds by Fenton's reagent and the ultraviolet irradiation of hydrogen peroxide. *J. Chem. Soc. B*, 1013-1018. DOI: 10.1039/J29690001013.

[14]. Pryor, W.A., Fuller, D.C., & Stanley, J.P. (1972). Reactions of radicals. 41. Reactivity patterns of the methyl radical. *J. Am. Chem. Soc.*, *94*, 1632-1638. DOI: 10.1021/ja00760a034.

[15]. Odian, G. (1991). *Principles of polymerization*. New York: Wiley.

[16]. Chapirò, A. (1962). Radiation polymerisation of vinyl monomers. In *Radiation chemistry of polymeric systems* (Chapter V). New York: Interscience Publishers.

[17]. Chapirò, A. (1950). On the polymerization of vinylic compounds initiated by gamma-rays. *J. Chim. Phys. Rev. Gen. Colloides*, *47*, 764-775.

[18]. Swallow, A.J. (1960). *Radiation chemistry of organic compounds*. Oxford, London, New York, Paris: Pergamon Press.

[19]. Chapirò, A. (1962). General aspects of radiation-initiated polymerization. In *Radiation chemistry of polymeric systems* (Chapter IV). New York: Interscience Publishers.

[20]. Stoffer, J.O., & Bone, T. (1980). Polymerization in water-in-oil microemulsion systems. I. *J. Polym. Sci. Polym. Chem.*, *18*, 2641-2648. DOI: 10.1002/pol.1980.170180822.

[21]. Candau, F. (1992). Polymerization in microemulsions. In C.M. Paleos (Ed.), *Polymerization in organized media*. Philadelphia, PA: Gordon and Breach Publishers.

[22]. Gan, L.M., & Chew, C.H. (1996). In J.C. Salamone (Ed.), *Polymeric materials encyclopedia* (Vol. 10, pp. 4321-4331). Boca Raton: CRC Press.

[23]. Anton, N., Benoit, J.P., & Saulnier, P. (2008). Design and production of nano-particles formulated from nano-emulsion templates-a review. *J. Control. Release*, *128*, 3, 185-199. DOI: 10.1016/j.jconrel.2008.02.007.

[24]. Acres, G.J.K., & Dalton, F.L. (1963). On Co-60 gamma ray-initiated emulsion polymerization. *J. Polym. Sci. Part A*, *1*, 3009-3020. DOI: 10.1002/pol.1963.100011001.

[25]. Xu, X.L., Ge, X.W., Zhang, Z.C., Wu, Z.C., & Zhang, M.W. (1997). Microemulsion polymerization of styrene initiated with gamma-ray. *Radiat. Phys. Chem.*, *49*(4), 469-472. DOI: 10.1016/S0969-806X(96)00163-6.

[26]. Xiangling, X., Xueewu, G., Qiang, Y., Zhicheng, Z., Ju, Z., Aizhen, N., & Manwei, Z. (1999). Growth of polymer nanoparticles in microemulsion polymerization initiated with γ ray. *Radiat. Phys. Chem., 54*, 279-283. DOI: 10.1016/S0969-806X(98)00254-0.

[27]. Wang, S., Wang, X., & Zhang, Z. (2007). Preparation of polystyrene particles with narrow particle size distribution bu gamma-ray initiated microemulsion polymerization stabilized by polymeric surfactant. *Eur. Polym. J.*, *43*, 178-184. DOI: 10.1016/j.eurpolymj.2006.09.010.

[28]. Chen, J., Qiao, J., Zhang, Z., & Zhang, Q. (2011). High monomer content batch microemulsion polymerization of butyl acrylate and acrylonitrile initiated with gamma ray. *Polym. Bull.*, *66*, 599-608. DOI: 10.1007/s00289-010-0295-9.

[29]. Melendez-Ortiz, H.I., Peralta, R.D., Bucio, E., & Zerrweck-Maldonado, L. (2013). Preparation of stimuli-responsive nanogels of poly [2-(dimethylamino) ethyl methacrylate] by heterophase and microemulsion polymerization using gamma radiation. *Polym. Eng. Sci.*, *54*, 1625-1631. DOI: 10.1002/pen.23703.

[30]. Antonietti, M., & Tauer, K. (2003). 90 Years of polymer latexes and heterophase polymerization: more vital than ever. *Macromol. Chem. Phys.*, *204*(2), 207-219. DOI: 10.1002/macp.200290083.

[31]. Chen, J., & Zhang, Z. (2007). Radiation-induced polymerization of methyl methacrylate in microemulsion with high monomer content. *Eur. Polym. J.*, *43*, 1188-1194. DOI: 10.1016/j.eurpolymj.2007.01.049.

[32]. Arshady, R. (1992). Suspension, emulsion, and dispersion polymerization: A methodological survey. *Colloid Polym. Sci.*, *270*(8), 717-732. DOI: 10.1007/BF00776142.

[33]. Tadros, Th.F. (1982). *The effect of polymers on dispersion properties*. London, New York: Academic Press.

[34]. Napper, D.H. (1983). *Polymeric stabilization of colloidal dispersions*. London: Academic Press.

[35]. Hu, Z., Tao, M., & Zhang, Z. (2007). "Gradient" polymer prepared by complex--radical terpolymerization of styrene, maleic anhydride, and *N*-vinyl pyrrolidone via gamma ray irradiation by use of a RAFT method: 2. Used in dispersion polymerization of styrene as a stabilizer. *Colloid. Surface. A*, *302*, 307-311. DOI: 10.1016/j.colsurfa.2007.02.049.

[36]. Ye, Q., Zhang, Z., Jia, H., He, W., & Ge, X. (2002). Formation of monodisperse polyacrylamide particles by radiation-induced dispersion polymerization: particle size and size distribution. *J. Colloid Interf. Sci.*, *253*(2), 279-284. DOI: 10.1006/jcis.2002.8465.

[37]. Ye, Q., Ge, X., & Zhang, Z. (2003). Formation of monodisperse PMMA particles by radiation-induced dispersion polymerization - I. Synthesis and polymerization kinetics. *Radiat. Phys. Chem.*, *66*, 11-16. DOI: 10.1016/S0969-806X(02)00307-9.

[38]. Dai, Q., Wu, D., Zhang, Z., & Ye, Q. (2003). Preparation of monodisperse poly(methyl methacrylate) particles by radiation-induced dispersion polymerization using vinyl terminus polysiloxane macromonomer as a polymerizable stabilizer. *Polymer*, *44*, 73-77. DOI: 10.1016/s0032-3861(02)00728-0.

[39]. Lamer, V.K., & Dinegar, R.H. (1950). Theory, production and mechanism of formation of monodispersed hydrosols. *J. Am. Chem. Soc.*, *72*(11), 4847-4854. DOI: 10.1021/ja01167a001.

[40]. Sakurada, I., & Ikada, Y. (1963). Effects of gamma radiation on polymer in solution. IV. Crosslinking and degradation of poly(acrylic acid) in aqueous solution. *Bull. Inst. Chem. Res. Kyoto Univ.*, *41*(1), 103-113. OSTI Identifier: 4703894.

[41]. Kaetsu, I. (1981). Immobilization of biofunctional substances. *Radiat. Phys. Chem.*, *18*(1-2), 343-356. DOI: 10.1016/0146-5724(81)90086-8.

[42]. Kaetsu, I. (1985). Recent progress on the immobilization of biocomponent by radiation polymerization and the application to biomedical uses. *Radiat. Phys. Chem.*, *25*(4-6), 517-528. DOI: 10.1016/0146-5724(85)90131-1.

[43]. Hoffman, A.S., & Allan, S. (1977). A review of the use radiation plus chemical and biochemical processing treatments to prepare novel biomaterials. *Radiat. Phys. Chem.*, *18*(1-2), 323-342. DOI: 10.1016/0146-5724(81)90085-6.

[44]. Rosiak, J.M., Janik, I., Kadlubowski, S., Kozicki, M., Kujawa, P., Stasica, P., & Ulanski, P. (2002). Radiation formation of hydrogels for biomedical application. In *Radiation synthesis and modification of polymers for biomedical applications. Final results of a co-ordinated research project 1996-2000* [and references herein]. Vienna: IAEA. (IAEA-TECDOC-1324).

[45]. Rosiak, J., Rucinska-Rybus, A., & Pekala, W. (1989). *Method of manufacturing of hydrogel dressings*. US Patent No. 4871490 A.

[46]. KIK-GEL Co. (1993). *AQUA-GEL dressings* [pamphlet]. Ujazd, Poland: KIK-Gel Co.

[47]. Charlesby, A., & Alexander, P. (1955). Reticulation of polymers in aqueous solution by γ-rays. *J. Chim. Phys. PCB*, *52*, 699-709.

[48]. Charlesby, A., & Alexander, P. (1957). Effect of X-rays and γ-rays on synthetic polymers in aqueous solution. *J. Polym. Sci.*, *23*, 355-375. DOI: 10.1002/pol.1957.1202310331.

[49]. Woods, R.J., & Pikaev, A.K. (1994). *Applied radiation chemistry, radiation processing*. New York: John Wiley and Sons, Inc.

[50]. Charlesby, A. (1991). *Irradiation effects on polymers*. New York: Elsevier Applied Science.

[51]. Saito, O. (1958). On the effect of high energy radiation to polymers I. Cross--linking and degradation. *J. Phys. Soc. Jpn.*, *13*, 198-206. DOI: http://dx.doi.org/10.1143/JPSJ.13.198.

[52]. Rosiak, J.M., & Ulanski P. (1999). Synthesis of hydrogels by irradiation of polymers in aqueous solution. *Radiat. Phys. Chem.*, *55*, 139-151. DOI: 10.1016/S0969-806X(98)00319-3.

[53]. Dispenza, C., Tripodo, G., Lo Presti, C., Spadaro, G., & Giammona, G. (2009). Synthesis, characterisation and properties of alpha, beta-poly(N-2-hydroxyethyl)--DL-aspartamide-graft-maleic anhydride precursors and their stimuli-responsive

hydrogels. *React. Funct. Polym.*, *69*, 565-575. DOI: 10.1016/j.reactfunctpolym.2009.03.010.

[54]. LoPresti, C., Vetri, V., Ricca, M., Fodera, V., Tripodo, G., Spadaro, G., & Dispenza, C. (2011). Pulsatile protein release and protection using radiation-crosslinked polypeptide hydrogel delivery devices. *React. Funct. Polym.*, *71*, 155-167. DOI: 10.1016/j.reactfunctpolym.2010.11.030.

[55]. Oh, J.K., Drumright, R., Siegwart, D.J., & Matyjaszewski, K. (2008). The development of microgels/nanogels for drug delivery applications. *Prog. Polym. Sci.*, *33*, 448-477. DOI: 10.1016/j.progpolymsci.2008.01.002.

[56]. Gonçalves, C., Pereira, P., & Gama, M. (2010). Self-assembled hydrogel nanoparticles for drug delivery applications. *Materials*, *3*(2), 1420-1460. DOI: 10.3390/ma3021420.

[57]. Ulanski, P., Kadlubowski, S., & Rosiak, J.M. (2002). Synthesis of poly(acrylic acid) nanogels by preparative pulse radiolysis. *Radiat. Phys. Chem.*, *63*, 533-537. DOI: 10.1016/s0969-806x(01)00549-7.

[58]. Dispenza, C., Grimaldi, N., Sabatino, M.A., Soroka, I.L., & Jonsson, M. (2015). Radiation engineered functional nanoparticles in aqueous system. *J. Nanosci. Nanotechnol.*, *15*(5), 3445-3467. DOI: http://dx.doi.org/10.1166/jnn.2015.9865.

[59]. Kadlubowski, S. (2014). Radiation-induced synthesis of nanogels based on poly(N-vinyl-2-pyrrolidone)-A review. *Radiat. Phys. Chem.*, *102*, 29-39. DOI: http://dx.doi.org/10.1016/j.radphyschem.2014.04.016.

[60]. Ulanski, P., & Rosiak, J.M. (1999). Use of radiation technique in the synthesis of polymeric nanogels. *Nucl. Instrum. Meth. Phys. Res. B*, *151*(1-4), 356-360. DOI: 10.1016/S0168-583X(99)00085-3.

[61]. Wang, B., Mukataka, S., Kodama, M., & Kokufuta, E. (1997). Viscometric and light-scattering-studies on microgel formation by gamma-ray irradiation to aqueous oxygen-free solutions of poly(vinyl alcohol). *Langmuir*, *13*, 6108-6114. DOI: 10.1021/la970599p.

[62]. Janik, I., Ulański, P., & Rosiak, J.M. (1998). Radiation formation of polymeric nanogels. *Radiat. Phys. Chem.*, *52*(1-6), 289-294. DOI: 10.1016/S0969-806X(98)00155-8.

[63]. Ulanski, P., Zainuddin, & Rosiak, J.M. (1995). Pulse radiolysis of poly(ethylene oxide) in aqueous solution. II. Decay of macroradicals. *Radiat. Phys. Chem.*, *46*(4-6), 917-920.

[64]. Plonka, A. (1991). Developments in dispersive kinetics. *Prog. React. Kinet.*, *16*(3-4), 157-333.

[65]. Plonka, A. (2001). *Dispersive kinetics*. Dordrecht, The Netherlands, Boston, MA: Kluwer Academic Publishers.

[66]. Janik, I., Ulanski, P., Hildenbrand, K., Rosiak, J.M., & von Sonntag, C.J. (2000). Hydroxyl-radical-induced reactions of poly(vinyl methyl ether): A pulse radiolysis, EPR and product study in deoxygenated and oxygenated aqueous solutions. *J. Chem. Soc., Perkin Trans. 2,* 2041-2048.

[67]. Dispenza, C., Grimaldi, N., Sabatino, M.A., Todaro, S., Bulone, D., Giacomazza, D., Przybytniak, G., Alessi, S., & Spadaro, G. (2012). Studies of network organization and dynamics of e-beam crosslinked PVPs: from macro to nano. *Radiat. Phys. Chem.*, *81*(9), 1349-1353. DOI: 10.1016/j.radphyschem.2011.11.057.

[68]. Sabatino, M.A, Bulone, D., Veres, M., Spinella, A., Spadaro, G., & Dispenza, C. (2013). Structure of e-beam sculptured poly(N-vinylpyrrolidone) networks across different length-scales, from macro to nano. *Polymer*, *54*(1), 54-64. DOI: 10.1016/j.polymer.2012.11.031.

[69]. An, J.C., Weaver, A., Kim, B., Barkatt, A., Poster, D., Vreeland, W.N., Silverman, J., & Al-Sheikhly, M. (2011). Radiation-induced synthesis of poly(vinylpyrrolidone) nanogel. *Polymer*, *52*, 5746-5755. DOI: 10.1016/j.polymer.2011.09.056.

[70]. Dispenza, C., Sabatino, M.A., Grimaldi, N., Spadaro, G., Bulone, D., Bondì, M.L., Adamo, G., & Rigogliuso, S. (2012). Large-scale radiation manufacturing of hierarchically assembled nanogels. *Chem. Eng. Trans.*, *27*, 229-234. DOI: 10.3303/CET1227039.

[71]. Grimaldi, N., Sabatino, M.A., Przybytniak, G., Kaluska, I., Bondì, M.L., Bulone, D., Alessi, S., Spadaro, G., & Dispenza, C. (2014). High-energy radiation processing, a smart approach to obtain PVP-graft-AA nanogels. *Radiat. Phys. Chem.*, *94*, 76-79. DOI: 10.1016/j.radphyschem.2013.04.012.

[72]. Dispenza, C., Sabatino, M.A., Grimaldi, N., Bulone, D., Bondì, M.L, Casaletto, M.P., Rigogliuso, S., Adamo, G., & Ghersi, G. (2012). Minimalism in radiation synthesis of biomedical functional nanogels. *Biomacromolecules*, *13*(6), 1805-1817. DOI: 10.1021/bm3003144.

[73]. Dispenza, C., Sabatino, M., Grimaldi, N., Mangione, M., Walo, M., Murugan, E., & Jonsson, M. (2016). On the origin of functionalisation in one-pot radiation synthesis of nanogels from aqueous polymer solutions. *RSC Adv.*, *6*(4), 2582-2591. DOI: 10.1039/c5ra23926e.

[74]. El-Rehim, H.A.A., Swilem, A.E., Klingner, A., Hegazy, E.S.A., & Hamed, A.A. (2013). Developing the potential ophthalmic applications of pilocarpine entrapped into polyvinylpyrrolidone-poly(acrylic acid) nanogel dispersions prepared by γ radiation. *Biomacromolecules*, *14*(3), 688-698. DOI: 10.1021/bm301742m.

[75]. El-Rehim, H.A.A., Hegazy, E.S.A., Hamed, A.A., & Swilem, A.E. (2013). Controlling the size and swellability of stimuli-responsive polyvinylpyrrolidone–poly (acrylic acid) nanogels synthesized by gamma radiation-induced template polymerization. *Eur. Polym. J.*, *49*(3), 601-612. DOI: 10.1016/j.eurpolymj.2012.12.002.

[76]. Dispenza, C., Grimaldi, N., Sabatino, M.A., Adamo, G., Rigogliuso, S., & Ghersi, G. (2013). Large-scale manufacturing of radiation sculptured therapeutic nanogels. In *Nanotechnology 2013: Bio Sensors, Instruments, Medical, Environment and Energy. Technical Proceedings of the 2013 NSTI Nanotechnology Conference and Expo* (Vol. 3, pp. 202-205). Washington, DC: NSTI.

[77]. Grimaldi, N. (2013). Water-borne polymeric nanoparticles for glutathione-mediated intracellular delivery of anticancer drugs. In *Nanotechnology 2013: Bio Sensors, Instruments, Medical, Environment and Energy. Technical Proceedings of the 2013 NSTI Nanotechnology Conference and Expo* (Vol. 3, pp. 155-158). Washington, DC: NSTI.

[78]. Adamo, G., Grimaldi, N., Campora, S., Sabatino, M.A., Dispenza, C., & Ghersi, G. (2014). Glutathione-sensitive nanogels for drug release. *Chem. Eng. Transact.*, *38*, 457-462. DOI: 10.3303/CET1438077.

[79]. Dispenza, C., Adamo, G., Sabatino, M.A., Grimaldi, N., Rigogliuso, S., & Ghersi, G. (2014). Oligonucleotides-decorated-poly(N-vinyl pyrrolidone) nanogels for gene delivery. *J. Appl. Polym. Sci.*, *131*(2), 39774-39782. DOI: 10.1002/app.39774.

[80]. Picone, P., Ditta, L.A., Sabatino, M.A., Militello, V., San Biagio, P.L., Di Giacinto, M.L., Cristaldi, L., Nuzzo, D., Dispenza, C., Giacomazza, D., & Di Carlo, M. (2016). Ionizing radiation-engineered nanogels as insulin nanocarriers for the development of a new strategy for the treatment of Alzheimer's disease. *Biomaterials*, *80*, 179-194. DOI: 10.1016/j.biomaterials.2015.11.057.

[81]. Lunkwitz, K., Brink, H.J., Handte, D., & Ferse, A. (1989). The radiation degradation of polytetrafluoroethylene resulting in low-molecular and functionalized perfluorinated compounds. *Int. J. Radiat. Appl. Instrum. C: Radiat. Phys. Chem.*, *33*(6), 523-532. DOI: 10.1016/1359-0197(89)90309-3.

[82]. Pasanphan, W., Rimdusit, P., Choofong, S., Piroonpan, T., & Nilsuwankosit, S. (2010). Systematic fabrication of chitosan nanoparticle by gamma irradiation. *Radiat. Phys. Chem.*, *79*, 1095-1102. DOI: 10.1016/j.radphyschem.2010.04.003.

[83]. Wasikiewicz, J.M., Yoshii, F., Nagasawa, N., Wach, R.A., & Mitomo, H. (2005). Degradation of chitosan and sodium alginate by gamma radiation, sonochemical and ultraviolet methods. *Radiat. Phys. Chem.*, 73, 287-295. DOI: 10.1016/j.radphyschem.2004.09.021.

[84]. Yoksan, R., Akashi, M., Miyata, M., & Chirachanhai, S. (2004). Optimal γ-ray dose and irradiation conditions for producing low-molecular-weight chitosan that retains its chemical structure. *Radiat. Res.*, *161*(4), 471-4810. DOI: http://dx.doi.org/10.1667/RR3125.

[85]. Caykara, T., & Guven, O. (1999). UV degradation of poly(methyl methacrylate) and its vinyltriethoxysilane containing copolymers. *Polym. Degrad. Stabil.*, *65*(2), 225-229. DOI: 10.1016/S0141-3910(99)00008-7.

Chapter 14

RADIATION MODIFICATION OF POLYSACCHARIDES AND THEIR COMPOSITES/NANOCOMPOSITES

Krystyna A. Cieśla
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

The trends to replace environmentally non-degradable polymers made from feedstocks based on petroleum or natural gas and to invent new products for biomedicine, and food or pharmaceutical industries, *etc.*, have spurred the development of materials derived from renewable resources. These natural materials should be more environmentally friendly, but require different processes and, in some cases, different manufacturing techniques. Polysaccharides are a large family of such natural polymers and have been extensively studied. The following are some areas of interest in pursuing these natural polymers:

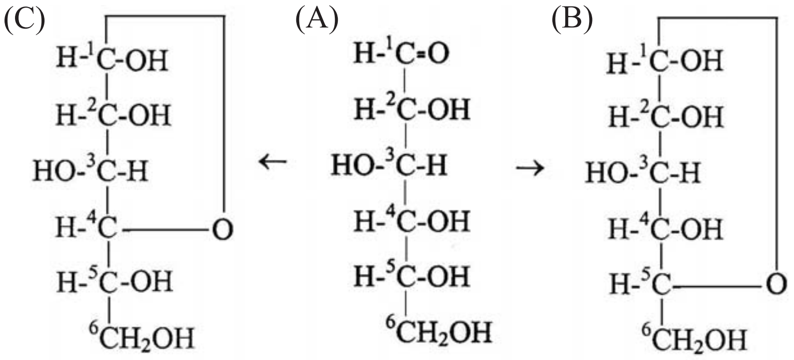
- natural polysaccharides produced by extraction from plant and animal tissues, and the derivatives of polysaccharides;
- products, by-products and wastes from agriculture and the food or paper industries (*i.e.* flours, bleached wood pulp, sugar cane bagasse, wheat straw);
- composites based on several polysaccharides or on polysaccharide-protein, polysaccharide-biodegradable synthetic polymers, polysaccharide-polyolefin and/or such containing some plasticizers, inorganic compounds (*i.e.* clays, TiO_2, SiO_2), lipids and surfactants;
- nanopolysaccharides and nanocomposites containing the above-mentioned polysaccharides and the addition of nanoparticles, such as inorganic nanoparticles (*i.e.* nanoclays, nanooxides, nanosilver), carbon or polymer/biopolymer nanoparticles, and all composites containing nanopolysaccharides.

Appropriate modifications of polysaccharides are done, often on an industrial scale, but using chemical, enzymatic or physical treatment to adjust properties for a given application. However, chemical processes rely on strong chemicals, while enzymatic methods can be rather expensive. Besides modifying the bulk polymer, surface modification can be conducted.

There has been increased interest in the use of radiation (*i.e.* ultraviolet radiation (UV), gamma or X-ray photons and fast electrons) in processing and modifying polysaccharides.

2. STRUCTURAL PROPERTIES OF POLYSACCHARIDES

The most common polysaccharides are: starch, cellulose and hemicelluloses, agar-agar, alginates, carrageenans, chitin and chitosan, pectin, and various plant gums. Although not a polysaccharide, lignin is a natural polymer that accompanies to celluloses in plant cells. Lignin is composed of three aromatic alcohols, whose structure determine the strong resistance of lignin to physical and chemical treatment.



Scheme 1. Fisher projections of aldoses: D-glucose (A), α-D-glucopyranose (B) and α-D-glucofuranose (C).

Polysaccharides are formed by monosaccharide units (Scheme 1) bonded by glyosidic linkages, as shown in Figs.1 and 2. There are a great number of

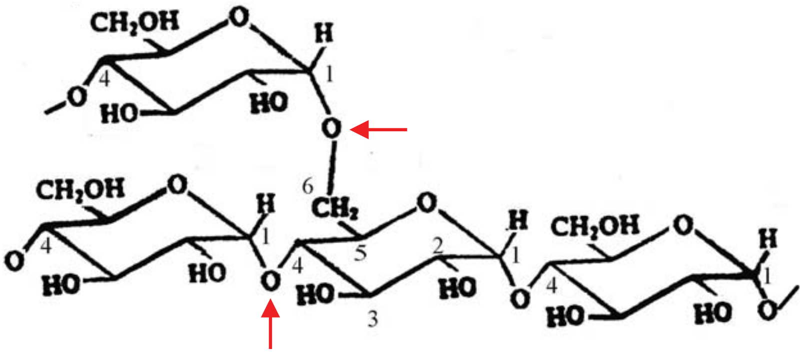


Fig.1. The structure of the starch amylopectin molecule (α-D-glucose unit, α1–4 and α1–6 linkages) with the most possible reaction paths (shown by the arrows). Starch amylose (non-branched) is formed by α-D-glucose units bound by α1–4 linkages.

possible monosaccharides differing in the molecular structure and conformation. Aldoses or ketoses (polyhydroxy aldehydes and polyhydroxy ketones) can be distinguished by their dependence on the position of C=O linkages in the molecule. An example of aldose is given in Scheme 1. Each saccharide can form several cyclic structures, as illustrated by the conformations B and C in Scheme 1. The positions of the OH groups at C1 and C2 in relation to the plane of the ring structure (*cis* or *trans*) are denoted as the α and β forms. The molecules can take the chair conformation (preferred in a majority of monosaccharides, as shown in Figs.1 and 2), or a twisted-boat conformation.

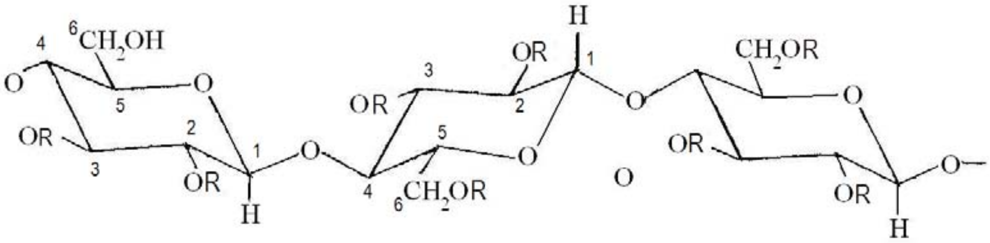


Fig.2. The structure of cellulose molecule (α-D-glucose unit, β1–4 linkages) or the ether and ester derivative of cellulose. Cellulose R = H, ether: R = H or CH_3 (methyl cellulose, MC), CH_2CH_2OH (hydroxyethylcellulose, HEC), *etc*. Ester: R = H or residue of carboxyl acid salt (*i.e.* $CH_2COO^-Na^+$ in the case of carboxymethylcellulose, CMC).

Polysaccharides can be composed of one type of the monosaccharide structural unit (homoglycans) or of several different types of structural units (heteroglycans) [1]. These can be connected by various types of glycosidic linkages, such as *1→4, 1→3, 1→6, 1→2,* as illustrated in Fig.1. Different functional groups, as COO^-, SO_3^-, $-NHCOCH_3$, NH_2^- in alginates, in carrageenans, in chitin and in chitosan, can substitute for the OH groups in the sugar units at different positions. These substitutions affect the conformation of the particular structural units of a polysaccharide. The presence of several types of the glycosidic linkages within the same polysaccharide may result in the formation of a branched molecule, as shown in Fig.1.

Accordingly, the structure/conformation of a polysaccharide macromolecule depends on all of the above factors. The most common conformations are the ribbon types (typical in cellulose fibers or alginates), the helix types (single or coiled double or triple helices; double helices are typical for starch) and the egg-box types (alginates stabilized by the Ca^{2+} ions). The ordered distribution of the chains results in the formation of ordered regions in the polysaccharide fibers or grains.

A great variety of possible polysaccharide structural types leads to a great variety of physical properties and of potential reactivity. The most important general physical property of all polysaccharides is their ability to capture water which results in the formation of hydrogels in aqueous environments. This can be achieved by heating a polysaccharide suspension, as for starch gelatinization, or by directly immersing a polysaccharide in water, as to swell agar-agar. This property determines numerous uses of polysaccharides as food hydrocolloids, in biomedicine, in technical industries and in environmental protection.

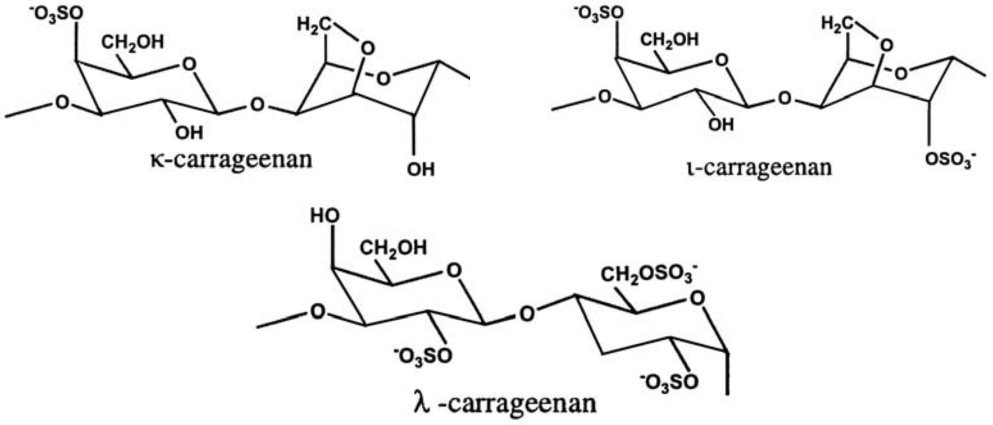


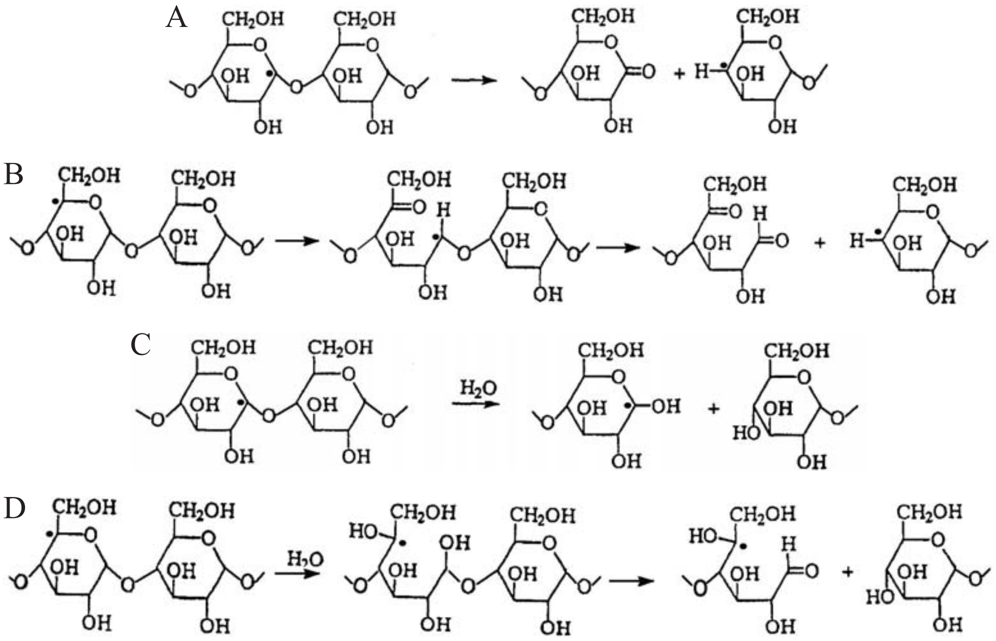
Fig.3. The structure of κ-carrageenan, ι-carrageenan, and λ-carrageenan.

Some oligosaccharides, such as chitosan, carboxymethyl chitosan (CM-chitosan), carrageenans or alginates, containing functional groups, as amide, sulfate or acid, show biological activity, as antibacterial, antiviral and antiphytoviral, antitumor, hemostatic, immunomodulation, *etc*., as well as antioxidant activity. Such activity may not be observed or is less efficient in the case of the same polysaccharide having a high molecular mass. Biological activity can be correlated to the oligosaccharide type, a specific range of the molecular mass, and the degree of substitution and conformation (which effects accessibility to active sites) [2-8]. Thus, chitosan shows antimicrobial activity, but this activity is higher in the case of oligosaccharides with a lower molecular mass [2-4] and might mainly be related to the presence of the amide groups. Macromolecular carrageenan does not show biological activity, while such activity, depending additionally on the sulfonation level, was found for some carrageenan oligomers. Carrageenans are a good example of the dependence of biological activity on the oligomer conformation, as in Fig.3; κ-carrageenan shows the highest biological activity.

3. BASIC RADIATION PROCESSES INVOLVING POLYSACCHARIDES

The differences in structure of particular polysaccharides affect their radiation processing and efficiency. Such differences in radiation processing can also happen for various conformations of the same polysaccharide (*i.e.* various forms of carrageenans). In the case of heteroglycans (*i.e.* alginates), the radiation processes depend on the participation of a particular monomer unit on the polysaccharide chain.

The formation of primary free radicals and their interaction with solvent are found with polysaccharides which follow the same rules as do free radical reactions with synthetic polymers. Free radicals are formed mainly by disruption of C–H linkages [8-10]. Secondary free radicals are formed on carbon atoms. For example, chain reactions of the primary and of the secondary free radicals lead to a disruption of the glicosidic linkages or C–O and C–C linkages in the glucose residues [9-11]. The transformations of free radicals formed on C1, C4 and C5 lead to fragmentation resulting in the formation of saccharides and carbonyl derivatives [9]. Examples of reactions taking place in the dry solid state and in an aqueous environment are presented in Scheme 2. Rearrangements of the oxide and superoxide radicals formed in the presence of oxygen result in the formation of carboxylic acids.



Scheme 2. Example free radical reactions taking place in the dry solid state (A, B) and in an aqueous environment (C, D).

Use of radiation processing for polysaccharides modification

Degradation resulting from the cleavage of glycosidic linkages is the most probable effect of ionizing radiation on solid polysaccharides and on polysaccharides in solution. Water soluble ether and ester polysaccharide derivatives (shown in Fig.2) degrade as do non-substituted polysaccharides when irradiated in the solid state or in aqueous solutions at low concentration (below *ca.*

10 wt%). An increase in the concentration above some critical value, which is well determined for each individual polysaccharide, leads to competitive crosslinking. In the systems characterized by a high polysaccharide concentration, in the so-called paste-like state, crosslinking occurs instead of degradation. Further increases in polysaccharide concentration result again in the predominance of degradation over crosslinking. Because of the decrease in mobility of the polymer chains with increases in concentration, the crosslinking reaction becomes restricted and at high polysaccharide concentrations, there is a predominance of degradation over crosslinking.

Besides crosslinking and degradation, polysaccharides can be grafted with monomers by using radiation processing.

4. DEGRADATION OF POLYSACCHARIDES

Radiation-induced degradation of alginates, carageenans, chitosan, pectin, cellulose, and starches are well recognized processes used mainly for making oligomers with well determined molecular mass. This relates to the potential uses of oligosaccharides in agriculture, as food hydrocolloids, in pharmacy, and in the plastics industry. An important reason for degrading or scissioning oligosaccharides is to modify their biological and antioxidant activity.

This degradation is accompanied by the formation of carbonyl and carboxyl products (compare Section 3).

4.1. DEGRADATION PROCESSES FOR POLYSACCHARIDES

A decrease in the mean molecular mass of a polymer (M_w/M_n) results from degradation, as shown in Fig.4. This is indicated by a decreased capability to form a gel and by a decrease in the viscosity of any gels that are formed.

Doses up to 500 kGy and sometimes even up to 1000 kGy have been used for polysaccharide degradation in dependence on polysaccharide type and the desired modifications. However, doses greater than 100 kGy were rarely used. To obtain the same level of depolymerization it was necessary to irradiate solid polysaccharides with an absorbed dose that was around thirtyfold higher as compared to irradiation carried out in a dilute aqua solution. This occurs due to the fact that irradiation in the solid state involves direct irradiation effects; whereas irradiation in water initiates indirect effects from water radiolysis products, their propagation and their subsequent reactions with the polymer. The extent of depolymerization was greater after irradiation of solutions done in air as compared to irradiation conducted under nitrogen. This is

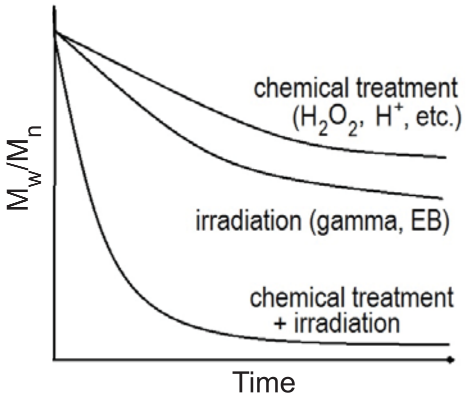


Fig.4. Schematic presentation of the degradation process of polysaccharides under: chemical treatment, gamma irradiation (at a defined dose rate), and the action of gamma irradiation on the solution of chemical agent.

related to the differences between the radiation processes and the products formed during irradiation. The irradiation of dilute solutions/gels done under nitrogen formed products containing C=C linkages; while irradiation under oxygen leads to the formation of C=O groups [11]. These differences were not noticed in the degree of depolymerization when the irradiation was carried out for solid samples either in air or in nitrogen, using the same irradiation doses, with there being smaller effects of irradiation performed on solid samples as compared to those irradiated in solution.

Differences were found between the sensitivity to irradiation for various forms of the same polysaccharides depending on their structure. For example, the following sequence was found to be the case for particular carrageenans structures, shown in Fig.3, based on both the formation of C=C linkages and the desulfonation level obtained after irradiation [8]: λ-carrageenan > ι-carrageenan > κ-carrageenan.

Synergistic effects of irradiation and chemical/enzymatic treatment

The combination of ionizing radiation with chemical treatments (acid or oxidative degradation) produces oligomers with a required molecular mass by using lower irradiation doses and has more efficient control of the structure and properties of the products as compared to using each of these processes separately [6, 12-14]. Examples are the irradiation of chitosan in diluted acetic acid solutions [13] or of the oxidative degradation of chitosan and alginate carried out in H_2O_2 solutions [6, 14] or of other systems that generate $^{\bullet}OH$ radicals. Figure 4 illustrates the effectiveness of combining processes. For example, it was found [14] that a dose of 4 kGy was sufficient for effective degradation when carried out in the 1% H_2O_2 solution, with no effect on the degree of deacetylation. M_w decreased to around 60% of the non-irradiated chitosan after treatment for 24 h with 1% H_2O_2, and up to around 10% after gamma irradiation in water solution using a 32 kGy dose. Irradiation of a 1%

H_2O_2 solution produced a similar degree of depolymerization after using a dose of 4 kGy.

Another example is the effective radiation-initiated degradation of solid chitosan which had been previously subjected to oxidative degradation carried out in solutions containing H_2O_2, $NaNO_2$ or NaClO.

Low molecular weight, active polysaccharides were made using irradiation of H_2O_2 solutions of chitosan, CM-chitosan, and alginate. These oligomers showed strong antioxidant properties, dependent on the molecular mass, and, in the case of the alginate, on the participation of two structural units (guluronic acid and mannuronic acid) in the polysaccharide chain [6]. Irradiation of alginates in 2% H_2O_2 solution produced a several-fold higher superoxide anion scavenging activity as compared to when irradiation was carried out in the absence of H_2O_2.

Conditions that limit undesirable degradation

Degradation is not desirable, for example, in the area of conservation of paper and wood artifacts which require some decontamination.

To protect systems containing polysaccharides against degradation that takes place under radiation decontamination various conditions were modified. Besides conducting the processes at low temperature, in the absence of oxygen, or after the addition of antioxidants, the irradiation of polysaccharides dispersed in protecting solvents that can act as free radicals scavengers was carried out. Some ionic liquids, *i.e.* 1-butyl-3-methylimidazolium chloride (Bmim), acted as radical scavengers [15]. Irradiation of wood moisten with Bmim improved the water resistance of the wood surface and limited water penetration [16].

Potential use of radiation-initiated degradation in industry and in environmental protection

The studies were carried out tending to support some industrial processes by ionizing radiation. Radiation pretreatment of lignocellulosic or cellulosic biomass or cellulose pulp, before enzymatic, acid or alkali hydrolysis, facilitated the degradation of the materials [17-19] and could be used as a step in the processes leading to the isolation of cellulose from biomass [17], in the production of alkali cellulose or bioethanol [18] as well as in utilization of waste products [19]. The simultaneous action of radiation treatment and acid hydrolysis (3% H_2SO_4) was also examined. The doses used varied in the range from 25 up to 1000 kGy. The radiation treatment alone is not effective enough for the degradation of lignocellulosic materials regarding the strong effect of lignin presence.

4.2. MODIFICATION OF THE ACTIVITY OF OLIGOSACCHARIDES

The activity of polysaccharides depends both on the molecular mass and on the presence of the specific functional groups. The radiation degradation process should be conducted at the conditions that enable to produce oligomers with the desired molecular mass and to preserve active functional groups.

For example, κ-carrageenan has the highest activity among the carrageenans. Irradiation induces smaller changes in it as compared to the other carrageenan conformations, as noted above (desulfonation) [8]. Using the appropriate irradiation conditions, κ-carrageenan can be made with a slightly decreased sulfonation level but with a high enough degree of depolymerization so that a long-lasting active agent may be produced. Thus, κ-carrageenan appeared to be the most promising polysaccharide for making the active carrageenan oligomer using irradiation [8].

Defense against phytoviruses

Phytoalexins are the defense substances synthetized by plants to protect them against phytoviral diseases. When used to feed plants, solutions of small amounts of oligosaccharides favor the formation of such compounds. Such oligosaccharides can be made by using radiation processing. Irradiation at a dose of 1000 kGy produces pectin and chitosan oligomers which have similar activity as enzymatically prepared products. The irradiation of chitosan produces particularly large amounts of phytoalexin, specifically pisatin [20, 21].

Increasing the antimicrobial, antifungal and antioxidant activity

Using of chitosan oligomers prevents the growth of bacteria, fungi and molds. Chitosan oligomers made using irradiation processing can extend the time of microbial incubation as compared to the non-irradiated chitosan.

For example, as reported in Ref. [16], *Escherichia coli* bacteria were detected immediately after incubation in a culture grown without chitosan. With non-irradiated chitosan, having an initial molecular mass equal to around 700 kDa, incubation time was about 7 h. With chitosan that was irradiated in the solid state to a dose of 50 kGy incubation time reached about 15 h, and no bacteria appeared when chitosan was irradiated to a dose of 100 kGy. However, use of a dose of 500 kGy and higher leads to decreases in the antimicrobial activity. The incubation times were as follows: 500 kGy – about 60 h, 1000 kGy – about 30 h, 1500 kGy – about 20 h, and 2500 kGy – *ca.* 3 h [4]. The most active fractions of chitosan have M_w in the range of 100-300 kDa.

For example, the use of irradiated chitosan was more efficient in protecting fruit against spoilage. When fruits were coated with non-irradiated and with irradiated chitosan, the irradiated chitosan extended shelf-life from 7 to 15 days [4].

Antioxidant activity was detected for the oligomers of chitosan, alginate and carrageenan made using irradiation processing [6, 7].

Promoting plant growth

Watering plants with the extracts of polysaccharide oligomers (carrageenans, alginate, chitosan, lignocellulose) made using gamma irradiation lead to an enhancement of plant growth [8, 20-22]. For example, when alginate having M_w equal to about 7000 kDa and made using irradiation (in the solid state with a dose of 500 kGy or in a 4% solution with 100 kGy) was introduced into the hydroponic cultivation of rice, there was a 15-40% increase in biomass yield with dependence on the irradiation conditions and on the concentration of the alginate solution [20, 21].

The differences in the structure and susceptibility to irradiation of particular carrageenans resulted in differences between their biological activities and the changes of this activity resulting from irradiation. Native κ-carrageenan has shown the highest activity compared to the other carrageenans [20]. A comparison of the action of carrageenans irradiated to doses of 100, 500 and 1000 kGy has shown that the highest biomass yield was obtained after using of κ-carrageenan irradiated to a dose of 100 kGy (Table 1).

Table 1. The approximate biomass yields estimated basing on Ref. [20] for the cultivation fed with κ- and ι-carrageenans.

Dose [kGy]	κ-carrageenan [%]	ι-carrageenan [%]
0	40	8
100	85	35
500	40	45
1000	40	5

Further studies [2] have shown that the best effect on the growth of potatoes was observed after using carrageenan irradiated to a dose of 30 kGy. The biological activity of κ-carrageenans in plants is related to their M_n in the following order: 1 kDa < 3 kDa < 5 kDa.

The following conclusions can be drawn about carrageenans action on plant growth (based on data from Refs. [20] and [8]):

- Native: κ-carrageenan > ι-carrageenan.
- Sensitivity to irradiation: κ-carrageenan > ι-carrageenan.

There is an optimum dose which can be used to obtain the highest effect on promoting plant growth for particular carrageenans. In the case of κ-carrageenan, irradiated in the solid state, the following sequence indicates that dose greater than 30 kGy is less effective [2]: 30 kGy > 100 kGy > 500 kGy (1000 kGy – inhibited, ineffective).

Suppression of environmental stress in plants

The contamination of soil with salt or heavy ions negatively effects plant growth. The presence of lignocellulosic materials extracted from biomass or of some other oligosaccharides diminishes this effect. The activity of such materials is increased by irradiation. For example, soil contaminated with salt reduces the biomass yield by 63%. The addition of non-irradiated and irradiated lignocellulosic extracts (from palm oil fiber) to the contaminated soil increased the yield to 93 and 103%, respectively [21].

5. CROSSLINKING OF POLYSACCHARIDES AND GRAFTING POLYSACCHARIDES

Although natural polysaccharides easily form gels in water, crosslinking produces hydrogels suitable for practical applications. Gels can also be made with hydrophobic derivatives of polysaccharides. In such cases, the other solvent must be trapped in the polysaccharide matrix.

Hydrogels for biomedical and industrial applications are commonly prepared by crosslinking water soluble synthetic polymers, such as poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO), poly(acrylic acid), polyacrylamide, and polyacrylonitrile. There is increased interest in "bio-artificial" polymers made from synthetic and natural polymers, often a polysaccharide or a polysaccharide derivative. Hydrogels based exclusively on natural polymers, polysaccharides or compositions of polysaccharides and proteins, are also of interest. Multicomponent hydrogels can show improved capability for swelling, modification of the sensitivity to pH, ionic strength or temperature as compared to hydrogels based on a single respective component. A low stability in water, however, is an important limitation for the use of polysaccharide hydrogels, despite of their beneficial properties.

As with hydrogels based on synthetic polymers, hydrogels based on polysaccharides can serve as the matrices for the immobilization (microencapsulation) of the "guest" molecules or particles. This process consists of immobilizing solid particles, microdrops of liquids or bioparticles (proteins, peptides, antibodies, cells or enzymes), in a matrix of a crosslinked polymer by physical bonding and/or physical entrapment in the gel network. This can be done by polymerization or crosslinking of polymer together with the entrapped component. Microencapsulation prolongs the action of the active components because of slower and controlled release, depending on environmental conditions, such as pH. The resulting hybrid materials can be used as the major components of artificial organs as well as in various controlled delivery systems. This deals with drug delivery as used in medicine and pharmacy, biocatalyzers, catalyzers used in the chemical industry, fertilizers used in agriculture, *etc*. The immobilization of microdrops of liquids permits the substitution of liquid oils by solid powders, which simplifies some processes in food industry.

Hydrogels based on polysaccharides can be made by crosslinking the polysaccharide alone, crosslinking a system containing a polysaccharide and a synthetic polymer, or by grafting the polysaccharide. The crosslinking of polysaccharides can be performed using a chemical method with the use of a crosslinking agent, such as glutaral aldehyde or genipin. Radiation processing is also widely used for the crosslinking and grafting of polymers. To obtain products with good properties, the processes must be carried out in such a way that the crosslinks will occur between two adjacent polymer chains and not within the same chain. In the case of grafting, the formation of the large amount of the grafted copolymer with a low amount of homopolymer is preferred. In the past two decades methods for the radiation crosslinking of polysaccharides have been developed which can be used in a variety of delivery systems. In the case of biomedical applications, it is beneficial to select the conditions for crosslinking a hydrogel such that the irradiation dose used for crosslinking relates to the sterilization dose of 25 kGy.

Materials crosslinked by irradiation have already found or are expected to find biomedical uses, in particular as wound dressings (including bioactive dressings), in drug delivery systems, as dietary supplements, for cushioning bedsores, as well as for use in the cosmetics industry. Many of these materials show appropriate properties to find use as absorbents and soil stabilizers. The ability of various crosslinked hydrogel materials to absorb metal ions and dyes has been confirmed.

Crosslinking of polysaccharide derivatives

Crosslinking can be effectively done using ether or ester derivatives of polysaccharides in a paste-like state. Crosslinking occurs through the mobile side chains (Fig.2).

First hydrogels made using the radiation processing of carboxymethylcellulose (CMC) were described by Fei *et al.* and Wach *et al.* in 2000 [23, 24]. The authors assumed that in the case of CMC, radiation crosslinking was more effective compared to crosslinking done by chemical methods. Radiation processing was used to make hydrogels based on systems that did not include any synthetic polymer; whereas the chemical crosslinking of highly substituted CMC could only produce a slight amount of crosslinked polymer [24].

Radiation processing experiments conducted with various ether and ester derivatives of polysaccharides produced hydrogels based on CMC, CM-chitosan, carboxymethyl chitin (CM-chitin), carboxymethyl starch (CMS), methyl cellulose (MC), hydroxyethylcellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose phthalate (HPMCP), *etc*. [25-30]. Some crosslinking of the non-substituted chitosan and starch was observed [31-32].

Several factors influence the radiation process and consequently the properties of the resulting products: polysaccharide type, degree of substitution (DS), concentration of the solution being irradiated, solvent type, absorbed dose and atmosphere during irradiation.

The evidence of crosslinking is shown by formation of gel, as illustrated in Fig.5. As crosslinking progresses, the gel content increases with an increase in the hardness of the gel and a decrease in swelling capability, as in Fig.5. The minimum dose needed to initiate gel formation is called the gelation dose. Doses that ensure appropriate high efficacy of the crosslinking processes might be considerably higher. It should be remembered that degradation and crosslinking are two competing processes taking place in all irradiated materials during the radiation process.

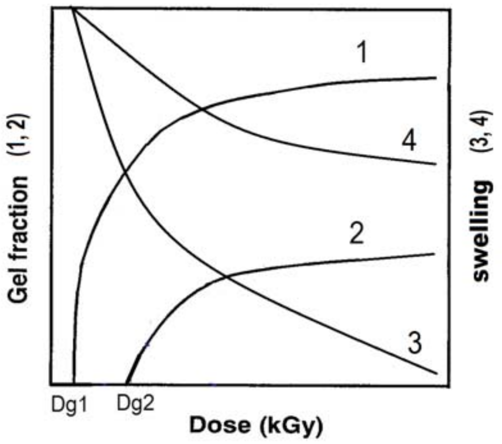


Fig.5. Schematic presentation of the dose dependence of gel formation and swelling for crosslinked polysaccharide systems: high efficiency – curves 1 and 3, low efficiency – curves 2 and 4. Dg1 and Dg2 mean the appropriate gelation doses for each type of process.

In general, a high degree of the polysaccharide substitution and a high concentration of the liquid medium favor making highly crosslinked materials, as in Fig.5. Fei *et al.* [23] observed that in the case of CMC, the efficiency of crosslinking increased when the degree of substitution increased to 2.2 and was the highest at concentrations of 20 to 30%. The effect of concentration is related to the fact that, at high concentrations, the nearest polymer chains can be close enough to each other to overcome any repulsive forces. However, with further increases in concentration, the mobility of the chains becomes too low and the probability of interaction between two adjacent chains decreases. Accordingly, the gelation dose depends on the concentration of the solution and reaches a minimum value (optimum) at a well-defined concentration. As a consequence, the optimum concentration for carrying out the most effective crosslinking should be determined separately for each particular crosslinked system.

As can be expected, the higher efficiency of crosslinking might be attained when the process is carried out in vacuum or under nitrogen, as compared to the process being carried out in the presence of oxygen (air) [23, 24].

The gelation doses for water soluble derivatives of cellulose, chitin and chitosan are relatively low, around 3 kGy. The doses needed to achieve effective crosslinking are, however, in the range of 20 to 40 kGy. Increasing dose above some critical values causes degradation of the crosslinked material.

In the case of CMS, effective crosslinking was found at lower doses compared to the carboxymethyl derivatives of other polysaccharides [27]. The effective dose determined for CMS, with a degree of substitution of 0.15, was 5 kGy in cases when irradiation was carried out in 15-50% water dispersions, and the highest efficiency of crosslink formation was observed after irradiation for dispersions with a concentration of 40%. In those instances in which there was an intermediate concentration, the content of the crosslinked material decreased when the dose was increased to above 10 kGy. The crosslinked CMS also forms hydrogels with high swelling capability, *i.e.* 1000 g/g after irradiation at a dose of 2 kGy. The lower costs resulting from the effectiveness at lower doses together with the lower price of CMS make it possible to produce hydrogels and adsorbents at lower costs compared to those based on other polysaccharides.

A majority of the crosslinking experiments were carried out in water and aimed at the preparation of hydrogels. However, crosslinking of the hydrophobic polymers is also possible when the polymer is dissolved in organic solvent or in a water solution of a salt, such as Na_2CO_3 [28, 29]. The type of solvent strongly affects the properties of the resulting gels. This effect is related to the formation of different free radicals which originate from each individual solvent due to irradiation, and to the further reactions of these radicals with polymers. For example, the formation of crosslinks in HPMCP takes place with the higher efficacy in methanol as compared to methyl acetate or to acetone [28]. The high mobility of polymer chains in a solvent also favors the formation of more crosslinks, as the polymer chains get closer one to another. Accordingly with solvents of the same type, the mobility of the polymer decreases when its chain length increases. This results in lower crosslinked density after irradiation. The gelation doses found for HPMCP were in the range of 50-60 kGy and the doses that are highly effective for crosslinking are even as high as 300 kGy [28]. This is considerably higher as compared to the water-soluble polysaccharides.

Hydrogels made by the above methods show good properties as adsorbents which are sensitive to the pH of the solution. In the cases of CMC, CM-chitosan and CM-chitin, the highest swelling ratio was achieved after using low doses, only 3 kGy. However, making hydrogels with an appropriately high mechanical resistance for use as the material in beds requires using higher doses [24, 25]. 1 g of CMC gels crosslinked in a 15% solution using doses of 3 and 40 kGy are capable of absorbing 500 or 300 g of water, respectively [30]. However, the higher crosslinked product made using a dose of 40 kGy is preferred. CMC hydrogels, crosslinked using a dose of 50 kGy, have similar mechanical resistance as hydrogels based on the synthetic polymers, and high enough swelling properties. This, together with the relatively low cost of CMC, creates opportunities for the wider use of those hydrogels as absorbents in industry and in agriculture. Functional groups in crosslinked chitosan and chitin are capable of selective binding of cations while having high swelling capability. These materials have thus the appropriate properties for use as absorbents for metal ions [26].

Crosslinked cellulose derivatives are used in pharmaceutical applications for drug encapsulation. Although the activity of the crosslinked material is lower than the base material, hydrogels made using radiation crosslinked CM-chitosan still show high antimicrobial potential and it makes them of interest in active wound dressings.

Crosslinked systems made with PVA, PVP, PEO

The introduction of the natural polysaccharides such as agar, carrageenans, chitosan or starch [33-40] into hydrogels based on PVA, PVP or PEO compositions before subjecting them to radiation crosslinking increases mechanical resistance, increases the water/solvent gain and, in some instances, imparts biological activity. In particular, the hydrogels of carrageenan with PVP or PEO absorb especially high amounts of water (over 13 000 g/g) [35] and show high mechanical strength allowing them to be used as absorbents in industry. The polysaccharide to synthetic polymer weight ratios varied from 1:10 to 3:1. Crosslinking was done in solutions containing 55 to 20% of the total polymer mass.

The structure of the mixed hydrogels is, in general, described in terms of the physical blend constructed from two interpenetrating polymer networks (IPN). However, two networks might entangle each other and interact *via* hydrogen bonding and electrostatic or ionic forces. The polysaccharide chains probably form a stiff skeleton while more flexible chains of the synthetic polymer can be entangled or entrapped within the gel matrix of polysaccharide.

The formation of crosslinks in radiation processing probably takes place with the participation of the synthetic polymer. Degradation is the major process taking place in the polysaccharide component. However, partial crosslinking or grafting of the polysaccharide and synthetic components can also take place. This concerns hydrogels of PVA or PVP with agar, carrageenan [33-35] and starch [39] (despite of the fact that majority of the starch is incorporated as a bulking agent in the PVA/PVP networks). Crosslinks form after the use of low doses in the range up to 10 kGy [34]. The other reports show that the structure resulting after irradiation of PVA (PVP)-agar and PVA (PVP, PEO)-carrageenan systems may constitute two tangled gel networks, whereas CM-chitosan is immobilized in the crosslinked PVA/PVP matrix [38].

The above studies were carried out using PVA(PVP)-polysaccharide solutions containing 5-10% of the synthetic polymer and irradiated at doses up to 100 kGy. The appropriate selection of the irradiation doses is especially important for the mixed hydrogels because of the concurrence process of polysaccharide degradation. The dose of 10 kGy was an optimum for making hydrogels containing carrageenan [36]. For example, for this polysaccharide and at this dose, the highest level of the crosslinked products, the highest strength and a high water absorption were attained. In the case of PVP/CM-chitosan, the use of higher doses of radiation might be more profitable [37], as in the cases of the systems containing only polysaccharides.

The introduction of chitosan or CM-chitosan into hydrogels based on PVA, PVP or PVA/PVP gives them an antimicrobial activity [36, 37] and results in an increase in the capability to bind to proteins, whereas hydrogels containing carrageenan show hemostatic activity [35]. These properties might be profitable for use in active dressings (*i.e.* antimicrobial, hemostatic) or in delivery systems for protein-based drugs.

Present development of hydrogels based on mixed systems is aimed at the preparation of multicomponent materials containing together several polysaccharides and synthetic polymers and the systems showing biological activity (antimicrobial, hemostatic). Such materials are foreseen for use as modern multifunctional adsorbents or in a biomedicine.

Grafting of monomers onto polysaccharide matrices

Radiation processing has been also used for grafting water soluble monomers onto starch and chitosan matrices [41-42] for use in products as absorbents. Acrylate monomers and their various derivatives were used as the graft monomers. The doses needed to attain a high degree of grafting (up to 70% of the monomer) were in the range of 2-8 kGy. Optimal properties were obtained at a monomer to starch ratio of 2:1 or 2.5:1.

The other purpose for grafting water soluble as well as water insoluble monomers (*i.e.* styrene [43]) onto starch matrices is to produce degradable materials that can be added to polyolefins in order to make partially biodegradable plastics having better mechanical properties compared to those manufactured with addition of just starch that was not grafted.

6. PREPARATION AND MODIFICATION OF BIODEGRADABLE AND EDIBLE PLASTICS

The environmental problem of increasing amounts of non-degradable plastic waste has generated interest in substituting some of these plastics, particularly those used traditional packaging materials as films and foams with novel materials based on natural and biodegradable polymers. Such materials could possibly be used as edible packaging (films and coatings) in the food and pharmaceutical industries. Such biodegradable materials should also have appropriate mechanical, barrier and sometimes sensory properties.

Polysaccharides have good film forming ability and make strong films when prepared by solution casting. However, some serious disadvantages of such materials are their high affinity to water and the dependence of mechanical properties on water content, which results in high strength films with low flexibility or low strength films with somewhat higher flexibility. Various strategies have been used to optimize polysaccharide film properties. Modification methods have been used for the polysaccharide substrates, such as degradation, crosslinking, esterification, etherification, and oxidation. Other solutions have dealt with compositions made from several polysaccharides or based on polysaccharide-protein systems. The blending of polysaccharides with biodegradable synthetic polymers, introducing hydrophobic additives (waxes, lipids, surfactants, *etc.*) or the use of reinforcing agents such as inorganic particles or fibers have also been looked at. Appropriate physical or chemical treatments are used to improve the cohesion of the polymer chains in blends. Bulk as well as surface modifications have been used for this.

Increasing interest in the use of safe and longer lasting packaged foods has generated interest in active packaging materials which would have antimicrobial or antioxidant activity [44]. This can be achieved by the introduction of active polysaccharide or other active additives (*i.e.* essential oils) into the material.

The use of the nano-sized particles or fibers results in plastics with the improved properties compared to the materials prepared with addition of the micro-sized additives. Nanocomposite systems can have also advantages when used for the delivery of active components.

Radiation modification was successfully used at the various steps in preparing films with improved functional properties or biodegradability. Radiation-initiated modification of the materials was done before the films were made. Radiation processes were also used to improve the compatibility of the film's components, to modifiy surface properties, as well as grafting the film material while in solution or on the surfaces of films. The irradiation of these packaging films has a high practical impact. This is related to the radiation decontamination of packaging materials and to the use of sterile packaging materials.

In majority of cases the doses used for systems containing polysaccharides were in the range up to 30 kGy, with higher doses being the exception. The best results were found after using doses in the range of 10 to 20 kGy.

Irradiation of solid polysaccharide before making films

The irradiation of a polysaccharide is profitable for some starch or a starch--surfactant compositions [45]. This is because good quality films or coatings could be more easily made when viscosity of the film forming solution was relatively low but with a high concentration of solids. Oxidized starches, which simultaneously degrade, are used. When radiation degradation is accompanied by oxidation, the irradiation can substitute for chemical methods. For example, the gamma irradiation of the potato starch substrate with absorbed doses in the range 5 to 30 kGy with an optimum of 10 to 20 kGy showed an improvement in the mechanical properties of films along with a decrease in hydrophilicity. The addition of a surfactant, sodium monolaurate, at an appropriate level in the composition along with using the irradiated starch produced films with hydrophobic properties. The contact angles for films made using non-irradiated starch and starch irradiated to 30 kGy were 58.4 and 100.4°, respectively. In addition to the starch being oxidized, the improvement in films properties resulted from the increased homogeneity of the films, as confirmed by scanning electron microscopy (SEM) [46].

Irradiation carried out using film forming solutions

Irradiation conducted for solutions containing polysaccharide or a composition based on polysaccharide-synthetic polymer-protein systems, with dry solids content being about 3 to 10 wt%, also produced better films. For example, improvements in the mechanical and barrier properties of the pectin-PVA (1:1), pectin-gelatin-PVA film, or the starch-locust bean gum-PVA films [47, 48] were observed after irradiation with gamma rays at doses up to 30 kGy. In the case of pectin-gelatin-PVA films (1:1:0.5) a dose of 10 kGy, when combined with crosslinking in a $CaCl_2$ solution, leads to 1.3-fold increase in tensile strength and a decrease in water vapor permeation of 0.8 of the initial value. However, in the case of alginates [49], the improvement of mechanical properties accompanied by decrease in swelling capability was found only after using a low dose of irradiation (optimum at 0.5 kGy), while additional dose leads to the films with the again inferior properties.

The improvement in the functional properties of these films can be explained by the crosslinking of the components that takes place in solutions.

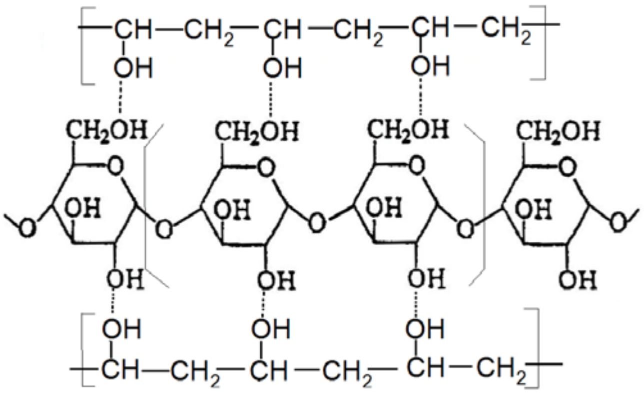
Irradiation carried out in the paste-like state

Pastes consisting of 25% of starch or up to 50% a total dry mass of polymer (starch, starch-chitosan and starch-bean protein) were irradiated then compression molded [32, 40, 50-52]. Irradiation up to 50 kGy increased the strength and elasticity of the films with a decrease in their hydrophilicity [32, 50, 51]. Using higher doses caused a decrease in the strength of starch and starch-chitosan films [32, 50]. Starch-chitosan films had increased antimicrobial and antifungal activity, compared to films based on non-irradiated compositions, demonstrating an occurrence of degradation processes (compare Section 4). The introduction of PVA leads to a deterioration the film properties [52], regarding the PVA crosslinking and initiating hydrogel formation [40] (compare Section 5). In such cases, good quality foams were produced [40].

Irradiated pastes containing about 50% dry solids have been successfully used for the compositions based on flours made from some leguminous plants [51].

Irradiation of films

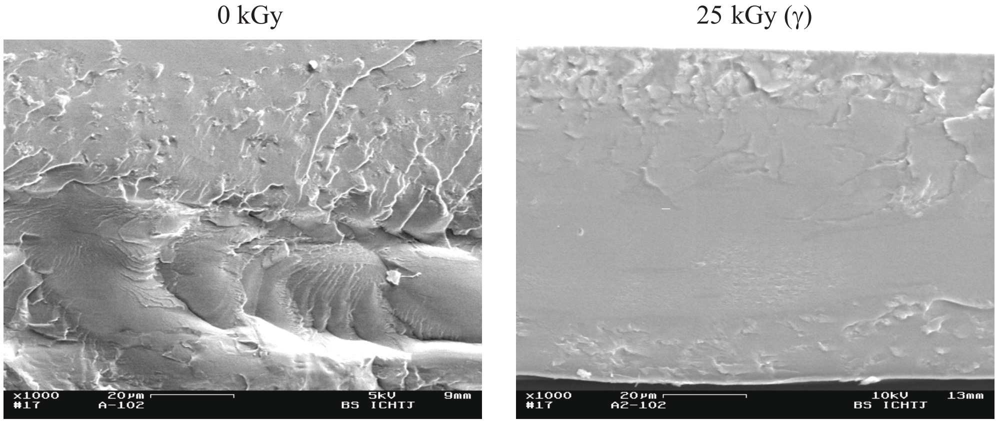
Although degradation of polysaccharide is expected with the use of pure polysaccharide, surface as well as bulk crosslinking also takes place when multicomponent systems based on several polysaccharides or on polysaccharide-protein-synthetic polymer systems are used [53, 54]. The proposed mechanism of hydrogen bonding in a starch-PVA system is shown in Scheme 3. This results in increased tensile strength in films and a decrease in elasticity. Although the radiation process took place in bulk, surface modification is especially important.



Scheme 3. The proposed mechanism of hydrogen bonding in a starch-PVA system.

Irradiation with gamma rays and with fast electrons in air causes oxidation, especially surface oxidation, as confirmed by the formation of C=O groups in films based on pure polysaccharides, as starches and chitosans, as well as starch-PVA films [55, 56]. This leads to increased hydrophobic properties of films, as shown by a considerable increase in contact angle to water (*i.e.* going from 69 to 88° [55]).

The improvement of the functional properties of multicomponent films after irradiation is due to their increased homogeneity besides chemical processes. Examples are starch-lignin films irradiated with fast electrons to 200 and 400 kGy [57] or starch-PVA films irradiated with gamma rays to 25 kGy, as shown in Fig.6 [55].



0 kGy

25 kGy (γ)

Fig.6. SEM images of the fracture of starch-PVA films (50:50, 30% of glycerol), non-irradiated and irradiated [55].

The use of gamma and/or electron beam irradiation was found to be an effective way to improve the properties of films based on starch-PVA, MC, MC-chitosan, starch-chitosan and CMC-sodium alginate compositions [53-55, 58-60], including those containing cellulose nanocrystallites (NCC). Irradiation improved the properties of films that contained natural antioxidants, such as gallic acid, ferulic acid or tyrosol. This effect was attributed to formation of crosslinks between the polymer chains *via* flexible molecules of the antioxidants [61].

Currently an important question arises concerning the effects of irradiation on the properties of bioactive films and coatings made by physical entrapment of guest molecules in the polymer network as their activity and possible release of the active component into a packaged product.

Radiation grafting of hydrophobic and active agents

Radiation processing can be used to improve the mechanical and barrier properties of the polysaccharide films by radiation grafting of appropriate monomers. 2-Hydroxyethyl methacrylate (HEMA) monomer was added to polysaccharide solutions before casting of films as based on MC, chitosan, starch or chitosan-starch compositions [62, 63]. Irradiation of the films with relatively low doses, from 1 up to 25 kGy, depending on the composition, improved the film strength, elasticity, and moisture barrier properties.

Radiation techniques can be also used to graft active components on films. This can be done by activation of the polymeric matrix using radiation treatment followed by immersion in the solution of the active component [64].

Introduction of NCC modified by radiation supported grafting a natural antioxidant (gallic acid) into gellan gum films improved the functional properties of the films, as compared to those containing none or the unmodified NCC [65].

Protection of food by edible coatings and irradiation

Protecting foodstuffs with coatings based on radiation-modified polysaccharides might help prolong their shelf-life as compared to the coatings based on non-modified materials. Food protection was more effective when active components were introduced into the film compositions, in particular when an active polysaccharide (*i.e.* chitosan) was used as the substantial component. In this case, the protective effect was strengthen after irradiation (compare Section 4).

The protection of foodstuffs by covering them with edible coatings was combined with the preservation of the food using irradiation. Two procedures have been proposed: (i) the first procedure is to irradiate the food and then cover it with the coatings, and (ii) the second is to irradiate the food after coating it with a protective layer [66]. The advantage of the second procedure is that it can modify the properties of the final coating using irradiation and to produce sanitized product and modified packaging within the same process. However, only relatively low doses, up to 2-3 kGy, are permitted for some food preservation. Thus, the possibility of using radiation modification of the coating during food irradiation is rather limited.

7. RADIATION MODIFICATION OF COMPOSITES AND POTENTIAL IN OTHER AREAS

Nanotechnology and advanced materials using polysaccharides

Irradiation is beneficial in making and functionalizing biopolymer plastics containing nanoparticles, such as metal or oxide particles, carbon nanotubes, nanopolysaccharides, *etc*. This includes the use of radiation to immobilize nanopolysaccharides in biopolymer matrices for tissue engineering. Modification of these materials is conducted in relation to the modification of properties as potential scaffolds.

Radiation methods can be used for making and functionalizing polysaccharide nanoparticles. Radiation method might thus substitute or support two "conventional" methods for making polysaccharide nanoparticles or nanofibers which rely on the mechanical destruction of the fiber or on the selective acid hydrolysis of the amorphous regions in the grain or fibers. Irradiation changes the polysaccharide similar to changes made by acid or mechanical treatments. The process consists of irradiation of a water dispersion of a polysaccharide followed by the precipitation of particles [67, 68]. It was possible to diminish the mean size of starch particles from 450 to 174 nm after irradiation with an absorbed dose of 300 kGy [68].

The surface of polysaccharide nanoparticles can be functionalized to impart hydrophobic or hydrophilic properties and to modify the activity of nanoparticles by grafting with appropriate functional groups [65].

The use of ionizing radiation for the restoration of cultural heritage objects

The deterioration of paper during storage is a consequence of cellulose degradation. This is an intrinsic process of oxidative degradation taking place under influence of atmosphere and of oxidative substances present in the paper or of acid hydrolysis due to the presence of acids. Biodeterioration and the destruction of wood and paper may also be due to the action of molds, fungi and insects.

Besides disinfection, consolidation techniques are used to improve the physical properties of wood and paper artefacts [69]. Consolidation consists of introducing monomers into the recovered object and internally polymerizing them using ionizing radiation. These processes were developed in several research centers in Europe (in France, Romania, and Germany) and are used for particular cultural artifacts. The technology paper consolidation was established at the Fraunhover Institute for Electron Beam and Plasma Technology in Germany.

Food industry (food additives, foodstuffs, feedstuffs)

The ability to form gels indicates a wide use of polysaccharides and their modifications in the food industry as additives for shaping and preserving food structure. Radiation-induced degradation [70] as well as crosslinking [71] can be used for the modification of the functional properties of food hydrocolloids and the functional properties of food containing polysaccharides as well as to facilitate polysaccharides extraction from grains. Rheological properties of food, emulsification and foaming properties, water and oil adsorption are dependent on food hydrocolloids. The degradation processes of starch, cellulose and proteins that take place when irradiating foodstuffs and feedstuffs were examined to see how they facilitated digestibility of the products [72]. The doses used during the studies were in the range of 3 kGy.

8. SUMMARY AND CONCLUSIONS

The large variety of possible structural types of polysaccharides provides a diversity of physical properties and potential reactivity. The most important physical property of polysaccharides is their high affinity for water. This property determines numerous uses in the food industry, in the biomedical area, in industry and in environmental protection. At the same time, this restricts the use of plastics based on polysaccharides. Depending on the required properties of the each particular product, it is necessary to optimize the polysaccharide system of choice.

Ionizing radiation initiates numerous processes in biopolymers. The differences in the structure of a particular polysaccharide or even its conformation as well as specific arrangements of structural units in the chain affect the radiation process, its course and efficiency. The basic reactions taking place in polysaccharides are still not fully understood, but it is possible to control the process result for a respective polysaccharide by modification of the irradiation conditions. In the case of non-substituted polysaccharides, the major process, taking place in the solid state and in an aqueous environment, leads to scissioning of the glycosidic linkages, although a variety of additional reactions take place. Oxidation processes play an important role. The irradiation of ether or ester derivatives of polysaccharides in the paste-like state leads to crosslinking. The relation between degree of degradation and crosslinking depends on the degree of substitution of the polysaccharide and on its concentration in solutions or pastes. Irradiation grafting of some monomers leads to materials characterized by some unique properties.

Trials are now being carried out to develop new fields for the use of ionizing radiation with systems containing polysaccharides. Using ionizing radiation generates new products which can find novel applications, improves the properties of the known products or can remove biological contaminants from new objects. In particular, irradiated polymers are used for making hydrogels suitable for medicinal use, for absorbents in industry or in agriculture. Oligosaccharides made by radiation processing, in particular active oligosaccharides, are foreseen for uses in medicine, agriculture and the food industries. Irradiation is used for the modification of biodegradable and edible plastics, especially for packaging films and coatings. This includes active packaging being looked at for a variety of delivery systems, especially those which can be used in the food and pharmaceutical industries, but which are also being explored for use in agriculture and chemistry. The grafting of the active components can be done using irradiation. Biodegradable plastics might also find use as coatings in tissue engineering and as coatings or adhesives in the paper or textile industries. Irradiation might be also used in the development of nanomaterials (nanoparticles and nanocomposites), based on polysaccharide systems, as well as for modification of food and food additives or for the consolidation of cultural artifacts.

Radiation-initiated degradation of polysaccharides or lignocellulosic materials can also be used in conjunction with degradation processes carried out by using chemical agents or enzymes. In some industrial processes, for example in the paper or textile industries, radiation can improve the methods of extraction the polysaccharides from raw sources and the use of industrial or agricultural wastes.

Besides new technologies based on polysaccharides, irradiation can be used for the decontamination of food and food additives as well as for the recovery of cultural heritage artifacts and for the sterilization of hybrid materials containing polysaccharides. Methods have been developed to protect those materials against undesired changes caused by irradiation. Accordingly the study of the radiation effects on polysaccharide-based materials is of importance.

The irradiation of polysaccharide containing systems has already found or has potential to find use in plastics technology, in nanotechnology, in medicinal and pharmaceutical areas, in the food industry, in the chemical and other technical industries, in the conservation field, in agriculture and in environmental protection. The ease and relatively low costs of regeneration, recycling or use of products based on natural polymers developed from renewable resources. as compared to petrochemical synthetic polymers, can have a positive impact on the environment and on the global economy.

REFERENCES

[1]. Belitz, H.D., & Grosch, W. (1987/1999). *Food chemistry*. Berlin, Heidelberg: Springer Verlag.

[2]. Liu, X.F., Guan, Y.L., Yang, D.Z., Li, Z., & Yao, K.D. (2001). Antibacterial action of chitosan and carboxymethylated cellulose. *J. Appl. Polym. Sci.*, *79*, 1324-1335.

[3]. No, H.K., Park, N.Y., Lee, S.H., Hwang, H.J., & Meyers, S.P. (2002). Antibacterial activity of chitosans and chitosan oligomers with different molecular weights on spoilage bacteria isolated from tofu. *J. Food Sci.*, *67*, 1511-1514.

[4]. Matsuahashi, S., & Kume, T. (1997). Enhancement of antimicrobial activity of chitosan by irradiation. *J. Sci. Food. Agric.*, *7*, 237-241.

[5]. Abad, L.V., Relleve, L.S., Racadio, C.D.T., Aranilla, C.T., & De la Rosa, A.M. (2013). Antioxidant activity potential of gamma irradiated carrageenan. *Appl. Radiat. Isot.*, *79*, 73-79.

[6]. Şen, M., & Atik, H. (2012). The antioxidant properties of oligo sodium alginates prepared by radiation-induced degradation in aqueous and hydrogen peroxide solutions. *Radiat. Phys. Chem.*, *81*, 816-822.

[7]. Yuan, H., Zhang, W., Li, X., Lu X., Li, N., Gao, X., & Song, J. (2005). Preparation and in vitro antioxidant activity of κ-carrageenan oligosaccharides and their oversulfated, acetylated, and phosphorylated derivatives. *Carbohyd. Res.*, *340*, 685-692. DOI: 10.1016/j.carres.2004.12.026.

[8]. Relleve, L., Nagasawa, N., Luan, L.Q., Yagi, T., Aranilla, C., Abad, L., Kume, T., Yoshii, F., & dela Rosa, A. (2005). Degradation of carrageenan by radiation. *Polym. Degrad. Stabil.*, *87*, 403-410. DOI: 10.1016/j.polymdegradstab.2004.09.003.

[9]. von Sontag, C. (2001). Carbohydrates. In: C.D. Jonah & B.S.M. Rao (Eds.), *Radiation chemistry. Present status and future trends* (pp. 481-511). Amsterdam, London, New York, Oxford, Paris, Shannon, Tokyo: Elsevier Sciences BV.

[10]. Stryer, L. (2003). *Biochemia* (Wyd. 2 popr.). J. Augustyniak & J. Michejda (Red.). Warszawa: Wydawnictwo Naukowe PWN. [Translation from the 4th American edition].

[11]. Nagasawa, N., Mitomo, H., Yoshii, F., & Kume, T. (2000). Radiation induced degradation of sodium alginate. *Polym. Degrad. Stabil.*, *69*, 279-285.

[12]. Kang, H.J, Byun, M.-W., Yook, H.S., Bae, C.-H., Lee, H.-S., Kwon, J.-H., & Chung, C.-K. (1999). Production of modified starches by gamma irradiation. *Radiat. Phys. Chem.*, *54*, 425-430.

[13]. Choi, W.-S., Ahn, K.-J., Lee, D.-W., Byun, M.-W., & Park, H.-J. (2002). Preparation of chitosan oligomers by irradiation. *Polym. Degrad. Stabil.*, *78*, 533-538.

[14]. Hien, N.Q., Phu., D.V., Duy, N.N., & Lan, N.T.K. (2012). Degradation of chitosan in the presence of hydrogen peroxide. *Carbohyd. Res.*, *87*, 935-938.

[15]. Hao, Y., Peng, J., Ao, Y., Li, J., & Zhai, M. (2102). Radiation induced effects on microcrystalline cellulose in 1-butyl-3-methylimidazolium chloride ionic liquid. *Carbohyd. Res.*, *90*, 1629-1633.

[16]. Croitorua, C., Patachiaa, S., Doroftei, F., Parparita, E., & Vasile, C. (2014). Ionic liquids influence on the surface properties of electron beam irradiated wood. *Appl. Surf. Sci.*, *314*, 956-966.

[17]. Shin, H.K., Jeun, J.P., Kim, H.B., & Kang, P.H. (2012). Isolation of cellulose fibers from kenaf using electron beam. *Radiat. Phys. Chem.*, *81*, 936-940. DOI: 10.1016/j.radphyschem.2011.10.010.

[18]. Chung, B.Y., Lee, J.T., Bai, H.-W., Kim, U.-J., Bae, H.-J., Wi, S.G., & Cho, J.-Y. (2012). Enhanced enzymatic hydrolysis of poplar bark by combined use of gamma ray and dilute acid for bioethanol production. *Radiat. Phys. Chem.*, *81*, 1003-1007. DOI: 10.1016/j.radphyschem.2012.01.001.

[19]. Czayka, M., & Fisch, M. (2012). Effects of electron beam irradiation of cellulose acetate cigarette filters. *Radiat. Phys. Chem*., *81*, 874-878. DOI: 10.1016/j.radphyschem.2012.03.003.

[20]. Kume, T. (2000). Utilization of polysaccharides by radiation processing. In T. Kume & Y. Maekawa (Eds.), *Proceedings of the Takasaki Workshop on Bilateral Co-operations – Radiation Processing of Natural Polymers – November 1 and 2, 1999, JAERI, Takasaki Japan* (pp. 87- 93). JAERI. (JAERI-Conf 2000-003).

[21]. Kume, T., Nagasawa, N., & Yoshii, F. (2002). Utilization of carbohydrates by radiation processing. *Radiat. Phys. Chem.*, *63,* 625-627.

[22]. Hien, N.Q., Nagasawa, N., Tham, L.X., Yoshii, F., Dang, V.H., Mitomo, H., Makuuchi, K., & Kume, T. (2000). Growth promotion of plants with depolymerized alginates by irradiation. *Radiat. Phys. Chem.*, *59*, 97-101.

[23]. Fei, B., Wach, R.A., Mitomo, H., Yoshii, F., & Kume, T. (2000). Hydrogel of biodegradable cellulose derivatives. I. Radiation-induced crosslinking of CMC. *J. Appl. Polym. Sci.*, *78*, 278-283.

[24]. Wach, R.A., Mitomo, H., Nagasawa, N., & Yoshii, F. (2003). Radiation crosslinking of carboxymethylcellulose of various degree of substitution at high concentration in aqueous solutions of natural pH. *Radiat. Phys. Chem.*, *68*, 771-779.

[25]. Zhao, L., Mitomo, H., Nagasawa, N., Yoshii, F., & Kume, T. (2003). Radiation synthesis and characteristic of the hydrogels based on carboxylated chitin derivatives. *Carbohyd. Polym.*, *51*, 169-175.

[26]. Waszkiewicz, M., Nagasawa, N., Tamada, M., Mitomo, H., & Yoshii, F. (2005). Adsorption of metal ions by carboxymethylchitin and carboxymethylchitosan hydrogels. *Nucl. Instrum. Meth. Phys. Res. B*, *236*, 617-623.

[27]. Nagasawa, N., Yagi, T., Kume, T., & Yoshii, F. (2004). Radiation crosslinking of carboxymethyl starch. *Carbohyd. Polym.*, *58*, 109-113.

[28]. Xu, L., Nagasawa, N., Yoshii, F., & Kume, T. (2004). Synthesis of hydroxypropyl methylcellulose phtalate gels in organic solvents by radiation crosslinking. *J. Appl. Polym. Sci.*, *92*, 3002-3007.

[29]. Xu, L., Nagasawa, N., Yoshii, F., & Kume, T. (2003). Syntheses of hydroxypropyl methylcellulose phtalate hydrogels in Na_2CO_3 aqueous solutions with electron beam irradiation. *J. Appl. Polym. Sci.*, *89*, 2123-2130.

[30]. Yoshii, F., Zhao, L., Wach, R.A., Nagasawa N., Mitomo, H., Yoshii, F., & Kume, T. (2003). Hydrogels of polysaccharide derivatives crosslinked with irradiation at paste-like conditions. *Nucl. Instrum. Meth. Phys. Res. B*, *208*, 320-324. DOI: 10.1016/S0168-583X(03)00624-4.

[31]. Sabharval, S., Varshney, l., Chaudhari, A.D., & Ramnani, S.P. (2004). Radiation processing of natural polymers: achievements & trends. In *Radiation processing of polysaccharides* (pp. 29-38). Vienna: IAEA. (IAEA-TECDOC-1422).

[32]. Zhai, M., Yoshii, F., & Kume, T. (2003). Radiation modification of starch-based plastic sheets. *Carbohyd. Polym*., *52*, 311-317.

[33]. Rosiak, J.M., Ulański, P., & Rzeźnicki, A. (1995). Hydrogels for biomedical purposes. *Nucl. Instrum. Meth. Phys. Res. B*, *105*, 335-339.

[34]. Abad, L.V., Relleve, L.S., Aranilla, Ch.T., & Dela Rosa, A.M. (2003). Properties of radiation synthesized PVP-kappa carrageenan hydrogel blends. *Radiat. Phys. Chem.*, *68*, 901-908.

[35]. Makuuchi, K., Yoshii, F., Aranila, C.T., & Zhai, M. (2000). Improvement of mechanical properties of hydrogel by irradiation of polymers in aqueos solution with κ-carrageenan. In H. Yamaoka, H. Hase & K. Makuuchi (Eds.), *Proceedings of the 8th Japan-China Bilateral Symposium on Radiation Chemistry, October 25-29, 1999, Kyodai Kaikan, Kyoto, Japan* (pp. 192-195). JAERI. (JAERI-Conf 2000-001).

[36]. Maolin, Z., Hongfei, H.. Yoshii, F., & Makuchi, K. (2000). Effect of kappa-carrageenaan on the properties of poly(N-vinyl pyrrolidine)/kappa carageenan blend hydrogel synthesised by γ-radiation technology. *Radiat. Phys. Chem., 57*, 459-464.

[37]. Zhao, L., Xu, L., Mitomo, H., & Yoshii, F. (2006). Synthesis of pH-sensitive PVP/CM-chitosan hydrogels with improved surface property by irradiation. *Carbohyd. Polym.*, *64*, 473-480.

[38]. Zhao, L., Mitomo, H., Zhai, M., Yoshii F., Nagasawa, N., & Kume, T. (2003). Synthesis of antibacterial PVA/CM-chitosan blend hydrogels with electron beam irradiation. *Carbohyd. Polym.*, *53*, 439-446.

[39]. Maolin, Z., Yoshii, F., Kume, T., & Hashim, K. (2002). Syntheses of PVA/starch grafted hydrogels by irradiation. *Carbohyd. Polym.*, *50*, 295-303.

[40]. Wongsuban, B., Muhammad, K., Ghazali, Z., Haskim, K., & Hassan, M.A. (2003). The effect of electron beam irradiation on preparation of sago starch/polyvinyl alcohol foams. *Nucl. Instrum. Meth. Phys. Res. B*, *211*, 244-250.

[41]. Kiatkamjornwong, S., Chomsaksakul, W., & Sonsuk, M. (2000). Radiation modification of water absorption of cassava starch by acrylic acid/acrylamide. *Radiat. Phys. Chem.*, *59*, 413-427.

[42]. Kiatkamjornwong, S., Chvajarenpun, &J., & Nakason, C., (1993). Modification of liquid retention property of cassava starch by radiation graftng with acrylonitrile. I. Effect of γ-irradaition on grafting parameters. *Radiat. Phys. Chem.*, *42*, 47-52.

[43]. KIatkamjorwong, S., Sonsuk, M., Wittayapichet, S., Prassarakich, P., & Vejjanukroh, P.-C. (1999). Degradation of styrene-g-cassava starch filled polystyrene plastics. *Polym. Degrad. Stabil.*, *66*, 323-335.

[44]. Campos, C.A., Gerschenson, L.N., & Flores, S.K. (2011). Development of edible films and coatings with antimicrobial activity. *Food Bioprocess Technol.*, *4*, 849-875. DOI: 10.1007/s11947-010-0434.

[45]. Cieśla, K.A., Nowicki, A., & Buczkowski, M.J. (2010). Radiation modification of the functional properties of the edible films prepared using starch and starch--lipid system. *Nukleonika*, *55*(2), 233-242.

[46]. Cieśla, K., & Sartowska, B. (2016). Modification of the microstructure of the films formed by gamma irradiated starch examined by SEM. *Radiat. Phys. Chem.*, *118*, 87-95. DOI: 10.1016/j.radphyschem.2015.04.027.

[47]. Kang, H.J., Jo, Ch., Lee, N., Kwon J.H., & Byun, M.W. (2005). A combination of gamma irradiation and $CaCl_2$ immersion for a pectin-based biodegradable film. *Carbohyd. Polym.*, *60*, 547-551.

[48]. Kim, J.K., Jo, Ch., Park, H.J., & Byun, M.W. (2008). Effect of gamma irradiation on the physico-chemical properties of a starch-based film. *Food Hydrocolloids*, *22*, 248-254.

[49]. Huq, T., Khan, A., Dussault, D., Salmieri, S., Khan, R.A., & Lacroix, M. (2012). Effect of gamma irradiation on the physico-chemical properties of alginate-based films and beads. *Radiat. Phys. Chem.*, *81*, 945-948.

[50]. Zhai, M., Zhao L., Yoshii, F., & Kume, T. (2004). Study of antibacterial starch/chitosan blend film under the action of irradiation. *Carbohyd. Polym., 57*, 83-88.

[51]. Salmoral, E.M., Gonzalez, M.E., Mariscal, M/P., & Medina, L.F. (2000). Comparison of chickpea and soy protein isolate and whole flour as biodegradable plastics. *Ind. Crop. Prod.*, *11*, 227-236.

[52]. Ghazali, Z., Wongsuban, B., Idris, S., Adzahan, N.M, Ithin, I., & Dahlan, K.Z. (2003). Radiation modified sago-blends and its potential for biodegradable packaging materials. In T. Kume & Y. Maekawa (Eds.), *Proceedings of the Takasaki Symposium on Radiation Application of Natural Polymers in Asia, October 1 and 2, 2001, JAERI, Takasaki, Japan* (pp. 32-46). JAERI. (JAERI-Conf 2002-003).

[53]. Senna, M.M., El-Shahat, H.A., & El Naggar, A.W.M. (2011). Characterization of gamma irradiated plasticized starch/poly(vinyl alcohol) (PLST/PVA) blends and their application as protected edible materials*. J. Polym. Res.*, *18*, 763-771.

[54]. Parvin, F., Khan, M., Saadat, A.H.M., Khan, M.A.H., Islam, J.M., Ahmed, M., & Gafur, M.A. (2011). Preparation and characterization of gamma irradiated sugar containing starch/poly(vinyl alcohol)-based blend films. *J. Polym., Environ.*, *19*, 1013-1022.

[55]. Abramowska, A., Cieśla, K.A., Buczkowski, M.J., Nowicki, A., & Głuszewski, W. (2015). The influence of ionizing radiation on the properties of starch-PVA films. *Nukleonika*, *60*(3), 669-677. DOI: 10.1515/nuka-2015-0088.

[56]. Ryzhkova, I., Jarzak, U., Schäffer A., Bäumer M., & Swiderek, P. (2011). Modification of surface properties of thin polysaccharide films by low energy electron exposure. *Carbohyd. Polym.*, *83*, 608.

[57]. Lepifre, S., Baumberger, S., Pollet, B., Cazaux, F., Coqueret, X., & Lapierre, C. (2004). Reactivity of sulfur free alkali lignins within starch films. *Ind. Crop. Prod.*, *20*, 219-230.

[58]. Khan, R.A., Salmieri, S., Dussault, D., Uribe-Calderon, J., Khamal, M.R., Safrany, A., & Lacroix, M. (2010). Production of nanocellulose-reinforced methylcellulose-based biodegradable films. *J. Agric. Food Chem.*, *58*, 7878-7885.

[59]. Khan, R.A., Salmieri, S., Dussault, D., Tufenkji, N., Uribe-Calderon, J., Khamal, M.R., Safrany, A., & Lacroix, M. (2012). Preparation and thermo-mechanical characterization of chitosan loaded methylcellulose-based biodegradable film: effects of gamma irradiation. *Radiat. Phys. Chem.*, *81*, 995-998. DOI: 10.1007/s10924-011-0336-y.

[60]. Ibrahim, S.M., & El Salmawi, K.M. (2013). Preparation and properties of carboxymethyl cellulose (CMC)/sodium alginate (SA) blends induced by gamma irradiation. *J. Polym. Environ.*, *21*, 520-527.

[61]. Benbettaïeb, N., Karbowiak, T., Brachais, C.-H., & Debeaufort, F. (2015). Coupling thyrosol, quercitin or ferrulic acid and electron beam irradiation to cross--link chitosan-gelatin films: A structure-function approach. *Eur. Polym. J.*, *67*, 113-127.

[62]. Khan, R.A, Dussault, D., Salmieri, S., Safrany, A., & Lacroix, M. (2012). Improvement of the mechanical and barrier properties of methylcellulose based

films by treatment with HEMA and silane monomers under gamma radiation. *Radiat. Phys. Chem.*, *81*, 927-931.

[63]. Khan, A., Huq, T., Khan, R., Dussault, D., Salmieri, S., & Lacroix, M. (2012). Effect of gamma irradiation on the mechanical and barrier properties of HEMA grafted chitosan-based films. *Radiat. Phys. Chem.*, *81*, 941-944. DOI: 10.1016/j.radphyschem.2011.11.056.

[64]. Vasile, C., Pâslaru (Stoleru), E., Sdrobis (Irimia), A., Zaharescu, T., Ioanid, G.E., Pricope, G.C., & Munteanu, B.S. (2014). Comparative study of the effect of γ-irradiation and cold plasma exposure on the various polymeric substrate modified to impart multifunctional properties for active/bioactive food packaging materials. In *Report of the 2nd RCM on Application of Radiation Technology in Development of Advanced Packaging Materials for Food Products, 8 to 12 September 2014, Bejaia, Algeria*. Retrieved March 16, 2016 from http://www-naweb.iaea.org/napc/iachem/working_materials/TR-RCM2-Oct14.pdf.

[65]. Criado, P., Fraschini, C., Salmieri, S., Becher, D., Safrany, A., & Lacroix, M. (2016). Free radical grafting of gallic acid (GA) on cellulose nanocrystals (CNCS) and evaluation of antioxidant reinforced gellan gum films. *Radiat. Phys. Chem.*, *118*, 61-69.

[66]. Kang, H.J., Jo, C., Kwon, J.H., Kim, J.H., Chung, H.J., & Byun, M.W. (2007). Effect of a pectin-based edible coating containing green tea powder on the quality of irradiated pork patty. *Food Control*, *18*, 430-435.

[67]. Akhavan, A., & Ataeevarjovi, E. (2012). The effect of gamma irradiation and surfactants on the size distribution of nanoparticles based on soluble starch. *Radiat. Phys. Chem., 81,* 913-914. DOI: 10.1016/j.radphyschem.2012.03.004.

[68]. Przybytniak, G., Cieśla, K., Kornacka, E., Sadło, J., Buczkowski, M., & Nowicki, A. (2015). Chapter 10: Radiation supporting synthezis and curing of nanocomposites suitable for practical applications. In *Radiation curing of composites for enhancing their features and utility in health care and industry* (pp. 148-166). Vienna: IAEA. (IAEA TECDOC-1764).

[69]. Egan, A., Madrian J., Foot, M., King, E., Millington, A., Nevin, M., Buttler, C., Barker, J., & Fletcher, D. (1995). The streghtening of embrittled books using gamma irradiation. *Radiat. Phys. Chem.*, *46*, 1303-1307.

[70]. Kang, I.-J., Byun, M.-W., Yook, H.S., Bae, C.-H., Lee, H.-S., Kwon, J.-H., & Chung, C.-K. (1999). Production of modified starches by gamma irradiation. *Radiat. Phys. Chem.*, *54*, 425-430

[71]. Katayama, T., Nakauma, M., Todoriki, S., Philips, G.O., & Tada, M. (2006). Radiation induced polymerization of gum arabic *(Acacia Senegal)* in aquas solution. *Food Hydrocolloids, 20,* 983-989.

[72]. Al-Kaisey, M.T., Mohammad, M.A., Alvan, A.-K.H., & Mohammad, M.H. (2002). The effect of gamma irradiation on the viscosity of two barley cultivars for broiler chicks. *Radiat. Phys. Chem.*, *63*, 295-297.

Chapter 15

ESTABLISHED AND EMERGING APPLICATIONS OF RADIATION-INDUCED GRAFT POLYMERIZATION

Olgun Güven
Hacettepe University, Department of Chemistry, 06800 Beytepe, Ankara, Turkey

1. INTRODUCTION

Among various physical and chemical methods, radiation-induced graft polymerization (RIGP) has advantages over the other grafting techniques. Radiation-induced grafting is a means of modifying base polymers wherein grafts can result in a combination of properites related both to the base polymer backbone and to the grafted chains. Through the proper choice of monomers with appropriate functionalities, new properties such as biocompatibility, hydrophilicity, hydrophobicity, adhesion, friction resistance, barrier properties, *etc*. can be incorporated onto the radiation-activated polymers, especially very inert ones, as fluoropolymers, by graft copolymerization.

Radiation-induced graft copolymerization has been used to produce graft copolymers with diverse functionalities, properties and configurations that meet the requirements of a variety of specific separation and purification applications which are of industrial interest. Various functional copolymers in form of selective membranes, ion-exchange resins, adsorbents and polymer electrolytes and solid polymer catalysts were found to be suitable for applications in the fields of water treatment, in the chemical industry, in environmental decontamination and in biotechnology and medicine. Details of the preparation and applications of a variety of functional copolymers obtained by radiation-induced graft copolymerization for separation and purification can be found in a review article published by Nasef and Güven [1].

Radiation-induced graft polymerization has been developing in three main directions: (i) polymeric membranes, (ii) polymeric sorbents, and (iii) graft polymers for medical and biotechnology applications. Among these applications, membranes play a key role in separation and purificaton processes. Specialty membranes have become an essential part of our daily life because of their use in areas such as biotechnology, nanotechnology and membrane-based energy devices, in addition to different membrane-based separation and purification processes. The development of these uses is very cost-effective due to low energy requirements for grafting and the ease of scale-up of membrane modular design. Various types of membranes have been developed for the use in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation, electrodialysis, solid polymer electrolytes, fuel cell applications, membrane--based sensors, medical uses such as artificial organs, controlled release drugs and tissue engineering. Among these membranes, ion-exchange membranes are among the most advanced separation membranes. Ion-exchange membranes are used to solve two important environmental problems: (i) the recovery and enrichment of valuable ions, and (ii) the removal of undesirable, hazardous ions from aqueous streams, especially the extraction of toxic metal ions from effluents. Such membranes or adsorbents in general have potential use as new functional materials in the separation of ionic species, mostly encountered in the solutions containing multiple components.

Many industries, such as electronics, fiber optics, and other materials based areas as nanotechnology as well as pharmaceutical and food processing have increasing requirements for extremely high purity materials. Parts per million levels of impurities are now common, and the need for parts per billion or less concentrations of impurities is becoming more frequent.

For a wide range of applications, the most desired properties required for successful ion-exchange membranes are [2]:

- High permeability selectivity – an ion-exchange membrane should be highly permeable to counter-ion, but should be impermeable to co-ions.
- Low electrical resistance – an ion-exchange membrane should have low electrical resistance and hence less potential drop during electro-membrane processes.
- Good mechanical stability – the membrane should be mechanically strong and should have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions.
- High chemical stability – the membrane should be stable over a wide pH range from 0 to 14 and in the presence of oxidizing agents.

All of the above listed properties may not be found in conventional commodity polymers. Hence the existing polymers need to be modified to cope with these expectations. For most of the applications, modification of surfaces only would be sufficient to meet these requirements. In polymer technology, surface modifications can be easily performed by grafting of a polymer to impart the properties lacking in the base polymer. Grafting of a second polymer chain on another polymeric substrate can be achieved by various free radical polymerization techniques.

Radiation-induced graft copolymerization has been used very often to prepare various types of membranes. However, most of the radiation-grafted membranes are ion-exchange materials because functional monomers can be easily grafted onto prefabricated polymer films, a process that is difficult to perform using other grafting techniques. The consistent and growing demand for ion-exchange membranes in separation, electrochemical and biological applications along with the high cost of commercial perfluorinated ionomeric membranes have driven research to develop alternative, less expensive membranes. A number of radiation-grafted neutral and specialty functional membranes have also been made and generated potential in various applications [3]. These applications that have already reached an industrial level of acceptance together with those with high market potential as highlighted below.

2. RADIATION-GRAFTED MATERIALS FOR SEPARATION AND PURIFICATION

In the design and development of radiation-grafted materials to be used in separation processes two approaches have been considered, either to collect valuable metal ions or to remove hazardous ionic species from aqueous media. The most remarkable application for the collection of valuable metal ions is the recovery of uranyl ions from seawater which can be used in the conversion into uranium oxide to be used as nuclear fuel. This topic has been elaborated in detail by the researchers from the Takasaki Radiation Chemistry Research Establishment of the Japan Atomic Energy Authority for the last couple of decades [4].

2.1. RADIATION-GRAFTED MATERIALS FOR RECOVERY OF URANIUM FROM SEAWATER

Although the concentration of uranyl ions in seawater is around 3 ppb, considering the vast volume of oceans and other seas, the total amount of uranium in seawater has been calculated to be 4.5 billion tons, which corresponds to 1000 times the amount available from terrestrial sources. The recovery of a rare earth metal like uranium from seawater has been considered a promising way to secure future fuel needs for atomic energy. In the development of an adsorbent for the selective adsorption of uranyl ions, the presence of other ions such as sodium, potassium, calcium and magnesium which are abundant in seawater has to be taken into account. Amidoxime (AO) adsorbents are considered as the most appropriate material for the recovery of uranium from seawater. Amidoxime groups are obtained by the chemical conversion of nitrile groups. Thus a nitrile group carrying monomer, such as acrylonitrile (AN), has been the monomer of choice for radiation grafting onto polyethylene

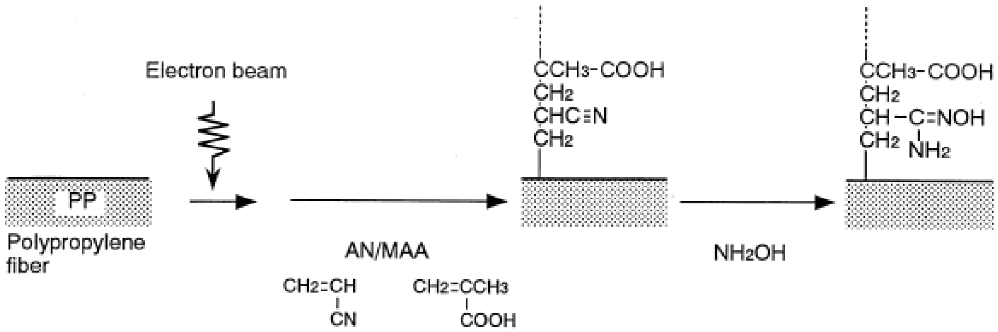


Fig.1. A simplified scheme for the preparation of amidoxime fibers by radiation-induced grafting.

(PE) or polypropylene (PP) fabrics for the preparation of amidoxime adsorbents. Adsorbents having AO groups exhibit a high selectivity for uranium complexes which exist as the tricarbonate-uranyl(VI) complex, $[UO_2(CO_3)_3]^{4-}$, in seawater. The adsorbed uranyl ions are easily recovered by elution with acid solutions. Polyethylene-coated polypropylene non-woven fibers (NF) are generally preferred as substrate materials for the radiation grafting of acrylonitrile monomer because of their environmental stability, chemical inertness, ease of radiation grafting and economics. The hydrophilicity of the adsorbents can be appended simply by using a monomer containing a hydrophilic group, such as 2-hydroxyethyl methacrylate or methacrylic acid (MAA) together with acrylonitrile. The hydrophilic amidoxime fibers are effective in accelerating uranium diffusion into the pores of the fibers. Katakai *et al.* [5] prepared MAA-cografted amidoxime fibers and demonstrated that these fibers exhibited an adsorption rate about four times that of fibers grafted with just amidoxime. A simplified scheme for the preparation of hydrophilic amidoxime fibers by radiation-induced grafting is shown in Fig.1.

The uranyl ion adsorption performance of adsorbents prepared by using different compositions of AN and MAA as monomers were tested and it was found that adsorbents prepared by using the ratio of AN/MAA at 60/40 showed the highest performance [6].

Kavakli *et al.* prepared a new type of fibrous adsorbent by incorporating two adjacent amidoxime groups in a repeating unit by radiation-induced graft polymerization [7]. The unique advantage of these polymers is that they contained double the amidoxime groups per repeating unit, an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit to improve the recovery of uranium and other transition metal ions from seawater and aqueous media at very low concentration levels (in ppb) more efficiently [8].

In the resultant structure shown in Fig.2, this adsorbent is enriched with amidoxime groups and the resulting adsorption efficiency for uranyl ions is more than 50% higher than adsorbents carrying a single amidoxime group per

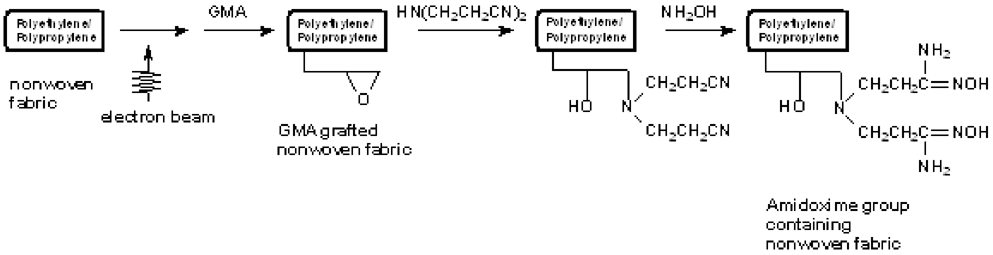


Fig.2. Scheme showing the synthesis of a novel non-woven adsorbent with enriched amidoxime groups.

repeat unit. There have been numerous attempts to develop special adsorbents for the uptake of uranyl ions from aqueous solutions and seawater. A comparative evaluation has been made to see which grafted groups have the best uranyl ion adsorption capacity.

2.2. COLLECTION OF URANIUM FROM SEAWATER

Most of the work on development and application of amidoxime adsorbents for the removal of uranium from seawater has been carried out by the Japanese scientists for the last three decades. Their findings are described below.

The amidoxime adsorbent fabric was prepared in a pilot facility at the Takasaki Radiation Chemistry Research Establishment in Japan. Rolls of polyethylene non-woven fabric, 200 m long and 1.5 m wide, were pre-irradiated by gamma rays to a dose of 200 kGy. The irradiated fabrics were then reacted with a monomer mixture of acrylonitrile and methacrylic acid. The grafting reaction proceeded for 5 h with the non-woven exposed to the monomer mixture and a degree of grafting of 120% was achieved. After amidoximation, a uranium adsorbent fabric of 6000 m^2 and 700 kg in weight was obtained for use in a marine experiment [9]. The collection system was composed of a floating frame carrying cages loaded with the adsorbent fabrics. At the end of about 20 to 30 days of seawater contact, the adsorbent fabrics were fractionally eluted by 0.5 M HCl to collect uranyl ions. The average capacity of the adsorbent was found to be 0.5 g-U/kg-adsorbent after 30 days of soaking. In order to reduce the operational costs, instead of using floating frames containing adsorbent beds, a new type of braid adsorbent was developed by the same group of researchers. The amidoximated braid type non-woven adsorbents of 60 m long were anchored at the sea bottom near Okinawa island in Japan and capacity of this type of adsorbent was determined to be 1.5 g-U/kg-adsorbent for 30 days' soaking which is three times higher than floating technique.

A group from the Oak Ridge National Laboratory, USA, presented a detailed cost analysis to verify the technical and economic feasibility of uranium recovery from seawater based on marine experiments performed at various locations [10]. Improvements in adsorbent performance, measured by number of viable reuses, degradation rate, and adsorption capacity, are considered as key factors that can reduce the costs of recovering uranium. The authors emphasized that as long as uranium recovery levels are in the range of grams per kilogram of adsorbent, minimizing the costs of fabrication of the adsorbant should be a key objective. The cost of producing the adsorbent itself was estimated by Schneider and Sachde at US$5.4/kg-adsorbent [10]. As the technology continues to develop, two pathways will be considered. If adsorbant capacity could be increased dramatically, this might lead to a very high-loading, single use material. Under this pathway, reducing adsorbent fabrication costs would benefit the uranium recovery cost most signicantly. Alternatively, the focus could turn to a very durable material that can sustain many uses without capacity loss. In this case, because the material would be moored at sea many times over its life cycle, deployment and mooring become the critical cost driver. Adsorption capacity and number of recycles are thus the main cost drivers for uranium recovery from seawater. The authors suggest that these economic analyses provide the motivation to develop robust adsorbents which can have high uranium capacity and which can be regenerated and recycled many times [10].

2.3. SCANDIUM RECOVERY FROM HOT SPRINGS

Scandium is the 30th most abundant element on the earth's crust. However, ores containing scandium as the main component are extremely rare, and scandium is primarily obtained as a by-product of uranium extraction from uranium ores. Thus, the price of scandium is 10 times higher than the price of gold, even though scandium is 1000 times more abundant. Because of the high price of scandium, advances in the research and development of its applications have been limited, with exceptions, such as new applications in catalysis. The conventional processes for recovering useful rare earth metals have disadvantages of not only environmental pollution, but also poor recovery efficiency at low capacity and low adsorption rates; therefore, finding adsorbents that can efficiently recover these metals, particularly scandium, by adsorption would be beneficial. In Japan, hot springs contain many dissolved metals such as vanadium and scandium. If these metals can be collected from hot springs, the industrial demand could be met. A suitable metal adsorbent was synthesized by radiation-induced graft polymerization by the direct grafting of 2-hydroxyethyl methacrylate phosphoric acid onto non-woven fabrics [11]. To test the performance of this newly produced adsorbent, a pilot-scale adsorption facility was installed. The hot spring water (pH 1.4) pumped from Yukawa river flowing through Kusatsu town in Japan was passed through the column filled with the adsorbent at a flow rate of 2.5 to 10 L/h (space velocity, SV: 60 to

500 h^{-1}). The breakthrough point and capacity were found to be almost same as those on a lab scale. Notably, the adsorbent volumes after scale-up were as much as 7500 times larger, and no decrease in performance was observed. From these results, if the column exchange time is set at 4 h, the total amount of scandium that can be collected per column was 100 mg. This system would allow scandium to be collected at 200 g/yr per column [11].

2.4. ARSENIC GRAFT ADSORBENTS

Various oxidation states of arsenic (As), which is a highly toxic element, exist in surface and ground waters all around the world. The most commonly used removal techniques for As(V) involve coagulation and ion-exchange of granular resins. However, it is difficult to remove As(V) to a low concentration rapidly with these techniques. Therefore, a new fibrous adsorbent using radiation-induced graft polymerization has been developed to effectively remove As(V) from water [12]. Synthesis of arsenic adsorbents at the pilot scale was carried out by radiation-induced graft polymerization of 2-hydroxyethyl methacrylate phosphoric acid monomer which consists of phosphoric acid mono-(50%) and di-(50%) ethyl methacrylate esters onto a non-woven cotton fabric (NCF), and then followed by chemical modification through contact with a zirconium (Zr) solution. The apparatus, which was equipped with reaction tanks, a washing tank and a pump, can produce up to 0.3-14 m size of the As(V) adsorbent in one reaction. A degree of grafting of 150% was obtained at an irradiation dose of 20 kGy with 5% of monomer solution made with deionized water for 1 h at 40°C. Finally, after Zr(IV) was loaded onto a NCF with 5 mmol/L of Zr(IV) solution, the graft adsorbent for the removal of As(V) was produced on a pilot scale. The adsorbent which was synthesized in pilot scale was evaluated in batch mode adsorption with 1 ppm (mg/l) of As(V) solution for 2 h at room temperature. The result was an adsorption capacity for As(V) for 0.02 mmol/g-adsorbent.

2.5. ADSORBENT FOR CESIUM

As a result of a nuclear accident that took place in Fukushima Daiichi Nuclear Power Station in March 2011, a significant amount of radioactive cesium (Cs) was released into the surroundings. An extremely vital task for the restoration process was to secure safe water sources. Japanese researchers immediately developed a Cs adsorbent for producing drinking water. The adsorbent was synthesized using radiation-induced graft polymerization of glycidyl methacrylate (GMA) with ammonium 12-molybdophosphate (AMP) onto a non-woven polyethylene fabric (NFPE) [13]. The radiation crosslinked poly-

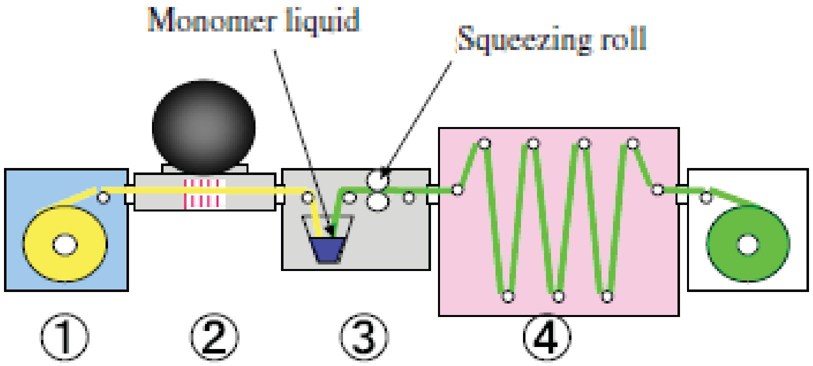


Fig.3. Schematic presentation of continuous radiation grafting system used by the Ebara Company [14] for the production of specialty membranes: 1 – trunk polymer feeding, 2 – electron accelerator, 3 – monomer impregnating zone, 4 – grafting reaction zone.

ethylene non-woven provided the adsorbent with a high stability of the loaded AMP. The Cs adsorption performances were evaluated using batch and column tests with various cesium solutions. The amount of adsorbed Cs was substantial enough for use in a wide pH range and even in the presence of coexistent ions. The amount of desorbed molybdenum from the Cs adsorbent was at a minimum at pH ranging from 5.8 to 8.6 (drinking water standard).

Figure 3 presents the scheme of continuous radiation grafting system used by the Ebara Company [14] for the production of specialty membranes.

2.6. ULTRA-PURE WATER PRODUCTION

Fine patterning in the electronics industry requires the use of ultra-pure water. Ultra-pure water is typically made by removing the contaminations such as metal ions, organic carbon, and small solid substance that may be present in wash water. The metal ions are generally removed by using a column packed with cation-exchange resins. Closely packed resins reduce the flow rate of water. To overcome this limitation in flow rate, an ion-exchange of a fibrous adsorbent was made by radiation-induced graft polymerization. An ion-exchange sulfonic acid group was bound onto a high density polyethylene non-woven fabric by radiation-induced grafting of glycidyl methacrylate and subsequent sulfonic acid chemical modification. The cation-exchange fabric was evaluated for adsorption of sodium ions in an experimental column. The effect of concentration, flow rate, and column height was investigated in terms of water purification. Total organic carbon eluted from the resulting ion-exchange fabric (IEF) could be reduced to concentrations less than 1 ppb after washing with organic solvents. Adsorption performance of the ion-exchange fabric was evaluated using a 10 ppb Na + solution. The results showed that the IEF made by graft polymerization was suitable for water purification in producing ultra-pure water [15].

2.7. AIR FILTERS

A facility for the continuous production of radiation-grafted non-woven fabrics is installed in Japan for making NH_3 gas removal filters for a large-scale integrated circuit facility. In this facility, the substrate is irradiated with a 300 keV electron beam (EB) in an inert atmosphere and then dipped into a monomer solution. The grafting proceeds as the monomer impregnates the non-woven while in the reactor [14]. The monomer is completely consumed during this grafting process, such that the removal of residual monomer is not necessary. The maximum production rate for this facility is 20 m/min. The grafted product can adsorb NH_3 quicker than conventional adsorbents such as charcoals and organic acid treated charcoal. Its adsorption capacity is 150 times higher than that of charcoal. As a spin-off technology, antimicrobial fabrics were also produced by radiation-grafting of N-vinyl pyrrolidone onto a non-woven polypropylene fabric and subsequent treatment with iodine. These fabrics have been commercialized to produce antimicrobial masks since 2002.

3. RADIATION-GRAFTED MEMBRANES FOR BATTERY AND FUEL CELL APPLICATIONS

3.1. MEMBRANES FOR BATTERIES

A battery is mainly composed of an anode (negative electrode), a cathode (positive electrode) and an electrolyte. There is also a separator and whose main function is to physically separate the positive and negative electrodes and prevent electrical short circuits while permitting the flow of ionic charge carriers necessary to complete the circuit. The separator, which is a film or membrane, must be a very good electrical insulator but also capable of conducting ions, and should be chemically and electrochemically stable. There are commercially available membranes meeting the requirements for fuel cell and battery applications and Nafion, a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer, is a frequently used separator membrane in fuel cells. Due to chemical, physical and mechanical property requirements for these applications, the base material is almost always a fluorinated polymer. Further modification of fluorinated polymers can best be achieved by radiation-induced grafting. In this way radiation-grafted membranes comparable in properties with that of Nafion are under development.

The most commercially successful radiation-grafted battery separators are for alkaline button type batteries where polyethylene is grafted with poly(acrylic acid) [16]. Lithium-ion (Li-ion) battery cells consist of a positive electrode, a negative electrode, a separator, and a non-aqueous liquid electrolyte. Microporous polyolefin separators have been widely used in Li-ion batteries because of their chemical and electrochemical properties. Microporous polyolefin separators have a low affinity for polar liquid electrolytes and a good thermal stability for the various applications. Some commercial polyolefin separators may shrink significantly at high temperatures leading to direct contact between the electrodes of opposite polarity. The separator should not shrink much at higher temperatures in order to ensure the safe operation of Li-ion batteries. In addition, the separators should have a thermal shutdown to insure a battery's safety. Poly(methyl methacrylate), PMMA-grafted PE separators were prepared by a research team at the Korea Atomic Energy Research Institute **(**KAERI), Korea [17], *via* irradiation of PE and then the grafting of methyl methacrylate to make a separator. The physical, chemical and electrochemical properties of the modified separators were tested. The results of these tests confirmed that the PE-g-PMMA separators showed better electrochemical stability than a PE separator. A PP-based battery separator was prepared by mutual irradiation grafting of acrylic acid (AA) onto microporous polypropylene films by the Bhabha Atomic Research Center in India [18]. The AA-grafted PP sheet was tested for its performance under actual battery conditions related to the battery separator membrane presently used by the battery industry in India. Samples grafted to > 20% gave satisfactory results. A sample grafted to ~20% was also used for a complete battery system consisting of 17 Ni and 16 Cd electrodes. The performance of the radiation-modified PP separator was found to be comparable to batteries made using a commercial battery separator that are being used in industry.

3.2. POLYELECTROLYTE MEMBRANES FOR FUEL CELLS

Fuel cells are a promising technology that can provide electrical energy that can satisfy the growing demand for emission free energy systems. Polymer electrolyte membranes are one of the key components in the development of fuel cells and there is a growing demand for more efficient, reliable and environmentally friendly energy systems. Amongst various methods, radiation-induced grafting is an attractive way for making polymer electrolyte materials to be used in fuel cells. Fluoropolymers, composed of synthetic polymers with structures of carbon–fluorine bonds, such as poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), poly(vinylidene fluoride) (PVDF), poly(ethylene-alt-

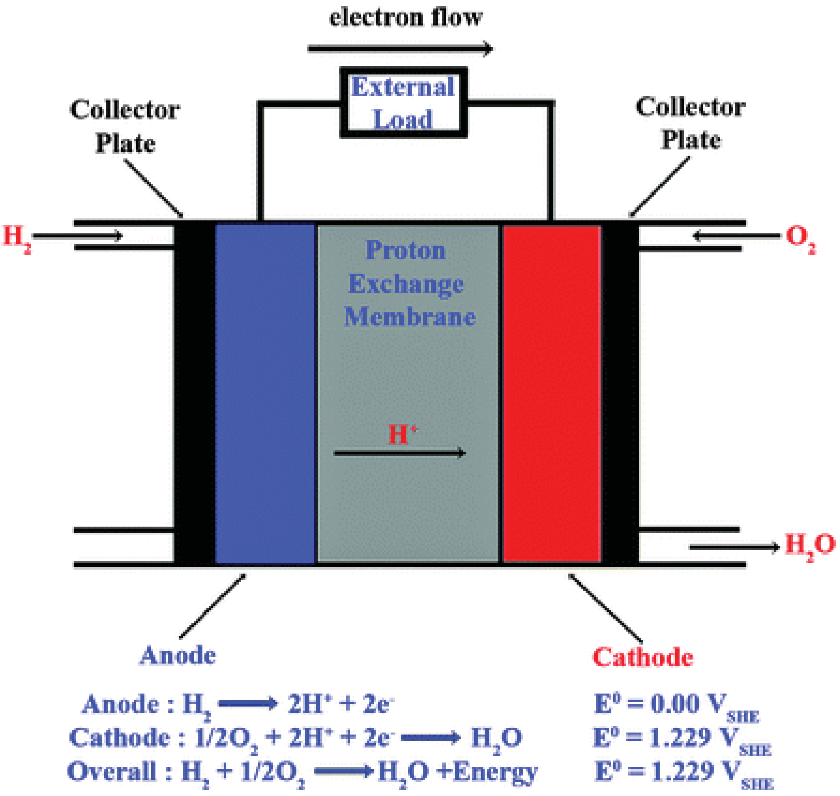


Fig.4. Sketch showing the assembly of a typical PEMFC and the electrochemical reactions involved.

-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA), and poly(tetrafluoroethylene) (PTFE), are very attractive materials as substrates for radiation-induced grafting because of their high thermal stability, good mechanical properties, and excellent chemical resistance. There are many studies in the literature reporting the use of various fluoropolymer films together with styrene for the preparation of proton exchange membranes (PEM) for use in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). Styrene is the most extensively used monomer to make proton exchange membranes by radiation grafting since it is available at reasonable cost, has established kinetics and the grafted styrene can be readily modified to introduce a variety of functionalities. A simplified sketch of PEMFC assembly and relevant reactions occurring at the anode and cathode generating electricity are shown in Fig.4.

The proton conducting membrane separates the anode and the cathode compartments such that it is impermeable to the fuels (methanol and oxygen) and has a high permeability for protons. With radiation-induced grafting of monomers onto FEP and ETFE films followed by sulfonation, proton exchange membranes for fuel cell application can be made. The use of commercial FEP and ETFE films avoids the problem of shaping the graft polymer into thin membranes of uniform thickness.

One of the most expensive components of a fuel cell is the proton conducting membrane. These are presently available at US$600-800/m^2, *e.g.* Nafion, and this has to be reduced to ~US$150/m^2 for the fuel cell technology to become more commercially viable [19]. Much work has been carried out in the search of more inexpensive membranes with comparable or better performance than those presently available. Fuel cell membranes based on fluorinated polymers made by radiation-induced grafting of monomers has been considered to be a very promising technique due to the advantages inherent in radiation grafting. Many reviews have been published covering the preparation, characterization, and performance assessment of radiation-grafted membranes obtained by radiation-induced grafting of styrene or its substituents with and without comonomers onto FEP and ETFE films in PEMFC [20-22]. The first radiation-grafted PEM was made by the radiation-induced grafting of styrene onto PE films with subsequent sulfonation. This was followed by a large number of studies using various substrate films made of hydrocarbon and fluorocarbon polymers in addition to commercial engineering plastics. The preparation of PEMs is carried out in two steps: (i) grafting and (ii) sulfonation. The stability of radiation-grafted membranes has been a subject of intensive research during the last decade and the following strategies have been established to enhance stability of membranes for PEMFC [23]:

- radiation-induced grafting of monomer with crosslinking followed by sulfonation,
- radiation-induced grafting onto new or modified polymer substrates followed by sulfonation,
- applying new radiation grafting techniques.

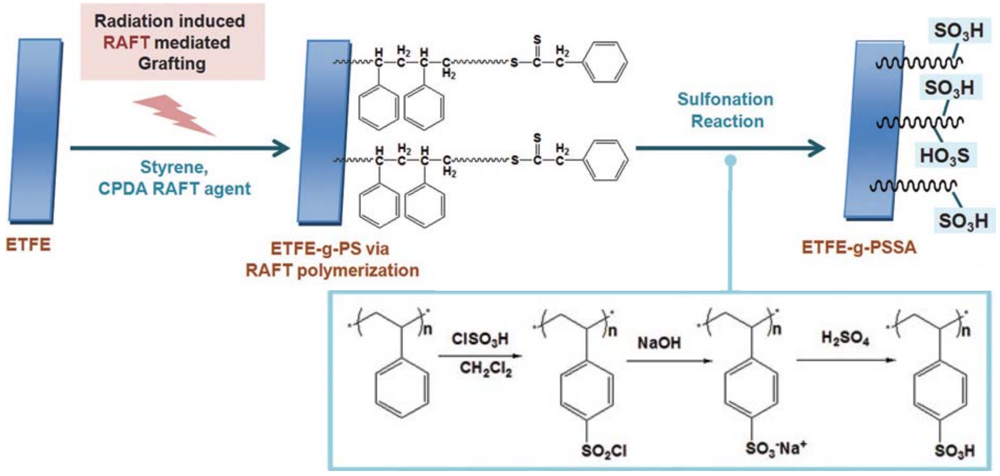


Fig.5. A scheme of the RAFT-mediated grafting process of styrene from ETFE surface and eventual sulfonation.

A comprehensive review on this subject, elaborating all the issues mentioned above, has been published by Nasef in *Chemical Reviews* [24]. The use of new radiation grafting techniques seems to have great potential for making fuel cell membranes with enhanced properties. We have shown that when free radical polymerization reactions involved in the grafting process can be controlled by so-called reversible addition-fragmentation chain transfer (RAFT) mechanism, the average molecular weight and distribution of graft chains can be controlled. Such a precise control of grafting imparts better properties to the membrane compared to grafting in the absence of RAFT polymerization [25]. Figure 5 shows a scheme of the RAFT-mediated grafting process of styrene from ETFE surface and eventual sulfonation.

By controlling the radiation-induced graft polymerization, it was shown that the introduction of RAFT polymerization in the PEM fuel cell preparation process enhanced the structural uniformity and performance in terms of proton conductivity compared to conventional methods.

4. RADIATION GRAFTING FOR HEALTH-CARE APPLICATIONS

4.1. RADIATION-GRAFTED CELL CULTURE DISHES

When tissue engineering was first proposed in the 1980s, the key materials used were biodegradable polymeric scaffolds. By combining preformed polymeric scaffolds and specific cell types, various tissues have been reconstructed. After transplantation of tissue-engineered contructs into hosts, the scaffolds degrade over weeks or months. The space formerly occupied by the scaffolds is filled with proliferated cells and deposited extracellular matrix (ECM) such as collagen. However this gave rise to the development of cell sheet engineering in trying to find solutions to avoid these limitations. In tissue reconstruction cell sheets are used but not single cells. Cell sheets are prepared on cell culture dishes having temperature responsive surfaces. Imparting thermo-responsive properties to the surfaces of culture dishes is best achieved by radiation-induced grafting of a thermo-reponsive polymer called poly(N-isopropylacrylamide) (PNiPAAm), on the surfaces where cells will be grown. This revolutionary approach was applied for the first time by Okano *et al.* [26]. This polymer exhibits a lower critical solution temperature around 32°C which means it acquires hydrophobic properties (polymer coils contracted) above this temperature and hydrophilic below it (polymer coils expanded), as shown in Fig.6.

The cell sheets grown at 37°C on the grafted polymer in a fully hydrophobic state can be easily detached by lowering the temperature below 32°C

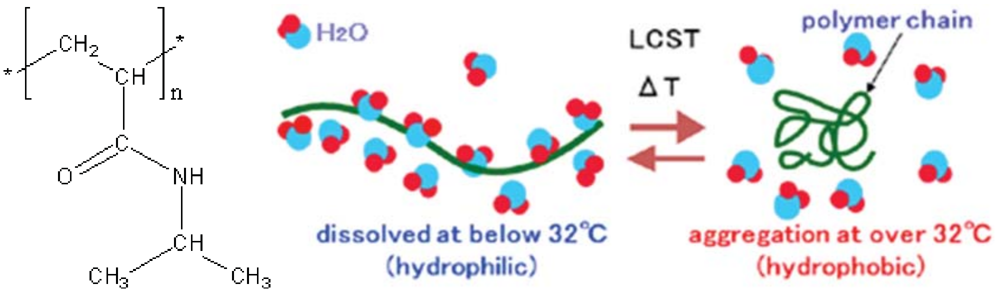


Fig.6. Chemical formula of poly(N-isopropylacrylamide) and its thermo-responsive behavior.

with polymer being transformed into hydrophilic state. Thus, the thermo-responsive behavior of poly(N-isopropylacrylamide) allows noninvasive control of cell attachment and detachment by only changing the temperature across 32°C without using any enzymatic treatment. The success of this technique depends strongly on the frequency of graft chains and their chain lengths [27].

As shown schematically in Fig.7, if the cell sheets grown on the surface of the culture dish were to be removed by using enzymes, the sheets disintegrate into individual cells (Fig.7A). However, by using the temperature responsive behavior of thin poly(N-isopropylacrylamide) layer grafted onto polystyrene culture dishes, sheets can be easily removed in tact (Fig.7B). For cell cultures, commercially available tissue culture polystyrene or polystyrene substrates are generally used for attachment of poly(N-isopropylacrylamide) on the surfaces. Using grafting methods, glass, silicon and poly(ethylene terephthalate) (PET) are also used as substrates. A review by Okano *et al.* focuses on the preparation and characteristics of poly(N-isopropylacrylamide)-modified surfaces and

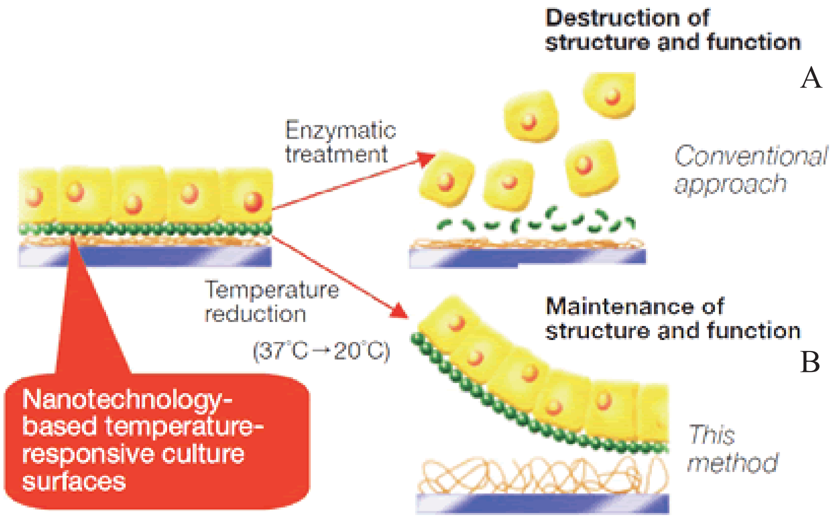


Fig.7. Noninvasive harvesting of cell sheets from PNiPAAm-grafted surfaces of cell culture dishes by temperature reduction.

discusses the effect of surface properties on cell adhesion and release [28]. Developments in improving the grafted surfaces for cell culture and for the clinical use of cell sheets harvested from the substrate surfaces are discussed. Among the clinical applications, culturing of epithelial cell sheets to heal damaged corneal surfaces, preparation of oral mucosal cell sheets to prevent post-operation inflammation, periodontal ligament cell sheets that are employed to induce tissue healing with bone, and periodontal ligament are listed [29].

4.2. ANTIBACTERIAL AND ANTIMICROBIAL SURFACES BY RADIATION GRAFTING

Worldwide, infectious diseases kill more people than any other single cause. These diseases are of particular significance in hospitals where there is considerable effort in warding off infections. Infections are triggered by germs (bacteria, viruses, fungi and protozoa), which are found everywhere, in air, soil and water. Generally, infections are combated with antimicrobial agents. In brief, the use of potent and/or specific antimicrobial systems helps to mitigate, combat and/or eradicate these infections, which means an improvement in the state of well-being. The use of polymeric materials with antimicrobial properties is of interest from both the academic and the industrial point of view. Reviews of the antimicrobial polymeric systems can be found in the literature [30, 31]. Polymers can act as a matrix for holding antimicrobial agents. Polymers with antimicrobial activity themselves is an area of research that is focused on solving the problem of contamination by microorganisms. This is a longer-term activity. Most bacterial cell walls are negatively charged, containing phosphatidylethanolamine (70%) as the major component; hence most antimicrobial polymers are positively charged. Polymers with quaternary ammonium groups are probably the most explored type of polymeric biocides. It is generally accepted that the mechanism of the bactericidal action of the polycationic biocides involves destructive interaction with the cell wall and/or cytoplasmic membranes [32].

As a typical application of radiation-induced grafting for producing antimicrobial fabrics, Ebara Clean Environment Co., Ltd. has made functional PE fabrics based a non-woven material using radiation-induced grafting of N-vinyl pyrrolidone with subsequent treatment with iodine to render it antimicrobal. To meet the huge demand for the antimicrobial materials used in face masks against the H1N1 epidemic in 2009, operational procedures were improved for high throughput reaching 133 000 m^2 [33].

To impart antibacterial properties to cotton which is a fabric widely used as a clothing material, mutual radiation grafting technique using ^{60}Co gamma radiation has been used to carry out grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton cellulose substrate. The VBT-grafted cotton samples showed excellent antibacterial activity against strains like *Escherichia* *coli* and *Staphylococcus aureus*. Samples with 25% VBT grafting showed a 6 log reduction in bacterial counts within 6 h of exposure time. The antibacterial activity of the grafted cotton samples was retained after several cycles of washing using a commercial detergent and drying [34]. The same group used gamma radiation to covalently link polymer chains of [2-(methacryloyloxy) ethyl]trimethylammonium chloride (MAETC) to cotton fabric by mutual radiation grafting. Radiation-polymerized poly(MAETC) and MAETC-g-cotton samples were tested for their antibacterial efficacy against various bacteria and were found to possess significant antibacterial activity [35]. In a similar study, a quaternary ammonium salt containing a monomer, that is [2-(acryloyloxy) ethyl)]trimethylammonium chloride (AETC), was grafted to cotton fabric by mutual radiation grafting using 2-hydroxyethyl methacrylate (2-HEMA) monomer to facilitate the grafting. Radiation-grafted poly(AETC) and AETC-g-cotton samples showed good antibacterial activity against gram-positive bacteria like *Staphylococcus aureus* and *Bacillus cereus* [36].

The development of antimicrobial polymers for food packaging has generated interest in maintaining the quality of food during long-term storage. One of the requirements of the food packaging has been to use antimicrobial packaging so that microbial infection can be prevented or controlled in food items during storage. This has resulted in a huge amount of work to incorporate antimicrobial agents into polymers and polymeric devices, so that they acquire ability to kill as well as inhibit the growth of microbes. The incorporation of antimicrobial agents on the surface of packaging materials seems to be an appropriate route. This can be achieved by either blending the antimicrobial agent into the polymer, or by immobilization of the agent on the polymer surface. Immobilization of any agent to the surface of a polymer is best achieved by radiation-induced grafting. PP surfaces were radiation-grafted with [2-(methacryloyloxy)ethyl]trimethylammonium chloride, which is a monomer with quaternary ammonium salt (QAS), for antimicrobial applications [37]. With a similar aim, radiation-induced grafting has been used to covalently bond low density polyethylene with antimicrobial additive, sorbic acid (SA), to develop a non-migrating antimicrobial active film [38]. Silver nanoparticles have found various uses because of their effective biocidal ability. The use of silver nanoparticles can be best done by surface grafting an appropriate polymer. Poly(acrylic acid) (PAA) chains were grafted onto PET film *via* γ-ray-induced graft copolymerization. The grafted PAA chains on PET film were neutralized by aqueous ammonia and then carboxylate anions were used to complex with silver ions from the silver nitrate solution. After chemical reduction of these silver ions, silver nanoparticles were immobilized on the surface of PET film. The amount of loaded silver nanoparticles can be controlled by the amount of grafted PAA, *i.e.* the degree of grafting of the PAA. The PET-g-PAA/Ag hybrid films possessed excellent bactericidal activity. The loaded silver nanoparticles were stable enough after ultra-sonication and then aging in air for 3 months [39].

5. CONCLUSIONS

Radiation-induced grafting is a simple technique for modifying base polymers because grafting may result in the combination of properties related to the backbone of the base polymer and of the grafted chains. Through the careful choice of monomers with appropriate functional groups, new molecular functionalities can be bound onto the surfaces of polymers *via* graft copolymerization. These combinations end up in countless industrial, environmental and health-care related applications. By the introduction of recently developed techniques for bringing a precise control over the molecular weight and narrow distribution of the graft chains, the prospect for radiation-induced controlled grafting is very high and will be used in the preparation of advanced materials.

REFERENCES

[1]. Nasef, M.M., & Güven, O. (2012). Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions. *Prog. Polym. Sci.*, *37*, 1597-1656.

[2]. Kariduraganavar, M.Y., Nagarale, R.K., & Kulkarni, S.S. (2006). Ion-exchange membranes: preparation methods for electrodialysis and fuel cell applications. *Desalination*, *197*, 225-246.

[3]. Nasef, M.M., & Hegazy, E.S. (2004). Preparation and applications of ion-exchange membranes by radiaton-induced graft copolymerization of polar monomers onto nonpolar films. *Prog. Polym. Sci*., *29*, 499-561.

[4]. Seko, N., Katakai, A., Hasegawa, S., Tamada, M., Kasai, N., Takeda, H., Sugo, T., & Saito, K. (2003). Aquaculture of uranium in seawater by a fabric-adsorbent submerged system. *Nucl. Technol.*, *144*, 274-278.

[5]. Katakai, A., Seko, N., Kawakami, T., Sugo, T., & Saito, K. (1998). Adsorption of uranium in sea water using amidoxime adsorbents prepared by radiation-induced cografting. *J. Atom. Energy Soc. Jpn*., *40*, 878.

[6]. Kawai, T., Saito, K., Katakai, A., Seko, N., Sugo, T., Sugita, K., Kanno, J., & Kawakami, T. (2000). Comparison of amidoxime adsorbents prepared by cografting methacrylic acid and 2-hydroxyethyl methacrylate with acrylonitrile onto polyethylene. *Ind. Eng. Chem. Res*., *39*, 2910-2915.

[7]. Kavakli, P.A., Uzun, C., & Güven, O. (2004). Synthesis, characterization and amidoximation of a novel polymer: poly(N,N'-dipropionitrile acrylamide). *React. Func. Polym*., *61*, 245-254.

[8]. Kavakli, P.A., Seko, N., Tamada, M., & Güven, O. (2004). Adsorption efficiency of a new adsorbent towards uranium and vanadium ions at low concentrations. *Sep. Sci. Technol*., *39*, 1631-1643.

[9]. Tamada, M. (2009). Technology of uranium recovery from seawater. *J. Jpn. Inst. Energy*, *88*, 249-253.

[10]. Kim, J., Tsouris, C., Mayes, R.T., Oyola, Y., Saito, T., Janke, C.J., Dai, S., Schneider, E., & Sachde, D. (2013). Recovery of uranium from seawater: A review of current status and future trends. *Sep. Sci. Technol.*, *48*, 367-387.

[11]. Hoshina, H., Ueki, Y., Saiki, S., & Seko, N. (2014). Synthesis of highly selective fibrous adsorbent by introducing 2-ethylhexyl hydrogen-2-ethylhexyl phosphonate for scandium adsorption. *Int. J. Org. Chem*., *4*, 195-200.

[12]. Hoshina, H., Kasai, N., Shibota, T., Aketagawa, Y., Tkahashi, M., Yoshii, A., Tsuroda, Y, & Seko, N. (2012). Synthesis of arsenic graft adsorbents in pilot scale. *Radiat*. *Phys. Chem*., *81*, 1033-1035.

[13]. Shibota, T., Seko, N., Amada, H., Kasai, N., Saiki, S., Hoshina, H., & Ueki, Y. (2016). Evaluation of a cesium adsorbent grafted with ammonium 12-molybdophosphate. *Radiat*. *Phys. Chem.*, *119*, 247-252.

[14]. Fujiwara, K. (2007). Separation functional fibers by radiation graft polymerization and applications. *NIM B*, *265*, 150-155.

[15]. Takeda, T., Tamada, M., Seko, N., & Ueki, Y. (2010). Ion-exchange fabric synthesized by graft polymerization and its application to ultra-pure water production. *Radiat. Phys*. *Chem.*, *79*, 223-226.

[16]. Ishigaki, I., Sugo, T., Senoo, K., Machi, S., Okamoto, J., & Okada, T. (1981). Synthesis of ion exchange membrane by radiation grafting of acrylic acid onto polyethylene. *Radiat. Phys. Chem*., *18*, 899-905.

[17]. Gwon, S.J., Choi, J.H., Sohn, J.Y., An, S.J., Ihm, Y.E., & Nho, Y.C. (2008). Radiation grafting of methyl methacrylate onto polyethylene separators for lithium secondary batteries. *Nucl. Instrum. Meth. B*, *266*, 3387-3391.

[18]. Goel, N.K., Bhardwaj, Y.K., Manoharan, R., Kumar, V., Dubey, K.A., Chaudhari, C.V., & Sabharwal, S. (2009). Physicochemical and electrochemical characterization of battery separator prepared by radiation induced grafting of acrylic acid onto microporous polypropylene membranes. *eXPRESS Polym. Lett.*, *3*, 268-278.

[19]. Horsfall, J.A., & Lovell, K.V. (2001). Fuel cell performance of radiation grafted sulphonic acid membranes. *Fuel Cells*, *1*, 186-191.

[20]. Gürsel, S.A., Gubler, L., Gupta, B., & Scherer, G.G. (2008). Radiation grafted membranes. *Adv. Polym. Sci*., *215*, 157-217.

[21]. Houchins, C., Kleen, G.J., Spendelow, J.S., Kopasz, J., Peterson, D., Garland, N.L., Ho, D.L., Marcinkoski, J., Martin, K.E., Tyler, R., & Papageorgopoulos, D.C. (2012). U.S. DOE progress towards developing low-cost, high performance, durable polymer electrolyte membranes for fuel cell applications. *Membranes*, *2*, 855-878.

[22]. Nasef, M.M., Gürsel, S.A., Karabelli, D., & Güven, O. (2016). Radiation-grafted materials for energy conversion and energy storage applications. *Prog. Polym. Sci*., in print.

[23]. Gubler, L. (2014). Polymer design strategies for radiation-grafted fuel cell membranes. *Adv. Energy Mater.*, *4*, 1300827-1300827.

[24]. Nasef, M.M. (2014). Radiation grafted membranes for polymer electrolyte fuel cells: Current trends and future directions. *Chem. Rev.*, *114*, 12278-12329.

[25]. Çelik, G., Barsbay, M., & Güven, O. (2016). Towards new proton exchange membrane materials with enhanced performance via RAFT polymerization. *Polym. Chem*., *7*, 701-714.

[26]. Yamada, N., Okano, T., Sakai, H., Karikusa, F., Sawasaki, Y., & Sakurai, Y. (1990). Thermo-responsive polymeric systems; control of attachment and detachment of cultured cells. *Makromol. Chem. Rapid Comm*., *11*, 571-576.

[27]. Takahashi, H., Nakayama, M., Yamato, M., & Okano, T. (2010). Controlled chain length and graft density of thermoresponsive polymer brushes for optimizing cell sheet harvest. *Biomacromolecules*, *11*, 1991-1999.

[28]. Haraguchi, Y., Shimizu, T.,Yamato, M., & Okano, T. (2012). Scaffold-free tissue engineering using cell sheet technology. *RSC Adv.*, *2*, 2184-2190.

[29]. Tang, Z., Akiyama, Y., & Okano, T. (2014). Recent development of temperature-responsive cell culture surface using poly(N-isopropylacrylamide). *J. Polym. Sci., Part B: Polym. Phys.*, *52*, 917-926.

[30]. Munoz-Bonilla, A., & Fernandez-Garcia, M. (2012). Polymeric materials with antimicrobial activity. *Prog. Polym. Sci*., *37*, 281-339.

[31]. Shintani, H. (2005). Bulk and/or surface modification of medical polymers to attain antimicrobial activity and/or biocompatibility. *Biocontrol Sci.*, *10*, 13-19.

[32]. Tiller, J.C., Liao, C-J., Lewis, K., & Klibanov, A.M. (2001). Designing surfaces that kill bacteria on contact. *Proc. Natl. Acad. Sci. USA*, *98*, 5981-5985.

[33]. Aoki, S., Fujiwara, K., Sugo, T., & Suzuki, K. (2013). Antimicrobial fabric adsorbed iodine produced by radiation induced graft polymerization. *Radiat. Phys. Chem*., *84*, 242-245.

[34]. Kumar, V., Bharwaj, Y.K., Rawat, K.P., & Sabharwal, S. (2005). Radiation-induced grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton fabric and study of its anti-bacterial activities. *Radiat. Phys. Chem*., *75*, 175-182.

[35]. Goel, N.K., Rao, M.S., Kumar, V., Bhardwaj, Y.K., Chaudhuri, C.V., Dubey, K.A., & Sabharwal, S. (2009). Synthesis of antibacterial cotton fabric by radiation induced grafting of [2-(methacryloyloxy) ethyl] trimethylammonium chloride (MAETC) onto cotton. *Radiat. Phys. Chem.*, *78*, 399-406.

[36]. Goel, N.K., Kumar, V., Rao, M.S., Bhardwaj, Y.K., & Sabharwal, S. (2009). Functionalization of cotton fabrics by radiation-induced grafting of quaternary salt to impart antibacterial property. *Radiat. Phys. Chem.*, *80*, 1233-1241.

[37]. Riquet, A.-M., Delattre, J., Vitrac, O., & Guinault, A. (2013). Design of modified platic surfaces for antimicrobial applications: Impact of ionizing radiation on the physical and mechanical properties of polypropylene. *Radiat. Phys. Chem*., *91*, 170-179.

[38]. Shukri, N.A., Ghazali, Z., Fatimah, N.A., Mohamad, S.F., & Wahit, M.U. (2014). Physical, mechanical and oxygen barrier properties of antibacterial active packaging based on LDPE film incorporated with sorbic acid. *Adv. Environ. Biol*., *8*, 2748-2752.

[39]. Ping, X., Wang, M., & Ge, X. (2011). Surface modification of PET films by gamma ray induced grafting of PAA and its application in antibacterial hybrid films. *Radiat. Phys*. *Chem*., *80*, 567-572.

Chapter 16

FUNDAMENTAL ASPECTS OF RADIATION-INDUCED CURING OF COMPOSITES

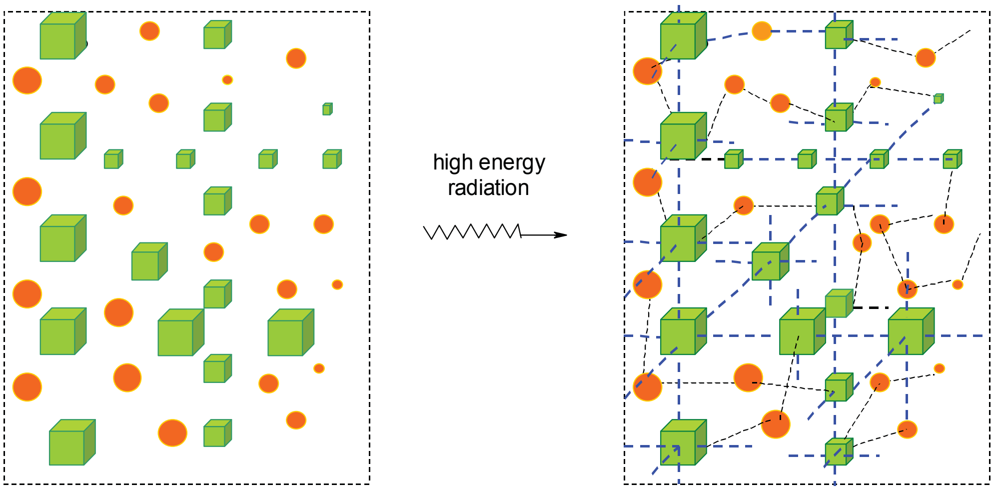
Xavier Coqueret, Guillaume Ranoux
Université de Reims Champagne-Ardenne, CNRS UMR 7312, Institut de Chimie Moléculaire de Reims, BP 1039, 51687 Reims Cedex 2, France

1. INTRODUCTION

Composites are engineered multiphase materials consisting of two or more materials with significantly different physical and/or chemical properties. The combination of these produces a material with characteristics different from the individual components which remain separate and distinct within the finished structure. By using properly selected materials in appropriate proportions, the resulting composite can exhibit new or improved properties, such as higher mechanical strength with a lower mass, specific optical, electrical, or magnetic properties, as well as many other possible functional properties, such as flame resistance. Composites are usually classified by the type of material used for the matrix [1]. Polymer matrix composites include a variety of reinforcements such as particles, aligned continuous fibers, discontinuous fibers, fabrics and braids and are by far the most widely used type of composites. The polymer matrix can either be a thermoplastic or a thermoset. The primary role of the continuous matrix is to bind together the embedded reinforcing component so that applied mechanical loads can be effectively transferred to it. The matrix also protects the reinforcing component from chemical and environmental attack.

Thermoset composites offer a number of advantages in terms of design options, ease of fabrication and mechanical performance with respect to weight. They are increasingly used to replace heavy structural parts and components, often made from metals, particularly in the aerospace and ground transportation industries. Such applications require composite materials exhibiting high glass transition temperatures and good compaction. Hence, the curing process is conducted at high temperatures under appropriate levels of pressure.

In a different area, inks and paints can be considered composite materials since they have a continuous polymer matrix and particulate fillers and pigments. The formation of polymer networks using radiation-initiated crosslinking-polymerization or curing in graphic arts and industrial coating is now a well-established technology that has been rapidly expanding since the 1980s [2]. This represents an alternative to solvent-based processes that are being banned and restricted because of their detrimental impact on the environment. Radiation curing technology offers several advantages in terms of eco-design (energy saving, reduction of volatile organic compounds (VOCs) and emissions, *etc*.) [3]. *In-situ* polymerization of restorative resins infused into damaged archeological objects made of wood or into weak artistic pieces of porous structure is another illustration of the unique in-depth effects that can be induced under mild conditions by high energy radiation [4]. High energy radiation treatment from electron beam (EB) accelerators is a more suited alternative to intense ultraviolet radiation (UV) for initiating in depth the crosslinking-polymerization of solvent-free compositions including monomers and reactive pre-polymers. The rapid polymerization process is triggered by exposure to ionizing radiation. Because of the presence of multifunctional monomers in a formulation, a three-dimensional covalent network is formed, resulting in the drying of the initial formulation and yielding mechanically toughened and chemically resistant materials, as illustrated in Scheme 1.



Scheme 1. Radiation-induced crosslinking-polymerization of monofunctional (○) and multifunctional (□) monomer blends.

Liquid or semi-solid formulations can be handled and applied to substrates by various means, spraying or rollor or blade coating as are solvent-based coatings. Acrylate derivatives and some vinyl aromatics are well-suited to give fast curing by free radical mechanisms. Epoxy or vinyl ether functional analogs can be cured by a cationic process requiring the addition of onium salt initiators. Pigments and additives are added to the formulation in order to facilitate the coating application, to enhance curing efficiency and to adjust performance and end-use properties of the coating. UV radiation is extensively used for labels, cartons and containers in the packaging industry. High energy radiation curing provides additional advantages compared to ultraviolet radiation. No initiator is needed for free radical polymerization and the penetrating power of electrons is greater than photons in the ultraviolet range at usual concentrations of photoinitiator and/or in formulations with high pigment or filler concentrations. Electrons are more efficient than ultraviolet radiation in that they penetrate opaque coatings and in composites they activate monomers even after vitrification of the network which undergoes gradual curing. This results in lower amounts of unreacted monomers and other extractables. Grafting reactions can also take place at the substrate-coating interface, thus improving adhesion.

Advances in formulations as well as in process control of radiation curing allow for major industrial developments in the food packaging industry and for industrial coatings (flooring, outdoor building parts, and such). Curing of fiber--reinforced polymer composites using high energy electron beams offers similar significant advantages for making a variety of aerospace, water vessels and ground vehicle components, as demonstrated by the Technicopolis programme [5]. The EB/X-ray curing process greatly reduces the time required to crosslink the polymer matrix compared to conventional heat curing. This process allows for curing without external thermal activation that results in high throughput. Radiation curing yields materials with reduced residual stresses for good part dimensional stability and fitting. Curing times are shorter and the curable formulations have long storage stability. The absence of highly volatile monomers renders the industrial process safer and more environmentally friendly.

Multifunctional monomers as aromatic acrylates or epoxies can be used as the resin matrix in high-performance composites due to their good mechanical, thermal, and electrical properties. Both types of monomers react according to specific mechanisms and yield networks with properties that can be adjusted by formulating the resin and by using the appropriate treatment under the radiation source.

2. RADIATION CURING

Ionizing radiation, EB, gamma or X-rays, is non-selectively absorbed by matter and thus generates at random a mixture of ionic species, free radicals, molecules in an excited state and solvated electrons. Depending on the medium subjected to irradiation, those active species can induce various types of chemical reactions, namely polymerization, crosslinking or scissioning of polymeric chains, grafting, oxidation, *etc*. [6]. Under irradiation, molecules with carbon-carbon double bonds, such as vinyl or acrylate monomers, undergo fast polymerization *via* a free radical mechanism. The cationic polymerization of epoxies, oxetanes and vinyl ethers requires a suitable initiator, as an onium salt.

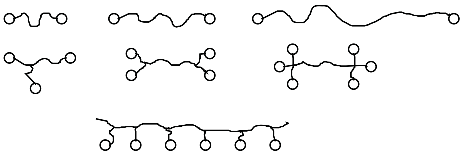
2.1. RADIATION-INDUCED POLYMERIZATION

Chain reactions are efficiently initiated with moderate radiation doses or exposure because modest exotherms result in the amplification of the kinetics of radiation-induced initiation. Processes involving single steps or short kinetic chain length reactions require much higher doses. This is generally the case for the radiation crosslinking of rubbers and thermoplastics. The matrices dedicated to electron beam processing of composites are generally designed for a specific application. In filament wound structures, where the properties of the roving are optimized to reach the maximum tensile strength of the fiber, the overall tensile properties are less important. But for other applications where the loading is complex, the off-axis material properties, such as transverse and shear, are important. These materials need to be developed to provide the maximum tensile yield, but the transverse properties of these composites are generally limited with radiation-cured materials. Two criteria are known to be of prime importance to improve the composite transverse properties: the transfer of the loading from the matrix to the fiber through an optimized fiber-matrix interface and a sufficient matrix toughness to avoid matrix dominated failure. In view of the broadening of electron beam curing applications, the search for materials with improved properties is actively ongoing in different research groups and companies worldwide.

2.2. RESIN SYSTEMS

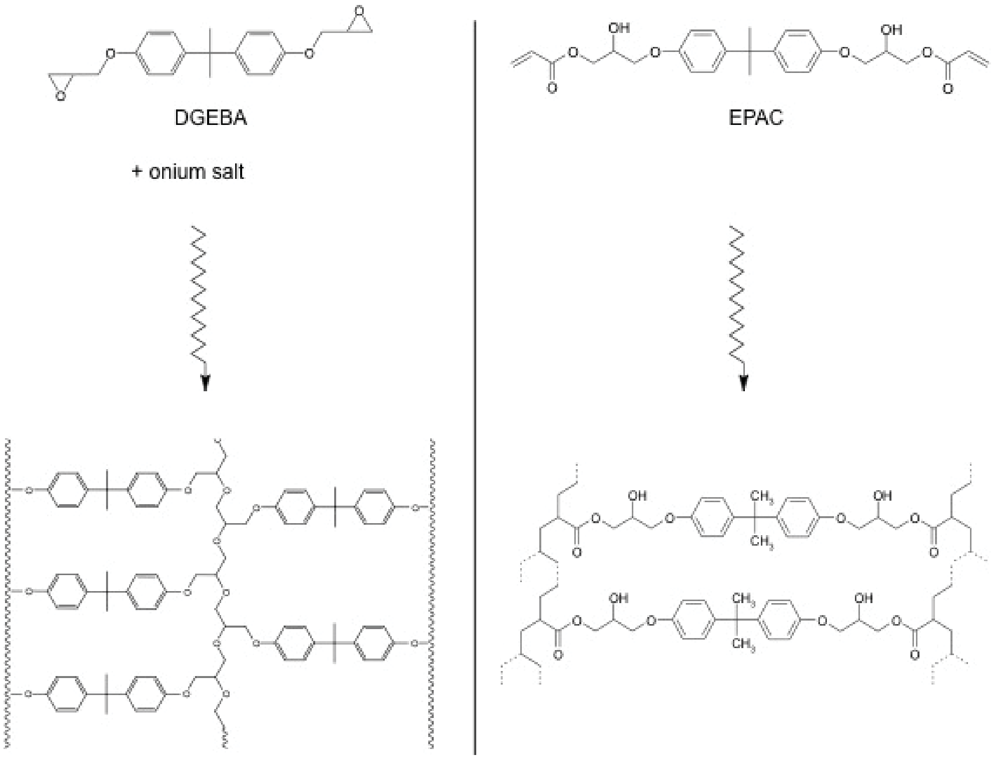
A variety of monomers and pre-polymers either with ethylenic unsaturations, mainly acrylates, or with epoxy functionality are commercially available. The molecular architecture, backbone and functionality of these monomers and pre-polymers influence both the reactivity of the radiation-sensitive composition and the physical properties of the resulting material.

The molecular architectures, shown in Scheme 2, exist for several classes of pre-polymers (polyurethanes, polyesters, polyethers, silicones and aromatic epoxies) with various molecular weights and functionalities. The degree of flexibility (or rigidity) of the pre-polymer backbone has a strong impact on the thermomechanical properties of the resulting network. Depending on the technical needs of the application, the viscosity of the pre-polymer blend can be adjusted by reactive diluents. Generally, the resin systems selected for high-performance applications must endure high service temperatures and exhibit high



Scheme 2. Typical architecture of monomers and pre-polymers available for radiation curable compositions.

mechanical properties together with a high toughness to avoid matrix dominated failure. For service temperatures higher than 120°C, resins based on aromatic monomers resembling or derived from the bisphenol A component of conventional thermosets are needed. Two representative monomers are shown in Scheme 3.

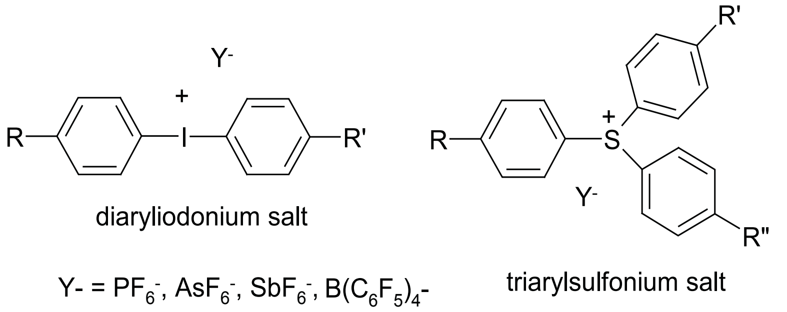


Scheme 3. Molecular structure of bisphenol A diglycidyl ether (DGEBA), of bisphenol A epoxy acrylate (EPAC) and of the networks resulting from their radiation-initiated crosslinking-polymerization.

Beyond the mentioned differences in monomer structure and in polymerization mechanisms, a number of other contrasting features may exert, in a direct or indirect manner, an adverse or a beneficial influence on the structure and on the properties of the final crosslinked materials.

The interaction between high energy radiation and organic materials generates free radical species that are efficient in initiating polymerization. The free radical process follows the same pathway as that of conventional crosslinking-polymerization initiated by thermal or redox processes. However, the dose rate of the irradiation source may strongly affect the efficiency of the process. At low dose rates, inhibition by oxygen may reduce the efficiency of initiation, and even completely preclude polymerization.

There are specific aspects of the cationic polymerization of epoxies. Radiation-initiated cationic polymerization of epoxies and vinylethers requires the use of onium salts with a low nucleophilicity anion. Aryl sulfonium or iodonium cations, as shown in Scheme 4, will be reduced by thermalized electrons or by the free radicals generated *in situ* as a consequence of radiation interaction with organic matter, yielding active cationic species (Bronsted acid, oxonium or carbenium ions).



Scheme 4. Examples of onium salts used for radiation-initiated cationic polymerization.

Cationic chain propagation proceeds *via* the reaction of the oxonium ions with epoxy monomers by the activated chain end (ACE) or activated monomer (AM) mechanisms [7]. The ACE mechanism consists of the repeated addition of monomer to the growing chain by the nucleophilic attack of the oxygen from the epoxy monomer on the carbon atom adjacent to the oxonium ion. The AM mechanism takes place in presence of hydroxyl containing species and involves their addition to the protonated monomer followed by a charge transfer; the activated monomer is then regenerated and can react again with a hydroxyl compound. As the epoxy ring opens, hydroxyl groups are formed which favor the AM mechanism. Others transfer reactions can take place between an active chain and nucleophilic species such as water, alcohol or any other hydroxyl compounds resulting in the liberation of a proton and an inactive oligomer [8].

As two cationic species cannot react together, no termination reaction occurs as a result of the self-quenching of active centers, as in the case of free radical processes. Once irradiation has ceased, cationic polymerization will continue without new initiation, by the so-called dark cure phenomenon [9], until the active centers are trapped in the glassy network or quenched by some inhibitor entering the material. This pseudo-living behavior enables further thermal activation giving rise to some beneficial post-cure effects [10].

2.3. NETWORK FORMATION AND VITRIFICATION

Radiation curing is generally achieved by processing composites at room temperature. During the process, the temperature rises a bit due to the absorption of radiation and to the exotherm of polymerization which generates typically 60 to 80 kJ per mole of reacted monomer group. The temperature reached by a sample increases when the dose, dose rate and/or initiator content increases resulting in a higher monomer mobility and a higher final conversion. The dimensions and the geometry of the cured sample are also very important since they control the kinetics of heat transfer. This explains why it is possible to achieve a high degree of conversion in vitreous samples, which have a glassy form. The curing of bisphenol A epoxy acrylate (EPAC)-based materials can yield networks with glass temperatures, T_g, as high a 180°C. The conversion dependence of T_g determined by dynamic mechanical analysis (DMA) of thin films treated under various conditions, as shown in Fig.1, exhibits a monotonous, unchanging increase suggesting a continuous build-up of the network as a consequence of increasing crosslinked density. The variations can be satisfactorily described by the Pascault-Williams relation:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1-(1-\lambda)x}$$

where: T_g – the glass transition temperature of network at conversion degree x, T_{g0} – the glass transition temperature of the uncured resin (x = 0), $T_{g\infty}$ – the glass transition temperature of the fully reacted resin (x = 1), λ – a structure-dependent parameter with value between 0 and 1, as represented by the continuous line in Fig.1 [11].

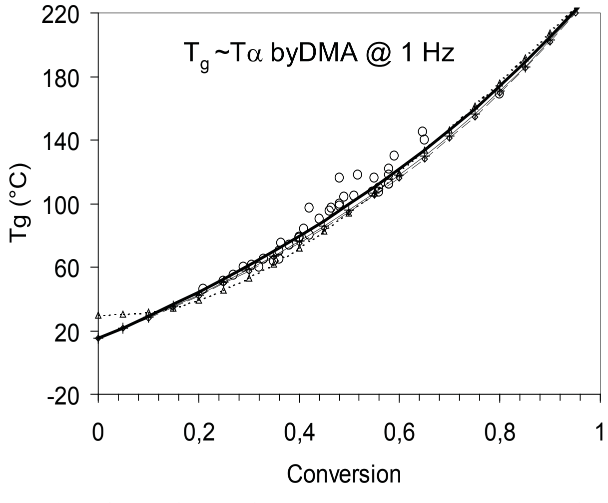


Fig.1. Plot of the T_g (tan δ maximum in DMA spectrogram) as a function of acrylate conversion for EB-cured EPAC films (for various EB doses, dose rates and dose increments).

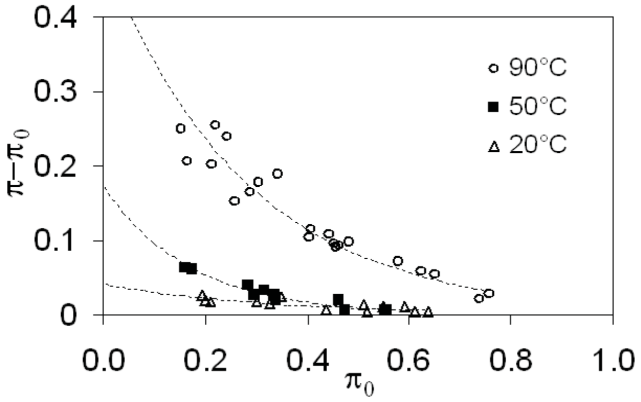
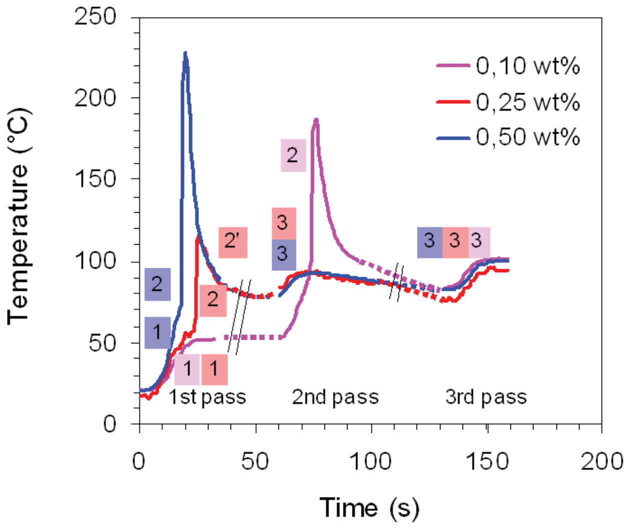


Fig.2. Conversion increase upon thermal aging *vs.* initial conversion (π_0) for EB-cured EPAC resin (35 days of aging).

The variation of acrylate conversion after thermal treatment *vs.* acrylate conversion after EB processing is illustrated in Fig.2 for EPAC resin aged at three different temperatures for 35 days. Post-polymerization increases with increasing temperature and with increasing residual unsaturation after EB processing, but is limited to less than 5% for EB-cured materials that have high conversions. Furthermore, no oxidation by-products (hydroxyl or carbonyl) were detected by FTIR after 3 months at 90°C.

Temperature monitoring during irradiation gives insight into the progress of network build-up. A thermocouple was placed in bulk bisphenol A diglycidyl ether (DGEBA) samples which included various amounts of initiator (diaryliodonium tetrakis(pentafluorophenyl)borate, Rhodorsil 2074). A 3 cm thick epoxy sample in an aluminum box was moved in front of a 10 MeV electron beam so as to receive a dose of 25 kGy per pass. The temperature profiles recorded during the EB processing of the DGEBA samples contained different amounts of an onium salt initiator and provided interesting and useful information, as shown in Fig.3. The thermal energy that caused the temperature rise in the irradiated samples not only came from the deposition of radiative energy by the electron beam into the samples, but also from the exotherm of polymerization.

With the lowest amount of initiator (0.1 wt%), one observes during the first 25 kGy pass a simple temperature step attributed to the conversion of the absorbed radiation into heat, since a similar step is recorded in the cured samples during the third and following passes. In the presence of this rather low amount of initiator, it is likely that the cationic species generated during the first pass are quenched by the nucleophilic contaminants contained in the unformulated resin itself which act as inhibitors. DGEBA resins are synthesized under basic conditions. The potentially initiating entities are not produced in sufficient concentration and the polymerization of epoxy functions does not start before the second pass.



0.5 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Exothermal polymerization, heating due to radiation absorption
3 - Heating due to radiation energy absorption (fully cured material)

0.25 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Kick off of the polymerization (partial cure), heating due to radiation absorption
2' - Vitrification
3 - Heating due to the radiation absorption, vitrified material: uncomplete curing

0.1 wt% initiator:
1 - Heating due to radiation absorption, inhibitor consumption
2 - Polymerization (total cure), heating due to radiation absorption
3 - Heating due to radiation absorption

Fig.3. Temperature profiles recorded during the dynamic EB irradiation of DGEBA samples with 0.1, 0.25 and 0.5 wt% of treated diaryliodonium salt by a dose increment of 25 kGy per pass (3 first passes shown in this figure).

The polymerization proceeds during the second exposure to the electron beam in a medium almost free of inhibitor and brought to a temperature of around 50°C. The temperature peak rises up to 180°C within approximately 10 s, just on exiting the irradiation zone.

The third pass does not lead to any significant polymerization exotherm, the temperature rise being limited to the absorbed radiation energy. With an onium salt content of 0.5 wt%, the polymerization starts and proceeds to completion during the first pass in front of the beam. The amount of initiator is sufficient to allow efficient consumption of the inhibiting species early during the first pass. The number of active centers produced is high enough to initiate the fast exotherm process that reaches completion in spite of the increase density of the network. The maximum temperature reached under these conditions is greater than 225°C. This impedes the vitrification of the sample at incomplete conversion, as observed for the intermediate content of onium salt (0.25 wt%). In this last case, the start of the exotherm from polymerization is delayed compared to the thermal effect due to the radiative energy deposition.

Polymerization is likely initiated by a smaller amount of cationic additive, possibly quenched by some residual inhibitors after some propagation steps. This results in a lower temperature rise and in a lower conversion following the first dose exposure. An important temperature decrease occurs by energy dissipation before the second pass which leads to a sample in the glassy state at 80°C. In the vitreous network, the propagation is expected to be slow and to generate a weak exotherm. As a consequence, the polymerization does not resume during the second 25 kGy pass, in spite of a significant amount of residual monomer functionality.

The effects of the thermal history on the glass transition and on monomer conversion in EB-cured DGEBA materials with diaryliodonium salts have been examined in some detail [12]. A series of samples containing various amounts of initiator were exposed to various doses so as to cover a broad conversion range. The plot of T_g variations as function of the monomer conversion exhibits a monotonous increase for low to medium conversion, up to a conversion degree of about 0.8 (the open circles in Fig.4), followed by an anomalous decrease of the T_g for conversion degrees exceeding that critical value (the open squares in Fig.4).

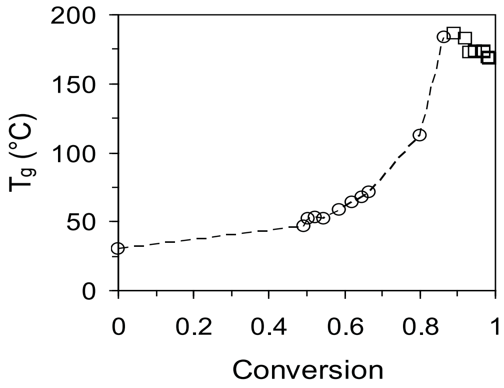
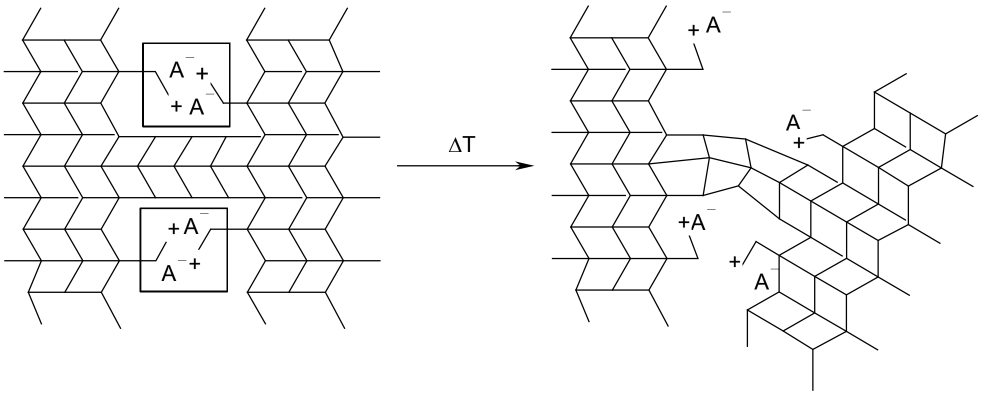


Fig.4. Plot of the T_g (E" maximum) as a function of epoxide conversion for EB-cured DGEBA samples with various initiator contents (diaryliodonium tetrakis(pentafluorophenyl)borate), EB doses, dose rates and dose increments.

Post-curing at a higher temperature than the glass transition pointed out that this decrease in the glass temperature is correlated to the amount of initiators used in the matrix.

This anomalous behavior can be explained by the relaxation of weak ion pair clusters. The build or increased density of the network likely traps the



Scheme 5. Simplified representation of the effect of a thermal treatment above T_g on the associated ion pairs within a poly(epoxy) network.

propagating oxonium and the counter-ion in vitreous clusters that contribute to the crosslinks of the network. A thermal treatment above T_g is thought to bring some segment mobility allowing for a rearrangement of the ionic clusters into ion pairs to take place. The total amount of crosslinks within the sample would decrease with amplitude correlated to the amount of ionic end groups in the network, which is observed experimentally. A simplified representation of this is illustrated in Scheme 5.

2.4. NETWORK PROPERTIES

2.4.1. Flexibilizing the matrix: the case of epoxy resins

As with thermosets, radiation curable resins can be formulated with various comonomers, reactive diluents or transfer agents to adjust the final properties of the matrix. The influence of hydroxyl compounds on the properties of the cured network has been studied by different groups [13-15]. The presence of hydroxyl groups as impurities or as additives affects the curing kinetics and, among other features of the material, the network T_g (as shown in Fig.5). Chain transfer which occurs by the activated monomer mechanism leads to shorter polymer chains and increases the mobility of the reactive species. This results in an accelerated curing, in higher final conversion of monomers, and in some decrease of T_g. It is possible to tailor the network structure of such systems by exploiting intrinsic differences in hydroxyl group reactivity. Water as a nucleophilic species is also a transfer agent which alters the polymeric network. A 23°C decrease of the T_g was observed when 1% of water was present in the matrix compared to a dry system [8].

The use of reactive diluents can facilitate the impregnation process by significantly reducing the viscosity of paste-like formulations. Reactive diluents also have an influence on the cure rate and on the final properties [16]. If the

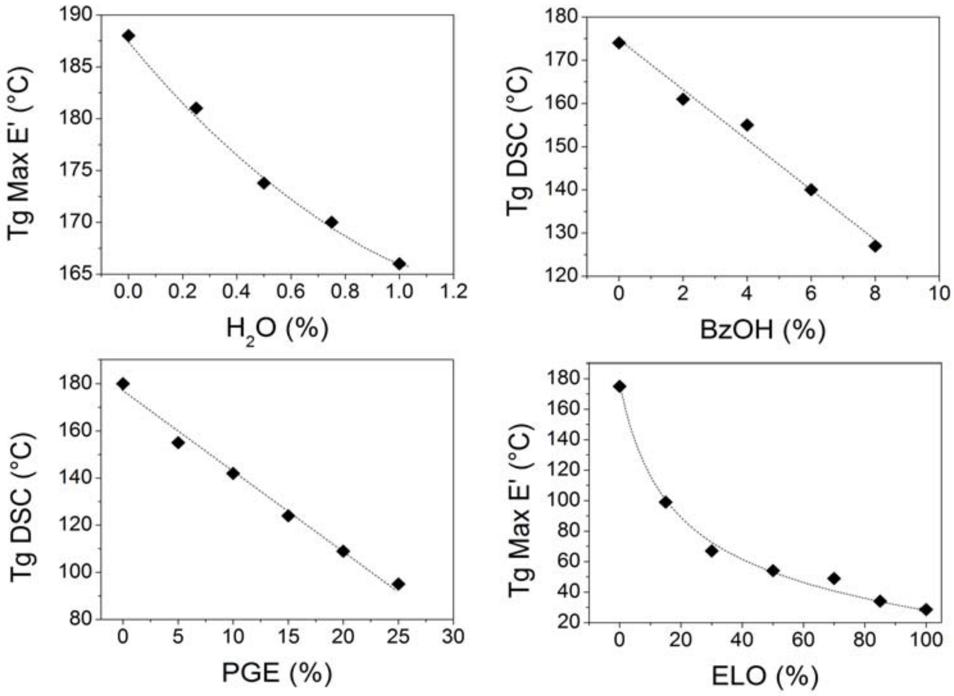


Fig.5. Influence of some reactive additives (water, benzyl alcohol (BzOH), phenylglycidyl ether (PGE) and epoxidized linseed oil (ELO)) for flexibilizing EB-cured DGEBA containing 0.5 wt% of an initiator (T_g determined by DSC (differential scanning calorimetry) or by DMA at 1 Hz).

diluent is a monofonctional monomer, the dilution causes a decrease of the crosslinked density. Some flexibilizing effect can be expected for the network.

The series of graphs shown in Fig.5 illustrate various possible formulations for adjusting the T_g of DGEBA-based resins cured by EB after an exposition to a dose 100 kGy (0.5 wt% of diaryliodonium tetrakis(pentafluorophenyl)borate, Rhodorsil 2074) with the presence of limited amounts of water or benzyl alcohol (BzOH) as transfer agents, of phenyl glycidyl ether (PGE) as a monofunctional reactive diluent and of epoxidized linseed oil (ELO) as multifunctional monomers with flexible alkyl side groups.

2.4.2. Micro-heterogeneities in matrix networks

The crosslinking-polymerization of multifunctional monomers is known to yield more brittle matrices, thus limiting the development of using such for the production of high-performance composite materials. A possible cause of such brittleness is the spontaneous formation of nano-heterogeneities during radiation-initiated polymerization, which is supported by atomic force microscopic imaging and by calorimetric analyses.

The local topography of samples cured by exposure to ultraviolet or EB radiation on NaCl plates was analyzed by atomic force microscopy (AFM).

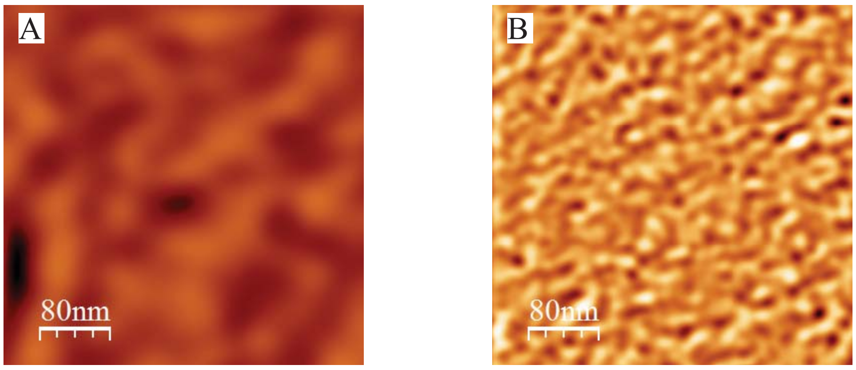
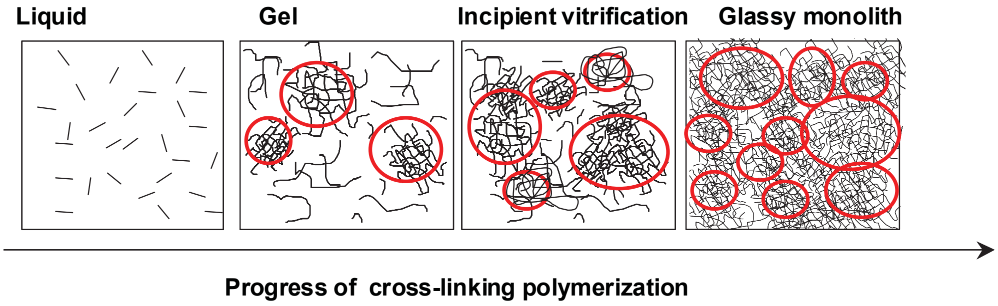


Fig.6. Height (A) and phase contrast (B) AFM images recorded in the tapping mode of partially EB-cured (20 kGy, conversion π = 0.41) epoxy diacrylate network.

The control of monomer conversion in the samples was determined by transmission FTIR to appraise simultaneously the local topography along with variations of crosslinked density as a function of the progress of the reaction. The pictures in Fig.6 show both the height and the phase contrast images the polymer network of a film made of bisphenol A epoxy diacrylate cured under an electron beam to a dose of 20 kGy yielding a conversion level of π = 0.41 for the acrylate functionality. The topographical image shows a very flat surface with a root mean square (RMS) roughness of 0.2 nm, whereas the phase contrast image highlights the more complex and heterogeneous structure of the network [17].

The sample morphology appears to be made of very stiff domains corresponding to the lower phase values, whereas the darker zones correspond to much more compliant material. Stiff domains can be reasonably associated with what can be named as clusters, originating from the initial microgels. Such clusters exhibit a densely crosslinked structure which contrasts with the softer interstitial zones that likely correspond to the loosely crosslinked and swollen portions of the matrix. This type of imaging reveals without ambiguity dense nodules with a mean diameter of about 15 nm. The description and understanding of structure-properties relationships in multi-acrylate networks by taking



Scheme 6. Sketch representing the heterogeneous build-up of networks prepared by radiation-induced chain polymerization of aromatic diacrylates.

into account their micro-heterogeneity is essential from both a fundamental and a practical viewpoint [18].

The scenario currently proposed for the build-up of the network is represented in Scheme 6. These sketches illustrate the measured variations of T_g and the broadness of the transitions in relation to the variety of defects and heterogeneities in the spatial distribution of crosslinks and their density [19, 20].

2.4.3. Matrix toughening with high T_g thermoplastics

The presence of nanoscale heterogeneities in the resulting vitreous monolithic material is one of the reasons for the brittle behavior generally observed when such materials are subjected to elongation or shear strain. The localized intensity of stress on incipient cracks results in the catastrophic failure of the material. In order to overcome this limitation, thermoplastic toughening agents have been introduced in an approach similar in some ways to the improvement of fracture resistance in thermosets with rubbers or with high T_g aromatic polyethersulfone (PES). Two notable differences with respect to the toughening methodology compared to heat curable networks are related to the particular thermal profile and kinetic conditions of radiation curing. Irradiation is generally conducted on materials at room temperature and subjected to the sudden initiation of chain polymerization with the generation of heat from the radiation energy itself and from the strong exotherm of polymerization. These two distinct features should favor the early occurrence of thermoplastic phase separation upon the polymerization of the reactive diluents and pre-polymers and should as well limit the growth of the nucleated thermoplastic domains, if the system starts vitrifying during the early stages of curing. This perspective seems particularly attractive for designing advanced radiation curable formulations.

The controlled polymerization-induced phase separation of nano-sized clusters of polyethersulfone was evaluated as a means for alleviating the inherent tendency of the diacrylate materials to brittle fracture, as shown in Fig.7.

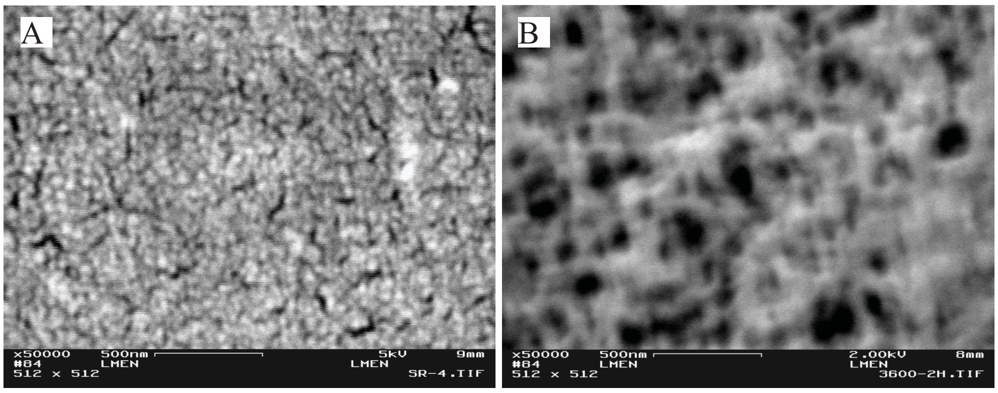


Fig.7. SEM micrographs showing the nano-sized morphology of neat (A) and toughened acrylate-based system including commercial high T_g thermoplastic (B) that exhibits typical K_{Ic} values of 2 $MPa \cdot m^{1/2}$.

Various homogeneous formulations including aromatic diacrylate monomers, polyethersulfone together with a compatible reactive diluent were prepared and polymerized by electron beam irradiation. The resulting toughened materials showed optimized critical stress intensity factor (K_{Ic}) over 2 MPa·$m^{1/2}$, whereas the K_{Ic} value is about 1 MPa·$m^{1/2}$ for the unmodified reference resin [21].

2.5. COMPARING EPOXY AND ACRYLATE CHEMISTRIES

On the basis of the knowledge and experience gained by academic and industrial research on networks with potential applications in coatings and in structural composites, the main features of the two types of chemistries, free radical and cationic, can be compared on a number of points including pre-cure properties, reactivity during cure, change of physical properties, mechanical properties and aging after curing [22]. Some of the general properties associated with each system are listed in Table 1.

Table 1. Comparison of acrylate- and epoxy-based radiation-cured formulations.

	Free-radical (acrylates)		Cationic (epoxies)	
	Advantages	Drawbacks	Advantages	Drawbacks
Pre-cure properties	Low cost chemicals, shelf stability		Compatibility with thermoplastic additives	Poor initiator compatibility, low stability
During curing	No initiator required, easier control of the reaction	Sensitivity to oxygen, high volume contraction	Insensitivity to oxygen, low volume contraction	Sensitivity to bases and nucleophiles (water)
Post-cure properties		Brittleness (strong), current carbon sizings not adapted	Toughness, flexibility, adhesion	No termination

This comparison reasonably leads to a conclusion that acrylates exhibit some advantages for conveniently handling and curing by a free radical process in spite of their sensitivity to oxygen inhibition. Such oxygen inhibition is limited to the surfaces that are in contact with air.

Cationic systems, in spite of their more complex and environmentally sensitive chemistry, being very sensitive to trace amounts moisture or humidity and to nucleophilic impurities, offer, in principle, a much more attractive set of cured physical properties, essentially associated with their low volume contraction and their molecular interaction parameters. A beneficial influence on mechanical properties of the matrix, as well as on fiber-matrix interactions can be expected and is effectively observed in several coating applications. This anticipated advantage on mechanical properties does not seem to be easily transferred to fiber-reinforced composites [23]. However, appropriate surface treatments have been proposed and validated for improving the interfacial properties of radiation curable carbon fiber-reinforced acrylate matrices [24].

Finally, both acrylate and cationic systems have their advantages and drawbacks. Whatever system is used, the knowledge of electron beam-induced chemistry and of the curing process is essential to attain and control the desired final materials properties. Ongoing research projects are focusing on the improvement of the transverse properties of composite materials through a better understanding of the fiber-matrix interface.

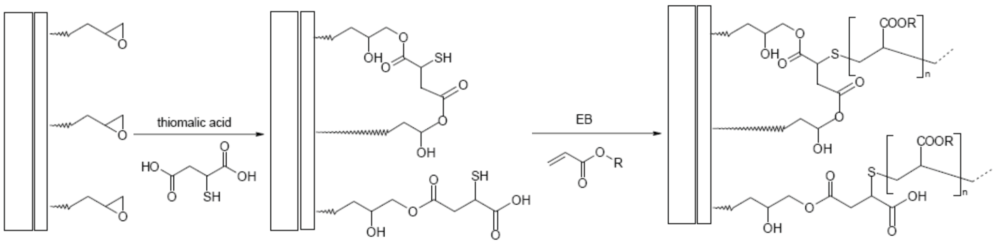
3. COMPOSITE PROPERTIES

Interfaces are among the most important yet poorly understood aspects of composite materials. There is a lack of understanding of processes occurring at the atomic level of interfaces and how those processes influence the behavior and the properties of the composite, whatever the chemical make-up (carbon, inorganic) and the geometry of the reinforcing component (short or long fibers, micro- or nanoparticles). There is a need for global understanding of the processes that take place on the atomic, microscopic, and macroscopic levels.

A weakness of radiation-cured carbon fiber-reinforced composite materials is their low transverse properties [24, 25], which are the result of a poor quality interface between fibers and the surrounding matrix. Several potential causes of this have been investigated.

Cure-induced volume shrinkage may, in some cases, influence adhesion between carbon fibers and the matrix. EB curable acrylate formulations have a higher cure-induced volume shrinkage (in the range of 3 to 5% for high-performance formulations) compared to thermally cured epoxy amine systems used for similar applications (commonly around 2 to 3%) [26]. This volume shrinkage is due to the polymerization process itself and can have a negative effect on the fiber-matrix adhesion. A low profile additive approach using polyvinyl acetate in some formulations resulted in a decrease of the cure-induced shrinkage from 6 to around 4.5% of the initial material volume. Such an improvement was attained without a significant decrease in the network's T_g and opens an interesting path for upgrading transverse properties.

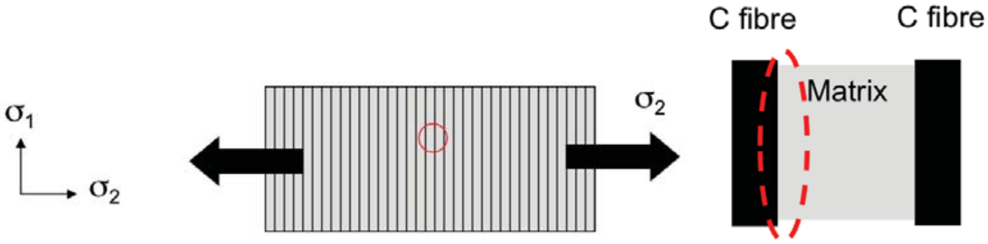
Fiber treatment using plasma treatment is another interesting approach [27]. Plasma treatment of fibers resulted in an interlaminar shear strength increase of 20 to 30% of composite samples. Adhesion improvement was demonstrated to be related to the oxidation of carbon fibers. X-ray photoelectron spectroscopy (XPS) analyses of the fibers show more than 15 to 20% of oxygen on the carbon surface after plasma processing.



Scheme 7. Schematic view of carbon fiber surface modification aimed at strengthening fiber-matrix interface.

Laboratory experiments were conducted on model formulations to try to reproduce in solution the chemistry that takes place at the fiber-matrix interface. The results emphasized the critical inhibiting influence of some chemical groups such as aromatic hydroxyls or amines. At the opposite end, the sensitizing effects of thiol groups on acrylate polymerization were also demonstrated. This led to the development of a treatment of the carbon fibers with thiomalic acid and an epoxy type sizing that yields a reactive coating particularly adapted to matrices curable by EB-initiated free radical mechanisms, as illustrated on Scheme 7. Covalent bonds between the carbon fiber sizing and the matrix are created with a great efficiency, as a result of the chain transfer reactions between grafted thiol groups and the growing polymer network [28-30].

Elementary composites using treated fibers and an epoxy acrylate formulation were found to exhibit transverse properties, measured by the transverse tensile strength, that were more than doubled (σ_2 = 70 MPa) compared to the same composite using fibers without treatment (σ_2 = 29 MPa) (Scheme 8).



Scheme 8. Principle of mechanical testing of the interface between carbon fiber and the radiation-cured matrix.

4. CONCLUSION AND PERSPECTIVES

Over the past 10 years, the knowledge of EB and X-ray processing has considerably increased. Curing kinetics, control and modeling of radiation processing, aging of EB-cured composites are now better understood on the basis of a multiscale investigation of network construction and of material properties. A variety of technical issues concerning EB curing have been addressed through a basic approach to radiation physics, radiation chemistry and materials science. Advanced studies aimed at the improvement of matrix toughness, at the reduction of the matrix cure-induced shrinkage, and at the design of fiber surface functionality have been addressed and significant results have been achieved with regard to each of these topics. Solutions for matrix toughening with greater processability and compatible with environmental considerations are under development. A next step will consist in aggregating the technical solutions developed for improving isolated aspects of curing, examined from the viewpoints of processing, of curing kinetics, of polymer network performance and of fiber-matrix interactions. Radiation-induced composite curing technology is being demonstrated that meets demanding product specifications. Encouraging results envision the mass production of structural composites as well as functional materials by means of a reliable, cleaner and more productive out-of-autoclave approach to manufacturing [31].

Acknowledgments

The authors express their gratitude to Dr. B. Defoort, Dr. M. Krzeminski and Dr. G. Larnac (Airbus DS) for their contribution and support to the work summarized in this chapter. Financial support by Conseil Regional Champagne Ardenne, MENESR and EU-FEDER Programme (CPER Project PlAneT) and by the EADS Foundation is gratefully acknowledged.

REFERENCES

[1]. Zweben, C. (2015). Composite materials (Chapter 10). In M. Kutz (Ed.), *Mechanical engineers' handbook. Vol. 1. Materials and engineering mechanics* (4th ed.). New York: John Wiley & Sons.

[2]. Glöckner, P., Jung, T., Struck, S., & Studer, K. (2008). *Radiation curing: coatings and printing inks; Technical basics, applications and trouble shooting*. Hannover: Vincentz Network GmbH & Co. KG.

[3]. Drobny, J.G. (2010). *Radiation technology for polymers* (2nd ed.). CRC Press.

[4]. Cœuré, P., & Khoi Tran, Q. (1999). Procédés radiochimiques pour la conservation des biens culturels. *Actualité Chimique*, 225, 141-143.

[5]. Boursereau, F., Dupillier, J.M., Larnac, G., & Roussel, D. (2000). Advanced electron beam composites and modeling approach for spacecraft and transportation applications. In S. Loud, V. Karbhari, D.O. Adams & A.B. Strong (Eds.), *Bridging the centuries with SAMPE's materials and processes technology: 45th International SAMPE Symposium and Exhibition* (Vol. 45, book 2, pp. 2235-2247). Society for the Advancement of Material and Process Engineering.

[6]. Coqueret, X. (2008). Obtaining high performance polymeric materials by irradiation. In S. Spotheim-Morizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basics to applications in material and life sciences* (pp. 131-150). EDP Sciences.

[7]. Ghosh, N.N., & Palmese, G.R. (2005). Electron-beam curing of epoxy resins: Effect of alcohols on cationic polymerization. *Bull. Mater. Sci.*, *28*, 603-607.

[8]. Lee, J., & Palmese, G.R. (2005). Cationic polymerization of glycidyl ethers and furans: Improved electron beam and UV cured epoxy networks. In *New horizons for materials and processing technologies: 50th International SAMPE Symposium and Exhibition* (Vol. 50, pp. 663-677). Society for the Advancement of Material and Process Engineering.

[9]. Sipani, V., Kirsch, A., & Scranton, A.B. (2004). Dark cure studies of cationic photopolymerizations of epoxides: Characterization of kinetic rate constants at high conversions. *J. Polym. Sci. Pol. Chem.*, *42*, 4409-4416.

[10]. Raghavan, J., & Baillie, M.R. (2000). Electron beam curing of polymer composites. *Polym. Composites*, *21*, 619-629.

[11]. Defoort-Vantorre, B. (1999). *Polymérisation sous rayonnement ionisant d'une résine acrylique pour composites: étude cinétique et modélisation*. Unpublished doctoral dissertation, Université des Sciences et Technologies de Lille, France.

[12]. Degrand, H., Cazaux, F., Coqueret, X., Defoort, B., Boursereau, F., & Larnac, G. (2003). Thermal effects on the network structure of diglycidylether of bisphenol-A polymerized by electron-beam in the presence of an iodonium salt. *Radiat. Phys. Chem.*, *68*, 885-891.

[13]. Mascioni, G., Ghosh, N.N., Sands, J.M., & Palmese, G.R. (2013). Electron beam and UV cationic polymerization of glycidyl ethers. Part II: Reaction of diglycidyl ether of bisphenol A. *J. Appl. Polym. Sci.*, *130*, 487-495.

[14]. Crivello, J.V., & Ortiz, R.A. (2002). Benzyl alcohols as accelerators in the photoinitiated cationic polymerization of epoxide monomers. *J. Polym. Sci. Pol. Chem.*, *40*, 2298-2309.

[15]. Bongiovanni, R., Malucelli, G., Sangermano, M., & Priola, A. (2002). Preparation of coatings via cationic photopolymerisation: influence of alcoholic additives. *Macromol. Symp.*, *187*, 481-492.

[16]. Allen, N.S., & Edge, M. (1993). UV and electron beam curable pre-polymers and diluent monomers: Classification, preparation and properties. In J.P. Fouassier & J.F. Rabek (Eds.), *Radiation curing in polymer science and technology. Vol. 1. Fundamentals and methods* (pp. 225-262). London: Elsevier Applied Science.

[17]. Krzeminski, M. (2010). *Renforcement à l'échelle nanométrique de matrices hautes performances polymérisées sous rayonnement ionisant*. Unpublished doctoral dissertation, Université de Reims Champagne-Ardenne, France.

[18]. Krzeminski, M., Molinari, M., Troyon, M., & Coqueret, X. (2010). Calorimetric characterization of the heterogeneities produced by the radiation-induced cross--linking polymerization of aromatic diacrylates. *Macromolecules*, *43*, 8121-8127.

[19]. Chuda, K., Smolinski, W., Defoort, B., Rudz, W., Gawdzik, B., Rayss, J., & Coqueret, X. (2004). Effects of vitrification on the isothermal polymerization of acrylate blends under radiation. *Polimery* (Warsaw, Poland), *49*, 505-513.

[20]. Krzeminski, M., Molinari, M., Troyon, M., & Coqueret, X. (2010). Characterization by atomic force microscopy of the nanoheterogeneities produced by the radiation-induced cross-linking polymerization of aromatic diacrylates. *Macromolecules*, *43*, 3757-3763.

[21]. Krzeminski, M., Molinari, M., Defoort B., & Coqueret, X. (2013). Nanoscale heterogeneities in radiation-cured diacrylate networks: Weakness or asset? *Radiat. Phys. Chem*., *84*, 79-84.

[22]. Janke, C.J., Yarborough, K.D., & Drzal, L.T. (1999). Fiber-matrix interface studies on electron beam cured composites. In L.J. Cohen, J.L. Bauer & W.E. Davis (Eds.), *Evolving and revolutionary technologies for the new millennium: 44th International SAMPE Symposium and Exhibition* (Vol. 44, book 1, pp. 647-658). Society for the Advancement of Material and Process Engineering.

[23]. Schultz, J., Lavielle, L., & Martin, C. (1987). The role of the interface on carbon fiber-epoxy composites. *J. Adhesion*, *23*(1), 45-60.

[24]. Coqueret, X., Krzeminski, M., Ponsaud, P., & Defoort, B. (2009). Recent advances in electron-beam curing of carbon fiber-reinforced composites. *Radiat. Phys. Chem*., *78*, 557-561.

[25]. Glauser, T., Hult, A., Johansson, M., Kornmann, X., & Berglund, L. (2000). Toughening of electron-beam cured acrylate resins. *Macromol. Mater. Eng.*, 280-281, 20-25.

[26]. Xu, L., & Drzal, L.T. (2004). Cure volume shrinkage of vinyl ester resins and their influence on adhesion between carbon fibers and vinyl ester matrix resins. In *Proceeding of the 26th Annual Meeting of the Adhesion Society, Myrtle Beach, SC, February 2003* (pp. 415-417).

[27]. Zhao, Y., Zhang, C., Shao, X., Wang, Y., & Qiu, Y. (2011). Effect of atmospheric plasma treatment on carbon fiber/epoxy interfacial adhesion *J. Adhes. Sci. Technol.*, *25*, 20, 2897-2908.

[28]. Ponsaud, P. (2005). *Amélioration des propriétés mécaniques transverses de matériaux composites polymérisés sous faisceau d'électrons: étude des facteurs influents*. Unpublished doctoral dissertation, Université de Lille I, France.

[29]. Defoort, B., Ponsaud, P., & Coqueret, X. (2007). *Method for enhancing adherence of carbon fibers with respect to an organic matrix*. Patent WO 2007031576.

[30]. Martin, A., Pietras-Ozga, D., Ponsaud, P., Kowandy, C., Barczak, M., Defoort, B., & Coqueret, X. (2014). Radiation-curing of composites including carbon fibres: A customized surface modification for improving mechanical performances. *Radiat. Phys. Chem*., *105*, 63-68.

[31]. Berejka, A., Montoney, D., Dispenza, D., Poveromo, L., Galloway, R., Cleland, M., & Driscoll, M. (2016). Power demands for curing carbon fiber composites for automotive components. *SAE Int. J. Mater. Manf.*, *9*(3), 811-818. DOI: 10.4271/2016-01-0527.

Chapter 17

RADIATION METHODS AND USES IN NANOTECHNOLOGY

Dagmara Chmielewska
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

Nanotechnology is a fast growing area in science and engineering. This multidisciplinary area has emerged from the convergence of electronics, physics, chemistry, biology, medicine and materials science to generate new functional materials of nanoscale dimensions. Figure 1 illustrates this convergence.

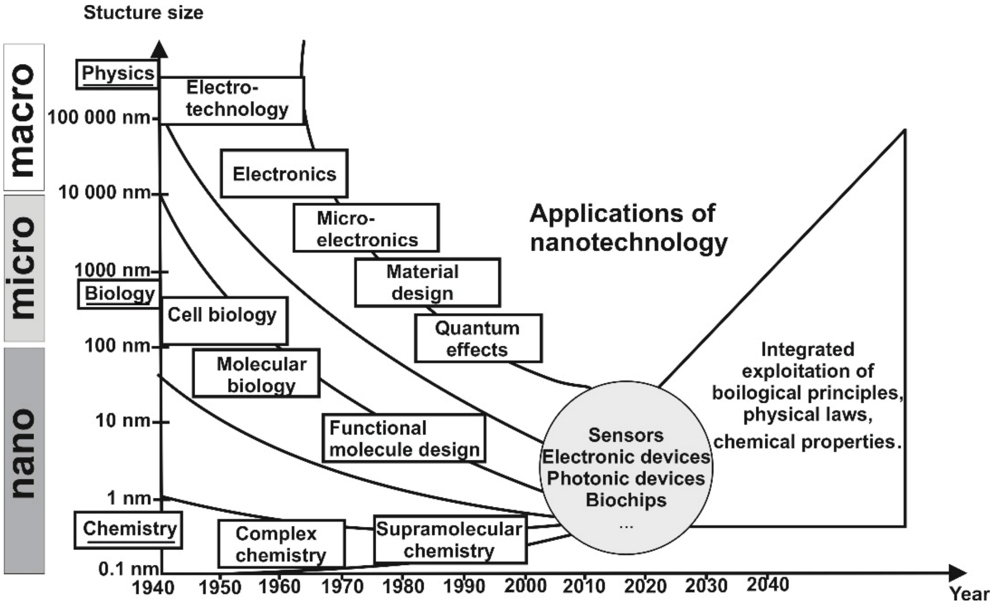


Fig.1. The convergence of the disciplines and multisector applications [1].

Nanotechnology is focused on the design, development, characterization and uses of materials which have at least one dimension that is less than 100 nm. One unique aspect of nanotechnology is that it offers a large increase in surface area for many nanomaterials, which generates new possibilities in surface-based technologies, such as catalysis and antibacterial applications. The physicochemical properties and functions of nanomaterials may differ significantly from those of the same material in bulk.

The use of radiation techniques in nanotechnology has been known for many years. X-ray, electron beam and ion beam lithography are good examples of such uses. By using electron beams, ion beams or X-rays, structures as small as 10 nm have been made. Ion track membranes with track diameters ranging from 10 to 100 nm are used directly or as templates for the electrodeposition of nanowires of metal, of semiconductors and of magnetic materials. Progress in X-ray, focused ion beam (FIB) and electron beam nanolithography, and in three-dimensional (3D) fabrication has been noted in recent years. Heavy ion beams can be used for the fabrication of nanopores which serve as templates for making nanowires. The use of radiation processing has proved to be an essential technique for the fabrication of nanostructures with high resolution since radiation beams can be focused down to a few nanometers or less. Four groups of nanoscale products are fabricated by radiation techniques: nanoparticles, nanogels, nanotubes and nanocomposites [1].

2. FUNDAMENTALS

The prefix “nano-” is derived from the Greek word “νᾶνος“ meaning “dwarf”. One nanometer (nm) is a unit of length in the metric system equal to one billionth of a meter or about the width of 6 carbon atoms or 10 water molecules. A human hair is approximately 80 000 nm wide and a red blood cell is approximately 7000 nm wide. Atoms are smaller than 1 nm, whereas many molecules including those of some proteins range between 1 nm and larger [2].

The concept of the nanotechnology was introduced in a presentation entitled “There’s plenty of room at the bottom” at the Annual Meeting of the American Physical Society on 29 December 1959 by Nobel laureate Richard P. Feynman. Feynman described a process for manipulating and controlling matter on a miniature scale, creating nanomaterials atom by atom or molecule by molecule. The term “nanotechnology” was first used in 1974 by Norio Taniguchi, a professor at the Tokyo Science University, and was defined as follows: “Nano-technology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule.” [3].

Two complementary approaches to nanomaterial fabrication are used (Fig.2):

- The “top-down” approach – where fabrication starts from the bulk material and reduces it down to the nanoscale.

- The “bottom-up” approach – where fabrication starts from the atomic or molecular level and by building atoms or molecules together complex nanostructures are created.

The term “nanomaterials” describes, in principle, materials that have at least one dimension in the range between 1 and 100 nm.

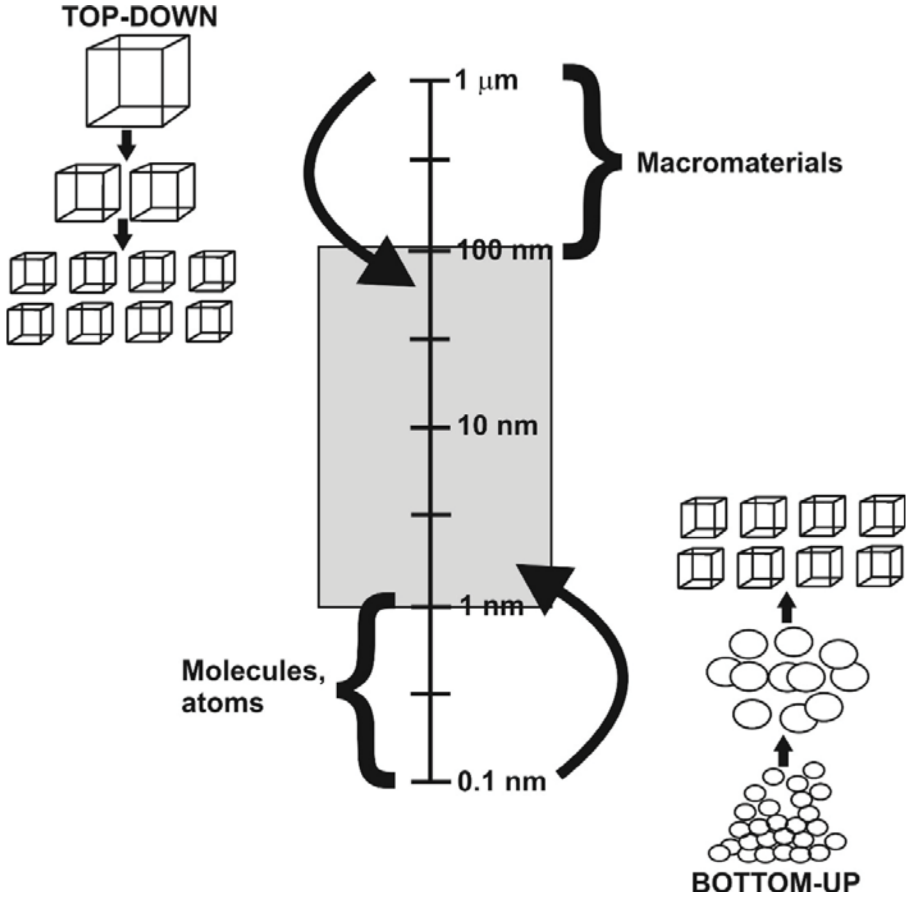


Fig.2. Scheme of the two approaches used in the fabrication of nanomaterials: “top-down” and “bottom-up” [4].

A great variety of nanostructures have been classified in different ways in the literature. Figure 3 shows the most relevant types of nanostructures in nanotechnology, classified according to four nonexclusive criteria [4].

Nanoparticles can be classified as natural, anthropogenic (incidental), or engineered in origin [5]. Taking into account the chemical composition, the dimensions of nanostructures and their distribution within a matrix, they can be homo- or heterogeneous. The chemical composition of nanostructures can be classified as inorganic (noble metal nanoparticles, quantum dots, *etc.*), organic (fullerenes, carbon nanotubes, dendrimers, *etc.*) or hybrid (gold nanoparticles modified with calixarenes, carbon nanotubes functionalized with ferrocene, *etc.*) [5]. The last classification of nanomaterials is based on the dimensions of the nanostructures and on two different approaches for terms used in nanometrology.

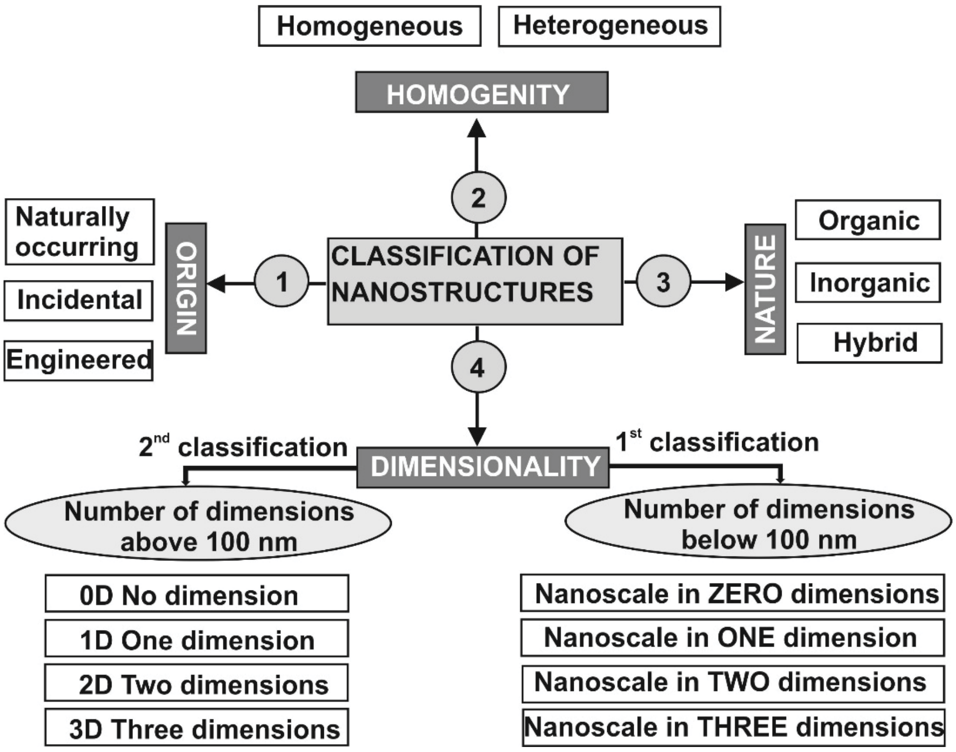


Fig.3. Classification of nanostructures according to the different criteria [4].

The Royal Society of Chemistry and the Royal Academy of Engineering classified nanostructures according to the number of dimensions in the nanoscale [6]. According to this classification three types of nanostructures can be distinguished:

- nanoscale in one dimension, such as surfaces, thin films and layers;
- nanoscale in two dimensions, such as tubes and wires;
- nanoscale in three dimensions, which includes nanoparticles and quantum dots, fullerenes, and dendrimers.

Classification of nanoscale at a zero dimension can also be added, such as materials composed by dispersed nanoparticles [4].

Other classification of nanostructured materials is based on the number of dimensions that are above the nanoscale [7]:

- 0-D nanostructures, such as nanoparticles, quantum dots and nanodots.
- 1-D nanostructures, such as nanowires and nanorods.
- 2-D nanostructures, such as coatings and surface layers. This category includes coatings made of nanocrystalline metals or nanocomposites.
- 3-D nanostructures, which include bulk materials.

The focus below is only on engineered nanostructures, which can be obtained with the use of radiation processing.

3. IONIZING RADIATION IN NANOTECHNOLOGY

Radiation-based methods play an important role in the development and modification of nanostructures.

Ion beams are used to fabricate track-etched membranes for ultrafiltration, membranes with electrical and magnetic properties and with potential uses as chemical detectors and biosensors [8]. The junctions between carbon nanotubes can be made by electron beam irradiation at elevated temperatures. Electronic devices require molecular connections between individual nanotubes. Microgels and nanogels produced by radiation techniques are well suited for biomedical applications since they are free of monomers, initiators and any other additives. Thus, they can be used as carriers for enzymes or antibodies used in diagnostics, as drug carriers for therapeutic purposes (controlled drug delivery) and possibly for artificial biological fluids and synthetic vectors for drug delivery.

Ionizing radiation is widely used in industry for the crosslinking of polymers and polymer blends. This technology can be extended to the crosslinking of nanopolymers and nanocomposites. Potential applications involve the irradiation of various types of polymers (natural rubber, polyolefins, polyimides, polystyrene, *etc.*) containing nanosized clays, silica or metal nanoparticles.

Radiation is an important tool in nanotechnology which has already been used (electron beam and X-ray lithography, track-etched membranes) and as results of recent studies indicate will to grow [1].

3.1. RADIATION IN THE PRODUCTION OF NANOMATERIALS

3.1.1. Nanogels

There are at least two definitions of polymeric nanogels and microgels. The first is derived from the definition of polymer gels. A polymer gel is a two-phase system consisting of a stable three-dimensional network of linked polymer chains and of molecules of a solvent filling the pores of this network. The second definition states that a nanogel or a microgel is an internally crosslinked macromolecule. This approach is based on the fact that, in principle, all the chain segments of a nanogel or microgel are linked together and are thus part of one macromolecule. This also reflects the fact that such gels can be made either by intramolecular crosslinking of single linear macromolecules or in a single polymerization event (*e.g.* initiated by one radical) that in the

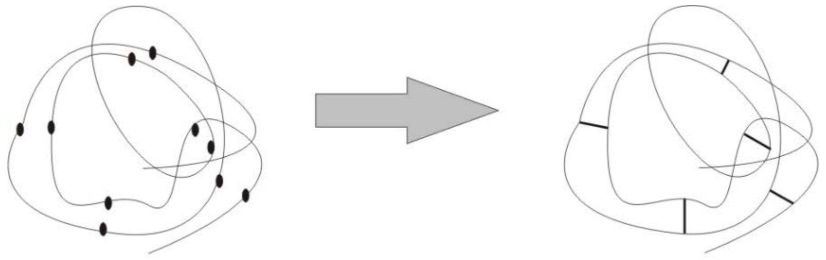


Fig.4. Formation of a nanogel from a single macromolecule by intramolecular recombination of polymer radicals.

absence of crosslinking would lead to the formation of a single linear polymer chain (Fig.4).

3.1.2. Metal nanoparticles

Noble metal nanoparticles have attracted interest because of their potential use in areas such as catalysis, nanoelectronics, sensors, health care and medicine [9-12].

During the electron beam or gamma-ray irradiation of liquids, most of the energy is absorbed by the water, so water radiolysis takes place, which results in the formation of reactive species such as the oxidizing hydroxyl radical ($^\bullet OH$) and very powerful reducing radicals as the hydrated electron (e^-_{aq}) and hydrogen atom ($H^\bullet$) [13]. Metal ions in solution are first reduced by these reducing agents to lower valence ions and then into metal atoms. Different parameters, as the initial concentration of metal cations in the solution, the irradiation dose, the dose rate, and the pH, can significantly influence the size of silver nanoparticles [14]. Making metal nanoparticles in an aqueous solution is difficult, because of a tendency for the particles to aggregate. The growth of metal nanoparticles must be controlled by the use of stabilizing (capping) agents, for example polymers with a high affinity for metal atoms, or the use of a solid support for nanoparticle binding. Different metal nanoparticles, Co, Zn, Pd [15], Cu, Hg [16], Ni [17], Ag [18], Au [19], Pt [20] and others [13], can be made with the use of ionizing radiation. Bi- and multimetallic nanoparticles can be also obtained in this way [13].

Metal clusters are generated by radiation-induced reduction either of ion precursors in solution or of ions impregnated in a solid support. The first step is the radiolysis of water which yields reactive free radicals, such as hydrated electrons, hydroxyl radicals and hydrogen atoms, and the molecular products H_2O_2 and H_2, according to the stoichiometry [21] included in reaction (1):

$$H_2O \rightsquigarrow 0.28\ e^-_{aq},\ 0.062\ H^\bullet,\ 0.28\ {}^\bullet OH,\ 0.047\ H_2,\ 0.073\ H_2O_2,\ 0.28\ H_3O^+ \quad (1)$$

The solvated electron (e^-_{aq}) and hydrogen atom are strong reducing agents (with standard reduction potentials $E^0(H_2O/e^-_{aq}) = -2.87\ V_{NHE}$ and $E^0(H^+/H^\bullet) = -2.31 V_{NHE}$, respectively [21]), so can easily reduce metal ions down to the zero-valence state:

$$M^+ + e^-_{aq} \rightarrow M^0 \qquad (2)$$

$$M^+ + H^{\bullet} \rightarrow M^0 + H^+ \qquad (3)$$

where M^+ is the symbol for monovalent metal ions and M^0 is the symbol for zero-valent metal.

In the water radiolysis process, $^{\bullet}OH$ radicals that are able to oxidize ions or atoms to a higher oxidation state are also generated. To prevent this reaction, a scavenger for $^{\bullet}OH$ radicals, such as a secondary alcohol or formate anion, is added to the solution. As the scavenger of $^{\bullet}OH$ radicals is added, substances whose oxidation by $^{\bullet}OH$ generate radicals that exhibit a strong reducing power, such as the radicals of secondary alcohols or of the formate anions [13]:

$$(CH_3)_2CHOH + {}^{\bullet}OH \rightarrow (CH_3)_2C^{\bullet}OH + H_2O \qquad (4)$$

$$HCOO^- + {}^{\bullet}OH \rightarrow COO^{\bullet-} + H_2O \qquad (5)$$

The $(CH_3)_2C^{\bullet}OH$ and $COO^{\bullet-}$ radicals are strong reducing agents too, with standard reduction potentials $E^0[(CH_3)_2CO/(CH_3)_2C^{\bullet}OH] = -1.8\ V_{NHE}$ and $E^0[CO_2/COO^{\bullet-}] = -1.9\ V_{NHE}$, respectively [13].

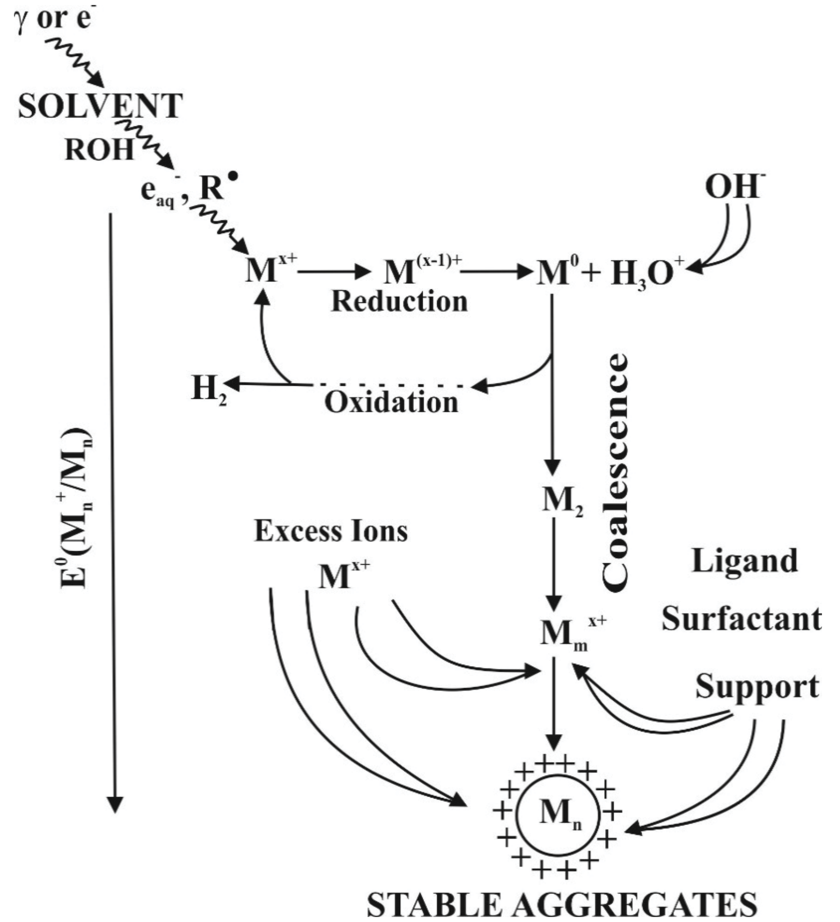


Fig.5. Scheme of metal ion reduction in solution with application of ionizing radiation [13].

In the next step, the generated radicals are able to reduce metal ions:

$$M^+ + (CH_3)_2C^\bullet OH \rightarrow M^0 + (CH_3)_2CO + H^+ \tag{6}$$

$$M^+ + COO^{\bullet -} \rightarrow M^0 + CO_2 \tag{7}$$

Metal atoms are formed with a homogeneous distribution throughout the solution. The binding energy between two transition metal atoms is stronger than the atom–solvent or atom–ligand bond energy. As a result, these atoms tend to dimerize when they encounter or associate with an excess of ions [13]:

$$M^0 + M^0 \rightarrow M_2 \tag{8}$$

$$M^0 + M^+ \rightarrow M_2^+ \tag{9}$$

By a continuation of this process, these species progressively coalesce into clusters following homogeneous kinetics [13]:

$$M_{m+x}^{\ x+} + M_{n+y}^{\ y+} \rightarrow M_{p+z}^{\ z+} \tag{10}$$

where m, n and p represent the nuclearites (*i.e.* the number of reduced atoms), and x, y and z are the numbers of associated ions, as illustrated in Fig.5. The redox potential of the clusters increases progressively with the nuclearity.

When a high dose rate is used, all of the reducing radicals are produced in a short time, which results in the coalescence of the atoms that were separately formed (Fig.6A). At a low dose rate, atoms dimerization and the coalescence

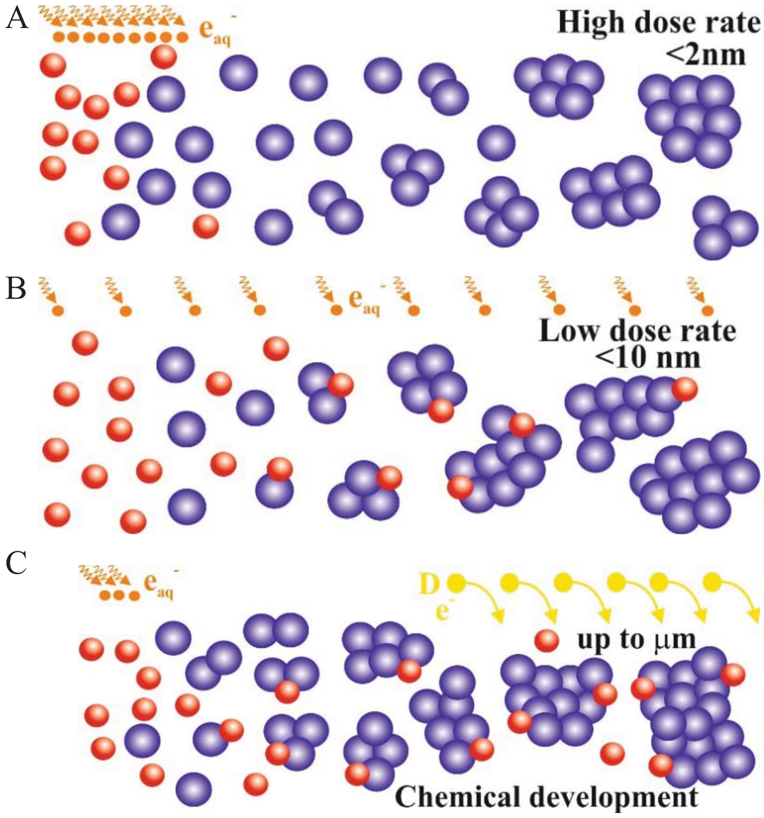


Fig.6. Nucleation and growth of metal clusters generated by radiolytic radicals at high dose rate (A), low dose rate (B) and with an electrons donor D (C).

process are faster than the production rate of the reducing radicals (Fig.6B). When a chemical that can play a role of an electron donor is added, the reduction potential is not negative enough to directly reduce isolated metal ions to atoms. In this case, the reduction of ions adsorbed on the nuclei generated by radiolysis act as seeds. This results in larger clusters being formed (Fig.6C) [22].

Metal atoms created by irradiation tend to coalesce into oligomers and then continually grow into larger clusters and eventually into precipitates. To prevent this growth, polymers acting as cluster stabilizers (capping agent) are added. Functional groups with a high affinity for the metals (*e.g.* $–NH_2$, –COOH and –OH) ensure the embedding of the molecule at the cluster surface and the polymeric chain protects the cluster from coalescing with a next one through electrostatic repulsion or steric hindrance [22]. Stabilizers should not chemically reduce metals ions bound on the surfaces of clusters. Different polymers, such as poly(vinyl alcohol) (PVA), sodium dodecylsulfate (SDS) [23], sodium polyvinyl sulfate (PVS) [24], polyacrylamide (PAM) or poly(N-methylacrylamide) (PNMAM) [20] and poly(ethylene glycol)s [25] have been used as metal cluster stabilizers. Some ligands (*e.g.* $CN^–$, EDTA – ethylenediaminetetraacetic acid) are also able to stabilize small-sized metal particles, because they are strongly connected with the cluster and prevent their coalescence by electrostatic repulsion. Another possibility for the limitation of the growth of metal nanoparticles is to make them in the presence of a solid support such as silica [14], titanium [26] and alumina. Ionizing radiation is able to penetrate the support and reduce the atoms of the metals to cations embedded on the surface or in the pores or *in situ* everywhere that the ions have diffused.

Bi- and multimetallic nanoparticles, composed of two or more different metal elements, are of greater importance than monometallic ones due to their improved catalytic properties in contrast to single-metal catalysts and to the development of new properties, which may not exist for the monometallic catalysts [27].

The preparation of bimetallic nanoparticles from metal salts can be divided into two groups: co-reduction and successive reduction of two metal salts. These processes yield an alloyed or a core-shell structure. Two ionic precursors of two different metal ions M^+ and M'^+ can be reduced by radiolytic radicals with equal probabilities:

$$e^-_{aq} + M^+ \rightarrow M^0 \tag{11}$$

$$e^-_{aq} + M'^+ \rightarrow M'^0 \tag{12}$$

However a further electron transfer from less noble metal atoms (for example M') to more noble metal ions M^+ systematically favors the reduction into M [13].

$$M' + M^+ \rightarrow (MM')^+ \rightarrow M + M'^+ \tag{13}$$

$$(M_m M_n')^{x+} + M^+ \rightarrow (M_{m+1} M_n')^{(x+1)+} \rightarrow (M_{m+1} M_{n-1}')^{x+} + M'^+ \tag{14}$$

If the ionic precursors are plurivalent, an electron transfer is also possible between the low valences of both metals. This increases the probability of segregation [13]. The less noble metal ions act as an electron relay towards the noble metal ions. As a result, monometallic clusters, M_n, are formed first and then, when the M^+ ions are spent, M'^+ ions are reduced at the surface of the M_n. The result is a core-shell bimetallic cluster where the more noble metal, M, is covered by the other metal M'.

Sometimes the inter-metal electron transfer does not occur. Then the initial reduction reactions are followed by mixed coalescence:

$$M' + M \rightarrow (MM') \tag{15}$$

$$(MM') + M \rightarrow (M_2M') \tag{16}$$

and association of atoms and clusters with ions as in reactions (13) and (14) [5]:

$$(M_mM_n')^{x+} + M^+ \rightarrow (M_{m+1}M_n')^{(x+1)+} \tag{17}$$

$$(M_{m+1}M_n')^{(x+1)+} + e^-_{aq}\ (\text{or R}) \rightarrow (M_{m+1}M_n')^{x+}\ (\text{or} + R^+) \tag{18}$$

Dose rate is a crucial parameter when deciding on the formation of an alloyed cluster or of a core-shell structure since these depend on the kinetic competition between the inter-metal electron transfer and the coalescence process during the radiolytic reduction of mixed metal ion solutions.

3.1.3. Carbon nanotubes

A new method using radiation techniques to grow carbon nanotubes was reported in 1996 by Yamamoto *et al.* [28]. In this work, carbon nanotubes were grown using an argon ion beam for the irradiation of an amorphous carbon target under high vacuum condition (4×10^{-5} Torr) [28]. The incident angle of the ion beam was normal to the target surface and the ion acceleration energy was 3 keV. Nanotubes were produced outside the sputtering region on the target surface after ion irradiation. The tubes had multilayered walls with the distance between carbon layers of 0.34 nm and tube wall thicknesses ranging from 10 to 15 sheets [28].

Single-walled nanotubes (SWNTs) have a diameter that is close to 1 nm, with a tube length that may be many thousands of times longer. The structure of a SWNT can be conceptualized by taking out the one-atom-thick layer from a graphite stack and wrapping it into a seamless cylinder. Single-walled carbon nanotubes have been found to possess the most remarkable electronic and mechanical properties and are used in various nanoscale devices.

Terrones *et al.* demonstrated that single-walled carbon nanotubes can be joined by electron beam irradiation to form molecular junctions [29]. Stable junctions of various geometries have been made *in situ* in a high voltage transmission electron microscope (TEM) with the specimen temperatures at 800°C. After a few minutes of irradiation of two crossing tubes, they consolidate at the point of contact, which results in the formation of a junction with an X shape. The ready-formed X junctions can be manipulated in order to create Y- and T-like molecular connections. The continuous sputtering of carbon atoms from the nanotube body occurs during irradiation, leading to dimensional changes and surface reconstructions [30]. The removal of one of the "arms" of an X junction generates a Y or T junction by using carefully chosen irradiation conditions. Exposing carbon nanotubes at high temperatures to an electron beam induces structural defects, which promote the joining of tubes *via* the crosslinking of pendant bonds. Junctions can be made *via* vacancies and interstitials, induced by a focused electron beam, to promote the formation of inter-nanotube links. It may now be possible to construct nanotube networks by growing crosslinked SWNTs followed by controlled electron beam irradiation at high temperatures.

3.1.4. Nanocomposites

Nanocomposite material consists of multiple nanoscale materials or a nanoscale material incorporated into a bulk material. The fabrication of nanocomposites has some challenges to make sure there is compatibility of the different material components in order to obtain desirable properties for the nanocomposite. Virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Nanocomposites can offer new uses in many fields, such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nanowires, sensors and other systems [1].

On the basis of their matrices, nanocomposites can be classified into three major categories:

- polymer matrix nanocomposites,
- metal matrix nanocomposites,
- ceramic matrix nanocomposites.

Polymer nanocomposites consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. Since many monomers can polymerize upon exposure to gamma rays, monomer polymerization has been used to make nanocrystalline materials [31, 32]. A novel strategy is to synthesize semiconductor/polymer nano-assemblies in a single step at room temperature by gamma irradiation. In general, a metal ion source, chalcogen salt and an organic monomer are mixed homogeneously as a deaerated aqueous solution with an appropriate amount of alcohol, as hydroxyl radical scavenger. The resulting mixture is then subjected to gamma irradiation (irradiation dose – 10^4 Gy) leads to the simultaneous formation of nanocrystalline metal chalcogenide particles and the polymerization of the monomers. The metal ion attached onto the surface or inside the polymer microspheres and the chalcogen ion, which is released by decomposition of the salt upon gamma irradiation, a homogeneous dispersion of nanocrystalline metal chalcogenide particles in microsphere polymer matrixes can be precipitated. Nanocomposites are thus formed at room temperature and under ambient pressure without the use of chemical initiators. By appropriate control of the reaction conditions, the gamma irradiation method may be extended to the preparation of a variety of spherical assemblies of metals and of semiconductors/polymer nanocomposites in aqueous systems. Analogously, several kinds of semiconductor/polymer nanowires have been made in a heterogeneous solution system. In this system, an organic monomer with polar groups can self-organize into amphiphilic supramolecules (micelles, microemulsions, vesicles and monolayers on surfaces), using the difference in the solubility of different fragments in the monomer. Under gamma irradiation, such supramolecules can polymerize to a pre-organized polymer tubule with a hydrophilic core and a hydrophobic sheath. The polymer tubule acts as both a template and a nanoreactor for the following growth of inorganic semiconductor nanowires in the hydrophilic cores from various water soluble systems [33].

Another example of the use of ionizing radiation in making polymer matrix composites is that of producing silver nanostructures in a cotton matrix using electron beam irradiation [12]. Ag-cotton nanocomposites exhibit antibacterial activity against gram-negative and gram-positive bacteria. Cotton samples were placed in silver nitrate solutions of different concentrations and then exposed to the electron beam irradiation using a 10 MeV, 8 kW linear accelerator. Water radiolysis generated very powerful reducing radicals that were able to overcome of the thermodynamic barrier of reducing the single metal ion while in solution. In this way, silver nanoparticles were embedded in the cotton fibers, as shown in Fig.7.

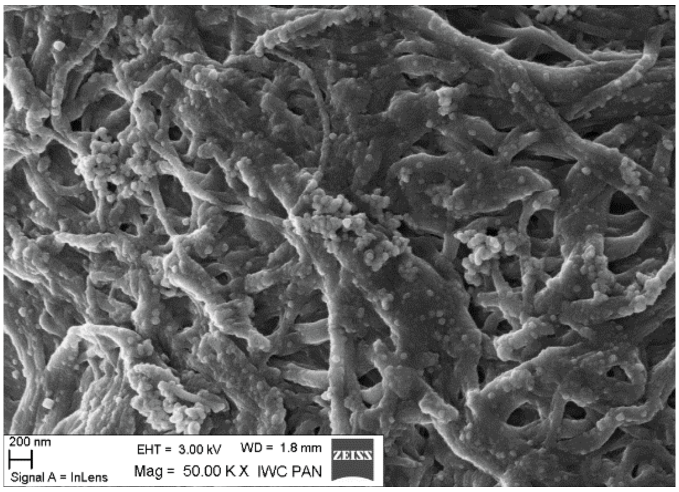


Fig.7. Silver nanoparticles embedded in a cotton matrix.

Among the large number of inorganic layered materials that exhibit intercalation capabilities, layered silicates are one of the most typical because of the versatility of their reactions. In particular, the smectite group of clay minerals, such as montmorillonite, saponite and hectorite, has been used since they have excellent intercalation ability. The combination of clay silicate layers and polymer matrices at the nanoscale level constitutes the basis for preparing an important class of inorganic-organic nanostructured materials.

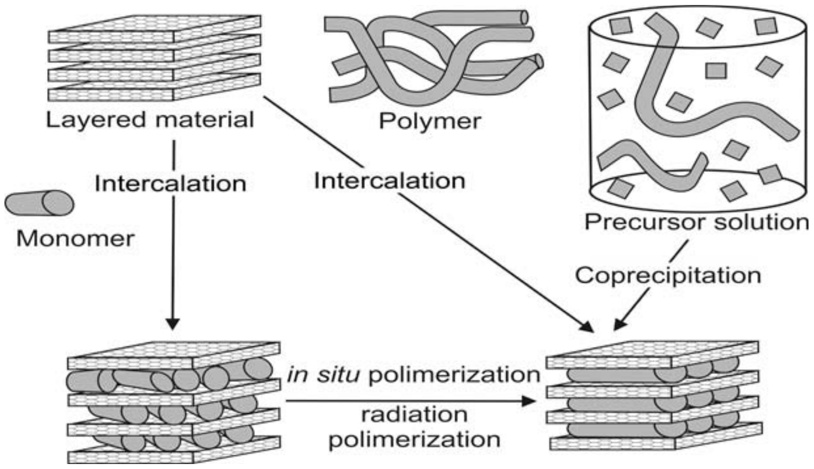


Fig.8. The overall process of preparing nanocomposites based on clay and polymer/monomers.

Clay such as montmorillonite consists of a dioctahedral aluminum sheet sandwiched between two silica tetrahedral sheets in a layered structure that is ~1 nm thick (Fig.8). Stacking layers lead to a regular Van der Waal's space between the layers called the interlayer. Clay has the ability to undergo extensive interlayer expansion or swelling, exposing a large active surface area, permitting guest molecules to enter into the interlayer. Interlayer cations such as Na^+, Ca^{2+}, and K^+ exist on the internal surfaces but can be exchanged with alkyl ammonium cations to give surfaces that are less ionic or polar. Such interlayers can be organically modified since they are more easily penetrated by polymers (either in the molten state or in solution) or by monomers which can be subsequently crosslinked or polymerized chemically or by using radiation [34]. In the process of making polymer-clay nanocomposites, it is important to ensure the compatibility of the entering polymer/monomer (hydrophobic) with the clay surface interlayer (ionic) by using intermediates, such as exchangeable organic based cations, intercalation agents or compatibilizers.

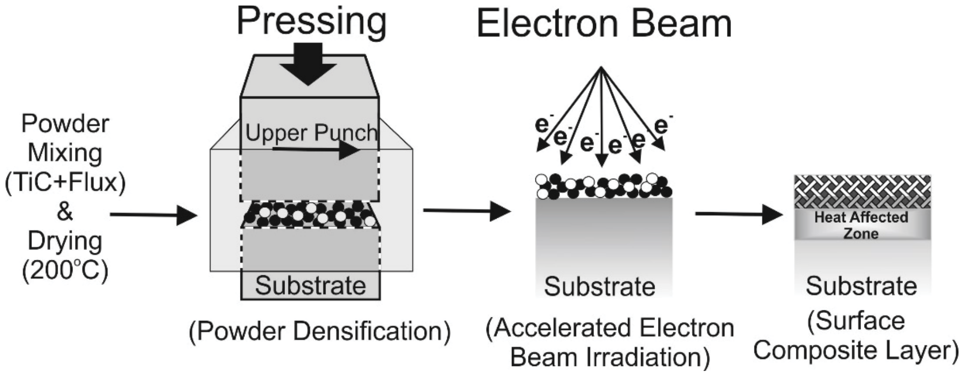


Fig.9. Scheme of the fabrication of TiC-reinforced surface composites [35].

Metal matrix composites reinforced with titanium carbide (TiC) particulates can be fabricated by high energy electron beam irradiation (Fig.9) [34].

A mixture of magnesium oxide (MgO) and calcium oxide (CaO) powders were used as a flux in order to obtain uniform TiC dispersion on a composite surface. Upon electron beam irradiation of a metal surface on which ceramic powders were evenly deposited, the metal surface melts, while the ceramic powders are either partially or completely melted and then precipitated again during solidification, thereby forming a surface composite [35]. Ferrous composites reinforced with TiC show high strength, high elastic modulus, and improved resistance to wear and oxidation.

3.2. LITHOGRAPHY

Lithography is the transfer of a pattern from a master slide/plate/mask to another surface. Nanolithography is suitable for use in the nanofabrication of electrical devices, data storage drives, sensors, drug delivery systems, *etc*. The two fundamental characteristics of an imaging system are its resolution (RES) and its depth of focus (DOF). The equations which define these are known as the Rayleigh criterion and are usually expressed as:

$$\mathrm{RES} = K_1\, \lambda/\mathrm{NA} \quad (19)$$

$$\mathrm{DOF} = K_2\, \lambda/(\mathrm{NA})^2 \quad (20)$$

where λ is the wavelength of the radiation used to carry out the imaging, and NA is the numerical aperture of the imaging system (or camera). These equations show that better resolution can be achieved by reducing λ and/or by increasing NA.

Ultraviolet radiation has been used to create patterns in lithography. The move of semiconductor technology towards the miniaturization of integrated circuits pointed out the limits of photolithography as technique for the fabrication of structures with dimensions on the submicron to nanometer scale. Due to diffraction effects, the resolution of the photolithography process is limited

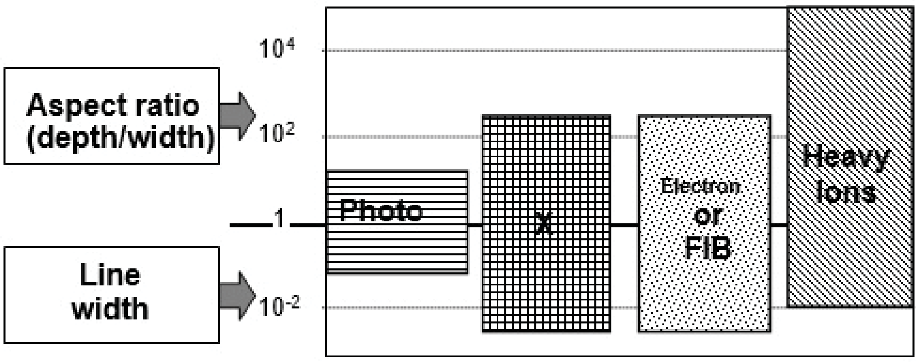


Fig.10. Optical and radiation sources for nanotechnology [36].

to a few microns. To obtain smaller and more precise chips, it was necessary to go to radiation-based technology using X-rays, electron beams and ion beams in order to approach submicron patterning (Fig.10) [36].

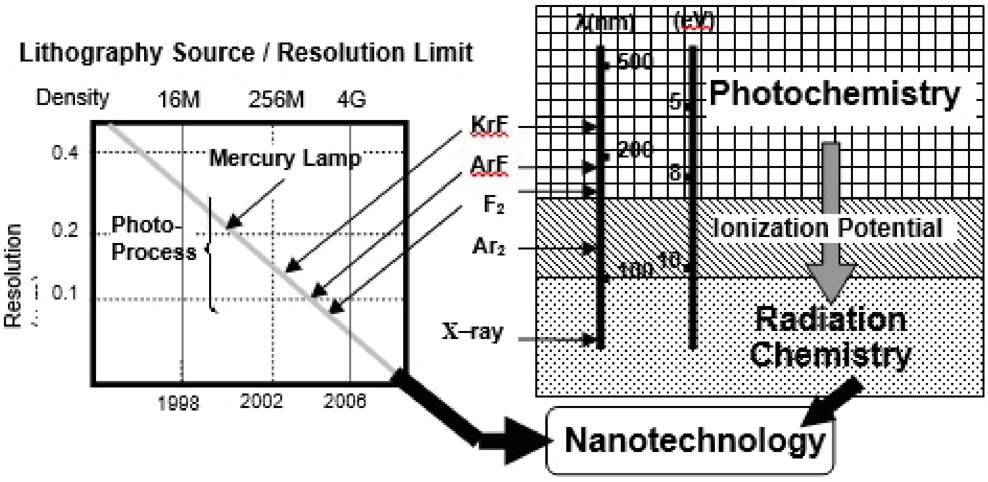


Fig.11. Aspect ratio and resolution limit of various lithographic methods [36].

Figure 11 [36] shows the aspect ratios and resolution limits (line width) of optical and radiation processes. Radiation methods are essential to nanotechnology because of their high resolution and high aspect ratios. Especially, nanofabrication requires electron beam and X-ray processes to attain resolutions lower than 10 nm. X-rays, electron beams, and low energy ion beams, such as electron beam scanning devices and focused ion beam, are useful in nanolithography, and in 3D nanofabrication. Heavy ion beam processes can be used for the fabrication of nanopores and nanowires since they too give high aspect ratio patterns.

3.2.1. Electron beam lithography

The concept of electron beam lithography (EBL) is to write patterns on thin films of electron sensitive material using a finely focused (submicrometer diameter) electron beam. The technology is capable of making very complex patterns with very high resolution, almost to the atomic level. EBL is a flexible technique that can work with a variety of materials and an almost infinite number of patterns, but it has some disadvantages, since it is one or more orders of magnitude slower than optical lithography.

Electron beam lithography was originally developed using an electron beam from a scanning or transmission electron microscope (SEM or TEM, respectively) to expose an electron-sensitive resist. A silicon substrate was first oxidized to form a layer of silicon dioxide (SiO_2) several nanometers thick, which was then spin-coated with a uniform layer of polymer (the resist) that was sensitive to ionizing radiation. The beam was controlled by a computer through a position generator interface which allowed writing any computer-defined patterns on the resist. Films with the desired geometry are made by covering areas where exposure is not wanted with a metallic pattern. Pattern transfer from the resist to the unpatterned SiO_2 film is done by wet or dry etching. Wet etching uses chemical or electrochemical processes to dissolve and remove the exposed areas of SiO_2. In dry etching, either ion bombardment (sputter etching) or plasma etching with activate species (ions, atoms, free radicals) is used to remove the unwanted materials. These dry etching processes can produce straight and sharp pattern edges with a better resolution. Thus, dry etching is more useful for patterning ultrafine nanostructures.

Three key parameters of the source are: (i) the virtual source size, (ii) its brightness (expressed in $A \cdot cm^{-2} \cdot sr^{-1}$), and (iii) the energy spread of the emitted electrons (measured in eV). As electrons penetrate the resist, they undergo a series of low energy elastic collisions, which deflect the electrons slightly. This results in beam broadening that increases with thickness. This effect is more significant at low incident energies [37]. Most of the electrons pass entirely through the resist and penetrate into the depth of the substrate. However part of those electrons will eventually undergo large angle scattering (backscattering). At higher energies, backscattered electrons can cause exposure microns away [38] from where the beam entered. This is related with the so-called proximity effect [39] where electrons writing a feature at one location increase the exposure at a nearby feature, causing pattern distortion and overexposure [40].

Backscattering can be minimized by exposing a thin membrane substrate. With sufficient exposure, the polymer chains in the resist are either broken (positive resist) or become crosslinked (negative resist), thus forming a positive or a negative image of the mask. After irradiation, the resist is developed to form the desired pattern, which, through an etching process, is then transferred onto the substrate.

The 3D nanopatterning and nanofabrication, called also stereolithography (SL), can be conducted by exposing a three-dimensional object to an electron beam. A special drive is needed to rotate the sample and the use of electron beam nanolithography, which has resolution 100 times higher than that which can be obtained using optical or X-ray sources. This results in reasonably fast 3D fabrication and patterning. One key technique is to rotate a 3D sample in such a way that any of its faces can be exposed to the electron beam. Another key technique is focusing the beam on a 3D sample. The height (Z coordinate) and horizontal position (X and Y coordinates) of any point on a sample must be determined. To measure the height, a confocal laser microscope has been used. A height map of the sample enables the height of any point on the sample to be determined, even if the sample is rotated [36].

3.2.2. X-ray and ion beam lithography

X-ray lithography uses X-rays from a synchrotron radiation facility or rays from a laser-induced plasma. Similar to electron beam lithography, the sample is covered with a resist layer of high sensitivity to X-rays and then exposed to the synchrotron X-radiation. Between the radiation source and the sample, at a few micrometers above the resist layer, a mask, having the same feature sizes as what will be made, is placed to define the pattern. X-ray masks are usually made of very thin (about 2 μm) films of silicon carbide, covered by a metal pattern having the desired geometry that is made of high-Z absorber material to prevent unwanted X-ray exposure of the sample. After irradiation, the resist is developed to yield the desired pattern, which, through an etching process, is then transferred onto the substrate. Both electron beam and X-ray lithography are capable of patterning down to lines and spaces well under 70 nm.

As with electron beams, ion beams can be used for the direct writing of nanostructure patterns on a surface being processed. Both electron and ion beams can be easily focused down to a narrow size, as small as a few nanometers, using electromagnetic lenses. Once focused, they can also be scanned across a surface with great precision. Focused beams can be computer controlled to reproduce a digitally stored image by rastering across the substrate without the need of resists or masks. This is useful in producing nanostructures which have high feature fidelity.

4. CONCLUSIONS

The ability to produce materials and structures with very high, nanometric precision is basic to the development of nanotechnology. Ionizing radiation is very powerful tool that can be used in this field. Radiation-based techniques using X-rays, electron beams and ion beams play important role in micropatterning. Another use of radiation in nanotechnology is making different nanostructures and nanocomposites. The use of ionizing radiation in nanotechnology has led to the development of new materials and advanced products for different branches of industry.

REFERENCES

[1]. Chmielewski, A.G., Chmielewska, D.K., Michalik, J., & Sampa, M.H. (2007). Prospects and challenges in application of gamma, electron and ion beams in processing of nanomaterials. *Nucl. Instrum. Meth. Phys. Res. B*, *265*, 339-346. DOI: 10.1016/j.nimb.2007.08.069.

[2]. Whitesides, G.M. (2003). The ‘right’ size in nanobiotechnology. *Nat. Biotechnol.*, *21*, 1161-1165. DOI: 10.1038/nbt872.

[3]. Nimesh, S. (2013). *Gene therapy. Potential applications of nanotechnology.* UK: Woodhead Publishing Limited.

[4]. Valcárcel, M., & López-Lorente, A.I. (2014). Gold nanoparticles in analytical chemistry. In D. Barcelo (Ed.), *Comprehensive analytical chemistry* (pp. 3-35). Amsterdam: Elsevier.

[5]. Lopez-Lorente, A.I., Simonet, B.M., & Valcarcel, M. (2012). Determination of nanoparticles in biological matrices. *Front. Biosci.*, *4*(3), 1024-1042. DOI: 10.2741/438.

[6]. The Royal Society & The Royal Academy of Engineering. (2004, July). *Nanoscience and nanotechnologies*. Retrieved October 21, 2015, from http://www.nanotec.org.uk/report/chapter3.pdf.

[7]. Daniszewska, A., Łojkowski, W., Fecht, H., Kurzydłowski, K.J., Narkiewicz, U., Salishchev, G.A., Zehetbauer, M.J., Kulczyk, M., Chmielecka, M., & Kuzmenko, D. (2006). Metallic nano-materials and nanostructures: Development of technology roadmap. *Solid State Phenom.*, *114*, 345-391. DOI: 10.4028/www.scientific.net/SSP.114.345.

[8]. Maekawa, Y., Koshikawa, H., & Yoshida, M. (2004). Anisotropically conducting films consisting of sub-micron copper wires in the ion track membranes of poly(ethylene terephthalate). *Polymer*, *45*, 2291-2295. DOI: 10.1016/j.polymer.2003.11.011.

[9]. Arabatzis, I.M., Stergiopoulos, T., Bernard, M.C., Labou, D., Neophytides, S.G., & Falaras, P. (2003). Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. *Appl. Catal. B-Environ.*, *42*(2), 187-201. DOI: 10.1016/S0926-3373(02)00233-3.

[10]. Shipway, N.A., Katz, E., & Willner, I. (2000). Nanoparticle array on surfaces for electronic, optical and sensor applications. *Chem. Phys. Chem.*, *1*(1), 18-52. DOI: 10.1002/1439-7641(20000804)1:1<18::AID-CPHC18>3.0.CO;2-L.

[11]. Haes, A.J., Zou, S., Schatz, G.C., & Van Duyne, R.P. (2004). Nanoscale optical biosensor: short range distance dependence of the localized surface plasmon resonance of noble metal nanoparticles. *J. Phys. Chem. B*, *108*(22), 6961-6968. DOI: 10.1021/jp036261n.

[12]. Chmielewska, D., & Sartowska, B. (2012). Radiation synthesis of silver nanostructures in cotton matrix. *Radiat. Phys. Chem.*, *81*, 1244-1248. DOI: 10.1016/j.radphyschem.2011.11.067.

[13]. Belloni, J., Mostafavi, M., Remita, H., Marignier, J.L., & Delcourt, M.O. (1998). Radiation-induced synthesis of mono- and multi-metallic nanocolloids and clusters. *New J. Chem.*, *22*, 1239-1255.

[14]. Ramnani, S.P., Biswal, J., & Sabharwal, S. (2007). Synthesis of silver nanoparticles supported on silica aerogel using gamma radiolysis. *Radiat. Phys. Chem.*, *76*, 1290-1294. DOI: 10.1016/j.radphyschem.2007.02.074.

[15]. Marignier, J.L. (1987). *Synthesis of metal nanoaggregates induced by ionizing radiations, structure and thermodynamical properties.* Thesis of “Doctorat d’Etat”, Paris-Sud University, Orsay.

[16]. Ershov, B.G., & Sukhov, N.L. (1990). A pulse radiolysis study of the process of the colloidal metal formation in aqueous solutions. *Radiat. Phys. Chem.*, *36*(2), 93-97. DOI: 10.1016/1359-0197(90)90220-C.

[17]. Marignier, J.L. Belloni, J., Delcourt, M.O., & Chevalier, J.P. (1985). Microaggregates of non-noble metals and bimetallic alloys prepared by radiation-induced reduction. *Nature*, *317*, 344-345. DOI: 10.1038/317344a0.

[18]. Liu, Y., Chen, S., Zhong, L., & Wu, G. (2009). Preparation of high-stable silver nanoparticle dispersion by using sodium alginate as a stabilizer under gamma radiation. *Radiat. Phys. Chem.*, *78*, 251-255. DOI: 10.1016/j.radphyschem.2009.01.003.

[19]. Mosseri, S., Henglein, A., & Janata, E. (1989). Reduction of dicyanoaurate (I) in aqueous solution: formation of nonmetallic clusters and colloidal gold. *J. Phys. Chem.*, *93*(18), 6791-6795. DOI: 10.1021/j100355a042.

[20]. Rafaeloff, R., Haruvy, Y., Binenboym, J., Baruch, G., & Rajbenbach, L.A. (1983). Radiolytic method of preparation of colloidal redox catalysts and their application in light-induced hydrogen generation from water. *J. Mol. Catal.*, *22*(20), 219-233. DOI: 10.1016/0304-5102(83)83028-4.

[21]. Buxton, G.V. (2008). An overview of the radiation chemistry of liquids. In M. Spotheim-Maurizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basics to applications in material and life science* (pp. 3-16). France: EDP Science.

[22]. Belloni, J., & Remita, H. (2008). Metal clusters and nanomaterials. In M. Spotheim-Maurizot, M. Mostafavi, T. Douki & J. Belloni (Eds.), *Radiation chemistry: From basics to applications in material and life science* (pp. 97-116). France: EDP Science.

[23]. Henglein, A. (1979). Reactions of organic free radicals at colloidal silver in aqueous solution. Electron pool effect and water decomposition. *J. Phys. Chem.*, *83*(17), 2209-2216. DOI: 10.1021/j100480a006.

[24]. Jonah, C.D., Matheson, M.S., & Meisel, D. (1977). Polyelectrolyte effects on rates of hydrated electrons. *J. Phys. Chem.*, *81*(19), 1805-1810. DOI: 10.1021/j100534a003.

[25]. Graetzel, M. (1981). Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light. *Acc. Chem. Res.*, *14*(12), 376-384. DOI: 10.1021/ar00072a003.

[26]. Hou, X.-G., & Liu, A-D. (2008). Modification of photocatalytic TiO_2 thin films by electron beam irradiation. *Radiat. Phys. Chem.*, *77*, 345-351. DOI: 10.1016/j.radphyschem.2007.04.003.

[27]. Toshima, N., & Yonezawa, T. (1998). Bimetallic nanoparticles—novel materials for chemical and physical applications. *New J. Chem.*, *22*, 1179-1201. DOI: 10.1039/A805753B.

[28]. Yamamoto, K., Koga, Y., Fujiwara, S., & Kubota, M. (1996). New method of carbon nanotube growth by ion beam irradiation. *Appl. Phys. Lett.*, *69*(27), 4174-4175. DOI: 10.1063/1.116976.

[29]. Terrones, M., Banhart, F., Grobert, N., Charlier, J.-C., Terrones, H., & Ajayan, P.M. (2002). Molecular junctions by joining single-walled carbon nanotubes. *Phys. Rev. Lett.*, *89*(7), 075505-1-075505-4. DOI: 10.1103/PhysRevLett.89.075505.

[30]. Ajayan, P.M., Ravikumar, V., & Charlier, J.-C. (1998). Surface reconstructions and dimensional changes in single-walled carbon nanotubes. *Phys. Rev. Lett.*, *81*(7), 1437-1440. DOI: 10.1103/PhysRevLett.81.1437.

[31]. Zhu, Y.J., Qian, Y.T., Zhang, M.W., Chen, Z.Y., & Xu, D.F. (1994). Preparation and characterization of nanocrystalline powders of cuprous oxide by using C-radiation. *Mater. Res. Bull.*, *29*, 377-383. DOI: 10.1016/0025-5408(94)90070-1.

[32]. Zhu, Y.J., Qian, Y.T., Li, X.J., & Zhang, M.W. (1997). γ-radiation synthesis and characterization of polyacrylamide-silver nanocomposites. *Chem. Commun.*, *12*, 1081-1082. DOI: 10.1039/A702946B.

[33]. Liu, H.R., Ge, X.W., Zhu, Y.J., Xu, X.L., Zhang, Z.C., & Zhang, M.W. (2000). Synthesis and characterization of polyacrylamide-nickel amorphous nanocomposites by γ-irradiation. *Mater. Lett.*, *46*(4), 205-208. DOI: 10.1016/S0167-577X(00)00170-1.

[34]. Komori, Y., & Kuroda, K. (2000). Layered silicate-polymer interlocation composites. In T.J. Pinnavia & G.W. Bell (Eds.), *Polymer-clay nanocomposites* (pp. 3-18). New York: J. Wiley & Sons.

[35]. Choo, S.-H., Lee, S., & Kwon, S.-J. (1999). Effect of flux addition on the microstructure and hardness of TiC-reinforced ferrous surface composite layers fabricated by high-energy electron beam irradiation. *Metall. Mater. Trans. A*, *30*(12), 3131-3141. DOI: 10.1007/s11661-999-0224-4.

[36]. Maekawa, Y. (2004). Nanotechnology and nanolithography using radiation technique in Japan. In *Emerging applications of radiation in nanotechnology, Proceedings of a consultants meeting held in Bologna, 22-25 March 2004* (pp. 221-232). Vienna: IAEA. (IAEA-TECDOC-1438).

[37]. Lee, Y.H., Browing, R., Maluf, N., Owen, G., & Pease, R.F.W. (1992). Low voltage alternative for electron beam lithography. *J. Vac. Sci. Technol. B*, *10*, 3094-3098. DOI: 10.1116/1.585935.

[38]. Kamp, M., Emmerling, M., Kuhn, S., & Forchel, A. (1999). Nanolithography using a 100 kV electron beam lithography system with a Schottky emitter. *J. Vac. Sci. Technol. B*, *17*, 86-89. DOI: 10.1116/1.590520.

[39]. Chang, T.H.P. (1975). Proximity effect in electron-beam lithography. *J. Vac. Sci. Technol.*, *12*, 1271-1275. DOI: 10.1116/1.568515.

[40]. Mohammad, M.A., Muhammad, M., Dew, S.K., & Stepanova, M. (2012). Fundamentals of electron beam exposure and development. In M. Stepanova & S.K. Dew (Eds.), *Nanofabrication* (pp. 11-41). Wien: Springer-Verlag.

Chapter 18

RADIATION USE IN PRODUCING TRACK-ETCHED MEMBRANES

Wojciech Starosta
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

Track-etched membranes are thin polymer films which have a system of fine, geometrically well-defined pores. A two-step process is used to achieve this. The first step consists of a thin polymer film being irradiated with a high energy heavy ion beam. During this step heavy ions penetrate the polymer film depositing part of their energy that results in ionization and excitation of target electrons. Because of the high energy depositions per unit length, discrete cylindrical regions extending along the ion trajectories and containing highly excited matter are formed. Through sequential relaxation steps, primary excitation energy is redistributed to electrons and ions in the film through a series of elemental processes involving the creation of radicals, of chemical bond breaking, of chain scissioning, the creation of small size chemical species, of gaseous product evolution (*e.g.* hydrogen) and of crosslinked fragments that finally lead to severe degradation of polymer chains inside the excited regions, which are called latent tracks [1-3]. In the second step, damaged polymer chains remaining after ion passage are etched using suitable chemicals to remove small size particles outside of the track by diffusion [4]. Assuming symmetrical etching conditions (etching from both sides of the film), cylindrical pores are formed, with the diameter dependent on the etching time.

Figure 1 is a scheme showing the pristine semicrystalline polymer (Fig.1A) and tracks created after the heavy ion passage through the polymer (Fig.1B). The reduced core density containing broken polymer chains and a hallo zone consisting of crosslinked polymer strands are illustrated (Fig.1B).

In Fig.2 the general photomicrographs of a final track-etched membrane made of poly(ethylene terephthalate) (PET) film are shown: the general view of the film surface (Fig.2A) and the cross-section view (Fig.2B).

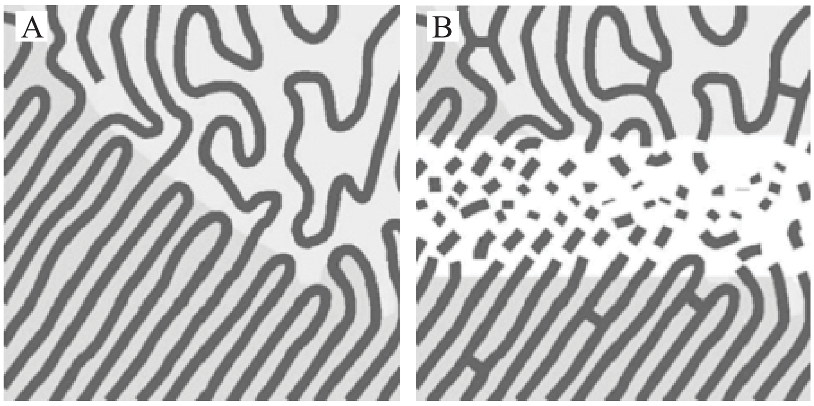


Fig.1. Scheme of ion tracks in a polymer: (A) initial semicrystalline polymer; (B) track consisting of a reduced core density, containing broken polymer strands surrounded by a track hallo zone crosslinked polymer strands. (Reproduced from Ref. [1]).

The phenomenon of track development in dielectrics were first documented in Young's paper published in *Nature* in 1958 [5]. Young noted that the heavy ions created as the result of uranium fission by slow neutrons, having a broad spectrum of energies, could be used for LiF irradiation. Track etching had been shown after contact with a strong alkali and tracks could be seen with an optical microscope. Further studies in this field were carried out by Price and Walker using mica irradiated with heavy ions from uranium fission. They patented their discovery entitled "The molecular sieves and the method of producing the same" in 1962 [6]. Shortly thereafter, the possibility of precise track etching in plastic materials was described in a paper by Fleischer and Price published in *Science* in 1963 [7]. The early researchers in track etching noted a broad scope of potential applications for etched tracks. Potential applications considered at that time included the determination of the age of geological and archaeological specimens containing natural uranium, the study of the early history of the solar system as recorded in meteorites, the determi-

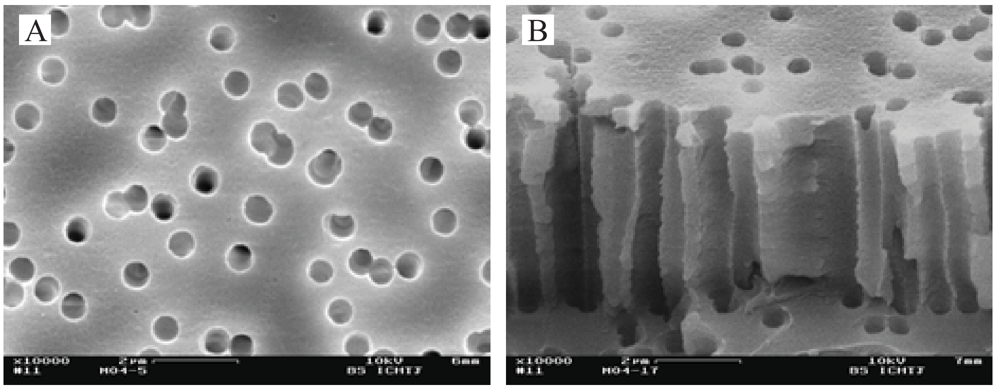


Fig.2. SEM (scanning electron microscopy) photomicrographs of a surface (A) and of a cross-section of track-etched membrane (B) made from a PET film.

nation of charged particle fluxes, the separation of biological cells having different sizes, aerosol sampling, *etc*.

The discovery of track etching to create pores in irradiated polymers was soon commercialized by the Nuclepore Company. Nuclepore track-etched polycarbonate membranes were manufactured from thin polycarbonate film irradiated with neutron-induced uranium fission products.

The major step in the advancement of track-etched technology was achieved around 1970 because of the developments in heavy ion accelerator technology. Heavy ion monoenergetic beams of multiple-charged ions, with precisely determined energy and mass, operated in a scanned mode, could be used for polymer film irradiation. The use of accelerator ion beams instead of uranium fission fragments enabled the irradiation of thicker polymer films and manufacture of pores of precise uniform diameter with controlled porosity and orientation – perpendicular or intentionally inclined to the surface of the film. Accelerator produced membranes were free of any possible radioactive contamination from fission fragments.

From then on, particle track-etched membranes have been routinely produced using heavy ion beam accelerators. Since 1970, polyester track-etched micro- and nanoporous membranes have been manufactured by the Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (JINR) in Dubna, Russia, using a heavy ion cyclotron. Other companies, as it4ip (a spin off from the Université Catholique de Louvain, Belgium), offer membranes made of polyester (PET), polycarbonate (PC) and polyimide (PI) films. Cyclopore and Poretics are other trademarks for these membranes. Research has been conducted in this field for many years by GSI Darmstadt, Germany.

Track-etched membranes possess a number of unique structural features that have made them distinct in comparison to other polymeric membranes, for example well-defined cylindrical geometry of pores, precise pore diameters and narrow pore size distributions enabling the exact exclusion limit in the case of particle filtration. At present, track-etched membranes made of polyester, polycarbonate or polyimide films are commercially available from the number of companies in a range of pore sizes, porosities and thicknesses. The key features of track-etched membranes are the following:

- well-defined cylindrical geometry of pores in the range of 10 nm to few μm,
- standard thicknesses in the range of 10-25 μm,
- narrow pore size distribution (variance of pore sizes below 5%),
- porosity in the range of 1-20%,
- low protein binding and low extractability ensuring no sample contamination,
- smooth and flat surfaces enabling particle collection for microscopic observation,

- chemical inertness and good thermal stability (up to 430°C in the case of membranes made from polyimide film).

Etched heavy ion tracks in polymers are suitable for a number of interdisciplinary uses in diverse fields. Track-etched membranes perform very well in applications where their unique structural properties are fully used. Due to their exact cut-off size, they perform well in the fine cleaning of small volumes of high value fluids from particulate material. They can be used for the efficient separation of medical and biological liquids from bacteria when a membrane with appropriate pore diameter is selected. In biosensors, they can be used for the controlled diffusion of biochemical reagents and for the protection of electrochemical detectors [8]. Due to their smooth surfaces, they can be used in the cell culture technologies for membrane-supported cell culture [9], cell nutrition, and cell collection by filtration for microscopic observation. The smooth surfaces are suitable for sample preparation for SEM (bacterial or air particulate matter analysis) and related analytical techniques.

A new area of use related to template synthesis of materials has emerged. In template synthesis, the cylindrical pores of track-etched membranes are used to directly deposit various materials inside the pores, such as polymers, metals or metal oxides. Monodispersed, one-dimensional nanostructures in the form of nanorods or nanotubes with a high length to diameter ratio and a strictly controlled radius by the membrane pore diameter can be made by this method [10-14]. Different architectures of nanostructures are possible. Materials may be left in the membrane which results in a flexible material with the filled pores. After the membrane polymer is dissolved, the discrete nanoparticles can be recovered by filtration for further use. When the membrane fixed to the solid support is filled and then dissolved after being made, brush-like nanostructures can be formed. Interest in one-dimensional structures stems from the fact that their physicochemical properties usually greatly differ in comparison to the properties of bulk structures and they can be used in the manufacture of electronics and sensors [15]. Such high aspect ratio nanostructures with length to diameter ratios reaching 1000 were not possible using standard methods of nanolithography based on ultraviolet (UV) or X-ray exposure.

There is a growing interest in track-etched pores in different areas of biology and medicine, where small diameter nanopores can be used as artificial model channels mimicking these encountered in biological membranes [16, 17]. Due to the higher stability of artificial channels, they can be used for the study of diverse biological processes, *e.g.* selective ion transport through the pores. Another broad area of use in biology is cell culture. There is also a growing interest in the development of microfluidic chips where membranes support cell cultures to simulate *in vivo* conditions. The microfluidic module presented in Ref. [9] consists of a fluidic supply channel and a cell culture chamber separated by a thin, low-dead-volume porous membrane (pore size – 0.015-0.2 μm). On one hand, these membranes serve as a physical barrier for a suspended cell culture against contaminants. On the other hand, the membrane permits controlled exposure of the cells to various concentrations of a drug that is transported *via* nanochannels through the membrane to interact with the cells. Such platforms should allow monitoring of various physiological processes and provide a large degree of freedom in the control of experimental conditions, while using reduced volumes of reagents and cells. These devices show great promise for high-throughput, automated drug screening in a point-of-care environment by relatively unskilled users.

It has been shown that diverse forms of the pores can be made, *e.g.* conical, cigar-like or a bowl-like shape, by properly choosing the etching process (asymmetrical, one-side etching or by adding surfactants on the one side of etched membrane) [18]. Detailed studies have confirmed the presence of charged species on the pore surfaces, resulting from polymer bonds being broken resulting in the formation of carboxylic or hydroxyl groups. This is important since pores with small diameters having charged groups on the pore surface can significantly influence the ion transport through the nanochannels, enhancing transport of counter-ions and diminishing transport of co-ions. The mechanism of ion and molecular transport through narrow channels is of great importance for biological studies. The developments achieved in track-etched techniques enable the making of artificial nanochannels, which better mimic those in the real biological world [19-24].

Another promising area of use for the track-etching technique is lithography. In the case of lithography based on ion beams, it is possible to create sub-100 nm features down to 10 nm in silicon and in polymers, which are not attainable using traditional optical lithography due to diffraction effects [25]. Different techniques can be used for making nanostructures, such as: ion projection lithography (IPL) and focused ion beam (FIB). The IPL technique follows traditional lithography, using large area masks through which a pattern is replicated in a resist material. In IPL, the complete absence of diffraction effects, the ability to tailor the depth of ion penetration to suit the resist thickness or the depth of modification, and the ability to pattern a large area in a single brief irradiation exposure without any wet processing are the prime characteristics of this technique. Ion tracks, specifically etched tracks, alone or in combination with lithography, enable many possibilities for creating novel deep micro- and nanostructures within polymer films that are difficult to produce or even unattainable by other techniques. Prototypes of a number of ion track-based electronic components, such as resistors, diodes, capacitors, magnets, transformers, transistors, and several types of sensors, have been made. The first hybrid track-based silicon polymer device has been successfully tested. However, this is still a long way to the industrial use. Nevertheless, the potential use of ion track-based microporous films is tremendous [26].

2. TRACK-ETCHED MEMBRANE MANUFACTURING

The manufacture of track membrane is the two-step process. In the first stage, polymer films are irradiated with heavy ions. The two typical methods of irradiation are shown in Fig.3. Figure 3A shows the irradiation with uranium fission products which were used at the early stages of research into track-etched materials, and Fig.3B shows the irradiation with an ion accelerator beam in the scan mode, as presently used. A special mode of beam scanning permits single ion track irradiation [27]. In that case, a low intensity beam is used and the irradiation is stopped immediately after the first ion pass through the film is detected. This variant of irradiation is used mainly for single track membrane preparation which is needed for high level research on ion transport phenomena inside a single pore and for different biological sensors manufacture. Recently, the preparation of single or few ion tracks based on a scanning ion beam has been achieved using set of small diameter diaphragms placed in the front of the film [28].

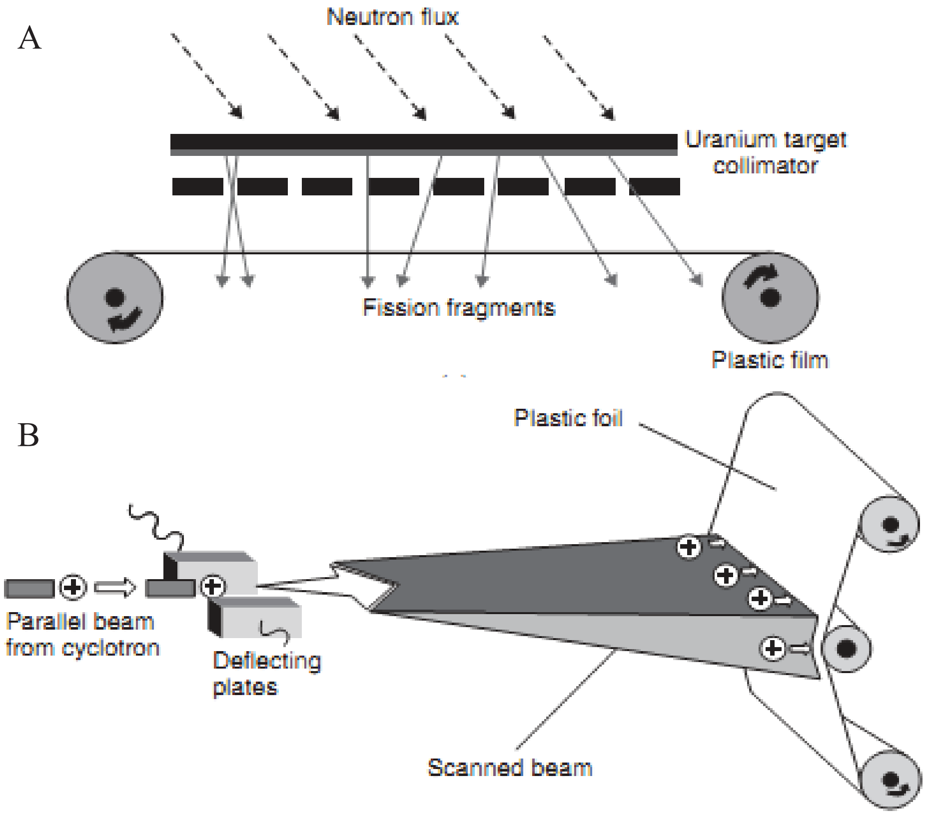


Fig.3. Scheme of irradiation of polymer films with uranium fission fragments (A) and heavy ion accelerator beam in scanning mode (B). (Reproduced from Ref. [2]).

While passing through a polymer film, heavy ions interact with the target nuclei and with target electrons. Such interactions can be described as series of discrete binary collision events, each one governed by electrostatic force of interaction between the charged particles, as described by Coulomb law. According to the rules of classical mechanic (conservation of energy and momentum), part of the energy of primary particle is transferred to the target particle and the incident particle is deflected from its primary direction. However, the details of these processes depend strongly on the specific energy (energy per unit mass) of the primary particle and on the mass ratio between the colliding particles. The transfer of energy to the target nuclei prevails at low values for ion specific energy (0.001 MeV/nucleon) and the transfer to target electrons prevails at higher specific energy values (at around few MeV/nucleon). This is shown for the case of Xe ions in PET films (Mylar) in Fig.4.

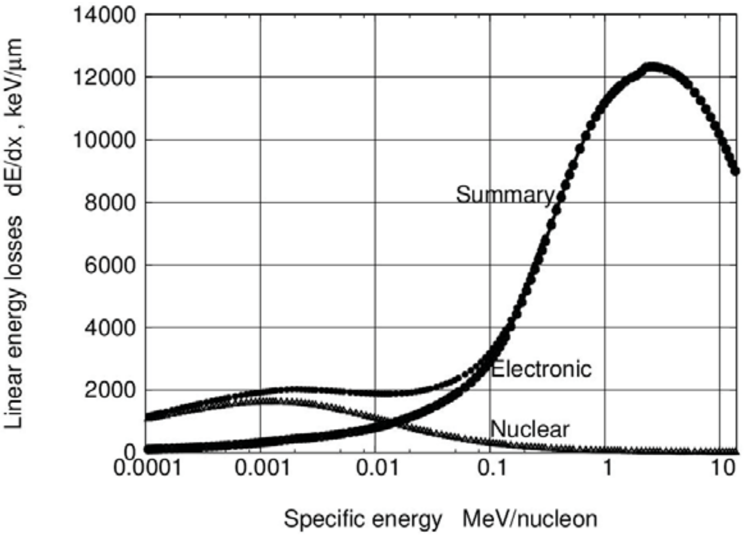


Fig.4. Dependence of energy losses per unit length for Xe ions with different specific energies penetrating PET film (Mylar). The functions were calculated using SRIM2013 software [29].

For the track-etched membrane manufacturing, heavy ions with sufficiently high specific energy are used, around 2 MeV/nucleon and higher. In this case, the transfer of energy in collisions with the nuclei can be neglected. Due to the large difference in the masses of electrons and ions, heavy ions do not change their direction in successive collisions and move approximately along a straight line. The quantitative description of the stopping of a heavy ion in matter is the energy loss per unit length. The electronic energy losses to target electrons per unit length are described by Bethe-Bloch formula:

$$-\frac{dE}{dx}=\frac{4\pi N_A Z\rho}{Am_m m_e c^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{z^2}{\beta^2}\left[\frac{1}{2}\ln\left(\frac{2m_e c^2\beta^2 T_{max}}{(1-\beta^2)\,I^2}\right)\right]-\beta^2-\frac{\delta}{2}$$

where: Z – charge of ion, β – velocity of ion in light velocity unit (v/c), I – target ionization potential, T_{max} – maximum energy transfer to target, m_e – electron mass, M – ion mass, γ – relativistic factor. T_{max} is available from the following equation:

$$T_{max} = \frac{2m_e c^2 \beta^2 \gamma^2}{1 + 2\gamma m_e / M + (m_e / M)^2}$$

where $\gamma = 1/\sqrt{(1-\beta^2)}$.

The energy deposited per unit length is related directly to the density of damaged polymer chains along the ion trajectory. The dependence between the density of energy deposition and the density of defects is a complex nonlinear relation. The process of ion interaction with a stopping material is statistical in nature, so there should be fluctuations in linear energy deposition. Correspondingly, fluctuations in the length of primary damaged micro-regions along the ion trajectory are expected. At sufficiently high values for the energy deposited

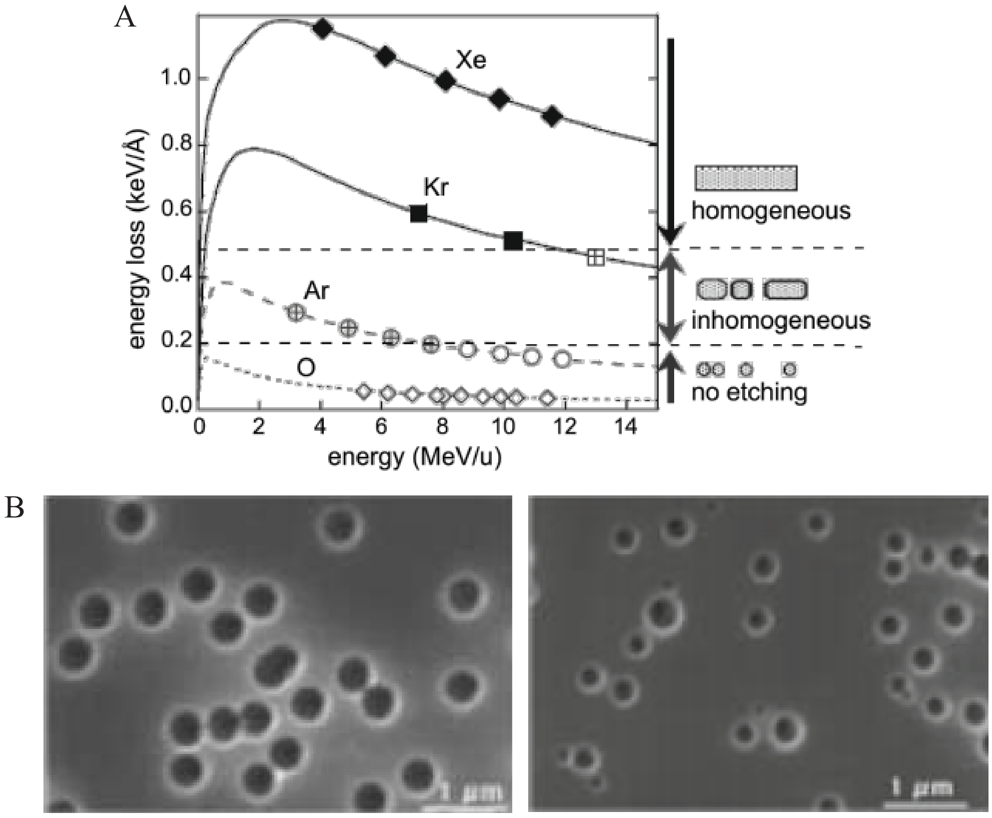


Fig.5. (A) Energy loss as a function of specific ion energy. The dashed lines separate the different regimes of track etching: homogeneous (full symbols), inhomogeneous (crossed symbols), and absence of etching (open symbols). (B) SEM images of uniform pores resulting from homogeneous tracks (left) and pores with broad size distribution due to inhomogeneous tracks (right). (Reproduced from Ref. [30]).

per unit length, the fluctuations will be smoothed and the overlapping of damaged micrograins can occur giving a continuous cylindrically shaped damaged latent track prior to the etching. It was experimentally found and reported in the literature that for the creation of continuous etchable latent ion tracks in polymer films able to perform as membranes, the energy deposition per unit length should be higher than some threshold estimated at 720-900 eV/nm for polycarbonate, polyimide and poly(ethylene terephthalate) [30].

To get an idea of possible quantitative energy depositions, the energy loss for four ions – Xe, Kr, Ar and O, were calculated using the SRIM software [29] and are presented in Fig.5. The dashed horizontal lines drawn at different values for energy losses separate the different regimes of track etching: homogeneous, inhomogeneous, and no etching.

The energy loss curves reach a maximum in the range of 1-5 MeV/u, depending on the ion type. Accelerated ions with specific energy in this range are the most efficient in energy deposition to a polymer target considering the deposited energy value and uniformity of linear energy deposition along the ion trajectory. For the case of the Xe ion with a specific energy of 3 MeV/u, linear energy deposition reaches the value of 1200 eV/Å and the range of the nearly uniform linear energy loss is sufficiently long, reaching about 20 μm as shown in Fig.6. Considering that the typical energy required to chain scission in polymers is in the range of 100 eV, severe damage to a polymer would be expected.

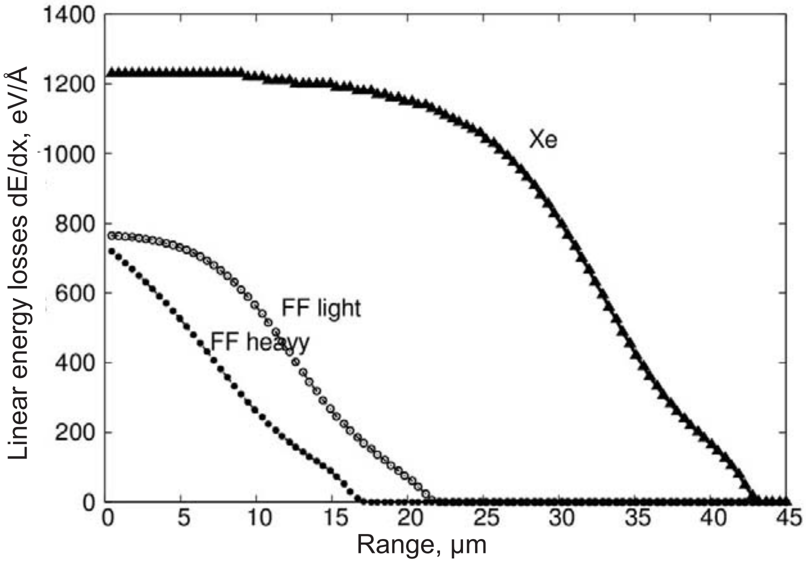


Fig.6. The energy loss of a light (atomic number Z = 36, atomic mass A = 92, energy E = 101 MeV) and a heavy (Z = 56, A = 141, E = 65 MeV) fission fragment of ^{235}U as a function of the range in poly(ethylene terephthalate). A curve for an accelerated Xe ion (Z = 54, A = 132, E = 396 MeV) is also shown. These curves were calculated using the stopping and ranges of ions in matter using the SRIM2013 code [29].

The structure of the damaged region is complex. However, the energetic electrons created in the primary processes of interaction (called δ-electrons), emitted mainly in the directions perpendicular to ion trajectory, can interact with matter further, leading to the creation of the electron cascades in the region surrounding the primary region of interactions. This process is connected with further ionization and excitation of atoms inside this region by direct electron impact or accompanying Auger relaxation processes of excited ions. As the result of these processes, the radii of severely damaged regions are extended up to 20 nm and a so-called halo region is formed around the track core. Therefore, the primary processes are completed with the central regions highly excited and electron clouds somehow shifted outside these regions. Next, the excitation energy is equilibrated in the relaxation processes in short time-scale of a femtosecond. The details of the relaxation of this far from equilibrium state are still under discussion. The difficulties in finding adequate theory are related to the proper description of the relaxation kinetics for the far from equilibrium state resulting from a high density of energy deposited into very small volume. The relaxation of these far from equilibrium states proceeds through cooperative action involving target electrons and ions leading to severe structural changes inside the primary damaged region and in the close vicinity around them, as a result of degradation of polymer chains through radical creation, chain scissioning, and chain crosslinking. Commonly used models for relaxation were elaborated on in early studies of track formation and include Coulomb explosion and a thermal spike model [1]. The first one takes into account the strong repulsive forces acting between ions remaining inside the track core while energetic electrons where moved outside. This interaction leads to rapid, explosive expansion of ions by atomic collision which cascades in the vicinity of the ion trajectory. The thermal spike model takes into account the rapid temperature rise inside the core at the ion passage step which leads to melting and disorder.

In the case of polymers the track core region undergoes severe structural transformation because of a chemical reaction initiated by radicals inside the core. Chain scission prevails inside the core, while outside the core in the track halo region (diameter – 10-100 nm) electron-induced radiation effects dominate, sometimes forming a crosslinked layer around the track core. Breaking of the most of the covalent bonds in the track core (including both the polymer backbone and side groups) is accompanied by around a 10% reduction of the density, which means that the free volume has increased proportionally. In polymers containing hydrogen, this local zone is depleted of hydrogen atoms, so unsaturated carbon–carbon bonds form. After the physical stage of track formation has been completed, the track in the polymer undergoes relatively slow chemical transformations, such as the decay of radiolysis intermediates, reactions with air (primarily oxygen), and creation of new groups (*e.g.* peroxide, hydroperoxide, hydroxyl, carboxyl), that enhance preferential etching.

Due to these structural changes accompanied by the formation of reduced density zones, the fast penetration of suitable chemical etchants are facilitated along the track enabling further degradation of oligomers present inside the track through chemical reactions initiated by etchant. Small weight clusters created in the etching process are removed to the outside by diffusion. The structural changes inside the track core enable the etching of the track. The free volume in the track core facilitates the penetration of the chemical reagent (etchant) along the particle's path and accelerates the chemical degradation of the macromolecular segments located there. In contrast, the modification of the polymer properties in the halo is not as strong. A typical feature of many polymers is that the halo material is etched at a lower rate than the pristine polymer. This phenomenon is likely caused by the preferential crosslinking of macromolecules in the halo region around the track core.

Chain scissioning in the latent tracks results in monomer segments at the end of a chain and only one chemical cleavage is required for etching. This simpler process contributes to the higher etch rate in the track. In addition, the etchant can diffuse faster into the track than into the non-tracked material. A combination of these effects qualitatively explains the much higher etch rates for the tracks compared to non-tracked materials.

The next stage of track-etched membrane manufacturing process consists of track sensitization using UV irradiation of the films. The stability of latent track and their susceptibility to etching can be increased by exposure to UV radiation in air. With a suitable chosen UV wavelength, a remarkable increase in etching rate along the track can be achieved with a minor effect on etching rate of the bulk polymer matrix. The mechanism responsible for that effect is

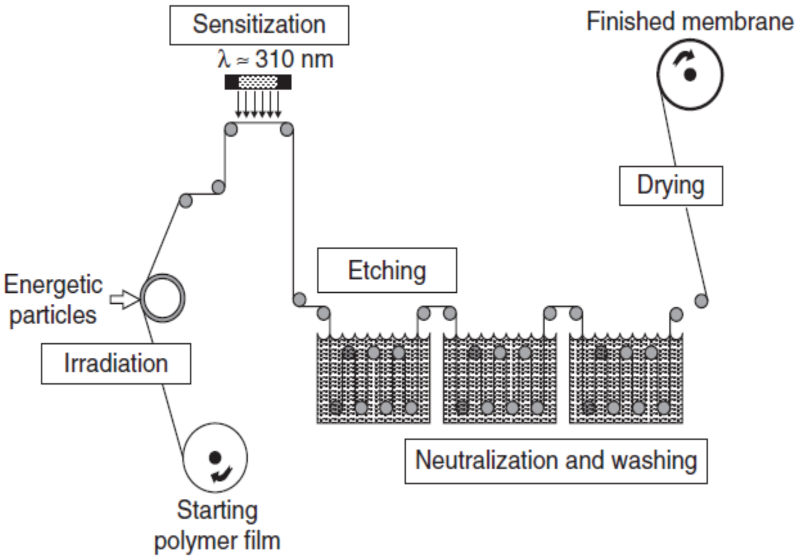


Fig.7. General scheme for track-etched membranes manufacturing. (Reproduced from Ref. [2]).

related to the photodecomposition of radiolysis products formed during heavy ion passage into low molecular weight species [31].

The final stage in track-etched membrane manufacturing is related to the etching of latent tracks with the irradiated film passing through the bath containing the etch solution. A typical scheme for this etching procedure is shown in Fig.7.

The process of etching consists of the penetration of a small-sized etchant molecules into the track core and in the selective breaking of chemical bonds inside the degraded core by chemical reactions [4]. Small size atomic clusters created in this process can be removed to the outside of the track by diffusion. The etching process is based essentially on two factors. One is related to large differences in the velocities for etching along the track core and in direction perpendicular to the track axis due to the easier transport of small etchant molecules in the less compact structure of the core. The second factor is kinetic in nature and is related to the lower chemical barriers for chemical bonds to break by reaction of the etchant with small low molecular weight units present in partially degraded core. Two values describe the kinetics of etching process: velocity of etching along the track, v_t, and velocity of etching for the unirradiated bulk matrix, v_b. For PET, the alkali etching solution is applied at temperatures in the range 50-80°C. The ratio of track to bulk etch velocities can reach up to 1000.

In PET etching, the mechanism is based on the alkaline cleavage of ester bonds. The corresponding chemical reaction scheme is shown in Fig.8. The free ethylene glycol and anion of terephthalic acid molecules as well as the bonded end groups, both carboxylate and hydroxyl, are created as the reaction products. It is worth noting that the pendant ionizable bonds present on the pore walls make them electrically active and are responsible for the selective ion transport through the small radius pore in an electrolytic solutions. This unique property in combination with the small pore radius is used for the selective sensing of macromolecule passage through the pore on the basis of current blockage in electrolyte solution.

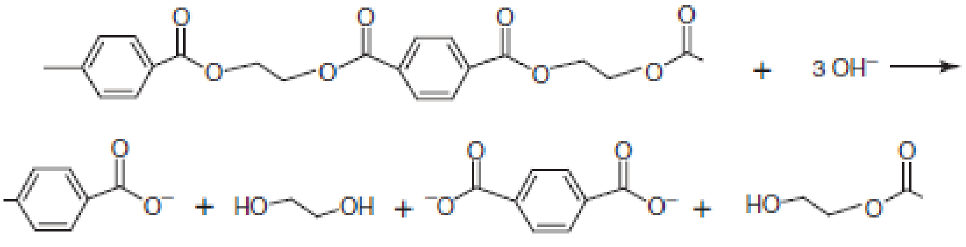


Fig.8. Chemical reaction scheme for ester bond cleavage in PET.

In large-scale track-etched membrane manufacturing, symmetrical etching conditions are used. In this case, the liquid etchant equally accesses both sides of the polymer film that is submerged in the etching bath. Due to the high

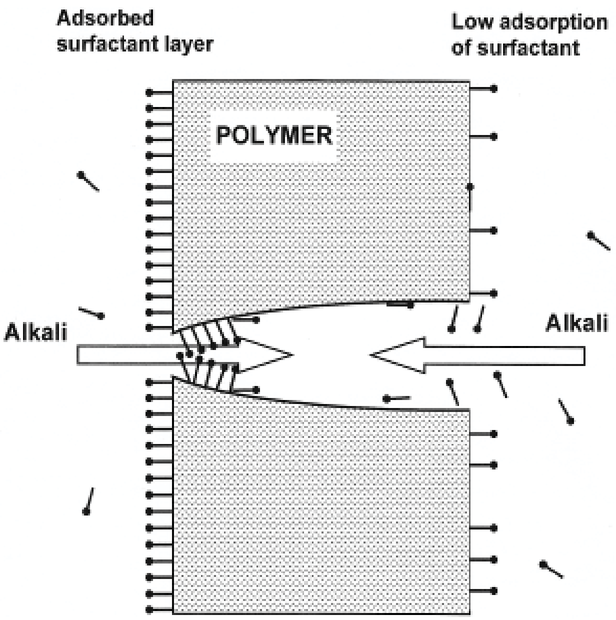


Fig.9. Scheme of track etching of irradiated film in the presence of nano-sized surfactant molecules. (Reproduced from Ref. [33]).

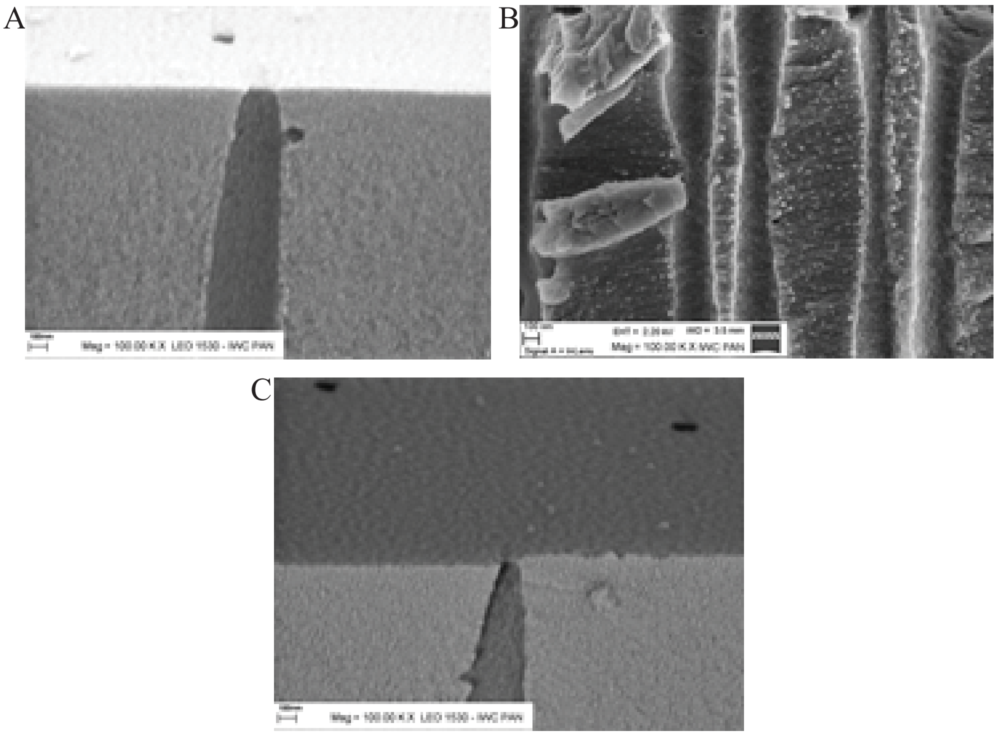


Fig.10. SEM micrographs of membranes with a conical pore (A), a bullet-like shape (B) and an hour glass (C) form.

value of the etch ratio, cylindrically shaped pores are created with diameters depending on the time of etching. On a laboratory scale, asymmetric etching conditions can be applied in order to get non-cylindrically shaped pores. In this case, one side of the membrane is in contact with etchant solution while other side is in contact with a so-called stopping solution containing an acid neutralizing solution. By this method, conical pores with small openings can be manufactured, which have found use as model systems for selective ion transport studies in electrolytic solutions and for single macromolecule detection.

Another possibility for the modification of the track form is the application of a surfactant solution on one side of membrane, as shown in Fig.9 [27, 32]. The surfactant diffusing through the openings made in the etching process binds to the surface of tracks and block them from etch attack. The detailed form of pore depends on balance of the surface coverage by the surfactant and by the etchant. Pores with the various forms, such as narrow and wide cones, spherical troughs, barrels, and bottle necked structures, can be obtained by this method. Some of them are shown in Fig.10.

3. APPLICATIONS OF TRACK-ETCHED MEMBRANES

3.1. TEMPLATES FOR ONE-DIMENSIONAL MATERIALS

The unique properties of track-etched membranes having well-defined shapes and precise pore diameters make them very attractive as hard templates for making one-dimensional, high aspect ratio nanomaterials like nanowires and nanotubes. Materials can be made from polymers, metals or metal oxides with diameters in the range of 10-200 nm and lengths of 10 μm. This gives a length to diameter ratio of up to 1000. In comparison to another well-known hard templates, like anodic alumina oxide membranes made by the electrolytic oxidation of aluminium foils, polymer track-etched membranes have a much wider range of pore diameters.

The template method is used to make free-standing arrays of one-dimensional materials in polymer films. After chemical dissolution of the polymer matrix, the nanoparticles can be recovered by filtration. A variation is the immobilization of arrays fixed on silicon/silicon oxide support covered with a conducting Au (or Pd) layer and spin coated with a thin polymer film for track etching.

Interest in exceedingly small dimensional materials is being driven by two stimuli. The first is related to the fact that physical and chemical properties become different at very small dimensions in comparison those of large bulk particles. The second is a common trend toward miniaturization in the field of sensing elements and a tendency to develop sensors operating at atomic scale level. In the case of sufficiently small diameter particles, a large fraction of atoms is lying on the surface occupying under-coordinated surface reactive sites. Attachment of external molecules on the surface of a semiconductor nanowire can strongly influence its conductivity due to the redistribution of the charge inside the nanowire needed to screen external molecular charges [34]. This happens when the Debye length for nanowire, the parameter describing the extension of electric field penetration into the bulk, is comparable to the diameter of nanowire. In the case of photosensitive materials, a relaxation processes of charge carriers generated by photon absorption depend strongly on the dimension of the absorbing particle. The time needed for photoinduced carriers to reach the surface by diffusion can be shorter than the hole-electron recombination time. Thus, a redox reaction on the surface would be possible with the participation of photogenerated charge carriers. Such a property is important for the photooxidation processes or, in the case of conductometric sensors, for their recovery and time response in the case of photoinduced analyte desorption. Thus, metal-oxide nanowires can function as sensitive and selective chemical or biological sensors. The active nanowire sensors in such devices can be configured either as resistors, whose conductance is altered by charge-transfer processes occurring at their surfaces or as field-effect transistors whose properties can be controlled by applying an appropriate potential onto a gate. Functionalizing the surface of these entities offers yet another way for expanding their sensing capability. Although research on the use of metal-oxide nanowires as sensors is still in its early stages, several encouraging experiments have been reported that are interesting in their own right and indicative of a promising future [35-38].

The template synthesis method of nanomaterials using track-etched membranes was pioneered by the Charles Martin's group at the University of Florida [39]. Their research has been directed to application of template made nanotubes and nanotube membranes for biosensors and for macromolecule detection and separation [8, 10, 13, 22]. At present, the template method for track-etched polymer membranes has become a mature method and is widely used by many research groups.

Various methods are used for making templates: electrochemical deposition in the case of metals, electrophoretic deposition in the case of non-conducting materials, vapour deposition, electroless deposition and chemical deposition from solution.

Table 1 presents information on materials and methods used for making nanostructures taken from recently published papers.

Electrochemical deposition proceeds according to the scheme shown in Fig.11. One face of the template must be covered with an inert conducting film (*e.g.* gold or platinum) serving as the anode. The metal is then electrochemically deposited within the pores of the membrane. The length of the nanowires

Table 1. Examples of nanostructures made by the membrane template methods.

No.	Product type	Membrane material	Technique	Ref.
1	Ni nanowires on Si/SiO_2 substrate, diameter – 20-60 nm, length – 2 μm	Polycarbonate	Electrodeposition	[40]
2	Bi single wire, cylindrical, conical	Polycarbonate	Electrodeposition	[41]
3	Ni, Co, Cu, Au, polypyrrole nanowires	Polycarbonate	Electrodeposition	[42]
4	Co, Ni-Au bisegment nanowires; NiFe/Cu/NiFe, Co/Cu/Co trisegment nanowires	Polycarbonate	Electrodeposition	[43]
5	Cu single nanowires, length – 30 μm	Polycarbonate	Electrodeposition	[44]
6	Cu nanowires, diameter – 0.2 and 0.4 μm, length – 10 μm	Polycarbonate	Electrodeposition	[45]
7	Au, poly- and single crystalline nanowires, length – 25 μm	Polycarbonate	Electrodeposition	[46]
8	FeNi (permalloy $Ni_{80}Fe_{20}$), Cu, Au nanowires	Polycarbonate	Electrodeposition	[47]
9	Au, conical nanowires	Polycarbonate	Electrodeposition	[48]
10	Au, Ag, Cu, Ni, Co, Rh, diameter – 40 nm, length – 3-5 μm	Polycarbonate	Electrodeposition	[49]
11	Au, Cu, Pt, Bi, Bi_2O_3, ZnO, CdTe nanowires	Polycarbonate	Electrodeposition	[50]
12	Bi_2Te_3	Polycarbonate	Electrodeposition	[51]
13	Ni-CdTe, Ni-ZnO-Ni multisegment nanowires	Polycarbonate	Electrodeposition	[52]
14	$Pb(Zr_xTi_{1-x})O_3$ nanowires, diameter – 100 and 200 nm	Polycarbonate	Electrophoretic deposition	[53]
15	TiO_2, SiO_2, $BaTiO_3$, $Sr_2Nb_2O_7$, $Pb(Zr_{0.52}Ti_{0.48})O_3$, diameter – 45-200 nm, length – 10 μm	Polycarbonate	Electrophoretic deposition	[54]
16	TiO_2, diameter – 45-200 nm, length – 10 μm	Polycarbonate	Electrophoretic deposition	[55]
17	TiO_2, diameter – 200 nm	Polycarbonate	Electrophoretic deposition	[56]
18	SiO_2 nanotubes, diameter – 100 nm	Polycarbonate	Atomic layer deposition	[57]
19	Al_2O_3 layer on conical nanochannels	PET	Atomic layer deposition	[58]
20	TiO_2 film, diameter – 200 and 400 nm, length – 10 μm	Polycarbonate	Atomic layer deposition	[59]
21	Fluorinated polymer layer, diameter – 50 nm	Polycarbonate	Chemical vapour deposition	[60]
22	Al_2O_3 film	PET	Atomic layer deposition	[61]

Table 1. Contd.

No.	Product type	Membrane material	Technique	Ref.
23	TiO_2, SiO_2, Al_2O_3 films, diameter – 18-55 nm, thickness – 5-22 nm	Polycarbonate	Atomic layer deposition	[62]
24	Au	Polycarbonate	Electroless deposition	[63]
25	TiO_2, length – up to 30 µm	Polycarbonate	Electroless deposition	[64]
26	Pt nanotubes, Pt/Ru bimetallic nanotubes	Polycarbonate	Electroless deposition	[65]
27	Ni, Ni-B nanotubes	Polycarbonate PET up to 30 µm	Electroless deposition	[66]
28	Ag film; Pt, Cu nanotubes	Polycarbonate	Electroless deposition	[67]
29	Au nanowires for DNA immobilization, diameter – 10 nm	Polycarbonate	Electroless deposition	[68]
30	Pd nanotubes, length – 30 µm	Polycarbonate	Electroless deposition	[69]
31	Au nanowires array	Polycarbonate	Electroless deposition	[70]
32	Ni, Pt, Cu, Ag, Au network, pore diameter – 400 nm	Polycarbonate	Electroless deposition	[71]
33	Au film functionalized with fluorinated thiols	Polycarbonate	Electroless deposition	[72]
34	Ag nanoparticles; Au, Cu, Pt nanotubes	Polycarbonate	Electroless deposition	[73]
35	Ni nanotubes, length – 10-100 µm	Polycarbonate	Electroless deposition	[74]
36	Au nanotube membrane, diameter – 50 nm	Polycarbonate	Electroless deposition	[75]
37	Ag microtubes, length – 10 µm	Polycarbonate	Electroless deposition	[76]
38	Cu doped Zn nanorods	Polycarbonate	Chemical solution	[77]
39	MgO nanorods, diameter – 70-160 nm, length – 5-6 µm	Polycarbonate	Chemical solution	[78]
40	In_2O_3 nanorods, diameter – 0.1 µm	Polycarbonate	Chemical solution	[79]
41	Polypyrrole nanotubes	PET	Chemical solution	[80]

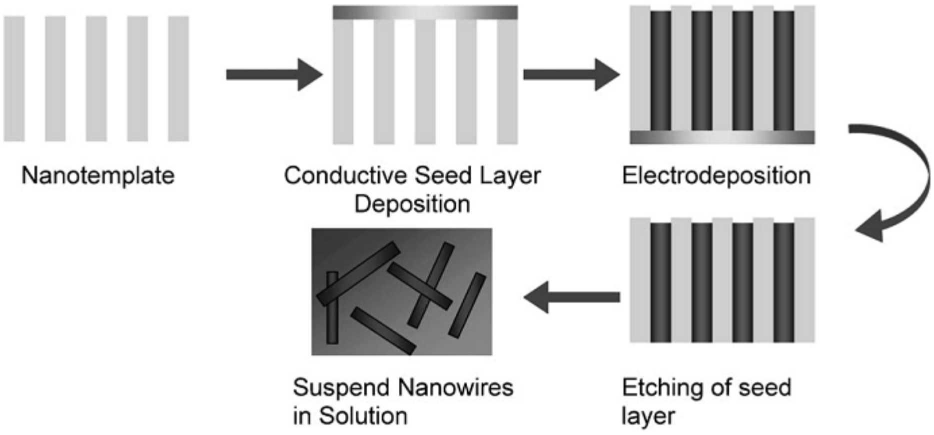


Fig.11. General scheme of electrochemical deposition of metal nanowires inside the pores of a track-etched membrane. (Reproduced from Ref. [37]).

is determined by the current density and deposition time, while the diameter of the nanowire is determined by the pore diameter of the template. After nanowires have been electrodeposited, the conducting film used for the electrochemical deposition as well as the template are then subsequently dissolved using appropriate acids or bases.

The scanning electron micrograph in Fig.12 shows the very smooth surface and uniform diameter of template made gold nanowires with diameters of 160 and 25 nm.

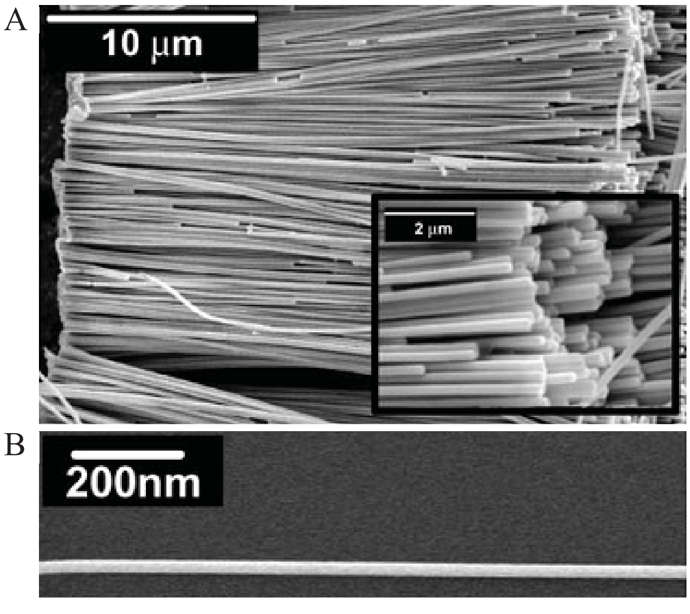


Fig.12. (A) SEM micrographs of 160 nm diameter gold wires; inset: end section of wires. (B) High-resolution scanning electron micrograph (HRSEM) of a 25 nm wire. (Reproduced from Ref. [46]).

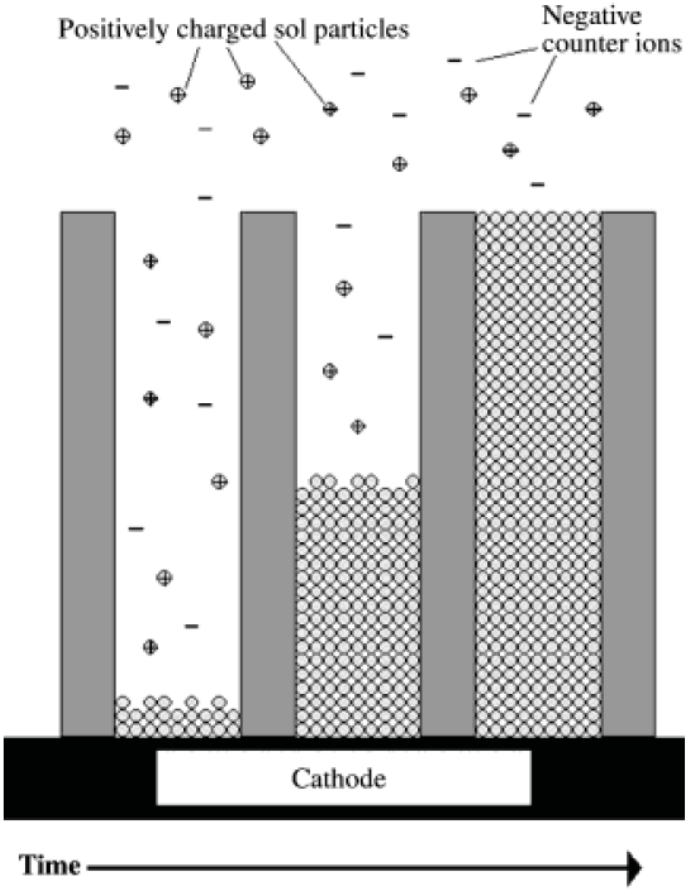


Fig.13. The scheme of electrophoretic deposition process. (Reproduced from Ref. [55]).

Electrophoretic deposition can be used in the case of non-conducting material deposition such as metal oxides. Nano-sized particles required for deposition can be prepared by sol-gel method. Using the sol-gel method, making monodisperse sol with particle dimensions in the range of 1 to 100 nm and easily controlled stoichiometry is possible. In a polar solvent or an electrolyte solution with proper conditions (zeta potential value), the surface of a nanoparticle develops an electrical charge preventing its agglomeration. Under the action of an external electric field, charged particles are set in motion, as schematically illustrated in Fig.13. When hitting an electrode, the electrostatic double layers present on the particle surfaces collapse and particles coagulate, forming a porous material of compacted particles [53]. A porous template is used to restrict the deposition to occur inside the pores only. Since monoliths grown by electrophoretic deposition are porous, post-deposition sintering at elevated temperatures is usually required to form a dense material. If the initial solid particles were amorphous, sintering would also induce crystallization. A variety of materials, such as TiO_2, SiO_2, $BaTiO_3$, PZT, and $Sr_2Nb_2O_7$, have been deposited by a combination of electrophoresis and the sol-gel method (see Table 1).

The atomic layer deposition (ALD) method is a thin film deposition method based on cyclic deposition of atoms from reactive precursors in gaseous form, supplied sequentially. It can be used for arbitrary shaped substrates and enable deposition of atomic thickness layers in one cycle. The ALD method has been successfully used with the track-etched membranes for the modification of pore surface properties and for the reduction of internal pore diameters. Conformal coatings on the pore walls of track-etched membranes with TiO_2, ZrO_2, and Al_2O_3 layers have been reported (see Table 1).

Many studies on ionic transport through small diameter nanochannels have shown a strong influence of pore wall surface charge on ion transport through the pores. There is a need to modify the pore wall surface properties. Specific local channel properties such as pore diameter variations, conformation variations of pendant bonds, swelling of pore walls, polymer surface layer or surface charge density variations due to the pH changes of a solution are usually not well known. But all of them may influence ion transport. Therefore, the development of methods for surface modification in a controlled manner in order to get a surface with well-defined properties is of great value. For macromolecular sensor development, the surface inside the nanopore should be carefully prepared, since the surface charge, roughness, and/or functional groups could significantly influence the signal-to-noise ratio and the capture rate of the analytes, and they could even lead to unwanted permanent adsorption of the analytes or clogging, if not enough attention was paid. Moreover, coating with

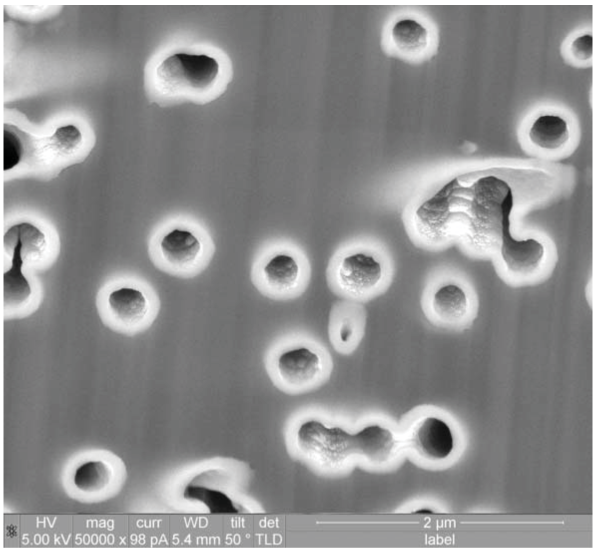


Fig.14. SEM BSE (scanning electron microscopy with back-scattered electrons) image of the FIB milled surface showing the TiO_2 conformal coating present inside the track-etched pores of the polycarbonate membrane. (Reproduced from Ref. [59]).

insulating durable material, like ceramic oxides, will protect the host material in some filtration applications.

The ability to reduce internal pore diameters in a controlled manner at the nanometre level is of great value for sensors development, especially in the range below 10 nm. For the protein sensor development, precise control of the pore size in the nanometre range is an important challenge, since the pore size needs to be just a little larger than the protein size in order to achieve very sensitive detection. A general view of a membrane after TiO_2 conformal coating is shown in Fig.14.

Electroless metal deposition uses a redox reaction to deposit metal on an object without the passage of an electric current, but using a plating bath. Due to its surface limitations, electroless deposition is a convenient and power saving method to produce hollow nanostructures. Most of the work on metal

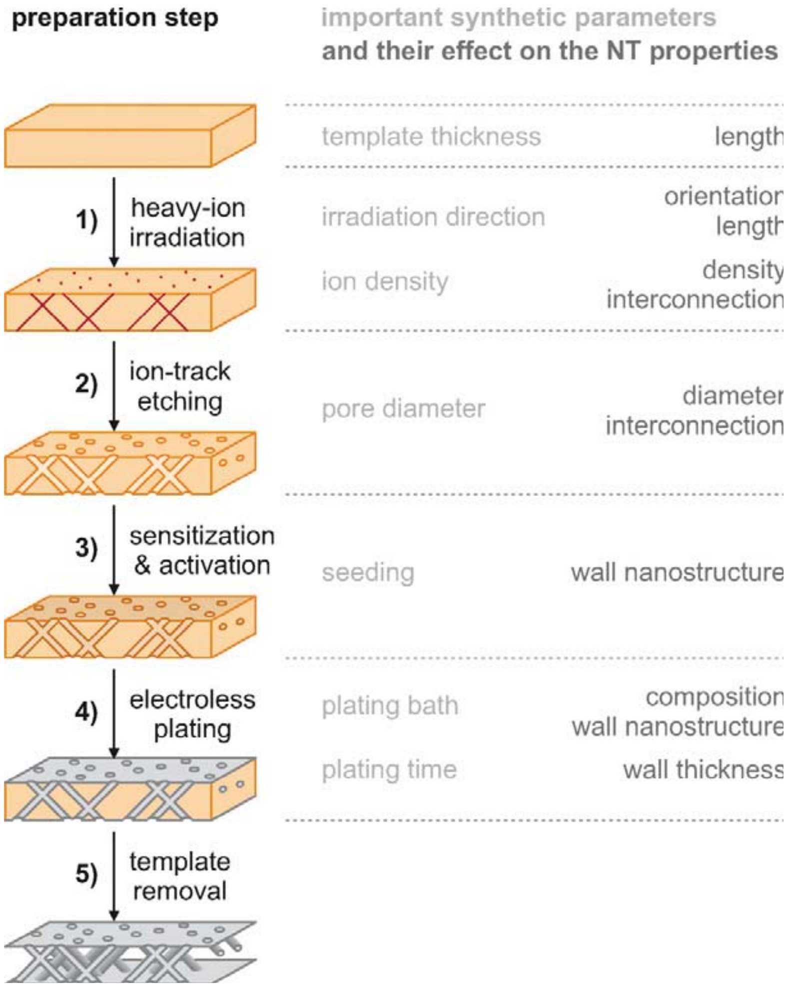


Fig.15. General scheme of electroless fabrication of self-supporting nanotube network. (Reproduced from Ref. [71]).

nanotubes made electrolessly in hard and passive templates is focused on Au. However, the making of anatase titanium dioxide nanotubes (TNT) with a diameter of approximately 100 nm and a wall thickness of approximately 10 nm has been reported recently [64].

The general scheme of the electroless process of self-supported nanotubes network is shown in Fig.15.

Bilateral, open cylindrical, largely anatase titanium dioxide nanotubes with controllable diameters and wall thickness were fabricated using electroless deposition based on aqueous solutions. The TNTs have potential uses in fields like sensing, photocatalysis or regenerative energy. Using polycarbonate as a template it is possible to produce TNT arrays within the polycarbonate having a tube density of a single such that there are up to 10^9 tubes/cm². These arrays can be directly used for sensor and photovoltaic applications.

Chemical template synthesis can be accomplished by immersing the membrane into a solution of a desired monomer and its oxidizing agent. This method can be used to make polymer nanotubes, nanowires (polypyrrole, polyaniline) as well for making metal oxide nano-sized features. Conducting polymers show preferential deposition along the walls of the polycarbonate membrane resulting in nanotubuler structures due to solvophobic interactions. These tubules close up as the deposition time is increased and eventually result in nanowires. Example of polypyrrole nanotubes is shown in Fig.16 [80].

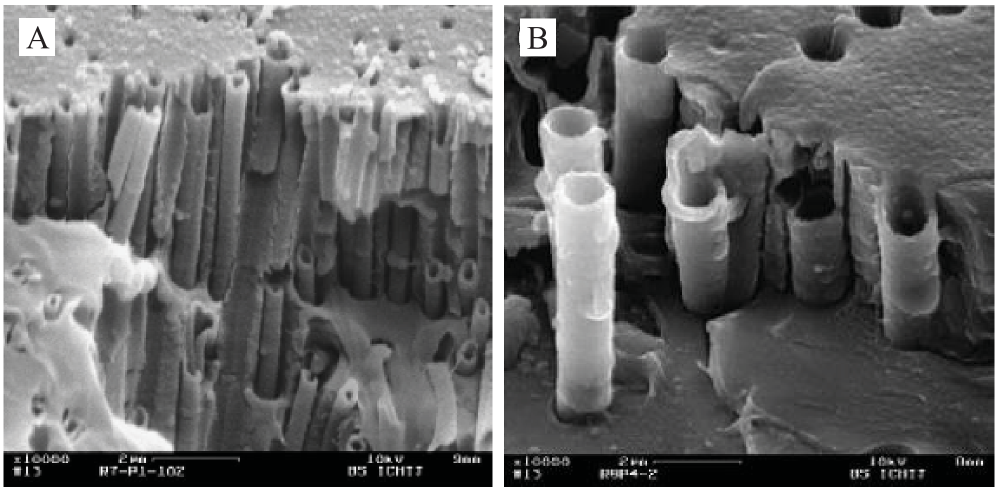


Fig.16. SEM micrographs of polypyrrole nanotubes made in track-etched membranes with pore of diameters: 0.4 µm (A) and 1.3 µm (B).

The series of metal oxides (MgO, Cu doped ZnO, In_2O_3) for gas sensor studies have been made by moderate thermal treatment of chemically prepared precursors filling the pores in Nuclepore polycarbonate track-etched membrane (see Table 1). The crucial step was the synthesis of a suitable oximato metal complexes. After infiltration of the precursor into the pores, a two-step moderate thermal treatment procedure (160°C, 450°C) was used to yield polycrystalline metal oxide rods [77-79].

3.2. USES OF TRACK-ETCHED MEMBRANES IN BIOLOGICAL RESEARCH

The achievements in the track-etching techniques, like asymmetrical nanochannel etching and chemical functionalization of nanochannel walls, give positive impetus to research and development in the field of biological applications. Fundamental to the understanding of process mechanisms in living organisms is to know the structure of ionic channels in biological membranes and the ion transport mechanisms through them. Experimental work based on the use of biological nanochannels, usually reproduced in laboratory by protein nanotubes embedded in lipid bilayers, *e.g.* using α-hemolysis biomolecule, has many disadvantages. These nanotubes are difficult to reproduce in practice, fragile and cannot withstand the complexity of the external environment. For experimental work, artificially made, durable nanochannels, mimicking those existing in the real biological world, would be preferable. Track-etched membranes are well-suited for this due to their biological and chemical inertness and the possibility of tuning their structural parameters by the chemical etching method. Besides nanochannels being formed with shape, diameter and length matching those found in the real biological world, pore walls can be functionalized with internal pore surface coatings, with a thin gold layer, and/or by covalent attachment of functional molecules or macromolecules, which are most important.

Thanks to the systematic studies of ionic flows in nanochannels and on the behaviour of molecules/macromolecules in confined space, it is possible to use artificial nanochannels mimicking those existing in real biological world. The main goal of this work was to quantitatively understand the fundamental laws governing the ionic and molecular transport through nanochannels, as well as to develop nanoscale devices for controlling and sensing biologically important macromolecules [20-24].

Pioneering research work [16, 17] conducted on artificial track-etched nanochannels confirmed that the ions flow through them and show features similar to these observed in biological nanochannels. These features included selectivity in ionic species transport, current fluctuations between high and low conducting state, and inhibition of ion flow by low pH and divalent cations. The encouraging results of the first experiments stimulated much broader interest and initiated more detailed research works conducted mostly by Martin's [18, 22] and Siwy's [22, 23] groups as well as work conducted at GSI Darmstadt [19, 20]. The next important step in development of artificial nanochannels, as the chemical functionalization of pore wall, has been done. The first work conducted by Martin's group was based on using electroless conformal coating to coat pore walls with gold and on attaching to the deposited layer thiol functionalized molecules. Soon, direct functionalization methods based on using native carboxylic groups remaining on the pore walls after chemical etching for chemical reactions with molecules possessing adequate functional groups, was developed. Thus, controlled manipulation of charge density on the pore wall became possible, opening the way to the modification of transport properties of small diameter nanochannels, particularly their selectivity for cationic and anionic species.

Generally, the pore wall functionalization process is based on the attachment of molecules or macromolecules having different functional properties. In the case of molecules with polar functional groups, the charge state can be pH-dependant. Thus, the effective charge of the pore wall can be changed by changing pH. In the case of macromolecule attachment, the conformational state properties depend on external factors, like pH, temperature, UV irradiation, salt ionic strength *etc.*, and it is then possible to change the "effective diameter" of a nanochannel used for the ionic transport. Since the detection methods of pore transport are usually based on measurements of full ion--voltage characteristics, including both possible polarization directions, any partial or complete blockage of the pore wall can be detected.

Up to now, different strategies have been employed for making artificial nanochannels mimicking biological ones. These methods have been developed using polymer track-etched techniques as well as different surface functionalization methods. They can be classified into four groups:

- designing a pore with asymmetric geometry and homogeneously charged inner surface;
- designing the cylindrical pore with inhomogeneously charged surface, particularly containing two segments with different electrical properties;
- designing the pore covered with a conducting metallic layer, enabling the control of the current flow through the pore by external voltage bias;
- designing the pore with electrochemical gating, containing attached single strand of DNA in the pore.

The molecular transport in nanochannels is a complex process requiring a detailed description of the interaction of mobile ions and fixed charges on the channel surface. Usually the detailed interpretation of experimental results requires solving the coupled charge and mass balance equation – the coupled Poisson-Planck-Navier-Stocks calculation of charge and mass fluxes. Surface charges on the pore wall in the presence of an electrolyte are screened by counter-ions. The detailed ion transport properties of the channel depend strongly on the relation of so-called Debye length describing the concentration dependant charge screening process to the diameter of the nanochannels. Generally, the surface charge on the pore wall influences the ion fluxes in the narrow channels and, in the case of a weak electrolyte, influence ionic strength as

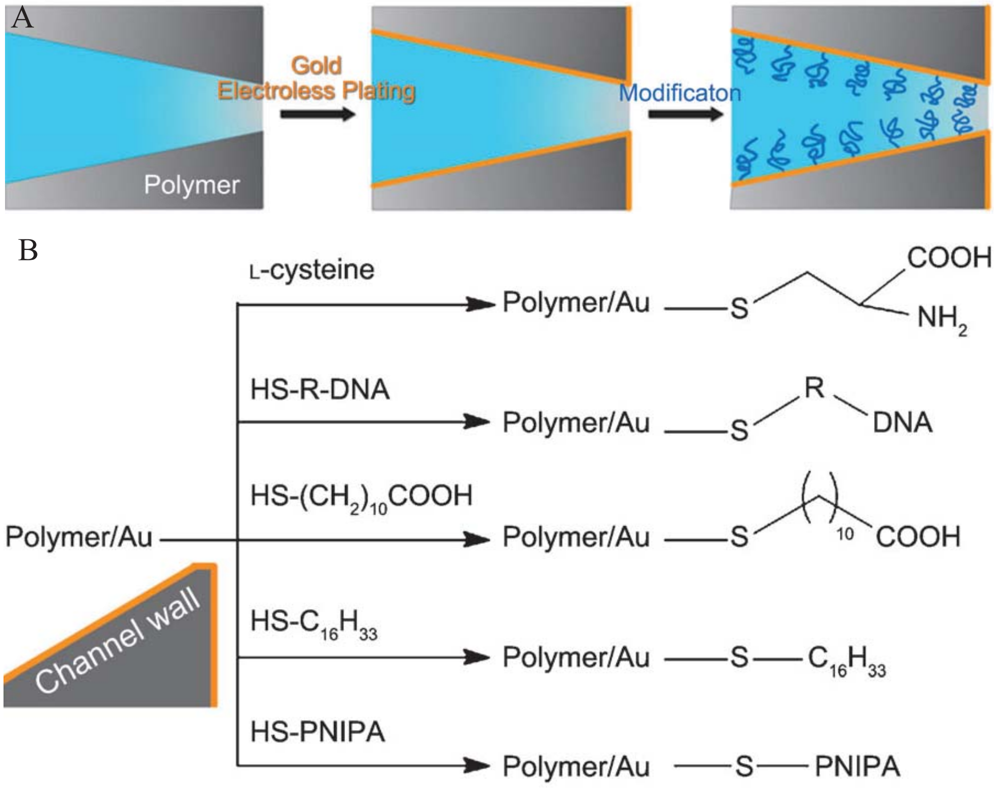


Fig.17. (A) Immobilization of functional molecules onto the inner wall of a nanochannel by electroless modification with Au and surface chemisorbing thiols. (B) A typical thiol self-assembled functional molecules for modifying the inner surface of a polymer/Au nanochannel (B). (Reproduced from Ref. [81]).

well. Detailed analyses of the ionic fluxes require solving differential equations describing charge and mass balance, the coupled Poisson-Planck-Navier-Stocks equations.

Figure 17 shows the general scheme of functionalization of pores walls of a track-etched membrane. The coating of pore walls with gold film by electroless deposition enables covalent linking of thiol-ended molecules of different lengths and functionalities using self-assembly mechanisms of the thiol-ended molecules on gold surfaces.

REFERENCES

[1]. Spohr, R. (1990). *Ions tracks and microtechnology. Principles and application.* Braunschweig: Friedr. Vieweg&Sohn Verlagsgesellschaft mbH.

[2]. Apel, P.Y. (2013). Track-etching. In *Encyclopedia of membrane science and technology* (pp. 332-356). Wiley.

[3]. Fink, D. (Ed.). (2014). *Fundamentals of ion-irradiated polymers*. Berlin, Heidelberg: Springer-Verlag. (Springer Series in Materials Science, Vol. 63).

[4]. Apel, P.Y., & Fink, D. (2004). Ion-track etching. In D. Fink (Ed.), *Transport processes in ion irradiated polymers* (pp. 147-202). Springer.

[5]. Young, D.A. (1958). Etching of radiation damage in lithium fluoride. *Nature*, *182*, 375-377.

[6]. Price, P.B, & Walker, R.M. (1967). *The molecular sieves and methods for producing same*. US Patent No. 3,303,085.

[7]. Fleischer, R.L., & Price, P.B. (1963). Tracks of charged particles in high polymers. *Science*, *140*, 1221-1222.

[8]. Kohli, P., & Martin, C.R. (2006). Smart nanotubes for biotechnology. *Curr. Pharm. Biotechnol.*, *6*, 35-47.

[9]. Vereshchagina, E., Mc Glade, D., Glynn, M., & Ducrée, J. (2013). A hybrid microfluidic platform for cell-based assays via diffusive and convective trans-membrane perfusion. *Biomicrofluidics*, *7*, 034101. DOI: 10.1063/1.4804250.

[10]. Hulteen, J.C., & Martin, C.R. (1997). A general template-based method for the preparation of nanomaterials. *J. Mater. Chem.*, *7*(7), 1075-1087.

[11]. Shang, H. (M.), & Cao, G. (2010). Template-based synthesis of nanorod or nanowire arrays. In Bharat Bhushan (Ed.), *Springer handbook of nanotechnology* (3rd ed., pp. 169-186). Springer.

[12]. Cao, G., & Liu, D. (2008). Template-based synthesis of nanorod, nanowire, and nanotube arrays. *Adv. Colloid Interface Sci.*, *136*, 45-64.

[13]. Martin, C.M. (1996). Membrane-based synthesis of nanomaterials. *Chem. Mater.*, *8*, 1739-1746.

[14]. Ferain, E., & Legras, R. (2003). Track-etch templates designed for micro- and nanofabrication. *Nucl. Instrum. Meth. Phys. Res. B*, *208*, 115-122.

[15]. Kuchibhatla, S.V.N.T., Karakoti, A.S., Vera, D., & Seal, S. (2007). One dimensional nanostructured materials. *Prog. Mater. Sci.*, *52*(5), 699-913.

[16]. Bashford, L. (1995). Membrane pores – from biology to track-etched membranes. *Bioscience Rep.*, *15*, 553.

[17]. Pasternak, C.A., Alder, G.M., Apel, P.Yu., Bashford, C.L., Edmonds, D.T., Korchev, Y.E., Lev, A.A., Lowe, G., Milovanovich, M., Pitt, C.W., Rostovtseva, T.K., & Zhitariuk, N.I. (1995). Nuclear track-etched filters as model pores for biological membranes. *Radiat. Meas.*, *25*, 675-683.

[18]. Apel, P.Yu., Blonskaya, I.V., Dmitriev, S.N., Orelovich, O.L., & Sartowska, B.A. (2015). Ion track symmetric and asymmetric nanopores in polyethylene terephthalate foils for versatile applications. *Nucl. Instrum. Meth. Phys. Res. B*, *365*, 409-413.

[19]. Ali, M., Ramirez, P., Nguyen, H.Q., Nasir, S., Cervera, J., Mafe, S., & Ensinger, W. (2012). Single cigar-shaped nanopores functionalized with amphoteric amino acid chains: Experimental and theoretical characterization. *ACS Nano*, *6*, 3631-3640.

[20]. Ali, M., Neumann, R, & Ensinger, W. (2010). Sequence-specific recognition of DNA oligomer using peptide nucleic acid (PNA)-modified synthetic ion chan-

nels: PNA/DNA hybridization in nanoconfined environment. *ACS Nano*, *4*, 7267-7274. DOI: 10.1021/nn102119q.

[21]. Zhang, H., Tian, Y, & Jiang, L. (2013). From symmetric to asymmetric design of bio-inspired smart single nanochannels. *Chem. Commun*., *49*, 10048-10063. DOI: 10.1039/c3cc45526b.

[22]. Siwy, Z., & Martin, C. (2007). Tuning ion current rectification in synthetic nanotubes in controlled nanoscale motion. In H. Linke & A. Månsson (Eds.), *Controlled nanoscale motion. Nobel Symposium 131* (pp. 349-366). Berlin, Heidelberg: Springer. (Lecture Notes in Physics 711). DOI: 10.1007/b11823292.

[23]. Siwy, Z., & Howorka, S. (2010). Engineered voltage-responsive nanopores. *Chem. Soc. Rev.*, *39*, 1115.

[24]. Hou, X., Zhang, H., & Jiang, L. (2012). Building bio-inspired artificial functional nanochannels: From symmetric to asymmetric modification. *Angew. Chem. Int. Ed.*, *51*, 5296-5307. DOI: 10.1002/anie.201104904.

[25]. Watt, F., Bettiol, A.A., Van Kan, J.A., Teo, E.J., & Breese, M.B.H. (2005). Ion beam litography and nanofabrication: A review. *Int. J. Nanosci.*, *4*, 269-286.

[26]. Fink, D., Alegaonkar, S., Petrov, A.V., Wilhelm, M., Szimkowiak, P., Behar, M., Sinha, D., Fahrner, W.R., Hoppe, K., & Chadderton, L.T. (2005). High energy ion beam irradiation of polymers, for electronic applications. *Nucl. Instrum. Meth. Phys. Res. B*, *236*, 11-20.

[27]. Spohr, R. (2005). Status of ion track technology – Prospects of single tracks. *Radiat. Meas.*, *40*, 191-202.

[28]. Apel, P.Yu., Ivanov, O.M., Lizunov, N.E., Mamonova, T.I., Nechaev, A.N., Olejniczak, K., Vacik, J., & Dmitriev, S.N. (2015). Production of multi-, oligo- and single-pore membranes using a continuous ion beam. *Nucl. Instrum. Meth. Phys. Res. B*, *365*, 641-645.

[29]. Ziegler, J.F. *SRIM – The Stopping and Range of Ions in Matter. SRIM-2013*. Retrieved May 16, 2016, from www.srim.org.

[30]. Trautmann, C., Bouffard, S., & Spohr, R. (1996). Etching threshold for ion tracks in polyimide. *Nucl. Instrum. Meth. Phys. Res. B*, *116*, 429-433.

[31]. Vilensky, A.I., Zagorski, D.L., Kabanov, V.Ya., & Mchedlishvili, B.V. (2003). UV- and γ-sensitization of latent tracks in polyethylene terephthalate. *Radiat. Meas.*, *36*, 131-135.

[32]. Apel, P.Yu., Blonskaya, I.V., Orelovitch, O.L., Root, D., Vutsadakis, V., & Dmitriev, S.N. (2003). Effect of nanosized surfactant molecules on the etching of ion tracks: New degree's of freedom in design of pore shape. *Nucl. Instrum. Meth. Phys. Res. B*, *209*, 329-334.

[33]. Apel, P.Yu., Blonskaya, I.V., Orelovitch, O.L., Ramirez, P., & Sartowska, B.A. (2011). Effect of nanopore geometry on ion current rectification. *Nanotechnology*, *22*, 175302. DOI: 10.1088/0957-4484/22/17/175302.

[34]. Zhang, Y., Kolmakov, A., Chretien, S., Metiu, H., & Moskovits, M. (2004). Control of catalytic reactions at the surface of a metal oxide nanowire by manipulating electron density inside it. *Nano Lett.*, *4*(3), 403-407.

[35]. Carretero-Genevriera, A., & Mestresb, N. (2015). Growth of 1-D oxide nanostructures. In *Encyclopedia of nanotechnology*. Dordrecht: Springer Science+Business Media. DOI 10.1007/978-94-007-6178-0_101005-1.

[36]. Kolmakov, A., & Moskovits, M. (2004). Chemical sensing and catalysis by one--dimensional metal-oxide nanostructures. *Annu. Rev. Mater. Res.*, *34*, 151-180.

[37]. Wanekaya, A.K., Chen, W., Myung, N.V., & Mulchandani, A. (2006). Nanowire--based electrochemical biosensors. *Electroanalysis*, *18*, 6, 533-550.

[38]. Stortini, A.M., Moretto, L.M., Mardegan, A., Ongaro, M., & Ugo, P. (2015). Arrays of copper nanowire electrodes: Preparation, characterization and application as nitrate sensor. *Sensor. Actuat. B-Chem.*, *207*, 186-192.

[39]. University of Florida (2016, July 12). *Martin Research Group*. Retrieved July 16, 2016 from https://martin.chem.ufl.edu/.

[40]. Walewyns, T., Scheena, G., Tootena, E., & Francis, L.A. (2011). Synthesis of patterned freestanding nickel nanowires by using ion track-etched polyimide. In Á.B. Rodríguez-Vázquez, R.A. Carmona-Galán, G. Liñán-Cembrano, R. Adelung & C. Ronning (Eds.), *Bioelectronics, Biomedical, and Bioinspired Systems V; and Nanotechnology V*. (Proc. SPIE, Vol. 8068). DOI: 10.1117/12.886775.

[41]. Chtanko, N., Toimil Molares, M.E., Cornelius, T., Dobrev, D., & Neumann, R. (2004). Etched single-ion-track templates for single nanowire synthesis. *J. Phys. Chem. B*, *108*, 9950-9954.

[42]. Schönenberger, C., van der Zande, B.M.I., Fokkink, L.G.J., Henny, M., Schmid, C., Krüger, M., Bachtold, A., Huber, R., Birk, H., & Staufer, U. (1997). Template synthesis of nanowires in porous polycarbonate membranes: Electrochemistry and morphology. *J. Phys. Chem. B*, *101*, 5497-5505. DOI: 10.1021/jp963938g.

[43]. Ferain, E., & Legras, R. (2009). Templates for engineered nano-objects for use in microwave, electronic devices and biomedical sensing application. *Nucl. Instrum. Meth. Phys. Res. B*, *267*, 1028-1031.

[44]. Enculescu, I., Siwy, Z., Dobrev, D., Trautmann, C., Toimil Molares, M.E., Neumann, R., Hjort, K., Westerberg, L., & Spohr, R. (2003). Copper nanowires electrodeposited in etched single-ion track templates. *Appl. Phys. A*, *77*, 751-755.

[45]. Ravish Garg, Samiksha Mehta, Amandeep Kaur, & Chauhan, R.P. (2012). Template based synthesis of low dimensional structures of copper and their characterization. *Int. J. Eng. Res. Dev.*, *3*, 4, 1-4.

[46]. Karim, S., Toimil-Molares, M.E., Maurer, F., Miehe, G., Ensinger, W., Liu, J., Cornelius, T.W., & Neumann, R. (2006). Synthesis of gold nanowires with controlled crystallographic characteristics. *Appl. Phys. A*, *84*, 403-407.

[47]. Ensinger, W. (2007). Formation of nanopore membranes and nanowires by high energy ion irradiation of polymer foils. *Surf. Coat. Technol.*, *201*, 8442-8447.

[48]. Karima, S., Ensinger, W., Mujahid, S.A., Maaz, K., & Khan, E.U. (2009). Effect of etching conditions on pore shape in etched ion-track polycarbonate membranes. *Radiat. Meas.*, *44*, 9-10, 779-782.

[49]. Tian, M., Wang, J., Kurtz, J., Mallouk, Th.E., & Chan, M.H.W. (2003). Electrochemical growth of single-crystal metal nanowires via a two-dimensional nucleation and growth mechanism. *Nano Lett.*, *3*, 7, 919-923.

[50]. Toimil-Molares, M.E. (2012). Characterization and properties of micro- and nanowires of controlled size, composition, and geometry fabricated by electrodeposition and ion-track technology. *Beilstein J. Nanotechnol.*, *2012*, 3, 860-883. DOI: 10.3762/bjnano.3.97.

[51]. Picht, O., Müller, S., Alber, I., Rauber, M., Lensch-Falk, J., Medlin, D.L., Neumann, R., & Toimil-Molares, M.E. (2012). Tuning the geometrical and crystallographic characteristics of Bi_2Te_3 nanowires by electrodeposition in ion-track membranes. *J. Phys. Chem. C*, *116*, 5367-5375.

[52]. Matei, E., Preda, N., Enculescu, M., Ansermet, J.-P., Toimil Molares, M.E., & Enculescu, I. (2010). Sequential deposition of multisegment nanowires. *Dig. J. Nanomater. Biostruct.*, *5*, 4, 1067.

[53]. Limmer, S.J., Seraji, S., Forbess, M.J., Wu, Y., Chou, T.P., Nguyen, C., & Cao, G.Z. (2001). Electrophoretic growth of lead zirconate titanate nanorods. *Adv. Mater.*, *13*, 16, 1269-1272.

[54]. Limmer, S.J., & Cao, G. (2003). Sol-gel electrophoretic deposition for the growth of oxide nanorods. *Adv. Mater.*, *15*, 5, 427-431.

[55]. Limmer, S.J., Chou, T.P., & Cao, G.Z. (2005). A study on the influences of processing parameters on the growth of oxide nanorod arrays by sol electrophoretic deposition. *J. Sol-Gel Sci. Technol.*, *36*, 183-195.

[56]. Mohammadi, M.R., Ordikhani, F., Fray, D.J., & Khomamizadeh, F. (2011). Template-based growth of titanium dioxide nanorods by a particulate sol-electrophoretic deposition process. *Particuology*, *9*, 161-169.

[57]. Sobel, N., Hess, Ch., Lukas, M., Spende, A., Stühn, B., Toimil-Molares, M.E., & Trautmann, Ch. (2015). Conformal SiO_2 coating of sub-100 nm diameter channels of polycarbonate etched ion-track channels by atomic layer deposition. *Beilstein J. Nanotechnol.*, *2015*, 6, 472-479.

[58]. Wang, C., Fu, Q., Wang, X., Kong, D., Sheng, Q., Wang, Y., Chen, Q., & Xue, J. (2015). Atomic layer deposition modified track-etched conical nanochannels for protein sensing. *Anal. Chem.*, *87*, 8227-8233. DOI: 10.1021/acs.analchem.5b01501.

[59]. Triani, G., Evans, P.J., Attard, D.J., Prince, K.E., Bartlett, J., Tan, S., & Burford, R.P. (2006). Nanostructured TiO_2 membranes by atomic layer deposition. *J. Mater. Chem.*, *16*, 1355-1359. DOI: 10.1039/B516499K.

[60]. Asatekin, A., & Gleason, K.K. (2011). Polymeric nanopore membranes for hydrophobicity-based separations by conformal initiated chemical vapor deposition. *Nano Lett.*, *11*, 677-686.

[61]. Chen, P., Mitsui, T., Farmer, D.B., Golovchenko, J., Gordon, R.G., & Branton, D. (2004). Atomic layer deposition to fine-tune the surface properties and diameters of fabricated nanopores. *Nano Lett.*, *4*, 1337.

[62]. Spende, A., Sobel, N., Lukas, M., Zierold, R., Riedl, J.C., Gura, L., Schubert, I., Moreno, J.M., Nielsch, K., Stühn, B., Hess, C., Trautmann, C., & Toimil-Molares, M.E. (2015). TiO_2, SiO_2, and Al_2O_3 coated nanopores and nanotubes produced by ALD in etched ion track membranes for transport measurements. *Nanotechnology*, *26*, 335301. DOI: 10.1088/0957-4484/26/33/335301.

[63]. Velleman , L., Shapter, J.G., & Losic, D. (2013). Gold nanotube membranes. In E.M.V. Hoek & V.V. Tarabara (Eds.), *Encyclopedia of membrane science and technology* (pp. 1-27). John Wiley & Sons, Inc. DOI: 10.1002/9781118522318.

[64]. Boehme, M., Fu, G., Ionescu, E., & Ensinger, W. (2010). Fabrication of anatase titanium dioxide nanotubes by electroless deposition using polycarbonate for separate casting method. *Nano-Micro Lett.*, *2*, 26-30. DOI: 10.1007/BF03353613.

[65]. Muench, F., Kaserer, S., Kunz, U., Svoboda, I., Brotz, J., Lauterbach, S., Kleebe, H.-J., Roth, Ch., & Ensinger, W. (2011). Electroless synthesis of platinum and platinum-ruthenium nanotubes and their application in methanol oxidation. *J. Mater. Chem.*, *21*, 6286-6291.

[66]. Muench, F., Oezaslan, M., Rauber, M., Kaserer, S., Fuchs, A., Mankel, E., Brötz, J., Strasser, P., Roth, Ch., & Ensinger, W. (2013). Electroless synthesis of nanostructured nickel and nickel boron tubes and their performance as unsupported ethanol electrooxidation catalysts. *J. Power Sources*, *222*, 243-252.

[67]. Muench, F. (2014). Polycarbonate activation for electroless plating by dimethylaminoborane absorption and subsequent nanoparticle deposition. *Appl. Phys. A*, *116*, 287-294.

[68]. Gasparac, R., Taft, B.J., Lapierre-Devlin, M.A., Lazareck, A.D., Xu, J.M., & Kelley, S.O. (2004). Ultrasensitive electrocatalytic DNA detection at two- and three-dimensional nanoelectrodes. *J. Am. Chem. Soc.*, *126*, 12270-12271.

[69]. Felix, E.M., Antoni, M., Pause, I., Schaefer, S. Kunz, U., Weidler, N., Muench, F., & Ensinger, W. (2016). Template-based synthesis of metallic Pd nanotubes by electroless deposition and their use as catalysts in the 4-nitrophenol model reaction. *Green Chem.*, *18*, 558-564.

[70]. Lapierre-Devlin, M.A., Asher, C.L., Taft, B.J., Gasparac, R., Roberts, M.A., & Kelley, S.O. (2005). Amplified electrocatalysis at DNA-modified nanowires. *Nano Lett.*, *5*, 6, 1051-1055.

[71]. Muench, F., De Carolis, D.M., Felix, E.-M., Brötz, J., Kunz, U., Kleebe, H.-J., Ayata, S., Trautmann, Ch., & Ensinger, W. (2015). Self-supporting metal nanotube networks obtained by highly conformal electroless plating. *ChemPlusChem*, *80*, 1448-1456.

[72]. Velleman, L., Shapter, J.G., & Losic, D. (2009). Gold nanotube membranes functionalised with fluorinated thiols for selective molecular transport. *J. Membr. Sci.*, *328*, 121-126.

[73]. Muench, F., Oezaslan, M., Seidl, T., Lauterbach, S., Strasser, P., Kleebe, H.-J., & Ensinger, W. (2011). Multiple activation of ion track etched polycarbonate for the electroless synthesis of metal nanotubes. *Appl. Phys. A*, *105*, 847-854.

[74]. Enculescu, I., Sima, M., Enculescu, M., Matei, E., Toimil Molares, M.E., & Cornelius, Th. (2008). Nickel nanotubes prepared by electroless deposition in ion track templates. *Optoelectron. Adv. Mat.*, *2*, 3, 133-136.

[75]. Shao, P. (2005). Gold nanotube membranes: Preparation, characterization and application for enantioseparation. *J. Membr. Sci.*, *255*, 1-11.

[76]. Kumar, V., Singh, R., & Chakarvarti, S.K. (2007). Novel electroless template based synthesis of silver microtubules and their characterization. *Dig. J. Nanomater. Biostruct.*, *2*, 1, 163-167.

[77]. Pashchanka, M., Hoffmann, R.C., Gurlo, A., Swarbrick, J.C., Khanderi, J., Engstler, J., Issanin, A., & Schneider, J.J. (2011). A molecular approach to Cu doped ZnO nanorods with tunable dopant content. *Dalton Trans.*, *40*, 4307.

[78]. Pashchanka, M., Hoffmann, R.C., & Schneider, J.J. (2010). Controlled synthesis and characterisation of MgO nanoparticles, thin films and polycrystalline nanorods derived from a Mg(II) single source precursor. *J. Mater. Chem.*, *20*, 957-963.

[79]. Pashchanka, M., Hoffmann, R.C., Gurlo, A., & Schneider, J.J. (2010). Molecular based, chimie douce approach to 0D and 1D indium oxide nanostructures. Evaluation of their sensing properties towards CO and H_2. *J. Mater. Chem.*, *20*, 8311-8319.

[80]. Starosta, W., Buczkowski, M., Sartowska, B., & Wawszczak, D. (2006). Studies on template-synthesized polypyrrole nanostructures. *Nukleonika*, *51*, Suppl. 1, S35-S39.

[81]. Xu Hou, Huacheng Zhang, Lei Jiang, (2012). Nanochannels: From symmetric to asymmetric modification. *Angew. Chem. Int. Ed.*, *51*, 5296-5307.

Chapter 19

RADIATION PRETREATMENT OF BIOMASS

Murat Torun
Hacettepe University, Department of Chemistry, 06800 Beytepe, Ankara, Turkey

1. INTRODUCTION

Biomass is organic matter derived from living or recently living organisms. With growing global concerns over renewable energy sources, biomass can be used as part of the energy supply chain. The main constituents of biomass are cellulose, hemicellulose and lignin. The relative amounts of these constituents change with type of lignocellulosic material as well as with where the biomass was grown. Cellulose is a polysaccharide made up of D-glucose units, linked by β-1,4 glycosidic bonds, and organized into crystalline and amorphous regions. Lignin and hemicellulose increase the mechanical properties of lignocellulosic materials.

Both physical and chemical methods are used to treat lignocellulosic material. Physical treatment is used to separate cellulose by eliminating lignin and hemicellulose as well as breaking down the crystallinity of the cellulose, so as to increase the accessible surface area and the size of pores in cellulosic materials. An effective pretreatment should break down the lignocellulose structure to give a digestible raw material, avoiding degradation of the target material and the formation of toxic by-products. Any pretreatment must be economically worthwhile [1]. The yield in the separation of the main components of lignocellulosic material depends on some parameters, such as the ratio of cellulose, hemicellulose and lignin to each other, the crystallinity of the cellulose and its water content. The general structure of lignocellulose is shown in Fig.1. The most important limiting parameter is the available surface area which influences the next processes, as when producing fine chemicals.

Several types of physical processes have been developed, mainly by using milling [2, 3], steam or fiber explosion [4-6], exposure to supercritical fluids [7, 8], irradiation [9-11] as well as chemical processes [12-14]. Some of these methods are not often satisfactory unless used with chemical ones in order to improve the process efficiency.

High energy irradiation (electron beams, X-rays or gamma rays) can produce ions and/or radicals in the biomass which initiate some chemical reactions

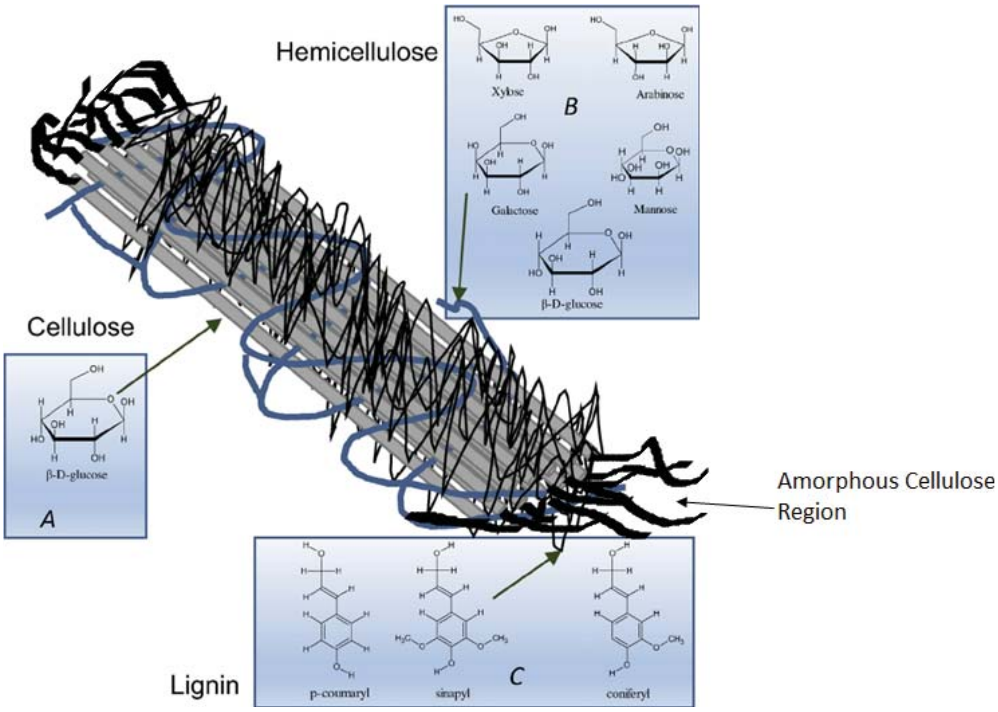


Fig.1. General structure of lignocellulose.

that mainly result in chemical bond cleavages [15-19] and decreasing molecular weight with increasing irradiation dose. Ionizing radiation is an effective method for the pretreatment of lignocellulosic biomass which can modify and disrupt the structure of biomass. The radiation-induced reactions in cellulosic materials are based on short- and long-lived radicals which produce secondary degradation through chain scissioning and crosslinking [20] which depend on the polymeric structure and radiation dose [21]. The irradiation dose needed can be reduced by adding low concentrations of sodium hydroxide. The degradation of the lignocellulosic material becomes accelerated and the process is more economically feasible [22]. The high degradation yield of lignocellulosic compounds using small irradiation doses is attributed to the weak chemical bonds between the lignin, the hemicellulose and the cellulose units and to alkali swelling [23]. Figure 2 illustrates this process.

During or soon after irradiation, radicals, which are produced mainly in amorphous regions of cellulose structure, extinguish quickly as well as radicals in the crystalline and semicrystalline regions which decay after a certain period which mainly causes the degradation aftereffect of lignocellulosic materials [24]. Investigations of the radiation-induced degradation of lignocellulosic materials include analyses of the formed radicals. A significant decrease of cellulosic radicals was observed with time after irradiation and the rate was dependent on temperature, humidity, the presence of oxygen and other envi-

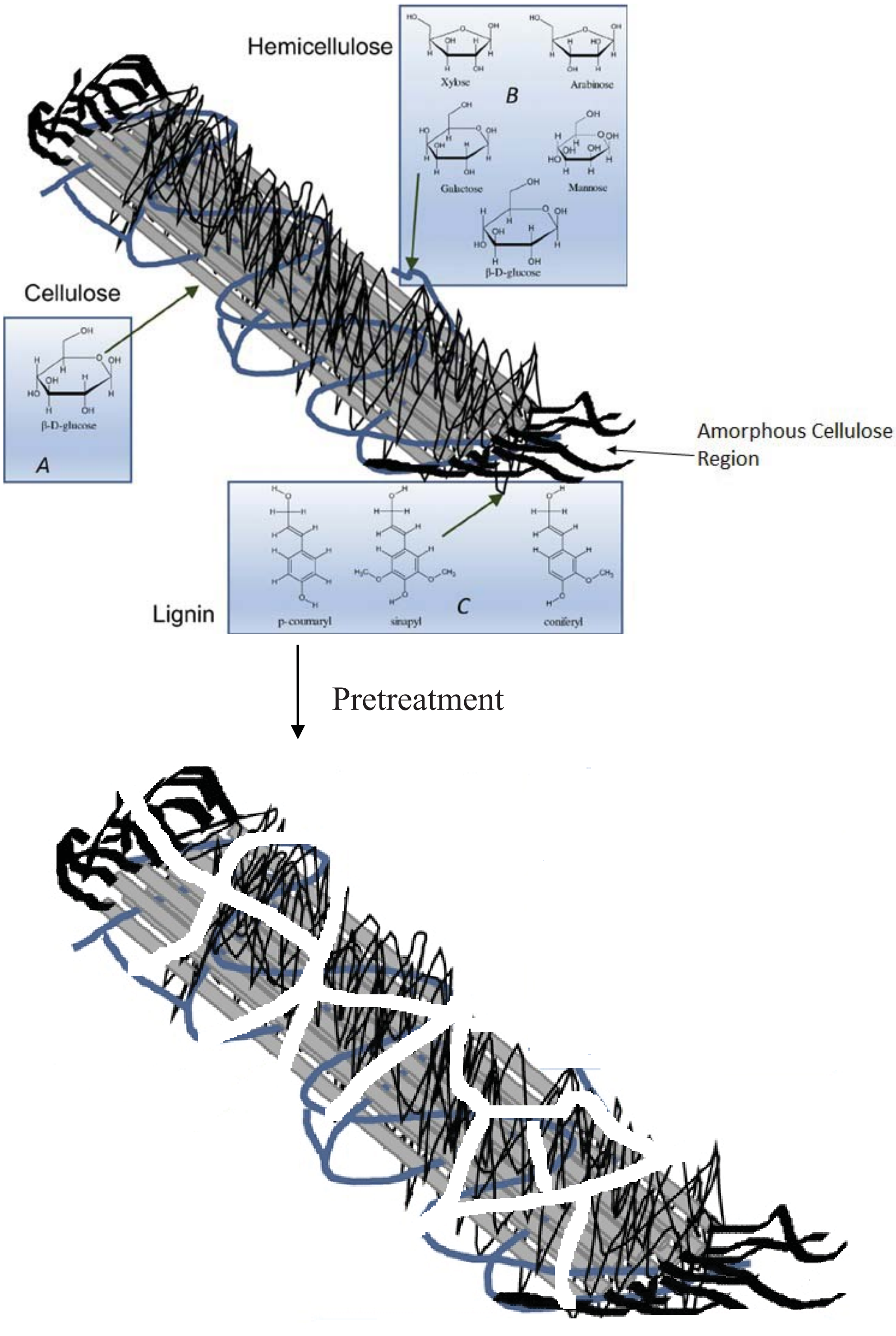


Fig.2. Pretreatment of lignocellulose biomass. Lignin and hemicellulose decompose before hydrolysis.

ronmental parameters [25-28]. A polyphenolic material, lignin, has some stabilizing effect on the radiation of lignocellulosic biomass [29] in which phenoxy radicals importantly become transformed into the o-quinonoid structures in lignin [30, 31].

1.1. GAMMA IRRADIATION

The ^{60}Co and ^{137}Cs isotopes undergo radioactive decay to produce gamma rays (γ-rays), ^{60}Co, which has a half-life of 5.26 years, is widely used in industrial irradiation processes as compared to other radioactive isotopes. Irradiation systems can be a batch (discontinuous), closed system process using a gamma chamber. This limits the amount of biomass that can be treated. In a batch-continuous process, the amount of irradiated biomass would be useful for further large-scale processing. Such systems have safety features and a long history of use in other areas. The energy of the gamma rays is transferred to the atoms of the biomass and results in the formation of radicals. The scission of glycosidic bonds results in the degradation of polysaccharides [21] as well as destructing cell walls [32, 33]. Gamma irradiation alone is an effective technique for biomass pretreatment and when the irradiation process is combined with other ones (chemical, physical) there is an increase in the efficiency of the entire process which can produce the same results using a lower dose.

1.2. ELECTRON BEAM IRRADIATION

Electron beam processing relies on electrically accelerated electrons, not on radioactive isotopes. When biomass is exposed to accelerated electrons, energy is transferred to the atoms of the biomass. The interaction of biomass with accelerated electrons results mainly in chain scission [34]. In addition, any heat generated in the target material may have a synergic effect in biomass treatment. As a result, both irradiation and physical transformations may occur together [35].

2. USES OF BIOMASS PRETREATMENT BY IRRADIATION

The are several uses of irradiation for biomass conversion:

- to facilitate enzymatic hydrolysis,
- to produce bioethanol,

- to facilitate protein synthesis,
- others.

The radiation pretreatment of biomass is mainly for bioethanol production, as well as for environmental purposes, and the combined use of radiation pretreatment with chemical pretreatment are discussed in the literature.

2.1. ENZYMATIC HYDROLYSIS

Kim *et al.* investigated radiation effects on mutated lignocellulose *Brachypodium* stems using a ^{60}Co gamma source. Changes in the cell walls and decrease in cell size were observed along with an increase in broken regions on cell surfaces with increase in irradiation dose [36]. This was due to the effect of reactive oxygen species formed after gamma irradiation and its synergistic effect on enzymatic hydrolysis. The reduction in lignin content was one of the most important steps for the development of bioethanol feedstock as well as for other aims. Kim *et al.* observed between 2.4 and 18.4% decrease of lignin content in irradiated cell walls [36]. Enzymatic hydrolysis of *Brachypodium* biomasses was performed to determine the irradiation yield of lignocellulosic biomass conversion to fermentable sugars by the amount of glucose change in structure. Samples were exposed to 0, 50, 100, 150, 200, 250 and 300 kGy doses of gamma rays. There was an increase in glucose yield with irradiation doses of 200, 250 and 300 kGy. At 50 and 100 kGy irradiation doses there was a lower glucose yield than the control plant samples (0 kGy, no dose). This lower glucose yield was attributed to insufficient pretreatment which failed to break the surface of lignocellulose or to the conversion of glucose to other by-products, as earlier reported by Yang *et al.* [23]. Crystallinity may affect enzymatic hydrolysis of lignocellulose [37] and irradiation pretreatment of *Brachypodium* may change the crystallinity of the lignocellulose surface. Very low dose-rate irradiation, which requires a long period of low energy irradiation, leads to depolymerization and further degradation as well as increases in the lignocellulose surface area which then yields enzymatic hydrolysis.

Yang *et al.* [23] investigated the effect of gamma irradiation pretreatment on the enzymatic hydrolysis of wheat straw. Increasing the irradiation dose increased the weight loss of the biomass as well as producing a more fine particle size distribution after pulverizing. The weight loss of the irradiated biomass wheat straw at 500 kGy was 3.70% due to the emission of by-product gases, including CO, CO_2 and H_2 as well as the loss of bounded water during chain scissioning process. The emission of molecular hydrogen among some volatile gases has been observed by various researchers [38, 39] after irradiation of cellulose. The yield of powder yield below 200 mesh screen size increased with irradiation dose and reached a value of 61.3% fine powder at 500 kGy from 15.2% of the control. This indicates the radiolytic degradation of biomass wheat straw resulted in a brittle structure and the combination of irradiation degradation and pulverization was effective in reducing the size of wheat straw particles. Yang *et al.* [23] also observed an increase in glucose yield with irradiation dose, which was moderate at 50 to 300 kGy but increased between 300 and 500 kGy irradiation doses with a maximum yield of 13.40% and then decreased with greater irradiation doses. This decrease of conversion to glucose was due to increased by-products which can act as inhibitors for the enzymatic hydrolysis of cellulose. The effect of the granularity of biomass wheat straw on radiation pretreatment was also examined by Yang *et al.* [23]. Powder fractions of 1 cm, 20, 60, 100, 140 and 180 mesh were studied. Biomass samples were irradiated to 500 kGy irradiation dose and the enzymatic hydrolysis was immediately studied. The correlation of granularity with glucose yield for unirradiated biomass powdered wheat straw between the 20 to 180 mesh sizes was relatively higher than that of 1 cm biomass. This can be explained by the increase in the surface area of cellulosic material after pulverizing or grinding which decreased the crystallinity that enhances the enzymatic hydrolysis. A synergistic effect between irradiation and grinding was observed for a granularity of 140 mesh biomass wheat straw irradiated to 500 kGy which gave a glucose yield of 10.24%. The aftereffect of radiation pretreatment of biomass wheat straw was also examined by Yang *et al.* [23]. The aftereffect was defined as the change of glucose (or reducing sugar) yield of a sample that was stored for different times after irradiation and compared with primary effects at the same irradiation dose. 140 mesh size biomass powder was irradiated to 400 kGy and the aftereffect at different storage times (0, 1, 4, 9, 15, 22, 30 days) was examined. The glucose yield increased up to twenty-second day after irradiation with a maximum value of 10.21% and then decreased at the thirtieth day, indicating the post-degradation of biomass proceeds with time. The decrease in glucose yield at the thirtieth day may be due to the accumulation of by-products that inhibit enzymatic hydrolysis.

Chung *et al.* examined the enzymatic hydrolysis of poplar bark by the combined use of gamma rays and dilute sulfuric acid for bioethanol production [40]. The combined pretreatment of biomass poplar bark at 1000 kGy gamma irradiation and dilute sulfuric acid process (3% w/w H_2SO_4) remarkably increased the yield of fermentable sugars. The dry basis content of poplar bark was 20.2% lignin. The xylose content of the biomass poplar bark with irradiation only decreased from 23.8 to 14.3%. When the use of a 3% dilute sulfuric acid solution was combined with 1000 kGy gamma irradiation, the xylose content was significantly reduced to 3.4%. In addition to this, the combined pretreatment process produced cellulose enriched solids. The xylose loss indicates the removal of hemicelluloses and provides a higher surface area of the cellulosic material for hydrolysis.

2.2. CONVERSION TO BIOETHANOL

There are many studies in the literature about the conversion of lignocellulosic biomass to bioethanol by various pretreatment methods including high energy radiation pretreatment.

Yoon *et al.* examined the production of saccharides from biomass *Undaria sp.* using gamma irradiation for bioethanol production [41]. The effect of low acid concentration for biomass conversion to fermentable sugars can be found elsewhere in literature as well as the use of a low pH to inhibit the microbial growth. The fermentation results in lower ethanol yields and this process requires acid recovery for economic reasons. Biomass samples were irradiated at various irradiation doses (0, 10, 50, 100 and 500 kGy) and the concentration of reducing sugar increased with irradiation dose from 0.017 to 0.048 g/L when irradiated to 500 kGy. Irradiation leads to the degradation of the starch in the *Undaria sp.* biomass through the cleavage of glycosidic bonds in the presence of water [42, 43]. Irradiation processing is free of toxic additives and is easier and more environmentally friendly since there is no need for additives, to tightly control temperature and for the use of special chemicals [22]. Irradiation of biomass in the presence of a dilute acid (1% sulfuric acid) enhances the degradation of the biomass to glucose. The sugar concentration was 0.017 g/L for 500 kGy irradiated biomass but this value increased to 0.235 g/L when combined with acid hydrolysis. This study showed that irradiation increased the saccharide yield from raw materials, biomass with high lignin content, that can be used for ethanol or biogas production.

Wang *et al.* examined the effect of gamma irradiation and steam explosion pretreatment on biomasses from agricultural residues for ethanol production [44]. Using a rice straw biomass, the degradation ratio for cellulose, hemicellulose and lignin increased with irradiation as could be done in the steam explosion process by increasing processing time or pressure. When compared, gamma irradiation was more efficient.

When compared with steam explosion pretreatment, irradiation is more useful for the enzymatic hydrolysis for bioethanol production since toxic compounds are not generated during the process. When treated biomass samples were compared with controls of untreated materials, the maximum concentrations of glucose and total reducing sugar were 43.3 mg/g of glucose and 90.4 mg/g of reducing sugar by enzymatic hydrolysis of biomass rice straw irradiated to 800 kGy. Using biomass samples which initially had 19.0 mg/g glucose and 37.2 mg/g reducing sugar, the steam explosion process at 2 MPa pressure for 2 min yielded 30.1 mg/g glucose and 85.4 mg/g reducing sugar. The concentrations of glucose and of total reducing sugar decrease with irradiation doses above 800 kGy and up to 2000 kGy. Toxic materials, such as glucuronic acid and galacturonic acid, were not found when using the irradiation pretreatment process. The concentrations of glucose and of total reducing sugar were at acceptable levels, indicating that irradiation processing is feasible for ethanol production. Morphology studies by scanning electron microscopy (SEM) compared lignocellulosic biomasses from rice straw, corn stalk and bagasse after gamma irradiation pretreatment at a dose of 1000 kGy with control samples. The irradiated biomasses show a wider distribution of lignin with an uneven surface and covered with small droplets, that may be ascribed to changes in lignin structure at an irradiation dose of 1000 kGy. The separation of cell wall components and an increase in the porosity were also found. Elimination of the interference of lignin droplets showed that three lignocellulosic biomasses have rough surfaces and large reactive areas after gamma irradiation treatment, which is very important for enzymatic hydrolysis. One of the important problems in industrial-scale bioethanol production from lignocellulose is the low efficiency from normally structured cellulose [45]. The gamma irradiation pretreatment process of biomass overcomes from this problem by degrading fibers and increasing the surface area needed to access cellulose. Acid hydrolyzed, gamma irradiation pretreatment of biomasses showed that the concentration of hydrolyzed sugars (glucose, xylose and arabinose) varied with agricultural types. The maximum concentration of glucose from bagasse was 0.18 g/L at a dose 2500 kGy followed by 1.0 (w/v) dilute sulfuric acid hydrolysis for 60 min. Under same conditions, the maximum concentration of xylose was 0.18 g/L for bagasse. Glucose, xylose and arabinose yields increase in the acid hydrolysis step with increasing irradiation doses from 500 to 2000 kGy. The effect of enzymatic hydrolysis on the radiation pretreatment for three lignocellulosic biomasses rice straw, corn stalk and bagasse was also studied. The maximum conversion ratios to hydrolyzed sugars were higher by 69% for the three investigated lignocellulosic biomasses. Glucose and xylose conversion was much higher and increased with irradiation dose from 500 to 2500 kGy following enzymatic hydrolysis. Arabinose conversion rate was relatively lower that decreased with irradiation dose from 500 to 2500 kGy following enzymatic hydrolysis. The pretreatment of lignocellulosic biomass with gamma irradiation was found to be more efficient than steam explosion. In addition, no toxic by-products are formed in the irradiation pretreatment process. Scanning electron microscopy showed the changes in lignocellulosic biomasses after the gamma irradiation pretreatment process which seems more suitable for industrial-scale bioethanol production.

2.3. CONVERSION TO PROTEINS

Some researcher has focused on the study of radiation pretreatment of lignocellulosic biomass for the bioconversion to protein rich materials for environmental purposes.

Awafo *et al.* examined the effect of radiation pretreatment of biomass corn stover to obtain protein rich organic substances [46]. Gamma irradiation at 100 kGy did not show an effect on the bioconversion of biomass corn stover into protein rich organic material. The irradiated material was equivalent to the unirradiated biomass. With additional irradiation, the protein profile becomes richer as discussed above because of a decrease in crystallinity, depolymerization and an increase in specific surface area available for bioconversion.

2.4. OTHER APPLICATIONS

Duarte *et al.* examined the effect of electron beam irradiation combined with a hydrothermal treatment process on the pretreatment of sugarcane bagasse [47]. The composition of biomass sugarcane bagasse was found to be 41.9% cellulose, 31.3% hemicellulose, 19.5% lignin, 6.3% soluble compounds and 1.0% ash. An increase in solubility was found with irradiation dose due to the hemicellulose cleavage that forms water soluble cello-oligosaccharides from xylanes. The main by-products of hemicellulose degradation were acetic acid, furfural and formic acid. When irradiated, moisture in the biomass forms an •OH radical that contributes to the radiation effects.

El-Batal *et al.* investigated the effect of radiation pretreatment of biomass *Aspergillus tamarii* on its adsorption capacity of dyes from textile manufacturing wastewater [48]. The cell walls of the biomass play an important role in dye adsorption and some pretreatment methods are used to increase the adsorption capacity by decomposition of such components as lignocellulosic biomass. The degraded cells have a larger surface area with more surface binding sites. The effects of ionizing radiation can be explained by the change in charges of the biomass which are based on the formation of more electrostatic charges that change the overall surface charge and modify binding sites. These enhance the formation of electrostatic bonds between the biomass surface and the dye molecules [49].

Ouallouche *et al.* investigated the effect of gamma irradiation pretreatment of *Rhizopus Stolonifer* biomass on the removal of mercury and lead from aqueous solutions and made a comparison with other methods [50]. All of the investigated pretreatment methods showed efficient removal of lead and mercury form water. The irradiation pretreatment of biomass increased adsorption of lead and mercury ions by 10% and by 33%, respectively. Although, the adsorption yield is relatively low compared to other pretreatment methods, the irradiation pretreatment is feasible since it easy to operate, economic over long periods of time, no additional chemicals are introduced into the system and is environment friendly without toxicity.

2.5. DEGRADATION

Khan *et al.* examined the changes in the physical and chemical properties of lignocellulose for jute after gamma irradiation [20]. The radiolytic degradation of biomass jute resulted in a biodegradable natural lignocellulose fiber formed mainly from 58-63% cellulose, 20-24% hemicelluloses and 12-15% lignin. The effect of gamma irradiation on jute was noted by several analytical methods which are given below. Tensile strength and elongation of jute was reduced with irradiation. The change in the mechanical strength of jute with irradiation was significant up to 30 kGy, but additional irradiation did not change the mechanical properties significantly due to concurrent chain scissioning and crosslinking reactions. Fluorescence and Fourier transform infrared (FTIR) spectrometry showed a decrease in the number and integral area of analytical peaks of pure jute with irradiation dose corresponding to radiolytic degradation. The thermal stability of jute was also decreased with irradiation since pyrolytic degradation occurs by glycosidic chain scission and the breakdown of other groups [51, 52]. Thermal reactions proceed more rapidly above 315°C in which glycosidic bond scissioning occurs. X-ray studies showed a decrease in crystallinity with irradiation dose which corresponds to a structural change in the lignocellulosic material.

Orozco *et al.* studied gamma irradiation induced degradation of orange peels [53]. A color change from yellow to brown was observed because of the formation of reducing sugars with irradiation. Sucrose, glucose, and fructose were determined by HPLC (high-performance liquid chromatography) analysis after irradiation of the orange peel biomass. Further irradiation of orange peels (1800 kGy) resulted in a decline in the amount of both glucose and fructose in the sugar concentration which was due to glycolytic degradation. Irradiated and unirradiated biomass orange peels both have the similar FTIR spectra with small changes in functional group. These changes were attributed to a decrease in chemical linkages by gamma irradiation. Thermal gravimetric results showed that when the irradiation dose reached 600 kGy or higher, hemicellulose and cellulose undergo chain cleavage but lignin is less affected by gamma irradiation. Lignin is more radiation resistant and protects the biomass structure from radiation. The formation of carbonyl groups on cellulose structure in the presence of oxygen enhances the conversion of cellulose to lower molecular weight compounds.

REFERENCES

[1]. Alvira, P., Tomás-Pejó, E., Ballesteros, M., & Negro, M.J. (2010). Pretreatment technologies for an efficient bioethanol production process based on enzymatic

hydrolysis: A review. *Bioresour.. Technol.*, *101*, 4851-4861. DOI: 10.1016/j.biortech.2009.11.093.

[2]. Tassinari, T.H., Macy, C.F., & Spano, L.A. (1982). Technology advances for continuous compression milling pretreatment of lignocellulosics for enzymatic hydrolysis. *Biotechnol. Bioeng.*, *24*, 1495-1505. DOI: 10.1002/bit.260240704.

[3]. Van Wyk, J.P.H., Mogale, A.M., & Seseng, T.A. (2001). Bioconversion of wastepapers to sugars by cellulose from Aspergillus niger, Trichoderma viride and Penicillium funiculosum. *J. Solid Waste Technol. Manage.*, *27,* 82-86.

[4]. Morjanoff, P.J., & Gray, P.P. (1987). Optimization of steam explosion as method for increasing susceptibility of sugarcane baggase to enzymatic saccharification. *Biotechnol. Bioeng.*, *29*, 733-741. DOI: 10.1002/bit.260290610.

[5]. Macmillan, J.D. (1994). Pretreatment of lignocellulosic biomass. In M.E. Himmel, J.O. Baker & R.P. Overend (Eds.), *Biomass for fuels production* (pp. 92-324). Washington, DC: American Chemical Society.

[6]. Öhgren, K., Bura, R., Saddler, J., & Zacchi, G. (2007). Effect of hemicellulose and lignin removal on enzymatic hydrolysis of steam pretreated corn stover. *Bioresour. Technol.*, *98*, 2503-2510. DOI: 10.1016/j.biortech.2006.09.003.

[7]. Liu, C., & Wyman, E.C. (2005). Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery and enzymatic digestibility of cellulose. *Bioresour. Technol.*, *96*, 1978-1985. DOI: 10.1016/j.biortech.2005.01.012.

[8]. Moiser, N., Hendrickson, R., Ho, N., Sedlak, M., & Ladisch, M.R. (2005). Optimization of pH controlled liquid hot water pretreatment of corn stover. *Bioresour. Technol.*, *96*, 1986-1993. DOI: 10.1016/j.biortech.2005.01.013.

[9]. Kumakura, N., & Kaetsu, I. (1983). Radiation and chemical pretreatment of chaff and its effect on enzymatic hydrolysis. *Process Biochem.*, *18*, 14-16.

[10]. Chosdu, R., Hilmy, N., Erizal, Erlinda, T.B., & Abbas, B. (1993). Radiation and chemical pretreatment of cellulosic waste. *Radiat. Phys. Chem.*, *42*, 695-698. DOI: 10.1016/0969-806X(93)90354-W.

[11]. Zhu, S., Wu, Y., Yu, Z., Zhang, X., Li, H., & Gao, M. (2006). The effect of microwave irradiation on enzymatic hydrolysis of rice straw. *Bioresour. Technol.*, *97*, 1964-1968. DOI: 10.1016/j.biortech.2005.08.008.

[12]. Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., & Penner, M.H. (1997). Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Bioresour. Technol.*, *59*, 129-136. DOI: 10.1016/S0960-8524(97)81606-9.

[13]. Kim, S., & Holtzapple, M.T. (2005). Lime pretreatment and enzymatic hydrolysis of corn stover. *Bioresour. Technol.*, *96*, 1994-2006. DOI: 10.1016/j.biortech.2005.01.014.

[14]. Silverstein, R.A., Chen, Y., Sharma-Shivappa, R.R., Boyette, M.D., & Osborne, J. (2007). A comparison of chemical pretreatment methods for improving saccharification of cotton stalks. *Bioresour. Technol.*, *98*, 3000-3011. DOI: 10.1016/j.biortech.2006.10.022.

[15]. Charlesby, A. (1955). The degradation of cellulose by ionizing radiation. *J. Polym. Sci.*, *15*, 263-270. DOI: 10.1002/pol.1955.120157921.

[16]. Charlesby, A., & Davison, W.H.T. (1957). Temperature effects in the irradiation of polymers. *Chem. Ind.*, 232-233.

[17]. Chapiro, A. (1967). Applications of radiation to the macromolecular chemistry of polymer crosslinking and grafting. *Rev. l'Assoc. Fr. Tech. Pet.*, *185*, 67-70.

[18]. Philips, G.O., & Arthur Jr, J.C. (1985). Effects of high-energy radiation on physical and chemical properties of purified fibrous cellulose. In T.P Nevell & S.H. Zeronian (Eds.), *Cellulose chemistry and its applications* (pp. 290-311). Chicester, UK: Ellis Horwood Ltd.

[19]. Cheng, S., & Kerluke, D.R. (2003). Radiation processing for modification of polymers. In *ANTEC 2003: Annual Technical Conference, May 4-8, Nashville, Tennessee. Conference Proceedings* (pp. 2694-2701). Society of Plastic Engineers.

[20]. Khan, F., Ahmad, S.R., & Kronfili, E. (2006). γ-Radiation induced changes in the physical and chemical properties of lignocellulose. *Biomacromolecules*, *7*, 2303-2309. DOI: 10.1021/bm060168y"10.1021/bm060168y.

[21]. Charlesby, A. (1981). Crosslinking and degradation of polymers. *Radiat. Phys. Chem.*, *18*, 59-66.

[22]. Lu, Z., & Kumakura, M. (1993). Effect of radiation pretreatment on enzymatic hydrolysis of rice straw with low concentrations of alkali solution. *Bioresour. Technol.*, *43*, 13-17. DOI: 10.1016/0960-8524(93)90076-N.

[23]. Yang, C.1., Shen, Z., Yu, G., & Wang, J. (2008). Effect and aftereffect of γ-radiation pretreatment on enzymatic hydrolysis of wheat straw. *Bioresour. Technol.*, *99*, 6240-6245. DOI: 10.1016/j.biortech.2007.12.008.

[24]. Glegg, R.E., & Kertesz, Z.I. (1956). Aftereffect in the degradation of cellulose and pectin by gamma rays. *Science*, *124*, 893-894. DOI: 10.1126/science.124.3227.893.

[25]. Polovka, M., Brezova, V., Stasko, A., Mazur, M., Suhaj, M., & Simko, P. (2006). EPR investigations of gamma-irradiated ground black pepper. *Radiat. Phys. Chem.*, *75*, 309-321. DOI: 10.1016/j.radphyschem.2005.07.007.

[26]. Bayram, G., & Delincee, H. (2004). Identification of irradiated Turkish foodstuffs combining various physical detection methods. *Food Control*, *15*, 81-91. DOI: 10.1016/S0956-7135(03)00018-5.

[27]. Bushan, B., Bhat, R., Rao, B.Y.K., Ahmad, R., & Bongirwar, D.R. (2003). Electron spin resonance studies on γ-irradiated coffee bean parts. *Int. J. Food Sci. Technol.*, *38*, 11-16. DOI: 10.1046/j.1365-2621.2003.00634.x.

[28]. Yordanov, N.D., & Aleksieva, K. (2004). X-and Q-band EPR studies on fine powders of irradiated plants. New approach for detection of their radiation history by using Q-band EPR spectrometry. *Radiat. Phys. Chem.*, *69*, 59-64. DOI: 10.1016/S0969-806X(03)00399-2.

[29]. Keller, A., & Ungar, G. (1983). Radiation effects and crystallinity in polyethylene. *Radiat. Phys. Chem.*, *22*, 155-181. DOI: 10.1016/0146-5724(83)90201-7.

[30]. Hon, D.N.S. (1992). Thermomechanical pulp and light photoactivity of α-carbonyl group in solid lignin. *J. Wood Chem. Technol.*, *12*, 179-196. DOI: 10.1080/02773819208545078.

[31]. Simkovic, I., Ebringerova, A., Tino, J., Placek, J., Manasck, Z., & Zilka, Z. (1986). ESR study of soda waste liquors. *Holzforschung*, *40*, 15-18.

[32]. Al-Masri, M.R., & Zarkawi, M. (1994). Effects of gamma-irradiation on cell wall constituents of some agricultural residues. *Radiat. Phys. Chem.*, *44*(6), 661-663. DOI: 10.1016/0969-806X(94)90227-5.

[33]. Betiku, E., Adetunji, O.A., Ojumu, T.V., & Solomon, B.O. (2009). A comparative study of the hydrolysis of gamma irradiated lignocelluloses. *Braz. J. Chem. Eng.*, *26*(2), 251-255. DOI: 10.1590/S0104-66322009000200002.

[34]. Henniges, U., Hasani, M., Potthast, A., Westman, G., & Rosenau, T. (2013). Electron beam irradiation of cellulosic materials-opportunities and limitations. *Materials*, *6*(5), 1584-1598. DOI: 10.3390/ma6051584.

[35]. Ershov, B.G., & Ponomarev, A.V. (2011). Prospects for electron beam technology in plant biomass processing. *Her. Russ. Acad. Sci.*, *81*(6), 623-628. DOI: 10.1134/S1019331611060025.

[36]. Kim, J.Y., Na, C.S., Kim, D.S., Kim, J.B., & Seo, Y.W. (2015). The effect of chronic gamma ray irradiation on lignocellulose of Branchypodium distachyon. *Cellulose*, *22*, 2419-2430. DOI: 10.1007/s10570-015-0687-y.

[37]. Park, S.K., Baker, J.O., Himmel, M.N., Parilla, P.A., & Johnson, D.K. (2010). Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulose performance. *Biotechnol. Biofuels*, *3*, 10. DOI: 10.1186/1754-6834-3-10.

[38]. Kovalev, G.V., & Bugaenko, L.T. (2003). On the crosslinking of cellulose under exposure to radiation. *High Energ. Chem.*, *37*, 247-254. DOI: 10.1023/A:1024790415083.

[39]. Smith, P.A., Sheely, M.V., Hakspiel, S.J., & Miller, S. (2003). Volatile organic compounds produced during irradiation of mail. *AIHAJ*, *64*, 189-195.

[40]. Chung, B.Y., Lee, J.T., Bai, H.W., Kim, U.J, Bae, H.J., Gon Wi, S., & Cho, J.Y. (2012). Enhanced enzymatic hydrolysis of poplar bark by combined use of gamma ray and dilute acid for bioethanol production. *Radiat. Phys. Chem.*, *81*, 1003-1007. DOI: 10.1016/j.radphyschem.2012.01.001.

[41]. Yoon, M., Choi, J., Lee, J.W., & Park, D.H. (2012). Improvement of saccharification process for bioethanol production from Undaria sp. by gamma irradiation. *Radiat. Phys. Chem.*, *81*, 999-1002. DOI: 10.1016/j.radphyschem.2011.11.035.

[42]. Raffi, J.J., Agnel, J.P., Thiery, C.J., Frejaville, C.M., & Saint-Lebe, L.R. (1981). Study of gamma-irradiated starches derived from different foodstuffs: A way for extrapolating wholesomness data. *J. Agr. Food Chem.*, *29*, 1227-1232. DOI: 10.1021/JF00108A032.

[43]. Sokhey, A.S., & Hanna, M.A. (1993). Properties of irradiated starches. *Food Struct.*, *12*, 397-410.

[44]. Wang, K., Xiong, X., Chen, J., Chen, L., Su, X., & Liu, Y. (2012). Comparison of gamma irradiation and steam explosion pretreatment for ethanol production from agricultural residues. *Bioamass Bioenerg.*, *46*, 301-308. DOI: 10.1016/j.biombioe.2012.08.013.

[45]. Chen, W.H., Pen, B.L., Yu, C.T., & Hwang, W.S. (2011). Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute acid and steam explosion for bioethanol production. *Bioresour. Technol.*, *102*, 2916-2924. DOI: 10.1016/j.biortech.2010.11.052.

[46]. Awafo, V.A., Chalal, D.S., & Charbonneau, R. (1995). Effect of irradiation as a pretreatment on bioconversion of corn stover into protein-rich mycelial biomass of Pleurotus Sajor-Caju. *Radiat. Phys. Chem.*, *46*(4-6), 1299-1302. DOI: 10.1016/0969-806X(95)00374-7.

[47]. Duarte, C.L., Riberio, M.A., Oikawa, H., Mori, M.N., Napolitano, C.M., & Galvao, C.A. (2012). Electron beam combined with hydrothermal treatment for enhancing the enzymatic convertibility of sugarcane bagasse. *Radiat. Phys. Chem.*, *81*, 1008-1011. DOI: 10.1016/j.radphyschem.2011.11.008.

[48]. El-Batal, A.I., Hashem, A.M., Hassan, M.S., & Helal, A.H. (2012). Removal of dyes from textile wastewater using treated *Aspergillus tamari* biomass in batch and column reactor. *World Appl. Sci. J.*, *19*(9), 1305-1310. DOI: 10.5829/idosi.wasj.2012.19.09.2792.

[49]. Zeroual, Y., Kim, C.S., Kim, M.B., & Lee, K.M. (2006). Biosorption of bromophenol blue from aqueous solutions by Rhizopus stolonifer biomass. *Water Air Soil Poll.*, *177*, *135-146*. DOI: 10.1007/s11270-006-9112-3.

[50]. Ouallouche, K.A., Kerrar, A.D., Amrani, S., & Zerrouki, S. (2014). Removal of lead and mercury from aqueous solutions by pretreated Rhizopus Stolonifer biomass. *IPCBEE*, *65*, 1-5. [5th International Conference on Food Engineering and Biotechnology].

[51]. Pandey, S.N., Day, A., & Mathew, M.D. (1993). Thermal analysis of chemically treated jute fibers. *Text. Res. J.*, *63*(3), 143-150. DOI: 10.1177/004051759306300303.

[52]. Basak, R.K., Saha, S.G., Sarkar, A.K., Saha, M., Das, N.N., & Mukherjee, A.K. (1993). Thermal properties of jute constituents and flame retardant jute fabrics. *Text. Res. J.*, *63*(11), 658-666. DOI: 10.1177/004051759306301107.

[53]. Orozco, R.S., Hernandez, P.B., Ramirez, N.F., Morales, G.R., Luna, J.S., & Montoya, A.J.C. (2012). Gamma irradiation induced degradation of orange peels. *Energies*, *5*, 3051-3063. DOI: 10.3390/en5083051.

Chapter 20

APPLICATION OF RADIATION TECHNOLOGY TO FOOD PACKAGING

Clara Silvestre[1/], Sossio Cimmino[1/], Elena Stoleru[2/], Cornelia Vasile[2/]
[1/] Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche, IPCB/CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Naples, Italy
[2/] "Petru Poni" Institute of Macromolecular Chemistry, Physical Chemistry of Polymers Department, Romanian Academy, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania

1. INTRODUCTION

The Food and Agriculture Organization of the United Nations (FAO), the World Health Organization (WHO) and the US Centers for Disease Control and Prevention (CDC) state that millions of cases of food borne disease are recorded every year. These food poisonings cause immense economic burden because of food recalls and the need for medical treatment. It has been also reported that food availability, abundance and safety are under threat and that by 2050, the global production of safe and nutritious food must increase by 70% in order to feed the growing world population and that a huge amount of food (~40%, ~1.3 billion tons/year) is lost between production and consumption, with a wasted investment for farmers and a parallel increase in cost for consumers and a burden on the environment. To solve these health, economic, and environmental problems, new solutions are needed.

To increase the availability of food, efforts are being made to increase production. Several methods for increasing food production have been identified and are being used, such as mechanization, irrigation, use of fertilizers, improved crop varieties, control of weeds and insects, new strains of disease resistant farm animals, infrastructure development, *etc*.

Improving yield is only one aspect of increasing food supply. It is equally important to conserve and protect what is produced. On the way from producer to consumer, if food products from plants and animals are not handled and packed with care, they can be prone to contamination by pathogenic microorganisms, causing additional food loss along with highly worrisome safety risks.

An innovative route to enhancing efficiency, reduce energy consumption and waste, and to provide safe food to everyone is through the convergence of different technical approaches. The use of current and older food processing and packaging technologies may be combined for different purposes. The advantage of combining emerging food packaging technology with food irradiation is an example. Another is the use of packaging materials containing bioactive nanoparticles and using this in combination with food irradiation. How packaging materials containing bioactive nanoparticles function and why they should be combined with food irradiation will be discussed and illustrated in selected case histories. Finally, some market analysis and future trends will be discussed.

2. FOOD PACKAGING

Modern food packaging started in 1810 with the invention of canning by Nicholas Appert. The introduction of plastics as food packaging materials began in the 1930s and have had a continuously increasing role.

Packaging protects foodstuffs during processing, storage and distribution from contamination by dirt (through contact with surfaces and hands), contamination by microorganisms (bacteria, molds, yeasts), contamination by parasites (mainly insects), contamination by toxic substances (chemicals), factors affecting color, smell and taste (off-odor, light, oxygen and other gases), loss or uptake of moisture (evaporation or water absorption) [1].

The market for food packaging and for plastic food packaging is as follows:

- The global market of food packaging is worth US$440 billion worldwide (about 2% of the gross national product of developed countries), with an annual increase of 10%.
- The food industry uses almost 65% of all packaging placed on the market, and the impact of the packaging on the retail cost of food is between 19 and 50%.
- Almost 40% of the total packaging is made of plastics.
- The growth rate of the market of plastic packaging in the last few years for both flexible and rigid plastic packages has been about 7%, the highest compared with other materials (glass – 2%, metal – 6%, paper – 6%, and others including wood – 3%).

These impressive numbers explain why many of the world's largest food packaging companies are exploring some emerging technologies to produce new food packaging materials with improved properties. They also want to be able to trace and monitor the conditions of food during transport and storage and to note what interacts with the food.

Most packaging materials are made from polymers derived from petroleum-based feedstocks. These materials have functional advantages, low cost and are widely available. Petroleum-based polymers can have such salient features as strength, flexibility, stiffness, barriers to oxygen and moisture, and resistance to attack from food components. However, their resistance to degradation and also to recycling and disposal pose some challenges when dealing with interests in environmentally sustainable materials, such as biodegradable polymers.

The most commonly used plastics in the food packaging are:

- Polyethylene (PE) polymers are characterized by low vapor permeability, good mechanical properties, flexibility, being non-toxic and available in direct food contact grades.
- Polypropylene (PP) is a polymer that is particularly lightweight, non-toxic, waterproof, resistant to chemical attack, but is oxygen permeable; when oriented, having good transparency.
- Polystyrene (PS) is used for protective packaging, because of its aesthetic qualities, ease of decoration, and the good transparency. Odorless and slightly water-permeable, polystyrene can sometimes be characterized by being fragile and having low heat resistance.
- Poly(ethylene terephthalate) (PET) was introduced to the market in the 1950s and has found use in the packaging industry, as for beverage bottles and for transparent containers.
- Poly(lactic acid) (PLA) is a thermoplastic linear aliphatic polyester made from starches that are derived from various renewable resources (corn starch, tapioca roots, sugarcane, *etc*.) which can be biodegradable. Although biodegradable polymers present a significant commercial potential, some of their properties, such as brittleness, low heat distortion temperature, high water vapor permeability, and low melt viscosity, may restrict their use for food packaging.

The materials suitable for food packaging are available mainly in the form of plastic films. Packaging films must be flexible, lightweight, odorless, hygienic (clean and toxicologically harmless), easy to recycle, and have mechanical strength, resistance to low and high temperatures, resistance to oil and fats, have good barrier properties against gases, sealing capability, and be available at low cost. They should also be easy to sterilize and when subjected to radiation sterilization, be resistant to irradiation which can be used with packaged foodstuffs [2-6].

3. RADIATION PROCESSING TO IMPROVE THE FUNCTIONALITY OF FOOD PACKAGING

The trend of replacing traditional materials such as glass, metals and paper with polymeric materials has been growing continuously within the various industrial sectors, including the food industry. In order to obtain polymer-based packaging materials with some desired properties, surface treatments are used. Surface treatments for packaging include surface functionalization (*i.e.* the introduction of specific functional groups onto the surface layer), surface cleaning or etching, and/or surface deposition which is usually carried out to improve wettability, sealability, printability, barrier characteristics, dye uptake, resistance to glazing, or adhesion to other polymers or materials, and to impart antimicrobial properties, *etc.*, without compromising the bulk properties of the packaging material [7-9].

Surface modification of polymeric packaging can be done either by chemical, physical or biological methods. Physical methods have gained preference over chemical techniques, offering greater precision, ease of process control, and are environmentally friendly. Classical physical and chemical methods for modifying polymer surfaces include flame treatment, corona treatment, low-pressure plasma, ultraviolet (UV) radiation, gamma irradiation, electron beam, ion beam, laser exposure, *etc*. as listed in Table 1. Physical modification either alters the surface layer or a coating is put on the existing packaging material.

Flame and corona treatments are commonly used on a continuous basis to modify the surface properties of polymeric packaging materials as when used to enhance the adhesion of inks and coatings to films.

3.1. GAMMA IRRADIATION

Gamma irradiation has some advantages, such as being non-polluting, having effects at ambient temperatures, and some flexibility through process control, *etc*. Gamma irradiation is not a surface treatment, since the photon energy is high enough to penetrate through materials. Under some experimental conditions, a modification of only the surface of a polymeric packaging material can be obtained. Gamma irradiation can lead to subsequent attachment of functional groups on a surface, allowing the material to immobilize enzymes or other bioactive species. The radiation grafting of acrylic acid (AA) onto polyethylene, polypropylene and polystyrene films was performed and it was found that the radiation yield of radicals and the hydrogen emission increased in the following order PS < PP < PE [10].

Table 1. Methods for the modification of polymeric packaging surfaces using irradiation from different sources [7-9].

Treatment method	Energetic species involved in the surface modification	Observations
Ultraviolet irradiation (UV lamps)	Energetic photons, cause crosslinking and free radical formation	Limited utility for extensive surface modification. Alteration of bulk properties if photocrosslinking occurs. Requires additional treatments as ultraviolet/ozone, plasma, *etc*.
Plasma exposure	Energetic neutrals (*i.e.* atoms, molecular components), ions, radicals, photons, electrons	Surface modification without altering bulk properties. Non-directional nature affects throughput and treatment characteristics. Availability of a wide range of surface modifications.
Corona treatment (corona discharge, dielectric barrier discharge)	Ozone, electrons, ions, excited molecular species, radicals	When applied in air, it proceeds through surface oxidation, which is accompanied by considerable chain scission leading to the formation of water soluble low molecular oxidized material. Degradation associated could occur with the formation of the so-called nodules. Morphological aspects depend on the relative humidity of environment.
Ion bombardment (ion gridless sources)	Highly directional ions, of variable energy	Selectable surface chemistries based on choice of discharge gas. Localized surface modification. Wide range of surface modifications or sputtering of the treated substrate, depending on the energy and the fluxes of the ion beam. Easily combined with deposition techniques.
Electron beam bombardment (electron sources)	Highly directional electrons, of variable energy	Possible degradation of polymers or their surface properties tailoring, depending on the energy and fluence of the electron beam. Sterilization.
Gamma irradiation (^{60}Co sources)	Energetic gamma photons	Sterilization. Functional groups attachment on the surface, allowing the material to immobilize bioactive species.

3.2. COLD PLASMA OR DIELECTRIC BARRIER DISCHARGE EXPOSURES

When used with a polymeric packaging material, a plasma can contain various energetic and reactive moieties, *e.g.* free radicals, positive and/or negative ions, electrons, photons, atoms, fragments and molecules that will interact with the surface of a material. The effects of plasma treatment vary with the fluence of these moiety depending on the plasma parameters (power, duration, type of gas and pressure). For example, the longer the plasma treatment, a higher the free radical concentration is obtained when using stronger conditions, as shown in Fig.1.

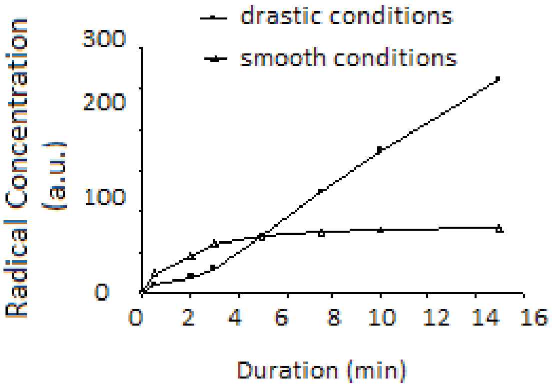


Fig.1. Radical concentration *vs.* N_2 plasma treatment duration of polypropylene. (Adapted from Ref. [11]).

For different experimental conditions, plasma treatment induces different effects on the modified surface, which can be cleaning, functionalization or crosslinking [11-14]. Surface modification/functionalization of PE with CO_2, H_2O and CO_2/H_2O plasma has been reported [11, 14].

It had been established that:

- the presence of oxygen in the polymer structure made the polymer more susceptible to plasma, but nitrogen in the polymer structure, for example polyimides, had an opposite effect;
- the polymeric structures most susceptible to plasma treatment are aliphatic polyethers with –O– ether linkage in the backbone and polysaccharides.

In many cases, a simple ablation of the surface layer has been observed, except for polyethylene and polypropylene where there is a highly oxidized surface layer [13]. Plasma processes are: plasma surface modification, plasma deposition, plasma-induced polymerization or grafting.

The immobilization of bioactive functional compounds like lysozyme, niacin, vanillin, sodium benzoate, glucose oxidase or antimicrobial peptides on a packaging material surface by plasma treatment has been extensively studied in the emerging field of antimicrobial and bioactive packaging [15-20]. Other antimicrobial compounds, like chitosan, silver and triclosan, have been immobilized on films by plasma treatment [21-26]. Following corona treatment, Joerger *et al.* [22] coated films with chitosan and chitosan/silver which showed good antimicrobial activity against *Escherichia coli* and *Listeria monocytogenes*.

The irradiation of prepackaged foodstuffs using electron beam or gamma irradiation can be used for food preservation. This irradiation also affects the morphology and the properties of packaging materials. Radiolysis products (RPs) have been detected, which are dose-dependent.

Dielectric barrier discharge (DBD) has been used to generate plasma inside sealed packages [27, 20], in fresh fish [28] and in meat [29]. The in-package plasma decontamination of foods and biomaterials relies on use of the polymeric package itself. Several packaging materials, such as low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene, Tyvek® (an air and water barrier made from high density polyethylene fibers), *etc*. demonstrated a significant reduction in the microbial population within the food products.

Ethylene-vinyl acetate (EVA) and ethylene-vinyl alcohol/ethylene-vinyl acetate (EVOH/EVA) films have been modified by the addition of clay or graphene and then exposed to ionizing radiation when producing prepackaged irradiated foods that have extended shelf life and provide some environmental sustainability advantages. Antimicrobial agents, such as potassium sorbate, organic acids (sorbic, propionic, benzoic, acetic, lactic), maleic anhydrides and few others, have been evaluated in grafts on commercial polyethylene film, which is normally used in the packaging for bakery and pastry products.

3.3. ELECTRON BEAM IRRADIATION

Two changes can result from electron beam irradiation:

- electron absorption, followed by bond cleavage to produce radicals, and/or radical recombination leading to the formation of crosslinks and end-links;

and/or

- disproportionation, which produces chain scissioning and gas evolution, mainly by radical recombination.

When polymers are exposed to ionizing radiation (*e.g.* electron beams), new chromophore groups are formed, which efficiently absorb electromagnetic radiation from the ultraviolet, visible and infrared (IR) regions of the spectrum. The main effects of electron beam irradiation are: crosslinking, degradation, resulting from the scissioning of bonds in the main chain and in the side chain, the formation of gases, such as H_2, CH_4, and CO, oxidation, changes in unsaturation resulting from the formation of various types of double bonds, C=C, cyclization through the formation of intermolecular bonds, which all depend on dose rate and the oxygen in the exposure environment.

The advantage of electron and also gamma irradiation over the chemical processing of polymers is due to crosslinking which occurs *in situ* and at lower temperatures in the solid state of finished products so that heating or melting of polymers is not needed.

Low energy (< 25 keV) electron beams can be used for surface treatment in order to improve the adhesion properties. This is might be due to the mechanically strengthening of the surface layer by oxygen containing functionalities introduced onto the surface, by the formation of radicals and by their consequent reactions with the atmospheric oxygen.

Using electron beam excitation, the coating of polymer surfaces by metal (metallization) can be achieved by an electrodeless process which is a well-developed industrial technique having low cost and operating at ambient temperatures. The most widespread use is the aluminum coating of plastic films or packaging materials, decorative and barrier.

Laser treatment has resulted in the modification of the hydrophilicity of the ablated areas and the surface potential of the ablated film goes from neutral to positive resulting from the redeposition of cationic fragments, the surface then becomes conducting.

4. EFFECTS OF IRRADIATION ON POLYMERS USED FOR PACKAGING APPLICATIONS

Examples of studies dealing with the irradiation effects on the most popular polymers are presented below.

Polypropylene (PP): The use of heat (steam), irradiation (electron beams or gamma rays) or chemicals in the products made from polypropylene significantly affects its mechanical and optical properties and sometimes also the organoleptic properties. Because the radiochemical yield for scissioning exceeds the radiochemical yield for crosslinking, PP is susceptible to degradation/oxidation in air. Sometimes there are problems in printing, coating and lamination, so additional surface treatments are needed to increase surface energy [30]. Gamma rays induce chain scissioning and degradation effects, resulting in a reduced melt viscosity and embrittlement. Due to radiation-induced oxidation, the polymer surface is enriched with oxygen containing hydrophilic groups, such as carbonyl, hydroxyl, carboxyl, *etc*., which have been detected by infrared spectroscopy [31]. In general, the polymer surfaces become hydrophilic after irradiation. Bio-components that are incorporated in PP are capable of scavenging hydrocarbon free radicals which delays of long-term oxidative degradation. Gamma irradiation of polypropylene and of polypropylene/biomass showed the antioxidant properties of bio-additives which can be derived from the labile protons of lignin hydroxyls. The activities of radical scavenging are different for different tested compositions, with the best stability being obtained from PP/*Eucalyptus globulus* which has a high lignin content.

Poly(ethylene terephthalate) (PET): Like other synthetic polymers, PET has a low surface energy, which requires surface modification to attain good adhesion for printing and dyeing [32]. In an oxygen and carbon dioxide plasma, chitosan was coated onto PET and PET/PP films with various preservatives used for antimicrobial properties [33, 34]. The surfaces became hydrophilic because of the new polar oxygen containing groups on the surface and chitosan was bonded to them through amino groups. The antimicrobial activity of these films against three kinds of microorganisms (*Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli*) indicated that the inhibition rates against *Bacillus subtilis* and *Escherichia coli* reached almost 100% while the inhibition rate against *Staphylococcus aureus* was lower than 85%. The accumulative release data of the antimicrobial substances migrating from these films into a media showed that their release rate increased with temperature and acidity, but decreased by enhancing the ionic strength controlled by sodium chloride or by lowering the ionic mobility by using sucrose.

Low density polyethylene (LDPE) (Unipac-PE-60) and polyamide (PA)-co/EVOH/PE (Lovaflex CH130): PE/PA laminated films were gamma- and electron beam irradiated. Antioxidant additives having phenolic and phosphate structures are usually present in polyolefins and undergo breakdown in irradiation processes due to partial radiolysis. Anti-slip and anti-static additives used in these films are also more sensitive to the conditions of irradiation and more susceptible to oxidative degradation than the polymers themselves. Scissioning reactions predominated over crosslinking reactions for both Unipac-PE-60 and Lovaflex CH 130 films, irradiated with both gamma rays or electron beams, at the interval doses from 0 to 30 kGy, at room temperature and in air.

Irradiated LDPE, PP, polyesters, PP-copolymer films, *etc*. [35] predominantly yield hydrocarbons, as alcohols, aldehydes, ketones and carboxylic acids as volatile compounds. Thus, leachates from packaging materials increase in quantity after irradiation. Laminated PET/PE films have a high leachable content after irradiation. PET12/PE70, Nylon/PE, and Nylon 15/PE 50 were found to be the most irradiation resistant packaging materials in terms of the quantity of radiolytic products. Polyamides present medium resistance to ionizing radiation with regard to the changes in its mechanical properties [36].

Polysaccharides: Radiation processing offers a clean and additive-free method for preparation of value-added novel materials based on renewable, non-toxic and biodegradable natural polymers, and natural polymer waste. Natural polymers like cellulose (carboxymethylcellulose) and other marine polysaccharides (chitin/chitosan, alginates, carrageenans) are predominantly chain scissioning polymers. After irradiation, there is a substantial decrease in molecular weight, as shown in Fig.2 [37]. This is accompanied by the formation of oxidation products and a reduction in crystallinity.

Poly(lactic acid) (PLA): PLA is an attractive substitute for classical polymer packaging materials because of its biodegradability and its having sufficient

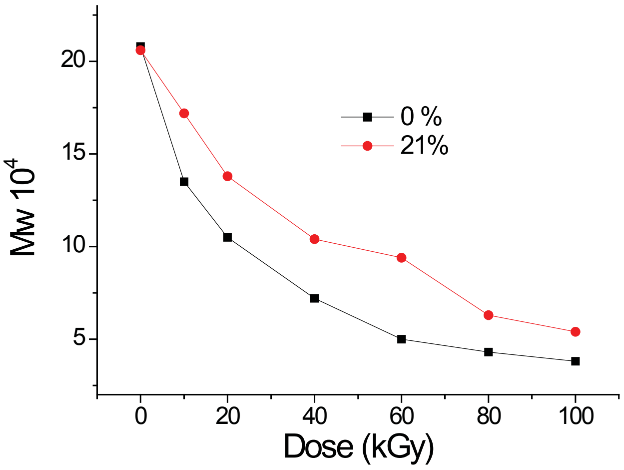


Fig.2. The change of weight-average molecular weight of carrageenans with different water contents as a function of irradiation dose. (Adapted from Ref. [37]).

mechanical and barrier properties. Ionizing irradiation with doses in the range of 2.5 to 25 kGy is commonly used for radiation sterilization and for the preservation of foods. The radiation resistance of PLA is sufficient for these packaging applications. Atmospheric plasma treatment improves the wettability of PLA substrates. Increased polarity is important for surface wettability, increasing up to 32.8 $mJ \cdot m^{-2}$. Polar groups as hydroxyl, hydroperoxide (COOH), and ethers are formed. More oxidized groups, such as carboxylic acids and esters, can also be formed [38]. Lactoferrin (LF) was immobilized on a PLA surface activated by high frequency plasma (1.3 MHz) discharge of 100 W or gamma irradiation (10, 20 and 30 kGy; at a dose rate of 0.4 kGy/h) [39]. The samples were tested for inhibiting the growth of three different bacteria: *Escherichia coli*, *Listeria monocytogenes* and *Salmonella typhymurium*. The lactoferrin-modified PLA substrate that was gamma pre-irradiated had a more pronounced antioxidant and antibacterial activity.

5. ACTIVE FOOD PACKAGING CONTAINING NANOPARTICLES

Food packaging no longer has just a passive role in protecting and marketing food products. New concepts of active and intelligent packaging play an increasingly important role by offering innovative solutions for extending the shelf life or maintaining, improving or monitoring food quality and safety.

The term “active packaging” was introduced by Labuza in 1989 [40]: “A packaging material is defined active when it has the ability to interact with food performing additional desired functions other than to providing a physical and passive barrier to the external environment".

Active packaging can have several uses as listed below:

- absorbing/scavenging: oxygen, carbon dioxide, moisture, ethylene, flavors, taints, ultraviolet radiation;
- releasing/emitting: ethanol, carbon dioxide, antioxidants, preservatives, sulfur dioxide, flavors, pesticides, antimicrobials;
- removing: catalyzing food component removal, as lactose, cholesterol;
- temperature control: insulating materials, self-heating and self-cooling packaging, microwave susceptors and modifiers, temperature-sensitive packaging.

Nanoparticles which have current and expected uses in food nano-packaging are:

- carbon black is an example of a material composed of nanoparticles that has been used in quantity for decades;
- silicate nanoparticles generally in the form of nanoscale flakes of clay;
- metal oxide (titanium, zinc, aluminum and iron oxides), TiO_2, being approved in European Community (EC);
- nanocrystalline cellulose (NCC).

The active and intelligent packaging market is witnessing a remarkable growth. There is an increase in demand for these packaging products because of changing lifestyles and the requirement by food processors to produce products with longer shelf life. The market for active and intelligent packaging is expected to grow at a compounded annual growth rate (CAGR) of 9.25% and to reach US$21.41 billion by the end of 2019, from the current estimate of US$13.75 billion. Some of the vendors mentioned for such packaging materials are: BASF, Amcor Limited, Landec Corporation, Bemis, Rexam Plc and Sonoco [2-5, 41-43].

6. FOOD IRRADIATION

Food irradiation is a food safety technology that can eliminate disease causing microorganisms, such as *Escherichia coli* O157:H7, *Campylobacter*, and *Salmonella,* from foods. The effects of irradiation on food and on animals and people eating irradiated food have been studied extensively for more than 40 years. These studies show clearly that when irradiation is used as approved for foods:

- irradiation is a safe and effective technology that can prevent many foodborne diseases (disease causing microorganisms are reduced or eliminated),
- the nutritional value is essentially unchanged,
- the food does not become radioactive.

The first patent on food irradiation is from 1905 [44] and proposed a way "to bring about an improvement in foodstuff" and "their general keeping quality" through the treatment of food, mainly cereal with alfa, beta or gamma rays from radium and other radioactive substances. It took a long time for this insight to have practical use since the radiation sources available at that time were not powerful enough to treat food in commercial quantities. Only after 1950 were radiation sources strong enough for industrial use and around then, the US Army and the US Atomic Energy Commission also started the development of the irradiation technology to improve safety quality of food, stimulated by President Eisenhower's initiative of "Atoms for Peace". Finally in 1980, the Joint Expert Committee of FAO/IAEA/WHO on Food Irradiation declared irradiated foods safe and wholesome for human consumption.

The actual progress of food irradiation is as follows:

- Food processing by ionizing radiation technologies such as cobalt-60, electron beam, and X-rays is approved in all continents and in commercial use over 60 countries.
- The radiation methodology has been endorsed as safe for foods and health by the World Health Organization and the European Food Security Agency, that found there are no health risks for the consumer linked to the use of food irradiation.
- The extent of clearances in the countries is varying from almost any food in Brazil, to selected items in several EU countries, as listed by the Official Journal of the European Union. In US between 2007 and 2013, the total volume of commodities treated by ionizing radiation increased by over 6000% from 195 000 kg in 2007 to approximately 13 million kg in 2013.
- Application: reduction of pathogenic microorganisms, decontamination, extension of shelf life, disinfestations, inhibition of sprouting and ripening.

The type of radiation used for food processing materials is limited to radiations from high energy gamma rays, X-rays and accelerated electrons. Two different radiation sources are used:

- radionuclide or radioactive isotopes that give off ionizing gamma rays (cobalt-60, cesium-137),
- machine sources of ionizing radiation (electron beam accelerators, X-rays generators).

The salient features of electron beam accelerators and X-ray generators are that they do not involve radioactive isotopes and that the process is very fast and cost-effective. The number of electron beams in industrial use is over 1700 worldwide and has now outnumbered gamma irradiation facilities by more than 10:1.

The food irradiation process involves exposing the food, either packaged or in bulk, to a controlled amount of ionizing radiation, dose, to achieve certain desirable objectives. If microbes are present in the food and it is irradiated, the energy from the radiation breaks the strands in the microbe's DNA molecules, making them unable to replicate. Unless this breakage of the DNA strands can be repaired, the organism will die and be unable to reproduce.

The effectiveness of the process depends on temperature and on the organism's sensitivity to irradiation, on the rate at which it can repair damaged DNA, and on the amount of the DNA in the target organism. In particular, parasites and insect pests, which have large amounts of DNA, are rapidly killed by an extremely low dose of irradiation. It takes more irradiation to kill bacteria, because they have less DNA. Viruses are the smallest pathogens that have nucleic acid, and they are, in general, resistant to irradiation at doses approved for foods. If the food still has living cells, they will be damaged or killed just as are the microbes. This is a useful effect, in that it can, for example, be used to prolong the shelf life vegetables because it inhibits sprouting and delays ripening.

Foods are not changed in nutritional value and they do not become dangerous as a result of irradiation. At the irradiation levels approved for use with food, levels of the vitamin thiamine are slightly reduced, but not enough to result in any vitamin deficiency. There are no other significant changes in the amino acids, fatty acids, or vitamin content in irradiated food. The changes induced by irradiation are so minimal that it is not easy to determine whether or not a food has been irradiated. A big advantage of irradiated food is that it is a cold process. Food is still essentially "raw", because it has not undergone any thermal process.

Food irradiation can be broadly divided into two categories based on the doses that are used, namely doses ≤ 1.0 kGy and doses ≤ 10 kGy. Doses ≤ 1.0 kGy are primarily used for eliminating insects and pests from fruits and vegetables and for the extension of shelf life; doses ≤ 10 kGy are used for eliminating microbial pathogens from meat and poultry products. The use of doses ≤ 1.0 kGy for the phytosanitary treatment of fruits and vegetables in international trade is the fastest growing market sector.

These doses are a balanced compromise between what is necessary for obtaining desired effects from the irradiation treatment and what could be tolerated by the product without the occurrence of side effects and sensory changes or in nutritional value of the treated product. Too high a dose can alter the organoleptic properties (development of odor and/or losses color and firmness) in foods with high moisture content.

Plastic packaging is widely used in products that undergo either the ≤ 1.0 kGy or the ≤ 10 kGy dose scenarios.

The US Food and Drug Administration (FDA) has required labeling of irradiated food products since 1966. A special label is required on irradiated foods, including the international symbol of irradiation, known as a "Radura", as shown in Fig.3, and a statement indicating that the food was treated with irradiation.

Fig.3. The label of irradiated food (“Radura”) [45].

The use of irradiation may also overcome the main drawback associated with conventional sterilization techniques that is the generation of liquid by-products. Gamma, electron beam, X-ray, ultraviolet irradiation, and plasma sterilization processes are chemical free, fast and safe approaches, applicable to a wide range of packaging materials and do not result in any residues [46]. The influence of gas humidity on the inactivation efficiency of a low temperature gas plasma has been demonstrated [46-49].

Irradiation can cause changes to a packaging material that might affect its integrity and functionality as a barrier, such as to chemical or microbial contamination. In addition to the base polymers, additives, such as antioxidants and stabilizers, are also of concern with regard to their radiolysis products (RPs). Such additives are prone to break down or degrade during polymer irradiation processing. During irradiation, they degrade preferentially over the polymer and could yield significant levels of RPs which could migrate into the food. Due to the possible occurrence of radiolysis products resulting from scissioning or crosslinking of polymers, as well as from the reactions of additives (antioxidants, stabilizers, *etc*.), the migration of additives and RPs must be evaluated in any pre-market safety assessment prior to their commercial use.

7. PREPARATION AND RADIATION MODIFICATION OF POLYMER NANOCOMPOSITES FOR FOOD PACKAGING USE

Biopolymers films (methyl cellulose (MC), chitosan and alginate) containing nanocrystalline cellulose (NCC) were gamma irradiated to between 2 and 25 kGy. These biopolymer films gained strength below a 5 kGy dose [50]. Monomer grafting onto the biopolymers was carried out in order to improve the NCC-biopolymer compatibility. Two monomers (trimethylolpropane trimethacrylate (TMPTMA) and 2-hydroxyethyl methacrylate (HEMA)) were grafted using gamma radiation at 5 to 25 kGy doses. These monomers were successfully grafted onto the biopolymers and NCC. The grafted films showed excellent mechanical properties.

NCC and carbon nanotubes (CNT) were also incorporated into polycaprolactone-based films made by compression molding. These films with 0.02% CNT were exposed to gamma irradiation from 5 to 25 kGy. The tensile strength and barrier properties of the films improved significantly after irradiation [50].

Alginate (95% alginate + 5% NCC) films were made from an aqueous alginate solution (3% w/w) [50] and were exposed to gamma radiation from 2 to 25 kGy doses. Irradiation improved the strength of the films significantly, as shown in Fig.4. A 10 kGy dose was found optimal [50].

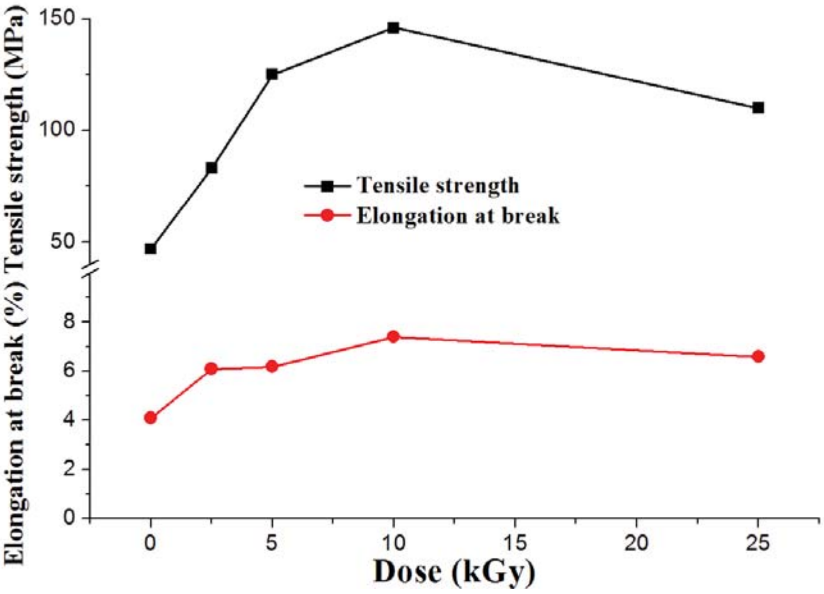


Fig.4. Effect of gamma radiation on the tensile strength and elongation at break of alginate films containing 5% NCC. (Adapted from Ref. [50]).

2-hydoxyethyl methacrylate and trimethylolpropane trimethacrylate monomers were grafted onto methyl cellulose and NCC-based films using gamma radiation to improve the NCC-MC compatibility. At a 10 kGy dose, HEMA reacted with MC and significantly improved the puncture strength of the films [50].

Gamma irradiation was also used to produce nano silver metal and graphene nano-sheets (GR) by the reduction of silver ions and graphene oxide (GO) [51]. This might be useful in producing biologically active packaging films. Chitosan/GO nanocomposites possess significantly improved physical properties, including mechanical, electrical conductivity, and structural stability when compared with pure chitosan [51].

Chitosan was immobilized (covalently attached) on a corona-treated polyethylene film surface by means of coupling agents 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS). The EDC coupling agent is used to couple carboxyl groups to primary amines [21, 52].

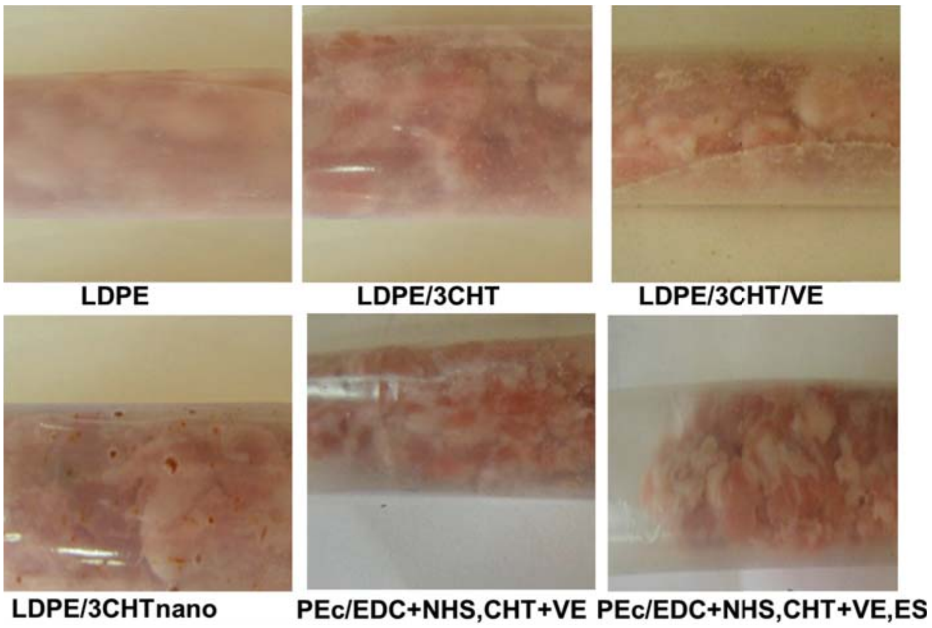


Fig.5. Microscopically aspects of the minced poultry cuts packed in films of LDPE grafted chitosan (CHT) after plasma activation, containing vitamin E (VE) and coated by electrospinning technique (ES). (Adapted from Refs. [53, 54]).

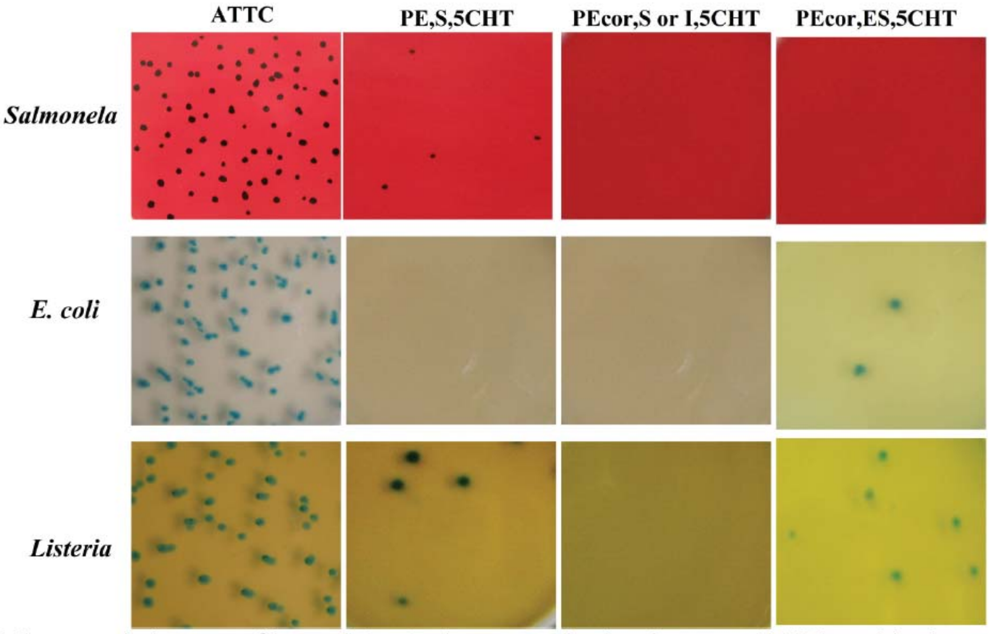


Fig.6. Microscopic images of bacterial colonies grown in the absence (ATCC) and in the presence of PE films coated with chitosan (CHT) by spreading (S) or electrospinning (ES) technique. (Adapted from Refs. [53, 54]).

Chitosan and vitamin E were grafted onto low density polyethylene films and shown to be effective in protecting poultry cuts, as shown in Fig.5, and in the inhibition of growth of both gram-positive and gram-negative bacteria, as shown in Fig.6 [53, 54].

Montmorillonite (MMT) was used as nano-filler to improve the properties of PLA (barrier and mechanical properties) [55]. MMT is hydrated alumina-silicate layered clay consisting of edge-shared octahedral sheets of aluminum hydroxide between two silica tetrahedral layers. MMT is relatively inexpensive and a widely available natural clay derived from volcanic ash and rocks. To

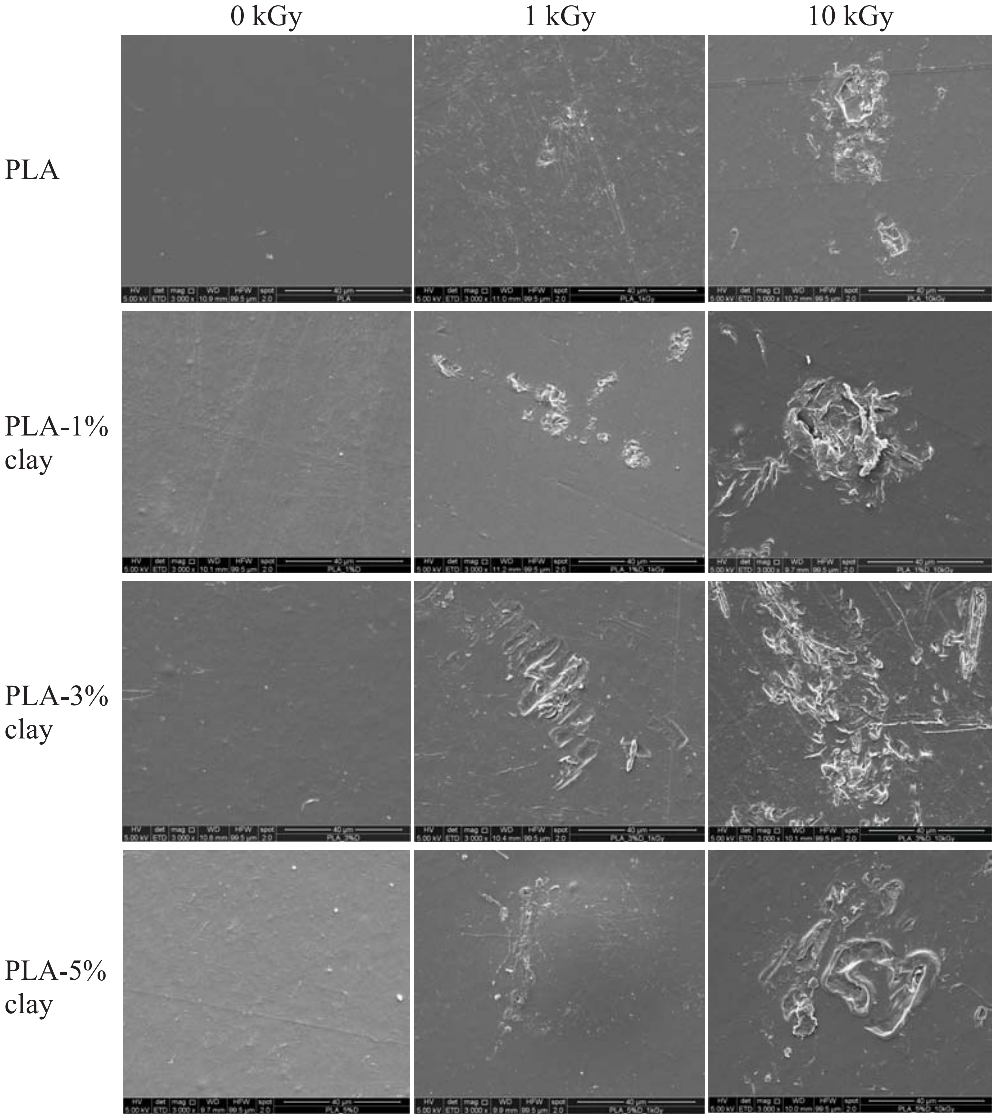


Fig.7. SEM (3000x magnification) of film surfaces of nanocomposites of PLA at 1, 3 and 5% by weight of clay irradiated at 1 and 10 kGy [55].

make the nanoparticles more homogeneous in the polymer matrix, MMT was modified by substituting the inorganic cations of the MMT with organic ammonium ions. Such films were designed for use with food that would be processed using electron beam technology for shelf life extension, phytosanitary treatment and pathogen elimination. Nanocomposite films were prepared at 1, 3 and 5% by weight of clay and exposed to electron beam doses of 1 and 10 kGy. The rationale for choosing these specific doses was that (as mentioned above) 1 kGy is approved by the US FDA for use on all fresh produce in the United States to extend the shelf life of fruits and vegetables. Thus, it was decided that this should be a target dose. Given the high market value for fresh produce and since biopolymers can serve as the packaging materials for fruit- and vegetable-based healthy food products sold in vending machines and for pediatric cancer patients, the maximum dose that was used was 10 kGy. This dose is at the upper limit for all foods that can be treated with irradiation in the US. The results of WAXD, TEM, ATR, SEM, DSC, TGA, tensile properties and barrier properties investigation before and after electron beam irradiation at 1 and 10 kGy show that the extrusion and subsequent calendaring used to make the films was able to create a homogeneous dispersion of the filler in the organic matrix, with a relevant intercalation of PLA into the clay galleries. PLA properties are influenced by the addition of clay and by electron beam irradiation. After electron beam exposure, samples showed some surface irregularities, increases in glass transition temperature, T_g, and in Young's modulus, and a decrease in oxygen permeability. These results were attributed to the presence the clay which creates a path for oxygen migration through the film, to crosslinking following the electron beam exposure, and to increases in crystallinity following the addition of the clay and the use of electron beam processing, as shown in Fig.7. These results lead to the conclusion that the PLA-based nanocomposites not only offer improved barrier and mechanical properties with respect to the PLA itself, but these nanocomposite materials can be customized for different applications that are needed in the food processing industry [55, 56].

8. SUMMARY AND FUTURE TRENDS

Packaging is an integral part of the modern food supply chain. It helps protect food, facilitate storage, transport and distribution. The use of nanotechnology can affect all of the packaging functions and also increase sustainability. Improved nano-packaging generally achieved with the incorporation of few percent of commercial nanoparticles in a polymeric binder results in several improvements starting from a decrease in permeability of gases and aroma and also allowing the food to have a longer shelf life.

Food processors prefer that food be prepackaged in the final packaging form. Irradiation of prepackaged food can prevent recontamination and facilitate prompt shipment to the market after irradiation.

There are several reasons for using irradiation in food processing:

- Health reasons: The Centers for Disease Control and Prevention (CDC) estimates that 48 million people/year got sick and 3000 deaths occurred in 2011 due to foodborne diseases (USA); foodborne illnesses are estimated at more than 11 million episodes/year.
- Health/economic reasons: The World Health Organization (2011) has underlined that because of growing global trade the world population has become more vulnerable to outbreaks of disease caused by contaminated food. Food poisoning outbreaks cause immense economic burdens because of the costs of food recalls and medical treatments. Post-process contamination caused by product mishandling and faulty packaging is reported to be responsible for about 2/3 of all microbiologically related recalls in USA. More than 40% of crops are destroyed each year due to pests and mold. Preventing this loss could feed 3 billion of people.
- Ethical: Recent reports by FAO (2009, 2011 and 2013) state that food availability, abundance and safety are under threat and that by 2050 global production of safe and nutritious food must increase by 70% to feed the growing world population. A huge amount of food (~40%, ~1.3 billion tons/year) is lost between the stages of production and consumption.

  Controlling pathogens in food products is very important. Improving yield is only one aspect of increasing food supply. It is equally important to conserve and protect what has been produced. On the way from producer to consumer, if foods products (plants and animals) are not handled and packed with care, they are prone to contamination from pathogenic microorganisms, causing additional food loss and concerns over food safety.
- Environmental: Food loss and waste have many negative economic and environmental impacts. Economically, they represent a wasted investment that can reduce farmers' incomes and increase consumers' expenses. Environmentally, food loss and waste inflict a host of issues, including unnecessary greenhouse gas emissions and inefficiently used water and land, which in turn can lead to a diminished natural ecosystem and the services it provides.

The possibilities and opportunities that can be had when irradiation is combined with nanotechnology have been explored. This convergence of technologies is useful and acceptable. This combination has the potential to enhance efficiency, reduce energy consumption, to reduce waste, and to facilitate recycling and reuse. Nanotechnologies used for active packaging and irradiation, when combined, present an opportunity to feed world's growing population by increasing food availability and minimizing food waste.

Several questions are still open and need to be studied:

- Research has shown that the irradiation of prepackaged food causes some chemical and physical changes in plastic packaging materials. These changes depend on a wide variety of factors including irradiation dose, temperature, oxygen availability, chemical/physical characteristics of the polymer. These changes are, in general, induced crosslinking and scissioning (degradation). Irradiation may also have radiolytic impact on the food with random production of assorted free radicals and unwanted chemicals that could possibly affect toxicity, texture, flavor and odor. Irradiation is intended to kill harmful organisms, and the technical problem is to do this through the polymer packaging (the food is prepacked) without harmful radiolytic impact either on the desired properties of the polymer (permeability, useful mechanical properties) or the food itself.
- Food could potentially become contaminated with radiolytic products formed in the packaging material when they are irradiated in contact with food. The possible migration of nanoparticles into the food must be taken into account. This may lead to a safety concern and, therefore, testing of packaging materials after exposure to irradiation is an integral part of any pre-market safety assessment of packaging materials when irradiated in contact with food. This is critical to the success of irradiation technology for prepacked food. All factors that are involved with the radiation response of polymers used for packaging, such as stability, and radiolytic products and nanoparticle migration, should be examined.

The controlled combination of these two innovative technologies, irradiation and nanotechnology, can bring significant improvement and contribute ensuring worldwide food quality, quantity and safety.

Acknowledgments

The authors acknowledge the financial support given by the Erasmus+ Programme through research project 2014-1-PL01-KA203-003611 and the International Atomic Energy Agency (IAEA) through research projects in the framework of the thematic area "Application of radiation technology in development of advanced packaging materials for food products" 2012-2016.

REFERENCES

[1]. Robertson, G.L. (2012). *Food packaging: Principles and practice* (3rd ed.). Boca Raton: CRC Press.

[2]. Lagarón, J.-M. (2011). *Multifunctional and nanoreinforced polymers for food packaging*. Cambridge: Woodhead Publishing Materials.

[3]. Lagaron, M., Ocio, M.J., & Lopez-Rubio, A.J. (2012). *Antimicrobial polymers*. New Jersey: John Wiley & Son.

[4]. Yam, K.L., & Lee, D.S. (Eds.). (2012). *Emerging food packaging technologies: Principles and practice*. Cambridge: Woodhead Publishing Limited. (Woodhead Publishing Series in Food Science, Technology and Nutrition No. 230).

[5]. Silvestre, C., & Cimmino, S. (2013). *Ecosustainable polymer nanomaterials for food packaging.* Boca Raton, FL: CRC Press.

[6]. Alavi, S., Thomas, S., Sandeep, K.P., Kalarikkal, N., Varghese, J., & Yaragalla, S. (2014). *Polymers for packaging applications*. Boca Raton: CRC Press.

[7]. Ozdemir, M., Yurteri, C.U., & Sadikoglu, H. (1999). Physical polymer surface modification methods and applications in food packaging polymers. *Crit. Rev. Food Sci. Nutr.*, *39*, 457-477.

[8]. Ozdemir, M., Yurteri, C.U., & Sadikoglu, H. (1999). Surface treatment of food packaging polymers by plasmas. *Food Technol.*, *53*, 54-58.

[9]. Schneider, J., Akbar, M.I., Dutroncy, J., Kiesler, D., Leins, M., Schulz, A., Walker, M., Schumacher, U., & Stroth, U. (2009). Silicon oxide barrier coatings deposited on polymer materials for applications in food packaging industry. *Plasma Process. Polym.*, *6*, S700-S704.

[10]. Przybytniak, G., Kornacka, E.M., Mirkowski, K., Walo, M., & Zimek, Z. (2008). Functionalization of polymer surfaces by radiation-induced grafting. *Nukleonika*, *53*(3), 89-95.

[11]. Poncin-Epaillard, F., Chevet, B., & Brosse, J.-C. (1994), Reactivity of a polypropylene surface modified in a nitrogen plasma. *J. Adhes. Sci. Technol.*, *8*(4), 455-468.

[12]. Yasuda, H., Lamaze, C.E., & Sakaoku, K. (1973). Effect of electrodeless glow discharge on polymers. *J. Appl. Polym. Sci.*, *17*(1), 137-152.

[13]. Hansen, R.H., Pascale, J.V., De Benedictis, T., & Rentzepis, P.M. (1965). Effect of atomic oxygen on polymers. *J. Polym. Sci. A*, *3*(6), 2205-2214.

[14]. Medard, N., Soutif, J.C., & Poncin-Epaillard, F. (2002). Characterization of CO_2 plasma-treated polyethylene surface bearing carboxylic groups. *Surf. Coat. Technol.*, *160*, 197-205.

[15]. Appendini, P., & Hotchkiss, J.H. (2002). Review of antimicrobial food packaging. *Innov. Food Sci. Emerg. Technol.*, *3*, 113-126.

[16]. Buonocore, G.G., Sinigaglia, M., Corbo, M.R., Bevilacqua, A., La Notte, E., & Del Nobile, M.A. (2004). Controlled release of antimicrobial compounds from highly swellable polymers. *J. Food Protect.*, *67*, 1190-1194.

[17]. Fernandez-Gutierrez, S.A., Pedrow, P.D., Pitts, M.J., & Powers, J. (2010). Cold atmospheric-pressure plasmas applied to active packaging of apples. *IEEE Trans. Plasma Sci.*, *38*, 957-965.

[18]. Ghanem, A., & Ghaly, A. (2004). Immobilization of glucose oxidase in chitosan gel beads. *J. Appl. Polym. Sci.*, *91*, 861-866.

[19]. Mastromatteo, M., Lecce, L., De Vietro, N., Favia, P., & Del Nobile, M.A. (2011). Plasma deposition processes from acrylic/methane on natural fibres to control the kinetic release of lysozyme from PVOH monolayer film. *J. Food Eng.*, *104*, 373-379.

[20]. Misra, N.N., Ziuzina, D., Cullen, P.J., & Keener, K.M. (2012). Characterization of a novel cold atmospheric air plasma system for treatment of packaged liquid food products. *Trans. ASABE*, *56*(3), 1011-1016.

[21]. Pâslaru, E., Fras Zemljic, L., Bračič, M., Vesel, A., Petrinić, I., & Vasile, C. (2013). Stability of a chitosan layer deposited onto a polyethylene surface. *J. Appl. Polym. Sci.*, *130*(4), 2444-2457.

[22]. Joerger, R.D., Sabesan, S., Visioli, D., Urian, D., & Joerger, M.C. (2009). Antimicrobial activity of chitosan attached to ethylene copolymer films. *Packag. Technol. Sci.*, *22*(3), 125-138.

[23]. Nobile, M.A., Cannarsi, M., Altieri, C., Sinigaglia, M., Favia, P., Iacoviello, G., & D'Agostino, R. (2004). Effect of Ag-containing nano-composite active packaging system on survival of *Alicyclobacillus acidoterrestris*. *J. Food Sci.*, *69*, E379-E383.

[24]. Popelka, P., Luptakova, O., Marcincak, S., Nagy, J., Mesarcova, L., & Nagyova, A. (2012). The effect of glaze and storage temperature on the quality of frozen mackerel fillets. *Acta Vet. Brno*, *81*, 397-402.

[25]. Vartiainen, J., Ratto, M., & Paulussen, S. (2005). Antimicrobial activity of glucose oxidase immobilized plasma-activated polypropylene films. *Packag. Technol. Sci.*, *18*, 243-251.

[26]. Zhang, W., Chu, P.K., Ji, J., Zhang, Y., Ng, S.C., & Yan, Q. (2006). Surface antibacterial characteristics of plasma-modified polyethylene. *Biopolymers*, *83*, 62-68.

[27]. Connolly, J., Valdramidis, V.P., Byrne, E., Karatzas, K.A., Cullen, P.J., Keener, K.M., & Mosnier, J.P. (2013). Characterization and antimicrobial efficacy against *E. coli* of a helium/air plasma at atmospheric pressure created in a plastic package. *J. Phys. D: Appl. Phys.*, *46*, 035401.

[28]. Chiper, A.S., Chen, W., Mejlholm, O., Dalgaard, P., & Stamate, E. (2011). Atmospheric pressure plasma produced inside a closed package by a dielectric barrier discharge in Ar/CO_2 for bacterial inactivation of biological samples. *Plasma Sources Sci. Technol.*, *20*, 10.

[29]. Rod, S.K., Hansen, F., Leipold, F., & Knochel, S. (2012). Cold atmospheric pressure plasma treatment of ready-to-eat meat: Inactivation of *Listeria innocua* and changes in product quality. *Food Microbiol.*, *30*, 233-238.

[30]. Suwanmala, P., Hemvichian, K., & Kangsumrith, W. (2014). Development of natural and synthetic polymers as suitable packaging materials for food products sterilized by radiation processing. In *Report of the 2nd RCM on Application of Radiation Technology in Development of Advanced Packaging Materials for Food Products, 8 to 12 September 2014, Bejaia, Algeria.* Vienna: IAEA. Retrieved March 15, 2016, from http://www-naweb.iaea.org/napc/iachem/working_materials/TR-RCM2-Oct14.pdf.

[31]. Parparita, E., Zaharescu, T., Darie, R.N., & Vasile, C. (2015). Biomass effect on gamma-irradiation behavior of some polypropylene biocomposites. *Ind. Eng. Chem. Res.*, *54,* 2404-2413.

[32]. Tkavc, T., Petrinič, I., Luxbacher, T., Vesel, A., Ristić, T., Fras-Zemljič, L. (2014). Influence of O_2 and CO_2 plasma treatment on the deposition of chitosan onto polyethyleneterephthalate (PET) surfaces. *Int. J. Adhes. Adhes.*, *48*, 168-176.

[33]. Lei, J., Yang, L., Zhan, Y., Wang, Y., Ye, T., Li, Y., Deng, H., & Li, B. (2014). Plasma treated polyethylene terephthalate/polypropylene films assembled with chitosan and various preservatives for antimicrobial food packaging. *Colloids Surface B*, *1*(114), 60-66.

[34]. Pankai, S.K., Bueno-Ferrer, C., Misra, N.N., Milosavljević, V., O'Donnell, C.P., Bourke, P., Keener, K., & Cullen, P.J. (2014). Applications of cold plasma technology in food packaging. *Trends Food Sci. Technol., 35*, 5-17.

[35]. Abad, L.V., Cabalar, P.J.E., & Laurio, C.D. (2014). Effects of gamma irradiation on commercial food packaging films. In *Report of the 2nd RCM on Application of Radiation Technology in Development of Advanced Packaging Materials for Food Products, 8 to 12 September 2014, Bejaia, Algeria.* Vienna: IAEA. Retrieved March 15, 2016, from http://www-naweb.iaea.org/napc/iachem/working_materials/TR-RCM2-Oct14.pdf.

[36]. Moura, E.A.B., Ortiz, A.V., Wiebeck, H., Paula, A.B.A., Camargo, A.O., & Silva, L.G.A. (2009). Effects of ionizing radiation on commercial food packaging. In *Controlling of degradation effects in radiation processing of polymers* (pp. 13-39). Vienna: IAEA. (IAEA-TECDOC-1617). Retrieved March 16, 2016 from http://www-pub.iaea.org/MTCD/publications/PDF/te_1617_web.pdf.

[37]. Güven, O. (2009). The use of radiation-induced degradation in: II. Controlling molecular weights of polysaccharides. In *Controlling of degradation effects in radiation processing of polymers* (pp. 174-184). Vienna: IAEA. (IAEA-TECDOC-1617). Retrieved March 16, 2016 from http://www-pub.iaea.org/MTCD/publications/PDF/te_1617_web.pdf.

[38]. Jordá-Vilaplana, A., Fombuena, V., García-García, D., Samper, M.D., & Sánchez--Nácher, L. (2014). Surface modification of polylactic acid (PLA) by air atmospheric plasma treatment. *Eur. Polym. J.*, *58*, 23-33.

[39]. Vasile, C., Pâslaru (Stoleru), E., Sdrobiș (Irimia), A., Zaharescu, T., Ioanid, G.E., Pricope, G.C., & Munteanu, B.S. (2014). Comparative study on the effect of γ-irradiation and cold plasma exposure on the various polymeric substrates modified to impart multifunctional properties for active/bioactive food packaging materials. In *Report of the 2nd RCM on Application of Radiation Technology in Development of Advanced Packaging Materials for Food Products, 8 to 12 September 2014, Bejaia, Algeria.* Vienna: IAEA. Retrieved March 15, 2016, from http://www-naweb.iaea.org/napc/iachem/working_materials/TR-RCM2-Oct14.pdf.

[40]. Labuza, T.P., & Breene, W.M. (1989). Applications of "active packaging" for improvement of shelf-life and nutritional quality of fresh and extended shelf-life foods. *J. Food Process. Pres.*, *13*(1), 1-69.

[41]. Ayhan, Z., Cimmino, S., Esturk, O., Duraccio, D., Pezzuto, M., & Silvestre, C. (2015). Development of films of novel polypropylene based nanomaterials for food packaging application. *Packag. Technol. Sci.*, *28*(7), 589-602.

[42]. Silvestre, C., Duraccio, D., & Cimmino, S. (2011). *Food packaging based on polymer nanomaterials. Prog. Polym. Sci.*, *36*, 1766-1782.

[43]. Cimmino, S., Duraccio, D., Marra, A., Pezzuto, M., Romano, I., & Silvestre, C. (2015). Effect of compatibilisers on mechanical, barrier and antimicrobial properties of iPP/ZnO nano/microcomposites for food packaging application. *J. Appl. Packag. Res.*, *7*(2), 108-127.

[44]. Appleby, J., & Banks, A.J. (1906). *Improvements in or relating to the treatment of food, more especially cereals and their products*. British Patent No. 1609.

[45]. Shafiur Rahman, M. (2007). *Handbook of food preservation* (Second edition). Boca Raton: CRC Press.

[46]. Muranyi, P., Wunderlich, J., & Heise, M. (2008). Influence of relative gas humidity on the inactivation efficiency of a low temperature gas plasma. *J. Appl. Microbiol.*, *104*, 1659.

[47]. Muranyi, P., Wunderlich, J., & Langowski, H.C. (2010). Modification of bacterial structures by a low temperature gas plasma and influence on packaging material. *J. Appl. Microbiol.*, *109*, 1875.

[48]. Donegan, M., Milosavljević, V., & Dowling, D.P. (2013). Activation of PET using an RF atmospheric plasma system. *Plasma Chem. Plasma Process.*, *33*(5), 941-957.

[49]. Komolprasert, V. (2007). Packaging for non thermal processing of food. In J.H. Han (Ed.), *Packaging for foods treated with ionizing radiation* (pp. 87-116). Ames, IA: Blackwell Publishing.

[50]. Lacroix, M., Salmieri, S., Khan, A., Huq, T., Criado, P., Becher, D., Khan, R.A., & Ibrahim, H. (2011). Using gamma irradiation for grafting and/or crosslinking of natural polymers for the fabrication of active beads and packaging films based on nanocellulose. In *Radiation curing of composites for enhancing the features and utility in health care and industry* (pp. 45-58). Vienna: IAEA. (IAEA-TECDOC-1764).

[51]. AbdEl-Rehim, H.A., Hegazy, E-S.A., & Raafat, A. (2011). Radiation processing of active biodegradable green nano composite materials for packaging purposes. In *Report of the 1st RCM on Radiation Curing of Composites for Enhancing the Features and Utility in Health Care and Industry, Vienna, 18-22 July 2011* (pp. 62-78). Vienna: IAEA.

[52]. Stoleru (Paslaru), E., Tsekov, Y., Kotsilkova, R., Ivanov, E., & Vasile, C. (2015). Mechanical behavior at nano-scale of chitosan-coated PE surface. *J. Appl. Polym. Sci.*, *132*(31), 4344-4356.

[53]. Darie, R.N., Sdrobiş, A., Pâslaru, E., Pricope, G., Baklavaridis, A., Munteanu, S.B., Zuburtikudis, I., & Vasile, C. (2014). Effectiveness of chitosan as antimicrobial agent in LDPE/CS composite films as poultry minced meat packaging materials. *Cell. Chem. Technol.*, *48*(3-4), 325-336.

[54]. Munteanu, B.S., Pâslaru, E., Fras Zemljic, L., Sdrobiş, A., Pricope, G.M., & Vasile, C. (2014). Chitosan coatings applied to polyethylene surface to obtain food-packaging materials. *Cell. Chem. Technol.*, *48*(5-6), 565-575.

[55]. Salvatore, M., Marra, A., Duraccio, D., Shayanfar, S., Pillai, S.D., Cimmino, S., & Silvestre, C. (2016). Effect of electron beam irradiation on the properties of polylactic acid/montmorillonite nanocomposites for food packaging applications. *J. Appl. Polym. Sci.*, *133*(2), 42219.

[56]. Silvestre, C., Pezzuto, M., Duraccio, D., Marra, A., & Cimmino, S. (2014). Exploiting nanotechnology and radiation technologies to develop new eco-sustainable nanomaterials for food packaging suitable for sterilization by irradiation. In *Radiation processed materials in products from polymers for agricultural applications* (pp. 99-104). Vienna: IAEA. (IAEA-TECDOC-1745).

Chapter 21

APPLICATION OF RADIATION TECHNOLOGIES FOR THE MODIFICATION OF ELECTRONIC DEVICES

Zbigniew Zimek
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

Radiation can change the properties of semiconductor devices and electronic circuits used in different fields as both on the ground and in space. This may be due to specific influences of a radiation environment on certain parameters of electronic components as when used in nuclear power plants, from particle accelerators and other equipment based on nuclear technology as used in medicine, science and industry. A terrestrial radiation environment is present because of the existence of naturally occurring radioactive elements and cosmic rays. Current leakage can increase or a threshold voltage shifted after electronic devices are exposure to a radiation environment. In general, semiconductors and the insulation materials of electronic devices can degrade or even be damaged under certain exposure conditions. The reliability of semiconductor devices exposed to ionizing radiation can be significantly affected. This is more important now because electronic devices are now much smaller and more complex.

The principal consequence of irradiation on electronic materials is radiation-induced effects (damages) of materials, which can disturb the functioning of the electronic devices made from these materials. These effects are related both to the properties of the irradiated material and to the type of irradiation. Research has focused on the development of new methods related to the hardening of electronic devices and to the improvement of their operation in radiation environments. Radiation-induced effects can also be used in the manufacture of electronic devices for intended modification of semiconductor materials and the properties of the final product.

There are different sources for ionizing radiation. Some originate in nature, whereas others are man-made. Ionizing radiation can be photons (electromagnetic quanta of gamma rays and X-rays) or particle beams (electron, ion or neutron beams). Accelerated electrons and ions, X-ray beams and thermal neutrons are produced by different types of equipment and are used for the modification of semiconductor material properties on an industrial scale. The worldwide semiconductor market has been estimated at US$147 billion, of which about 45% was shared by the USA and Japan [1].

2. IONIZING RADIATION-INDUCED EFECTS IN ELECTRONIC DEVICES

Accelerated electrons, ion beams, X-rays, cosmic rays and gamma rays transfer their energy by ejecting atomic electrons, which can then ionize other atoms in the absorbing material. Radiation-induced effects depend primarily on the absorbed dose and type of semiconductor material, and are less dependent on type of radiation. The irradiation of silicon crystals with high energy particles or gamma rays or X-ray results in the generation of electron-hole pairs (ionization, which can be recognized as a transitory damage) and of a variety of defects in the crystal lattice (displacement damage, which can be considered as permanent).

Figure 1 illustrates the radiation paths for electron, ion and photon beams in an irradiated semiconductor material. Heavy charged particles (ion beams) lose energy in small steps. Their well-defined short penetration range depends on ion energy and the target material properties. Ion beams may cause frequent atomic displacements, whereas electrons can generate only some. Gamma rays

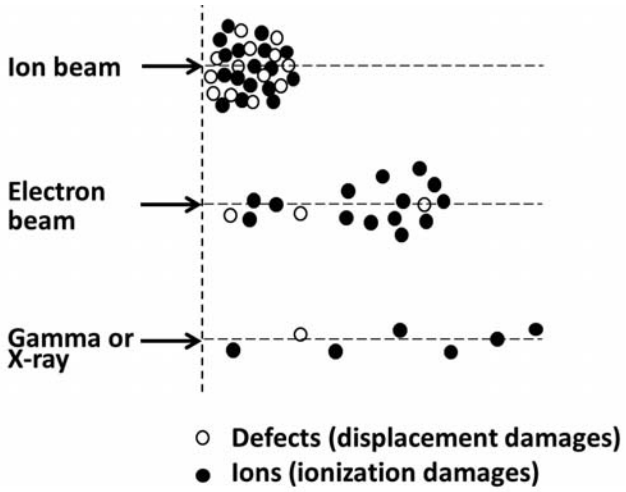


Fig.1. Radiation paths of electron and ion beams and gamma rays and X-rays in an irradiated semiconductor material.

and X-rays can generate rare atom displacements through the Compton effect. Ion beams can be also used to introduce impurities into the irradiated semiconductor material for certain electronic devices as well as to introduce dopants in substrates for state-of-art integrated circuit fabrication. The main advantages of ion implantation are: a low temperature process, precise dose, penetration depth control, possible implantation through thin layers of insulation, and a short process time.

The cumulative effects of semiconductor irradiation may occur during the entire lifetime exposure of the device or irradiation can be an intended step during the manufacturing process. In the first case, the irradiation may lead to damage of the semiconductor device if the radiation level has reached its tolerance limits. The sensitivity of such failure depends also on the type of semiconductor device and its construction. Several other parameters are also important: temperature, dose rate, device polarity, surface doping, and type of radiation. In some specific cases, a single event caused by the energy deposition of a single particle may also lead to catastrophic failure of device's operation. Dose effects can be evaluated in relation to the energy deposited in the irradiated material (dose level). The energy absorbed in an irradiated material liberates charge carriers which diffuse or drift to a place where they are trapped. In general, this leads to unintended concentrations of charge and consequently creates parasitic electronic fields.

Displacement damages are usually described in terms of the particle fluence (particles/cm^2). An elastic collision can be responsible for ejecting an atom from its normal lattice position. Displacement damages depend on the energy transferred to the lattice atoms. Displacements are specific for the types of particles and particle's kinetic energy. The primary knock-on atom may cause a cascade of atomic displacements before coming to rest. Certain levels of displacement energy are needed to overcome the semiconductor lattice forces and allow the atom to move for more than one atomic distance away from its original site. The threshold energy for an atom displacement in semiconductors is: 27.5 eV for Ge and 25 eV for Si. Displacement damages alter the electronic properties of the semiconductor crystals.

The crystalline structure of a semiconductor material can be modified by inelastic and elastic collisions which may occur during irradiation processing. Figure 2 shows the possible atom displacements from their original crystalline position. A displaced atom becomes an interstitial, thus its previous position is called a vacancy. Displaced atoms (interstitial) and vacancies are called a Frenkel pair. Vacancies and interstitials are mobile at sufficiently high temperatures and can be annealed by recombination. Damages may serve as charge--carrier donors and traps. Displacement defects play a major role in the reduction of the time interval needed for the transition between conduction and non-conduction states at semiconductor junctions. The presence of displacement effects in a semiconductor material is related to the reduction of a carrier lifetime. A carrier lifetime is defined as the average time it takes for a minority of the carriers to recombine.

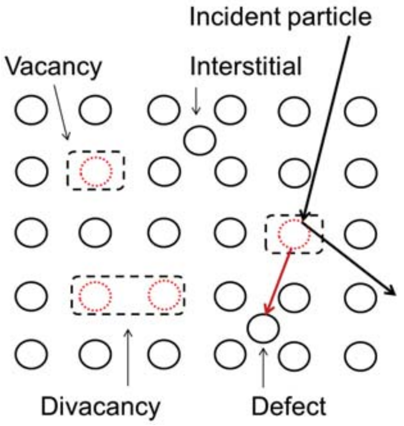


Fig.2. Defects created by atom displacement.

Displacement damages create trap levels, which help in transitioning electrons from valence to a conduction band. This leads to an increase of the reverse biased current. In the case of forward biased current, the trap level helps in the recombination of electrons and holes, which decreases the current. Traps that are close, either to the valence or conductive band, may capture charges (electrons and holes) and release them after a certain time. This leads to density variations of donors and acceptors. Ionization is a process that leads to the generation of ions by removing an electron from or adding an electron to a neutral atom. The principal result of ionization is the generation of electron-hole pairs within an irradiated material. Due to the specific configuration of energy levels, the radiation-induced effects in metals, semiconductors and insulators are quite different, as shown in Fig.3. Ionization-induced conductivity changes

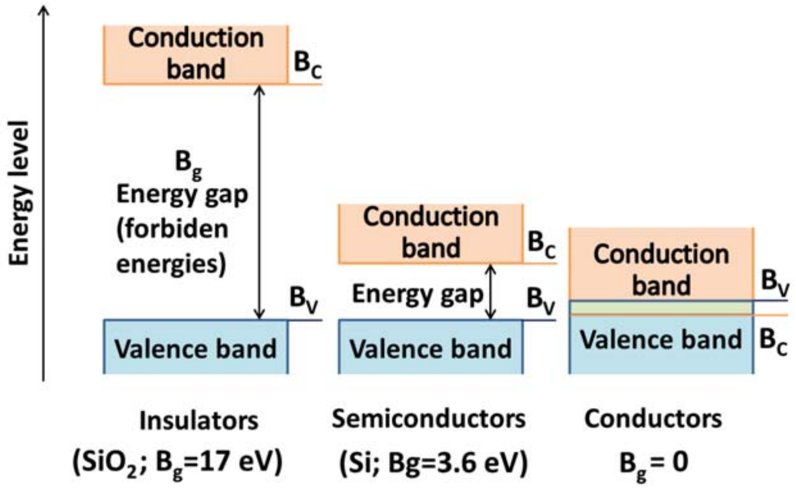


Fig.3. Energy band diagrams for insulators, semiconductors and conductors.

in metallic conductors are negligible. A quite different situation can be observed in irradiated semiconductors and insulators. The valence band in semiconductors and insulators is filled by electrons whereas conductive band is empty. A large number of electrons from the valence band can be excited to the conduction band because of irradiation. Time holes are produced in the valence band. Irradiation generates electron-hole pairs. Electron-hole pair generation energy amounts 2.8 eV for Ge and 3.6 eV for Si semiconductors. Since the direct recombination of electrons from conduction band with the vacancies in the valence band cannot happen, the electrons are free to drift through the irradiated material.

Electrons transferred to the conduction band can significantly increase the electrical conductivity of the semiconductor. Therefore ionizing radiation can modify certain electrical parameters of semiconductor devices, but also, in the extreme case, can ruin their performance and finally lead to the breakdown of the component or of a system.

Some semiconductor devices are more sensitive to radiation-induced ionization effects; some others are affected by a dominant radiation displacement damage. Permanent radiation damage can be observed only in the dielectric layers, like the gate oxide isolation in MOSFET (metal-oxide-semiconductor field-effect transistor) devices. When an electric field is present in the semiconductor material, part of the defect pairs do not recombine. Both electrons and holes start to drift in the electric field. Holes can be trapped in the defect centers inside the material, whereas electrons, having much higher mobility, can easily leave the material. In extreme cases, charges build up and defect activation may lead to degradation of the electronic device. If there is not an electric field, any unbalanced charges disappear due to recombination. The recombination process depends on the carrier lifetime and does not lead to material degradation.

Semiconductors of the n-type are characterized by electrical conduction made by the movement of electrons; whereas in p-type semiconductors, electrical conduction is mainly due to the movement of positive holes. In n-type semiconductors, the majority of carriers are electrons. In p-type semiconductors, the carriers are positively charged holes. A minority of carriers are responsible for carrying the lesser part of the current in a semiconductor.

In case of a p-n junction, the electric field separates electrons and holes. This leads to transient charging.

Semiconductor junctions are the basic components of diodes and more complex devices, as transistors and integrated circuits. They consist of p-type semiconductors where the majority of carriers are holes and n-type semiconductors where the majority of carriers are electrons, as show in Fig.4. A semiconductor junction is formed by direct contact between p- and n-type semiconductors which allows for the diffusion of charge carriers from one to another side of the contact. In this way, some of electrons are transferred from

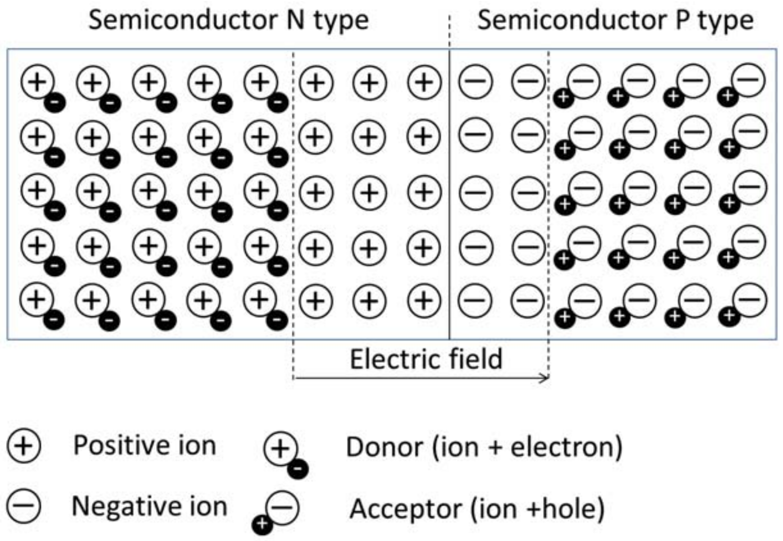


Fig.4. Semiconductor junction structure.

n- to p-type semiconductors; whereas holes in n-type semiconductors remain located on the same side of the junction. Thus narrow positive and negative charge barriers are formed indicating the appearance of an internal electrostatic electric field.

When the polarity of the battery is such that electrons are allowed to flow through the diode, the diode is said to be forward-biased. Conversely, when the battery is "backward" and the diode blocks current, the diode is said to be reverse-biased. A diode may be thought of as like a switch: "closed" when forward-biased and "open" when reverse-biased. A scheme of a diode is presented in Fig.5A. Different materials are used for the manufacture of p-n diodes: silicon, gallium-arsenide, silicon-carbide and others depending on how the device will be used.

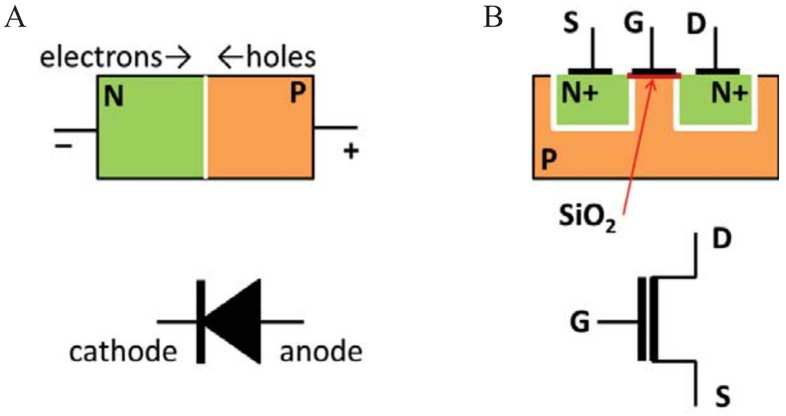


Fig.5. Schematic diagram of basic electronic devices: A – diode, B – MOSFET transistor (S – source, G – gate, D – drain, SiO_2 – gate insulator layer).

MOSFET transistors, as shown in Fig.5B, are also commonly used in electronic circuits. This device is very sensitive to the effects of the radiation environment because of the charge formation in the SiO_2 gate insulation layer. When the gate insulator is irradiated, free electrons and holes are created. These are then influenced by an applied electric field. Because of their mobility, electrons are able to move to the positive electrode. The holes move more slowly promoting the probability of getting trapped in the gate material. Trapped holes accumulate a charge which may significantly change a transistor's properties. A loss of drain control and transistor failure can be the result. Voltage-current properties of a transistor depend on the charge states in the gate insulator, which are determined by ionization damages. Discharging (a breakdown process) of a charged insulator is possible which may cause electrical damage of certain components of an electronic device.

3. RADIATION PROCESSING OF ELECTRONIC DEVICES

Semiconductors are used as a fundamental base for electronic components. Semiconductor devices are diodes, transistors, and integrated circuits and are used throughout computer and digital technology up to high power electronic devices, which are used to commutate high currents in power supply systems. There are a very broad range of uses for a variety of electronic devices with specific properties and technical specifications for each use. Some parameters for electronic devices, such as high switching speed (a reduction in the time interval between conduction and non-conduction states) or unified gain coefficient can be achieved by selective use of radiation processing. The semiconductor junction is usually described as a basic component of a diode. Diodes are the basic components of more complex devices, as transistors, FET (field effect transistors), thyristors and integrated circuits. A minority carrier's lifetime can be reduced by the introduction of efficient recombination centers. The recovery time for diodes and the switch off time for thyristors are directly proportional to the lifetime of minority carriers. Thus, all methods that lead to the shortening of the lifetime of minority carriers are used in the manufacturing of fast semiconductor devices. The generation of the recombination centers in the crystalline net of the silicon is the physical condition which shortens the lifetime of minority carriers. This may be achieved by introducing metallic impurities, like gold or platinum, into the silicon as a recombination centers of the semiconductor lattice. A similar effect can be obtained by the irradiation of the semiconductors with high energy elementary particles or photons. The irradiation process forms the primary and secondary defects in the crystalline net, and creates the effective recombination centers for minority carriers.

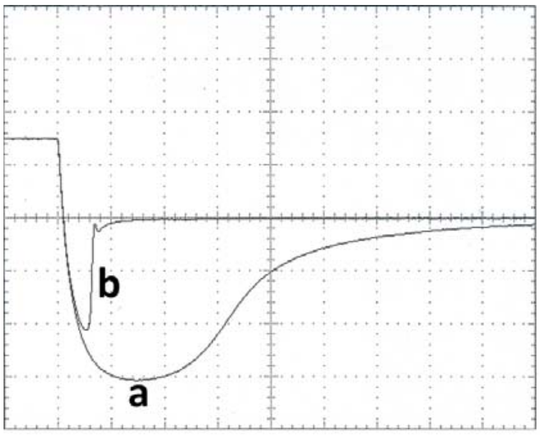


Fig.6. Current switching off characteristic of a diode: a – before irradiation, b – after electron beam treatment. Vertical scale: loading current – 2 A/div, horizontal scale: time – 1 μs/div.

The metal diffusion process is very sensitive to disturbances during fabrication procedure. High energy irradiation, in contrast, may be used for well controlled processing of high power diodes and of thyristors with known properties. The irradiation of semiconductor devices can also be performed in a final stage of the manufacturing process. An essential advantage of radiation processing is the ability to partially or totally remove the radiation effects by heating the samples. This can be very useful in the case of accidental overdosing. Electron beam (EB) irradiation was found to be the shortest, most useful and economic way for semiconductor processing.

Figures 6 and 7 show the loading current switching capabilities before and after electron beam irradiation for commercial semiconductor devices which were evaluated during experiment performed at the Institute of Nuclear Chem-

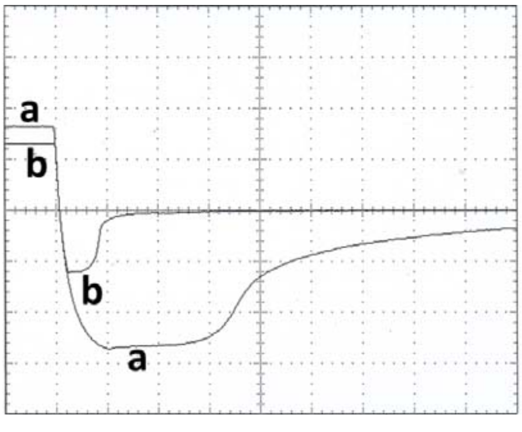


Fig.7. Thyristor current switching off characteristic: a – before irradiation, b – after electron beam treatment. Vertical scale: loading current – 2 A/div, horizontal scale: time – 1 μs/div.

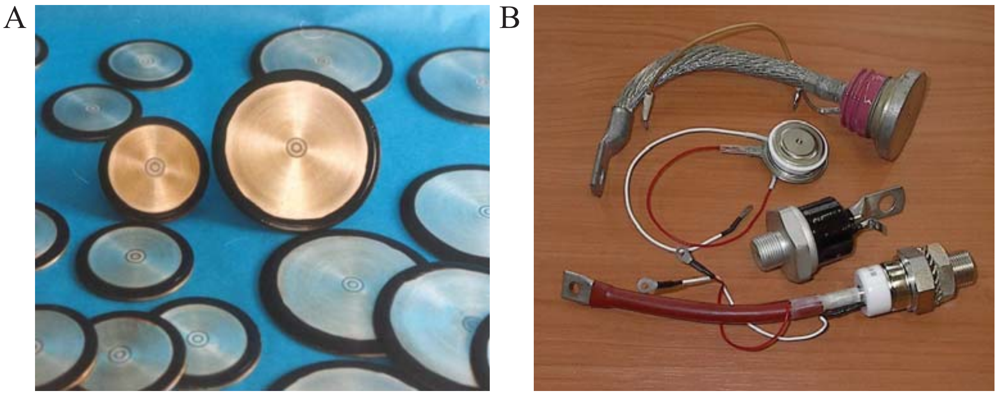


Fig.8. The general view of thyristor structures (A) and commercial power thyristors (B).

istry and Technology (INCT, Poland). Figure 8A shows the general view of a thyristor structure. Some commercial thyristors are shown in Fig.8B.

The dependence of the reverse recovery time (t_{rr}) as well as of the forward voltage drop (V_F) from a 10 MeV electron fluence (dose) on irradiated commercial diodes are presented in Fig.9 [2]. The minority carrier's lifetime and switching speed can be easily controlled by the fluence (dose) used in the irradiation process.

The major advantage of high energy electron irradiation is the depth of penetration of electrons in matter and the penetration into encapsulated semiconductor power devices. The possible high cost of radiation processing is compensated by a major improvement in semiconductor device performance and a simplification of the device manufacturing process. The following radiation-induced modifications of parameters of diodes and thyristor are possible:

- Shortening the recovery time of diodes and thyristors as a consequence of the shorter lifetime of minority carriers. This parameter depends on dose. Modifications are very effective but some saturation has been observed for

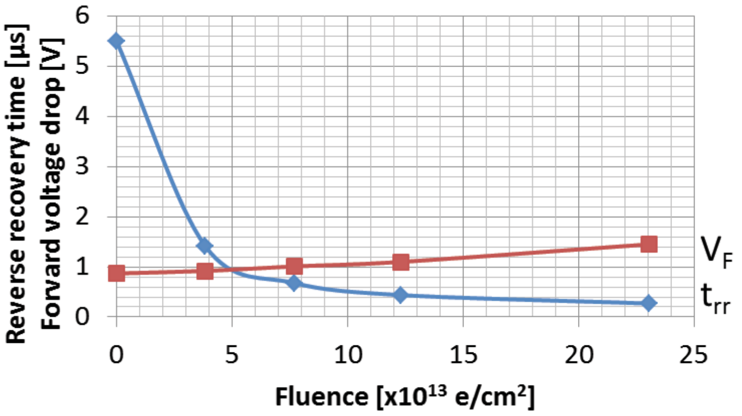


Fig.9. The relation between the fluence of 10 MeV electrons and reverse recovery time (t_{rr}) as well as forward voltage drop (V_F) of irradiated commercial diodes [2].

the high doses. It is quite common to reduce the switching-off time for thyristors by a factor of 3 and in parallel to reduce the diode's recovery time by approximately 10 times.

- An unfavorable fall of the load current has been observed (the increase of voltage in the conductive state) as a consequence of the decreasing lifetime and the average free diffusing distance of the carriers. This effect is much stronger if the voltage of the diode and silicon resistivity is higher after irradiation. A comparison of semiconductor devices properties after irradiation clearly shows advantages for the use of the radiation process for devices which can be used up to 1500 V.
- Radiation-induced defects in a silicon matrix are stable over a period of 40 years if the temperature of the semiconductor device does not exceed 125°C.

Figure 10 shows semiconductors packed for radiation processing at the INCT radiation facility that is equipped with an electron accelerator (beam energy – 10 MeV, beam power – 10 kW). The ratio between the price for a given performance level (higher unit price) and the unit cost of irradiation is, when using an electron beam, the highest for all radiation processing technologies used on a commercial scale. The price/cost ratio can be as much as 10 to 20 times of the irradiation cost.

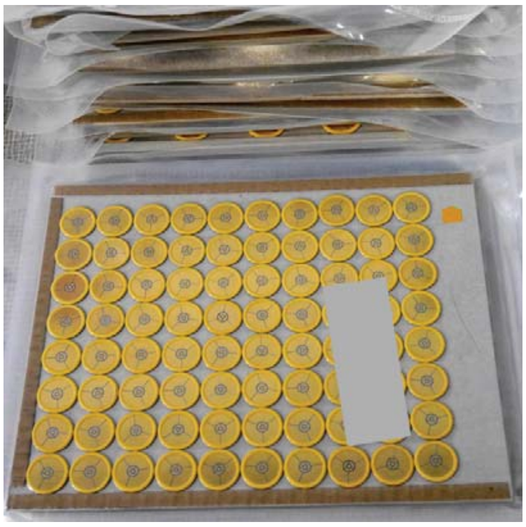


Fig.10. Semiconductors packed for radiation processing.

The large spread use of semiconductor devices containing doped gold or platinum impurities may lead to situation when a number of components do not meet required performance parameters. These components too can be improved by radiation processing.

Another important feature is related to the trimming process which is used after the radiation-induced modification of semiconductor devices. Significant reduction in the variations of certain semiconductor properties help to produce devices for parallel configurations. These devices require good matching of the reverse recovered charge or unification of the forward voltage drop [3].

The reduction of switching time of high power semiconductor devices may significantly reduce the thermal energy losses because in transit period the resistivity and the loading current are relatively high, capable of generating heat through resistance heating. Because of this effect, it was estimated that the Polish industry could save 32 GWh of power over a one year period. This would reduce the requirements for installed electrical power and generator plants by over 200 MW. The radiation modification of semiconductors on industrial scale was started in Poland over 40 years ago [4, 5].

Gamma irradiation gives similar effects as does electron beam processing but at significantly lower efficiency. Sometimes both electron and ion beam treatment methods are used to optimize certain properties (like switching characteristics). In such a case electron beam processing allows for the control of carrier lifetime in a material volume. Ion beam treatment, with limited penetration, can be used for precise changes of carrier lifetime in specific regions of the device. Electron doses ranging from 0.05 to 400 kGy and ion beam fluences (*e.g.* proton and helium) varying from 10^9 to 10^{13} ions/cm^2 are used. Exact irradiation conditions for certain types of semiconductor devices, like beam energy and dose rate, are confidential with each company.

4. DOSIMETRY BASED ON SEMICONDUCTOR SENSORS

Dosimetry plays an important role in nuclear research and in particular in radiation processing, where the absorbed dose should be established on a routine basis. The use of semiconductor devices, like Si diodes and MOSFET transistors, are recognized as one of innovative methods which can be used for dosimetry measurements as performed in the medical area at doses of 0.5 to 10 Gy and also in typical industrial irradiators where the absorbed dose can range from 10 Gy to 50 kGy [6]. One of the important features of the use of semiconductors in dosimetry measurements is simplicity and precise electrical readout.

The characterization of semiconductor devices as routine dosimeters revealed the possible influence of different environmental conditions on the final results [7]. A post-irradiation heat treatment protocol for stabilizing the dosimeter response is recommended. This is important in order to attain reliable dosimetry results and also to be able to read the dosimeter again at some future time. Semiconductor dosimetry is valid for both high activity gamma sources and for high energy, high power electron beam facilities.

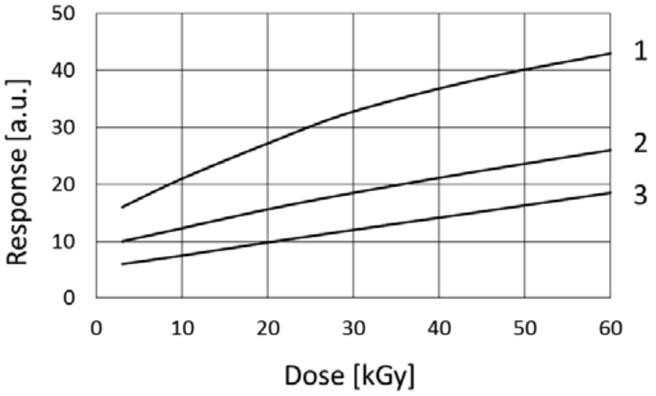


Fig.11. Calibration curves for transistor dosimetry system for cobalt-60 gamma rays: 1 – after irradiation; 2 – post-irradiated, after heating for 30 min at 100°C; 3 – post--irradiated, after heating for 30 min at 150°C [7].

The results presented in Figs.11 and 12 were obtained using commercially available, high voltage, fast switching n-p-n bipolar power transistors. A decrease in the charge carrier lifetime for these devices is proportional to the absorbed dose. The response of the transistor to irradiation was measured and compared with dose as absorbed in water according following reference dosimeter protocols.

Different dose responses of irradiated transistors were found for measurements performed just after irradiation, after heating for 30 min at 100°C and after heating for 30 min at 150°C. Significant differences between gamma and electron beam treatment were noted in the sensitivity of dose measurements and the ability to anneal irradiated semiconductor devices [8].

Experimental results obtained during the investigation of bipolar power transistors, which were tested as dosimeters, revealed that that they can be used

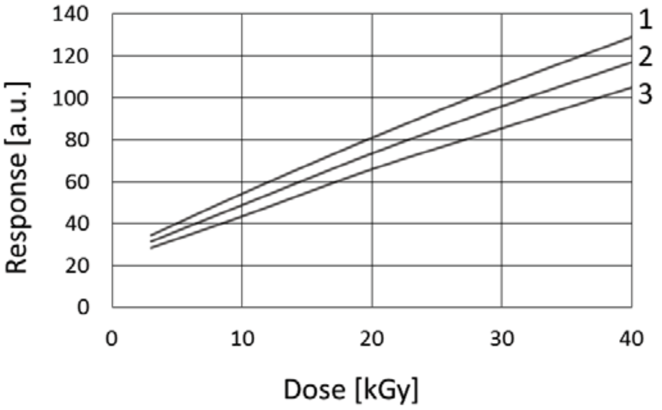


Fig.12. Calibration curves for transistor dosimetry system for 10 MeV electrons: 1 – after irradiation; 2 – post-irradiated, after heating for 30 min at 100°C; 3 – post-irradiated, after heating for 30 min at 150°C [7].

for routine dosimetry at gamma and accelerator facilities. However, each batch of transistors should be carefully evaluated because of variations in their response to irradiation. There is a limited dependence of transistor response to the temperature at which the measurements were made. A laboratory with a controlled temperature for ambient conditions should be used. The post-irradiation heat treatment protocol is recommended to stabilize the dosimeter response. This makes it possible to obtain reliable readouts of dosimeters in the future and were archived for months. The main advantages of using transistors for dosimetry are: low cost, a relatively inexpensive readout system, ease of use, and a very short time to perform dose measurements [9].

5. SUMMARY

Electron beam modification of semiconductor devices is based on the decrease of the lifetime of minority carriers after radiation treatment. To obtain suitable conditions for this process a number of defects are created in silicon crystals by high energy electrons. Certain irradiation conditions should be followed to obtain a compromise between decreasing carriers' lifetime, which leads to the faster switching properties, but at the same time reduces load current level. The major advantages of high energy electron beam use for the modification of the properties of electronic devices rely on the electron's depth of penetration into the matter and its generation of a uniform distribution of recombination centers. Because of this, a device's switching time can be tailored according to user needs even in finished or encapsulated power devices.

Electron beam processed fast switching power thyristors and diodes are used in a growing number of applications for which the long-term stability, the efficiency and energy savings semiconductor components are important and assured through competitive pricing. Power interruptions at data processing centers and at hospitals with life-support equipment are examples of the need for such power thyristors and diode devices, along with many other applications in metallurgy, mining, transportation, household uses and other areas. Electron beam technology does not require additional investment. The cost of using an existing electron beam facility can be melded into the total product cost. This can be quickly recovered because of the major improvement in devices and the simplification of the device manufacturing process.

The main factors (if not under control) that may cause the electronic component damage are: energy of the ionizing radiation, radiation flux and exposure time. Larger particles may cause higher damage due to their mass and cross section area. On the other hand, electromagnetic radiation (gamma rays, X-ray) requires a lot of energy to cause bulk damage in semiconductors. That is why X-ray inspection is rather safe for electronic devices.

The penetration of ionizing radiation through the silicon oxide layer formed on the semiconductor surface causes the buildup of a trapped charge in the insulator's layer. If the charge moves towards the SiO_2-Si interface, the basic characteristics of the semiconductor will be changed. Single radiation-induced effects are not recognized as permanent damage but have the potential to alter the microcode of certain devices and memory circuits.

The radiation processing technique, as compared to the introduction of metal impurities in semiconductors, offers: precision, reliability and reproducibility of required properties. Precise control of the concentration of defects that are generated provides more uniform electrical properties. Electron beam technology helps solve common diffusion problems present, when metal impurities are introduced into a semiconductor: non-uniform depth distribution of impurities and high leakage currents. The irradiation process is very flexible and can be used for the processing of raw semiconductor components and for final products as well as for the improvement of the device properties. The stability of radiation-induced defects is assured for over a period of 40 years, if the temperature of the semiconductor device does not exceed 125°C, which is close to upper limit of junction temperature during normal device operation. There is also the possibility to control and remove radiation-induced defects through a proper annealing process.

REFERENCES

[1]. Tagawa, S., Kashiwagi, M., Kamad, T., Sekiguchi, M., Hosobuchi, K, Tominaga, H., Ooka, N., & Makuchi, K. (2002). Economic scale of utilization of radiation (I): Industry. *Nucl. Sci. Tech.*, *39*, 9, 1002-1007.

[2]. Quanfeng, L., Huiyong, Y., Taibin, D., & Peiqing, W. (2001). Irradiation of semiconductor devices using 10 MeV travelling wave electron linear accelerator. *Nucl. Instrum. Meth. Phys. Res. B*, *174*, 194-198.

[3]. Fouchi, P.G. (1994). Irradiation of power semiconductor devices by high energy electrons: the Italian experience. *Radiat. Phys. Chem.*, *44*, 4, 431-440.

[4]. Drabik L., Panta P., & Szyjko J. (1981). Fast thyristor and fast diodes families development (in Polish). *Elektronizacja*, *14*, 42-46.

[5]. Szyjko, J., Bany, B., Bułhak, Z., Drabik, L., Panta, P., Stambuldzys, A., Świderski, W., & Wincel, H. (1980). *Sposób modyfikacji dynamicznych właściwości przyrządów półprzewodnikowych przy użyciu promieniowania jonizującego*. Polish Patent No. 116059. Polish Patent Office.

[6]. McLauglin, W.L., & Dersrosiers, M.F. (1995). Dosimetry systems for radiation processing. *Radiat. Phys. Chem.*, *46*, 4-6, 1163-1174.

[7]. Fuochi, P.G., Lavalle, M., Corda, U., Kovacs, A., Peimel-Stuglik, Z., & Gombia, E. (2009). Characterization of power transistor as high dose dosimeters. *Nucl. Instrum. Meth. Phys. Res. A*, *599*, 284-288.

[8]. Fuochi, P.G., Lavalle, M., Gombia, E., Mosca, R., Kovacs, A.V., Vitanza, A., & Patti, A. (1999). On the use of a bipolar power transistor as routine dosimeter in radiation processing. In *Techniques for high dose dosimetry in industry, agriculture and medicine. Proceedings of a symposium held in Vienna, 2-5 November 1998* (IAEA-SM-356/47, pp. 95-102). (IAEA-TECDOC-1070).

[9]. Fuochi, P.G., Corda, U., Gombia, E., & Lavalle, M. (2006). Influence of radiation energy on response of bipolar power transistor tested as dosimeter in radiation processing. *Nucl. Instrum. Meth. Phys. Res. A*, *564*, 521-524.

Chapter 22

FUTURE DEVELOPMENTS IN RADIATION PROCESSING

Andrzej G. Chmielewski
Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland
International Irradiation Association, Hardwick House, Prospect Place, Swindon Witshire, UK SN1 3LJ

1. INTRODUCTION

Radiation chemistry is a branch of physical chemistry, like photochemistry, plasma chemistry, ultrasonic chemistry, *etc*. Shortwave electromagnetic radiation (gamma radiation or X-rays) and high-penetration corpuscular (electrons) radiation transfer energy on a continuous, even into high density matter. Ionizing radiation, in the form of X-rays, gamma radiation, and electrons, produces abundant secondary electrons. The collision of a photon with a molecule usually causes an electron to be ejected *via* the Compton effect. Thus, nearly all of the physical and chemical changes in the system are produced by energetic electrons and not by the initiating photons. The kinetics of reactions induced by photons are similar to those obtained if electrons are used as the primary radiation. Therefore, there is no major difference in the effects caused by these different forms of radiation. Depending on the energy transferred, molecules can undergo ionization, excitation, or thermal transfer. Interaction with matter can be divided by time scale into the following stages: initial physical processes, pre-chemical reactions, chemical reactions, and, finally, radical diffusion. The time scale for the physical stage is on the order of 10^{-16} s. Electron excitation occurs in the range shorter than $\sim10^{-10}$ s and vibrational excitation in the range 10^{-14} to 10^{-11} s. Molecular dissociation takes place in the range 10^{-14} to 10^{-6} s, centered at 10^{-10} s. Reactions governed by diffusion take place in the range $\sim10^{-10}$ to $\sim10^{-6}$ s. In liquid systems, it takes an ion pair about 10^{-5} s to separate and become free ions. Following these primary events, the ions, secondary electrons, and excited molecules undergo further transformations, exchanging charges and energy and reacting with the surrounding molecules, thereby producing free radicals and other reactive species which finally evolve into new stable products.

The physical, chemical, and biological effects of ionizing radiation on matter form the basis for many practical applications [1]. The number of such applications is growing, and the sources for gamma radiation and X-rays are now being operated in diverse environments. They play an important role in the economic development of many countries.

2. RADIATION SOURCES AND PROCESSING PLANTS

Three main sources of radiation are used in radiation processing. These are electron accelerators, gamma sources, and X-ray units based on the e^-/X conversion process. Accelerators are available for supplying electron beams (EB) in the energy range up to 10 MeV, and sources of the radionuclides cobalt-60 and cesium-137 emit gamma rays at 1.17/1.33 and 0.662 MeV, respectively. The introduction of new powerful X-ray (bremsstrahlung) radiation sources opens up new, until now largely unexplored, fields. Electron beams are corpuscular radiation and have limited penetration. The entire energy of electrons is deposited into relatively thin layers in materials. In the case of X-rays and gamma rays, ionizing radiation is produced by photons, which have no mass, and are thus able to penetrate deeper into materials. Cobalt-60 emitted gamma rays penetrate ~300 mm of unit density material on an equal entrance-equal exit basis. By contrast, the highest electron energy used in commercial applications, 10 MeV, only penetrates ~38 mm. The dose rates for gamma and X-rays are four to five orders of magnitude lower compared to EB. Therefore, the product throughput for gamma and X-rays is significantly lower than that of electron beams: electron beams are capable of delivering 100 kGy/s, whereas the typical dose rate for gamma rays is 2.8×10^{-3} kGy/s or ~10 kGy/h. X-rays are one order of magnitude higher in dose rate than gamma rays at 2.7×10^{-2} kGy/s or ~100 kGy/h. The radiation dose delivered over the same time period by an electron accelerator of just 15 kW power is approximately equal to that delivered by a 1 MCi cobalt source. X-ray target conversion efficiencies vary with the atomic number of the metal used; they are typically in the range of 8 to 12%. In practice, this means that in order to X-ray process products with the same manufacturing rate as a 10 MeV, 50 kW electron beam, the EB source for X-ray generation will have 417 kW of power, but will provide significantly greater depth of penetration.

2.1. GAMMA IRRADIATORS

The radiation processing industry gained significant impetus with the advent of nuclear reactors, which have the capability of producing radioisotopes such as cobalt-60. These gamma-ray emitters became popular radiation sources for research, medical and industrial applications. Many commercial sized gamma-ray irradiators have been built, 200 of which are estimated to be in current operation. Recently, the use of electron accelerators as radiation source equipped with an X-ray converter is increasing. However, gamma sources are difficult to replace, especially for use with non-uniform, high density products. Currently, cobalt-60 is almost solely used as an industrial gamma radiation source, mainly because it is easy to produce and it is not soluble in water. Based on the total cumulative sale of cobalt-60 by all suppliers, it is estimated that the installed capacity of cobalt-60 is increasing at the rate of about 6% per year. It is interesting to note that the worldwide use of disposable medical devices is also growing at approximately the same rate (5-6%), which seems to be driving the growth of cobalt-60 sales. The most suitable gamma radiation sources for radiation processing are cobalt-60 and cesium-137 because of the relatively high energy of their gamma rays and fairly long half-lives (30.1 years for cesium-137 and 5.27 years for cobalt-60). However, the use of cesium-137 has been limited to small, self-contained dry storage irradiators, used primarily for the irradiation of blood and for insect sterilization. In the United States, the use of cesium-137 has come under more stringent regulatory control with the National Academies of Sciences, Engineering, and Medicine recommending that it should be removed from the market and replaced by alternatives, such as small X-ray devices. Currently, all industrial gamma-ray radiation processing facilities employ cobalt-60 as the gamma radiation source [2].

The high capital costs and increasing regulatory demands have limited the growth of industrial gamma-ray processing facilities. However, the Nordion GammaFIT™ market-entry irradiator offers a gamma source at minimal capital investment. It is designed for optimal processing and flexibility to support future growth. Customers

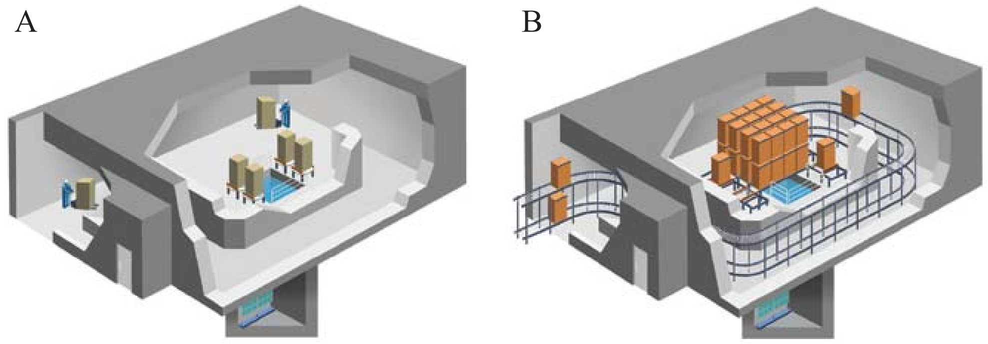


Fig.1. R&D small-scale irradiator (A) upgraded to a four-pass automated tote unit (B) [3].

can choose to start at the irradiator configuration which best suits their current business needs, with the option to change and upgrade as their business needs grow. Higher volumes or changes in product mix warrant an upgrade to a configuration with higher capacity. A scheme of a research and development small unit which can be upgraded to a four-pass automated tote irradiator is presented in Fig.1. The modular design minimizes irradiator downtime during an upgrade [3].

2.2. ELECTRON ACCELERATORS AND e$^-$/X UNITS

Electron beam accelerators have emerged as the preferred radiation source for industrial processing since they offer advantages over isotope radiation sources, such as (i) increased public acceptance with no storage, transport or disposal of radioactive material issues; (ii) the ability to configure a manufacturing process for in-line processing; and (iii) higher dose rates resulting in much higher throughputs. During the 1980s and 1990s, accelerator manufacturers dramatically increased the beam power available for high energy electron accelerators. Some of this effort helped in meeting the demands of the sterilization industry. In this timeframe, the perception that bigger, higher power, higher energy equipment was better prevailed. The operating and capital costs of accelerators did not increase with power demand and energy output as much as the throughput increased. High power provided low unit cost for radiation treatment. In the late 1980s and early 1990s, advances in electron beam technology produced new higher energy, higher power EB accelerators suitable for use in the sterilization market on an industrial scale. The main challenge for EB was the limited penetration of electrons in irradiated materials, which

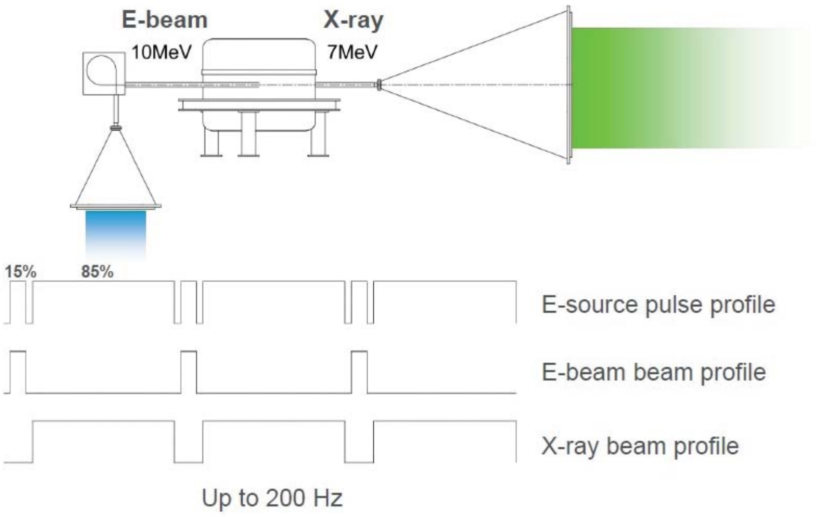


Fig.2. IBA system for X-ray or electron beam irradiation [4].

hampered the use of this technology for treatment of high density products and whole pallets. A solution has been high-powered IBA Rhodotrons™ with e$^-$/X converters. The relatively low X-ray conversion efficiency is overcome by increased beam power. Such a solution [4] is an IBA system for X-ray or electron beam irradiation, as shown in Fig.2.

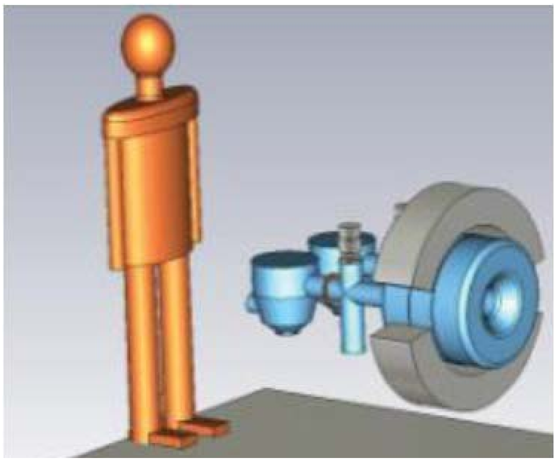


Fig.3. The new compact TT50 Rhodotron™ [4].

Another development from IBA is a compact TT50 Rhodotron™, as shown in Fig.3. The design target is a 80 cm cavity diameter unit [4] with the beam energy of 10 MeV and power of 10 kW. With its 20% energy efficiency, this unit will be a good tool for small- to medium-sized service providers and for research and development institutions.

3. MATERIALS PROCESSING

3.1. POLYMERS

Radiation processing has been used for nearly 60 years in industry for polymer modification [5]. The irradiation of polymeric materials with ionizing radiation (gamma rays, X-rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates, free radicals, ions and excited states. These intermediates can follow several reaction paths that result in disproportion, hydrogen abstraction, arrangements and/or the formation of new bonds. The extent of these transformations depends on the structure of the polymer and the conditions of treatment before, during and after irradiation. Thorough control of all of these factors facilitates the modification of polymers by radiation processing. The modification of polymers covers radiation crosslinking, radiation-induced polymerization (graft polymerization and curing) and the degradation of polymers. The success of radiation processing of polymers can be attributed to two reasons: (i) the ease of processing various shapes and sizes and (ii) many polymers undergo a value-added crosslinking reaction upon exposure to radiation. Some naturally occurring polymers have been difficult to process and degrade when exposed to radiation. Recently, some natural polymers are being looked at again with renewed interest because of their unique characteristics such as their inherent biocompatibility, biodegradability and availability. Many processes of the radiation treatment of natural polymers, though known for a long time, have not yet been commercialized, either because of the high cost of irradiation (high dose) or because of the reluctance on part of an industry to adapt to radiation technology. It is important to consider combining the beneficial effects of conventional technology along with radiation technology to overcome such issues. For synthetic polymers and natural rubber, there are well established irradiation processes. Naturally occurring polysaccharides have a wide range of uses in agriculture, medicine, cosmetics, food industry, and wastewater treatment. Some products based on radiation processed cellulose derivatives or chitosan have been developed and introduced to the market. Chitin is, next to cellulose, the second most abundant polysaccharide on earth. It is present in crustacean shells, insect exoskeletons, and fungal cell walls. Chitosan, (1-4)-2-amino-2-deoxy-β-D-glucan, is the deacetylated derivative of chitin. Commercially available chitosan is characterized by high molecular weight and low solubility in most solvents which limits its use. The solubility of chitosan can be increased by lowering the molecular weight. Water soluble chitosan can be prepared by oxidative degradation with H_2O_2 at a concentration higher than 1 mol/L. Low molecular weight chitosan can be prepared by chemical, radiation, or enzymatic degradation of the high molecular weight polymer. Radiation is one of the tools for the modification of polysaccharides. To decrease the molecular weight, a combination of chemical and radiation methods can also be used [6]. Chitosan oligomers have been obtained through irradiation of chitosan dissolved in acetic acid. Treating plants with oligochitosan increases their disease resistance and also stimulates their growth. Degraded polysaccharides such as alginate, chitosan, or carrageenan can increase tea, carrot, or cabbage productivity by 15 to 40%. Chitosan irradiated within the range of 70 to 150 kGy strongly affects the growth of plants as wheat and rice and reduces damage caused by vanadium. Radiation-degraded alginate in concentrations 20 to 50 ppm promotes the growth of rice seedlings, in concentrations at 100 ppm causes an increase of peanut shoots by approximately 60% compared to a control. Further progress in natural polymer processing is foreseen. One breakthrough factor could be the use of X-rays [7].

3.2. NANOTECHNOLOGY

Nanotechnology is a fast growing area in science and engineering. Radiation is used as a tool in this area. For many years, atoms and ions have been arranged using ion or electron beams. Radiation chemists in material processing follow a similar approach as do chemists in general, namely, that is treatment in the bulk. However, trends of more precise treatment technology have been followed as well, such as the use of surface curing, the development of ion track membranes and of controlled release drug-delivery systems. The ability to fabricate structures with nanometric precision is of fundamental importance to any exploitation of nanotechnology [8].

3.3. OTHER MATERIALS

Radiation processing can include gem stone colorization, the development of high temperature resistant fibers (SiC), and semiconductor modification [9].

4. STERILIZATION

Commercial radiation sterilization has been used for more than 50 years. Over the decades, there has been a substantial growth in the market for disposable medical products. With this, there has been significant growth in the use of ionizing radiation as a method for sterilization [10]. At present, 40 to 50% of all disposable medical products manufactured in North America are sterilized by radiation. Worldwide, there are now some 160 commercial cobalt-60 irradiators being used for radiation sterilization, operating in 47 countries and containing approximately 240 to 260 million Ci (8.9-9.6 × 10^{18} Bq) of gamma--emitting cobalt-60. Included in this calculation are service-type facilities operated in research and development centers. Because of the ability to down-scale cobalt-60 units, there are many research and development pilot-scale, small facilities as well, that are almost equal in number (~150). When other uses are taken into account, there are a total of over 300 gamma irradiators being operated for a variety of purposes in 55 different countries. Syringes, surgical gloves, gowns, masks, band-aids, dressings, medical tetra packs, bottle teats for premature babies, artificial joints, food packaging, raw materials for pharmaceuticals and cosmetics, and even wine corks are being gamma sterilized. An increasing number of electron beam accelerators are also being used, but for only a minority of radiation sterilized products.

5. FOOD IRRADIATION

A joint FAO/IAEA/WHO (Food and Agriculture Organization/International Atomic Energy Agency/World Health Organization) Expert Committee approved the use of radiation treatment of foods up to 10 kGy dose in 1980. After 1980, new regulations permitted the irradiation of foods which were not previously approved for this process in the United States. Experts agreed that radiation does not cause any toxicological changes or activation of irradiated food products. Therefore, toxicological tests for food treated by this method are not needed. Gamma rays or X-rays up to 7.5 MeV and electrons up to 10 MeV energy can be used for this purpose. The approvals of the irradiation treatment of packaged fresh or frozen uncooked poultry in 1990 and for the treatment of fruits, vegetables, and grains in 1986 are some of the examples of these new regulations. Today, more than 40 countries have permitted the use of irradiation for over 60 food products. The use of irradiation is becoming a common treatment for sterilizing packages in the aseptic processing of foods and pharmaceuticals. Spices represent the largest volume of irradiated food products. In 1988, the great International Conference on the Acceptance, Control of and Trade in Irradiated Foods, jointly sponsored by FAO, IAEA, WHO and ICT-UNCTAD/GATT (International Trade Centre-United Nations Conference on Trade and Development/General Agreement on Tariffs and Trade) was held in Geneva. The Document on Food Irradiation, adopted by consensus by government designated experts from 57 countries who attended the Conference, includes an important statement promoting the worldwide action on the development of detection methods for irradiated foods: ‟Governments should encourage research into methods of detection of irradiated foods so that administrative control of irradiated food once it leaves the (irradiation) facility can be supplemented by an additional means of enforcement, thus facilitating international trade and reinforcing consumer confidence in the overall control system” [11].

5.1. SPICES AND HERBS

Despite the great advances observed in modern synthesis-based pharmacy, medicinal plants still play an important role in contributing to health care. There has been a growing interest in alternative therapies in recent years, especially those derived from plants. The WHO estimates that about 65 to 80% of the world’s population living in developing countries depends essentially on medicinal plants (herbs) for use in primary health care. Spices and herbs are often contaminated with high levels of bacteria, molds and yeasts. Most often the microorganisms, which are present on the surface of the plant, are a mixture of epiphytic microflora, growing on specific varieties of plants, and the microflora originating from the plant environment, namely soil, water and air. Pathogenic microorganisms may grow on some herbs and spice plants, and quite often they grow not only on the surface, but inside of the plant's tissue as well. If untreated, the herbs and spices will rapidly spoil the products which are supposed to enhance health. When contaminated with pathogenic bacteria, they can also result in serious food borne illnesses. Spices are usually decontaminated by irradiation or by fumigation with ethylene oxide gas (EtO). Some spices can be also steam treated. There is an extensive body of research available on the irradiation of spices, herbs and vegetable seasonings. Most products have been studied with at least preliminary if not extensive research, and the effects of irradiation on microbial contamination and sensory properties have been quantified. Since irradiation is a clearly preferable sanitation method, its use has been allowed by the Codex Alimentarius and by most countries worldwide [12]. While the use of EtO is allowed in North America, its use is not allowed in many European countries since EtO is a carcinogen when inhaled and it leaves harmful chemical residues on the spice. Typical pathogenic microorganisms present in herbs are *Staphylococcus aureus*, *Salmonella*, *Pseudomonas aerginosa, Clastridium perfringens* and *Candia albicans*. Opportunistic microorganisms are present as well; these are nonpathogenic microorganisms which, under specific conditions, may cause infection. These are the *Staphylococcus* type, *Enterococcus* and other rods from the *Enterobacteriaceae* family and *Pseudomonas* type, other nonfermentous rods, aerobic rods *Bacillus* type, most of the anaerobic rods of the *Clostridium* type, fungi imperfecti of the *Candida* and *Rhodotorula* type, and mold fungi, mostly *Mucor*, *Rhizopus* and *Aspergillus* types. There are different reasons as to why human organisms are infected by a nonpathogenic microorganism. These are metabolic aberrations (diabetes, renal insufficiency *etc*., long-lasting antibiotic therapy, radiotherapy, *etc*.). Especially sensitive to such a type of infections are children and elderly people. The other actions of microorganisms which are present in herbs may affect the quality of the final product. A chemical compound being a component of the drug may be destructed or its composition changed. Enzymes produced by microorganisms may react with other components of the drug to produce toxins or compounds having other pharmaceutical effects. The requirements regarding the microbiological purity for herbs were established by the WHO.

High contamination of herbs due to the presence of endospores of *Bacillus* and *Clostridium* and spores which are very resistant to the chemical and physical methods of decontamination, pose significant difficulties in the production of phyto-preparations. The use of physical or chemical methods, which reduce microbiological contamination to the desired level, quite often leads to the reduction of the content of the biologically active components. The sensory properties of most spices are well maintained between 7.5 and 15 kGy.

Research clearly indicates that irradiation maintains the sensory properties of spices, herbs and vegetable seasonings better than EtO treatment. Generally, the sensory properties of spices are more resistant to irradiation than are some herbs. Also, herbs are more damaged by EtO treatment. Herbs are more sensitive to treatment of any kind. At the doses required to control microbial contamination, insects and other pests will be killed in all life stages. Radiation treatment results in cleaner, better quality herbs and spices compared to fumigation with EtO. While both decontamination and sterilization methods result in some changes to some spices, radiation does not change the sensory or functional properties to the same extent as does EtO [12]. This is an important consideration when exporting these products.

6. POLLUTION CONTROL

Municipal and industrial activities of man have led to environmental degradation. The pollutants emitted to the atmosphere are off-gases from industry, power stations, residential heating systems and vehicles. Fossil fuels, which include coal, natural gas, petroleum, shale oil and bitumen, are the main source used to generate heat and electrical energy. Ironically, coal, which is the dirtiest fuels among hydrocarbons, will be the main fossil fuel for the next two centuries [13]. All of these fuels contain major constituents (carbon, hydrogen, oxygen) as well as other materials, such as metals, sulfur and nitrogen compounds. During the combustion process, different pollutants as fly ash, sulfur oxides (SO_2 and SO_3), nitrogen oxides ($NO_x = NO_2 + NO$) and volatile organic compounds, are emitted. Fly ash contains different trace elements (heavy metals). The gross emission of pollutants is tremendous on a worldwide basis. These pollutants remain present in the atmosphere under such conditions that they can effect man and his environment. Air pollution, caused by particulate matter and other pollutants, not only directly affects the environment, but also contaminates water and soil and leads to their degradation. Wet and dry deposition of inorganic pollutants leads to the acidification of environment. These phenomena all affect human health, increase corrosion, and destroy plants and forests. As a result, widespread forest damage has been reported in Europe and in North America. Many cultivated plants are not resistant to these pollutants either, especially in their early period of vegetation.

Mechanisms of pollutant transformation in the atmosphere are described by environmental chemistry. Photochemistry plays an important role in these transformations. SO_2 and NO_x are oxidized, sulfuric and nitric acids are formed in the presence of water vapor, fog and water droplets. Another problem caused by human activities is the emission of volatile organic compounds to the atmosphere. These emissions cause stratospheric ozone layer depletion, ground level photochemical ozone formation, and toxic or carcinogenic human health effects, which contribute to the global greenhouse effect, and accumulate and persist in the environment. Waters in open and underground reservoirs are being polluted, cultivated soil and forests degraded. Most of the plants, especially coniferous trees, are not resistant to the sulfur oxides discharged from municipal and industrial facilities. Water pollution had been primarily a local problem, with identifiable sources of pollution from liquid waste. Until a few decades ago, most of the wastes discharged into waters came from animal and human excreta and from other organic components from industry. In areas with low population density and without sewerage systems, such problems were alleviated to a great extent by the natural self-purification capacity of the receiving water. However, with the increasing urbanization of the last two centuries and a subsequent expansion of sewerage systems without any or adequate treatment, liquid waste loads have become so large that the self-purification capacity of receiving water downstream of large human settlements can no longer prevent adverse effects on water resources. Another problem concerns industrial effluents, which carry chemical contaminations, heavy metals, organic pollutants, often petrochemicals, pesticides, dyes, *etc*. Some pollutants are synthesized *in situ*, as, for example, chloroorganic compounds originate from chlorine use for water/wastewater disinfection. The result of discharging such materials include dyeing living water reservoirs and their inhabitants, the risk of infection, health effects caused by contaminated drinking water and offensive smells. Over the years, the pollution load on most receiving waters has further increased. In addition to the impacts from point sources, pollution from non-point (diffuse) sources, for example, leaching and runoff from agricultural areas and long-range transported air pollutants, have become increasingly important. Consequently, the associated problems are no longer just local or regional, but have become continental in scope. The situation regarding environment contamination is becoming critical. Economic and technically feasible technologies for pollution control of gaseous and liquid effluents are being sought. Radiation offers an advanced solution to these problems as well. Radiation technology may greatly contribute to the environmental protection [13]. Industrial electron beam installations for flue gases containing SO_x and NO_x treatment have been already built in China and Poland. The same technology for high sulfur and high humidity off-gases (low quality lignite) has been successfully tested in an industrial pilot plant in Bulgaria. Pilot plant tests performed in Japan have illustrated that by using electron beam for municipal waste incinerator off-gas treatment the concentration of dioxins can be reduced by 80%, other persistent organic pollutants can be depleted as well. The positive results the electron beam wastewater treatment are the basis for a full-scale industrial plant being built in the South Korea. A pilot gamma plant for sludge irradiation, producing a high-grade organic fertilizer, is in operation in India.

In most of continuous flow systems (flue gases, wastewater) electron accelerators are being used [14].

6.1. GASEOUS POLLUTANT EMISSION CONTROL

Different air pollution control technologies are being sought. The conventional technologies most often used for air pollution control are: (i) wet flue gas desulfurization (FGD), based on SO_2 absorption in lime or limestone slurry; and (ii) selective catalytic reduction (SCR), based on NO_x reduction over a catalyst to atmospheric nitrogen with ammonia as the reductive specie. However, technologies which treat different pollutants in one step are of special interest. Electron beam flue gas treatment (EBFGT) technology is such a process. EBFGT technology is among the promising advanced technologies. It is a dry-scrubbing process for the simultaneous SO_2 and NO_x removal, where no waste is generated. After the irradiation of the polluted gas, fast electrons interact with the gas, creating various ions and radicals, and the primary species formed include e^-, N_2^+, N^+, O_2^+, O^+, H_2O^+, OH^+, H^+, CO_2^+, CO^+, $N_2^\bullet$, $O_2^\bullet$, N, O, H, OH, and CO. In the case of high water vapor concentration, the oxidizing radicals $^\bullet OH$ and $HO_2^\bullet$ and excited ions such as O(3P) are the most important products. The SO_2, NO, NO_2, and NH_3 present cannot compete with the reactions because of their very low concentrations, but will react with N, O, $^\bullet OH$, and $HO_2^\bullet$ radicals. Ammonia, as mentioned above, is added to the gas to neutralize the acids formed in these reactions, with an aerosol of ammonium sulfate and ammonium nitrate being the final products of the reaction. In this technology, the temperature and humidity of flue gas are modified in the spray cooler, then almost stoichiometric amounts of ammonia is added to the flue gas and such a gas mixture is irradiated in the process vessel by an electron beam from

Fig.4. ELV-12 accelerator for environmental applications.

accelerator. The by-product is collected by the electrostatic precipitator (ESP) and may be used as an agricultural fertilizer or as a component of NPK (nitrogen-phosphorus-potassium) or NPKS (nitrogen-phosphorus-potassium-sulfur) commercial fertilizer. This technology was implemented in a full-industrial scale at the Electric Power Station (EPS) "Pomorzany" in Szczecin for the purification of flue gases emitted from two low-sulfur coal-fired Benson boilers. In this industrial plant with a nominal flow rate of 270 000 Nm^3/h, SO_2 and NO_x are removed from flue gas with the efficiency exceeding 90 and 70%, respectively [15]. A problem in implementing this technology was the need for reliable high power, mid-voltage, self-shielded accelerators. A new unit manufactured by the Budker Institute of Nuclear Physics in Novosybirsk, Russia, and EB Tech Co., Ltd., Republic of Korea, meets these requirements. The ELV-12 accelerator provides a 0.6 to 1.0 MeV electron beam and power that is equal to 400 kW, as shown in Fig.4.

Fig.5. Pilot plant at oil refinery: 1 – stack of F 1001 boiler, 2 – boiler F 1001, 3 – flue gas duct, 4 – pilot plant control room, 5 – gas conditioning column, 6 – pilot plant stack, 7 – cartridge bag filter, 8 – thermal insulated duct, 9 – cyclone, 10 – ammonia dosing unit, 11 – mobile accelerator unit.

A new use of concern is the treatment of flue gas from oil fired boilers [16] and diesel engines on cargo ships. The pilot plant for the use of EBFGT from an oil fired boiler was constructed in a refinery, using EB a mobile unit manufactured by EB Tech Co., Ltd., as shown in Fig.5. Tests have proved a high removal efficiency of pollutants in this case as well.

6.2. WASTEWATER POLLUTANTS DISCHARGE CONTROL

Because of the increasing levels and complexity of polluted effluents from municipalities and industry, current wastewater treatment technologies may not be successful for the remediation of polluted waters and for disinfection. The development and implementation of alternative technologies for the cleanup of industrial wastewater, municipal water, groundwater, and drinking water are critical to sustainability in many countries. Research and development work using a large scale wastewater treatment facility was performed at the Miami Electron Beam Research Facility. The water purification process relied on water radiolysis to degrade pollutants. Some of the free radicals formed are oxidative species ($^{\bullet}$OH), and the others reductive (H, e^{-}_{aq}). Thus, there is competition between oxidation and reduction processes in the system. A possible synergistic effect with ozone may improve the overall efficiency of the destruction of organic pollutants. In this case, ozone would react with the strong reductive species leading to the formation of hydroxyl radicals. Aqueous effluents that have been treated by irradiation include polluted drinking water and liquid industrial and agricultural wastes. The formation of some possible toxic by-products could limit implementation of this process. An industrial plant has been constructed in the Republic of Korea. Based on the data obtained in the laboratory and from pilot plant experiments, suitable doses were determined to be around 0.2 kGy for a flow rate of 10 000 m^3 of effluent per day. In this case, a high power accelerator (1 MeV, 400 kW) manufactured by the EB Tech Co., Ltd. was used. High energy electron disinfection of sewage wastewater in flow streams has been proposed and tested. The hybrid use of controlled chemical-oxygen-demand (COD) and microbiological load with electron beam processing looks the most promising for future use.

Another use for accelerator-generated electron beams is the degradation of antibiotics and leftover drugs that are in liquid effluents. Antibiotics for animal husbandry, administered drugs, metabolites, or their degradation products enter the ecosystem *via* the use of manure or slurries on areas used for agricultural purposes or from pasture-reared animals that excrete directly onto the land. The degradation of ampicillin in a pig manure slurry and an aqueous ampicillin solution have been studied using electron beam irradiation. The results demonstrate that EB technology is an effective means of removing antibiotics from manure and bodies of water.

6.3. SOLID WASTE TREATMENT

The problem of water contamination by chemical and biological matter is well known. In many regions there are deficits in the water supply for municipal, agricultural, and industrial use. Water in reservoirs, drawn mainly from rivers, is reused many times. The purification and disinfection of water is needed to protect the health of consumers. Even so, bottled water and household filters are very popular as a source of quality drinking water. The most popular and efficient wastewater purification systems are biological treatment plants. These plants then become a source for biological sludge, which is a waste that contains approximately 3% solids of higher if a dewatering process is used. Unfortunately, the sludge of municipal wastewater origin is biologically contaminated by viruses, bacteria, and the eggs of parasites. In the case of landfill disposal, these contaminants survive for many years. Even in regions with severe winters, the sludge undergoes continuous fermentation and the temperature is higher than the freezing point of water. Some years ago, different countries solved this problem by dumping such wastes into the sea, which is now prohibited. The sludge is a good organic fertilizer and is especially good for use with sandy soils. Some countries are using injection under the soil, which is not so safe from a health point of view if the field is used for the cultivation of food crops. In the European Union, sludge incineration is the current direction taken to solve this problem. However, all combustion processes emit pollutants and greenhouse gases to the atmosphere. Different methods of disinfection have been proposed: heat pasteurization, mixing with lime, and ionizing radiation treatment. The destruction of the microbes by radiation is achieved by direct and indirect DNA double- and single-strand breaks and other damage to cell components. Again, due to the high concentration of water in a living organism, the free radicals formed play a most important role in the indirect damage to the living organism's structure. The indirect action of ionizing radiation, which is very similar to that discussed earlier for nonliving physicochemical matter, involves water radiolysis and the effect of active species on DNA. Research has shown that sewage sludge can be disinfected successfully by exposure to high energy radiation. Doses of 2 to 3 kGy destroy more than 99.9% of bacteria present in sewage sludge. Higher doses (up to 10 kGy) are required to inactivate more radiation-resistant organisms. Both gamma sources (cobalt-60, cesium-137) and electron accelerators can be used for the irradiation of sewage sludge. Gamma source radiation has better penetration, allowing thicker layers of sludge to be irradiated, although they have less power and require a longer irradiation time than do electron sources. The irradiated sludge, being pathogen-free, can be beneficially used as manure in agricultural fields as it is rich in nutrients required for soil. Initial field trials of sludge as manure in agricultural fields used for winter wheat crops as well as for summer green grain crops have been very encouraging. Since the irradiated sludge is free from bacteria, it can also be used as a medium for growing bacteria that is useful for the soil like rhizobium and azotobacter and to produce biofertilizers, which can be used to enhance crop yields. In the case of sludge or soil irradiation, high energy accelerators are preferable. An accelerator of 10 MeV at 10 kW is able to irradiate 70 tons of sludge a day at a dose of 5 to 6 kGy. The estimated cost of such installation is US$4 million.

Acknowledgments

Work was partly supported by iia (International Irradiation Association)-INCT (Institute of Nuclear Chemistry and Technology) contract (No. 01/INCT-iiA/2015) and Ministry of Science and Higher Education (Poland) co-financing grant (No. 3520/IIA/15/2016/0).

REFERENCES

[1]. Chmielewski, A.G. (2007). Practical applications of radiation chemistry. *Russ. J. Phys. Chem. A*, *81*, 9, 1488-1492.

[2]. IAEA. (2005). *Gamma irradiators for radiation processing*. Vienna: IAEA. Retreived June 20, 2016 from http://www-naweb.iaea.org/napc/iachem/Brochure%20on%20gamma%20irradiators.pdf.

[3]. Nordion. (2014). *Introducing GammaFIT™ – the latest in flexible irradiator technology*. Nordion. Retrieved June 20, 2016 from http://www.nordion.com/wp-content/uploads/2014/10/GT_GammaFIT_Irradiator_datasheet.pdf.

[4]. Dethier, P. (2015, September 7). *The second generation Rhodotron*. IAEA Technical Meeting on New Generation of EB-accelerators for Emerging Radiation Processing Applications, Vienna, Austria, 07.09.2015.

[5]. Chmielewski, A.G., Haji-Saeid, M., & Ahmed, S. (2005). Progress in radiation processing of polymers. *Nucl. Instrum. Meth. Phys. Res. B*, *236*, 44-54.

[6]. Chmielewski, A.G., Migdal, W., Swietoslawski, J., Swietoslawski, J., Jakubaszek, U., & Tarnowski, T. (2007). Chemical-radiation degradation of natural oligo-amino-polysaccharides for agricultural application. *Radiat. Phys. Chem.*, *76*(11), 1840-1842.

[7]. Chmielewski, A.G., Al-Sheikhly, M., Berejka, A.J., Cleland, M.R., & Antoniak, M. (2014). Recent developments in the application of electron accelerators for polymer processing. *Radiat. Phys. Chem.*, *94*(1), 147-150.

[8]. Chmielewski, A.G., Chmielewska, D.K., Michalik, J., & Sampa, M.H. (2007). Prospects and challenges in application of gamma, electron and ion beams in processing of nanomaterials. *Nucl. Instrum. Meth. Phys. Res. B*, 265, 339-346.

[9]. Chmielewski, A.G. (2006). Worldwide developments in the field of radiation processing of materials in the dawn of 21st century. *Nukleonika*, *51*(S1), S3-S9.

[10]. IAEA. (2008). *Trends in radiation sterilization of health care products*. Vienna: IAEA. Retrieved June 20, 2016 from http://www-pub.iaea.org/MTCD/publications/PDF/Pub1313_web.pdf.

[11]. Stachowicz, W., Malec-Czechowska, K., Dancewicz, A.M., Szot, Z., & Chmielewski, A.G. (2002). Accredited laboratory for detection of irradiated foods in Poland. *Radiat. Phys. Chem.*, *63*, 427-429.

[12]. Chmielewski, A.G., & Migdał, W. (2005). Radiation decontamination of herbs and spices. *Nukleonika*, *50*(4), 179-184.

[13]. Chmielewski, A.G. (2005). Application of ionizing radiation to environment protection. *Nukleonika*, *50*(S3), S17-S24.

[14]. Chmielewski, A.G. (2011). Electron accelerators for environmental protection. *Rev. Accel. Sci. Tech.*, *4*, 147-159.

[15]. Chmielewski, A.G., Licki, J., Pawelec, A., Tyminski, B., & Zimek, Z. (2004). Operational experience of the industrial plant for electron beam flue gas treatment. *Radiat. Phys. Chem.*, *71*, 439-442.

[16]. Basfar, A.A., Fageeha, O.I., Kunnummal, N., Al-Ghamdi, S., Chmielewski, A.G., Licki, J., Pawelec, A., Tyminski, B., & Zimek, Z. (2008). Electron beam flue gas treatment (EBFGT) technology for simultaneous removal of SO_2 and NO_x from combustion of liquid fuels. *Fuel*, *87*, 1446-1452.