

RADIATION CHEMISTRY OF ORGANIC SOLIDS

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1. INTRODUCTION

Radiation chemistry deals with chemical reactions produced by interactions of ionizing radiation with materials. The effects of radiation on matter depend on the type of the radiation and its energy level, as well as on the composition, physical state, temperature and the atmospheric environment of the absorbing material. The type and yield of the final products produced by exposure of an organic compound to ionizing radiation are often dependent on its physical state (gas, liquid or solid) and its molecular structure [1]. The effects of radiation on organic solids (polymers, lignocellulosic materials, *etc.*) are an area of increasing interest. Ionizing radiation can modify the physical, chemical, and biological properties of polymers; the changes occurring when polymer materials are in a solid state are different, as compared to chemical or thermal reactions carried out in melted polymers. After the interaction of ionizing radiation (gamma rays, X-rays, accelerated electrons, ion beams) with macromolecules, very reactive intermediates (primary entities, radicals and ions) are formed. These intermediates can follow several different reaction paths, that result in the formation of oxidized products, grafts, scissioning of main chains (degradation) or crosslinking. The type and degree of these transformations depend on the structure of the material (*e.g.* polymer) and the treatment applied before, during and after irradiation [2].

2. PRIMARY AND SECONDARY EFFECTS

Ionizing radiations can be classified in three categories:

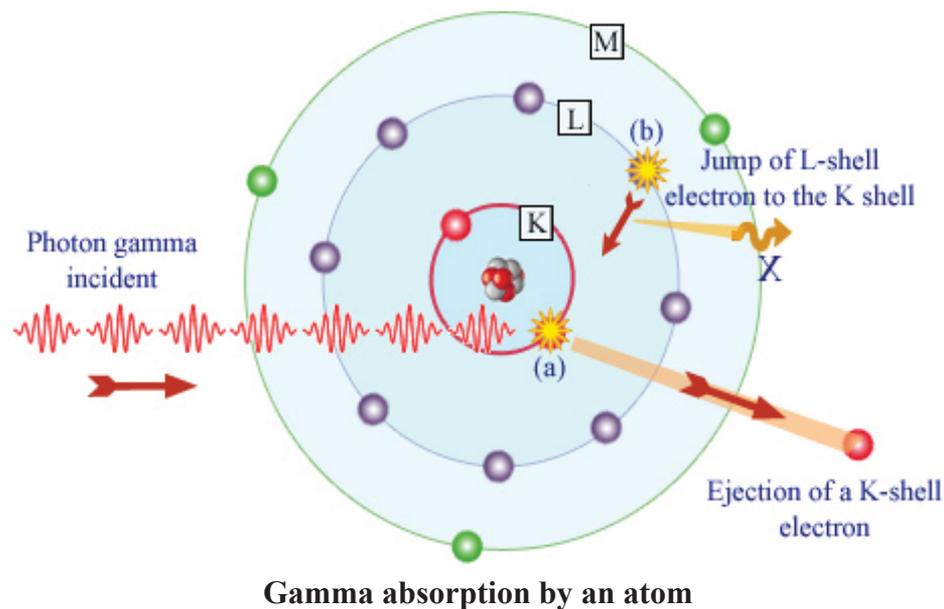
- charged particles: electrons (e^-), positrons (e^+), and heavy ions;
- photons: gamma (γ), X-rays and light;
- neutrons (n).

The term “ionizing radiation” in a wider sense also applies to photons or particles having sufficient energy to ionize a molecule of a material. This involves photons with energies ranging from the first ionization energy of the material (~ 10 eV) up to several million eV (MeV), as well as energetic charged particles, such as electrons, positrons, accelerated heavy ions, *etc.* The result of such energy absorption is the breaking or rearrangement of chemical bonds, *i.e.* decomposition of some of the initial material.

Radiation principles explain how the gamma rays, electron beams (EB) and X-rays interact with matter. Independently from the type of radiation (electromagnetic or particle) most of the radiation effects are produced by secondary electrons. According to calculations by Bethe with primary electrons of 10^{3-15} eV more than 80% of the absorbed energy is transferred to secondary electrons.

These interactions result in the formation of energetic electrons which are random throughout the materials and which cause the formation of energetic molecular ions. These ions may be subject to electron capture and dissociation, as well as to rapid rearrangement through ion-molecule reactions, or they may dissociate with time depending on the complexity of the molecular ion. The chemical changes in matter can occur *via* primary radiolysis effects, which occur as a result of the adsorption of the energy by the absorbing matter, or *via* secondary effects, which occur as a result of the high reactivity of the free radicals or electrons and the excited ions or molecules produced as a result of the primary effects. These highly reactive intermediates can undergo a variety of reactions leading to stable chemical products. In general, these chemical products can be detected and are referred to as radiolysis products. Understanding gamma-ray interaction with matter is important from the perspective of shielding against their effects on biological matter. These chemical changes can ultimately have biological consequences in the case where the target materials include living organisms.

The main types of interactions of gamma and X-radiation with substances are the photoeffect both in its photoelectric and photonuclear forms, Compton effect and scattering and generation and/or annihilation (elastic collisions) of the pairs (electron positron pair production). To a minor extent, photofission, Rayleigh scattering and Thompson scattering also occur [3]. The photoelectric effect can displace atomic electrons, whereas the photonuclear reaction would displace elementary particles from the nucleus.



Gamma absorption by an atom

Fig.1. Schematic representation of photoelectric effect.

Photoelectric effect is the most effective mechanism of photon absorption, as shown in Fig. 1.

The photoelectric effect occurs in two stages. First, a photon (a) removes a bound electron in one atom. In the case of gamma photons, it is usually an electron belonging to the innermost atomic shells, L or K (as shown in Fig. 1). Then the atom that has lost one of its inner electrons is left in an excited state. An electron from an outer layer ((b) in Fig. 1) moves to occupy the vacancy left by the ejected electron. If the ejected electron belonged to the K shell, an X-ray is emitted during this transition which is accompanied by the emission of a characteristic soft electromagnetic radiation in the X-ray, ultraviolet (UV) or visible region of the electromagnetic spectrum.

The photoelectric effect is the phenomenon that transforms light, infrared and ultraviolet rays into electricity in solar panels and photodiodes of cameras. It is also involved in the completely different field of radioprotection by transforming penetrating X- and gamma rays into electrons easy to stop and thus protects humans from the effects of these radiations.

The photoelectric process is always accompanied by a secondary emission since the atom cannot remain in an excited state indefinitely, thus:

- The atom emits X-rays and returns to the ground state.
- Auger electrons are emitted from the outer electronic shells carrying out the excitation energy. The secondary radiation is also later absorbed and occurs in scintillators used in gamma radiation detection.

The photoelectric effect is the most effective physical phenomenon in mitigating these radiations. The gamma-ray or X-ray photon absorbed by interact-

ing with a bound electron to form an atom radical (\bullet) disappears. The photon simply vanishes. If the energy of the photon is greater than 0.339 MeV, an electron may be ejected from the atom producing an ion pair. The ejected electron will then produce secondary ionization events in its surrounding atoms in a similar manner to beta particles (electrons or positrons). The photoelectric effect has a high probability of occurring with lower energy photons and atoms having high atomic numbers. The shell structure of atoms plays a crucial role. The photon removes an electron only if its energy exceeds the binding energy of the electron on its shell. The probability (called cross section) of removing an electron from a shell becomes different from zero beyond this threshold. Where there is a certain small probability of a photoelectric effect type phenomenon, gamma rays tend to interact more with not only deeper, core-level energy states, but also with the nucleus of the material. In this case, a number of different phenomena go on such as nuclear excitation, different types of scattering, *etc.* [4]. Photonuclear reactions can be used to produce neutron sources which can be used in a variety of applications such as nuclear medicine and radiography.

In the Compton effect, the photon undergoes a collision with an atom thus being deviated from its trajectory and releasing part of its energy. This energy is usually enough to abstract an electron from the atom. Compton scattering is the inelastic scattering of a photon by a charged particle, usually an electron. It results in a decrease in energy (increase in wavelength) of the photon (which may be an X-ray or gamma-ray photon). This is called the Compton effect. The electrons in matter are neither free nor at rest. However, in some cases, one can approximate the state of an electron in a simple model as free and at rest. In this case a gamma rays can interact with a loosely bound electron by being scattered with an appropriate loss in energy, as illustrated in Fig.2.

The scattering of photons from charged particles is called Compton scattering after Arthur Compton, who was the first to measure photon-electron

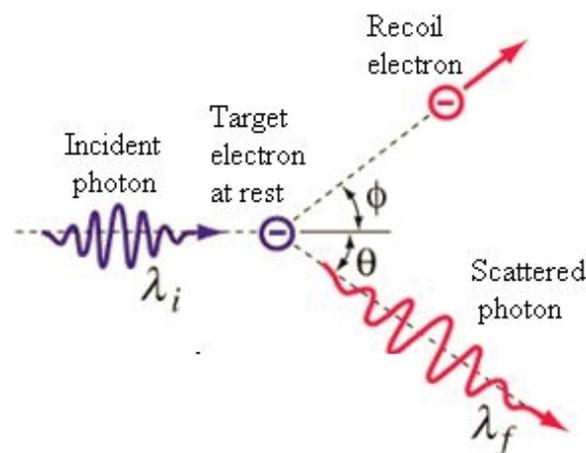


Fig.2. Compton scattering.

scattering in 1922. When the incoming photon gives part of its energy to an electron, then the scattered photon has lower energy and according to the Planck relationship has a lower frequency and longer wavelength. The wavelength change in such scattering depends only upon the scattering angle for a given target particle. The constant in the Compton formula (Eq. (1)) can be written as in Eq. (2) and is called the Compton wavelength for the electron:

$$\lambda_f - \lambda_i = \Delta\lambda = \frac{h}{m_0 c} (1 - \cos \theta) \quad (1)$$

$$\frac{h}{m_e c} = \frac{hc}{m_e c^2} = \frac{1240 \text{ eV} \cdot \text{nm}}{0.511 \text{ MeV}} = 0.00243 \text{ nm} \quad (2.43 \times 10^{-12} \text{ m}) \quad (2)$$

where: λ_i – the initial wavelength, λ_f – the wavelength after scattering, h – the Planck constant, m_0 – the electron rest mass, c – the speed of light, and θ – the scattering angle.

Part of the energy of the photon is transferred to the recoiling electron. Inverse Compton scattering also exists, in which a charged particle transfers part of its energy to a photon. Compton scattering is of prime importance in radiobiology, as it is the most probable interaction of gamma rays and high energy X-rays with atoms in living cells and is applied in radiation therapy. In material physics, Compton scattering can be used to probe the wave function of the electrons in matter. The primary effect of the Compton interaction is ionization.

3. CHEMICAL EFFECTS OF RADIATIONS

The primary effect of high energy radiation is ionization and, to a minor extent, excitation of molecules and atoms. The radiation gradually releases its energy through the material giving rise to a track of reactive species (ions, excited molecules, radicals, electrons) whose reactions are responsible for the irreversible chemical transformations of the matter (radiolysis). Primary ionization generates electrons, whose energy is large enough to give rise to further ionizations and excitations. Thus, secondary electrons are responsible for a major part of radiation chemical effects. This explains the substantial analogy of the effects stemming from the different type of radiations either electromagnetic (gamma rays, X-rays) or charged particles (electrons, alpha, protons, deuterons, *etc.*). The probability that electrons with energy < 10 MeV and gamma radiations of 0.5-1 MeV (Compton effect) will interact with atoms and molecules is proportional to the electron density of the material and it is therefore relatively unselective and largely independent of chemical structures. A general radiolysis mechanism for a condensed phase is illustrated in Fig.3.

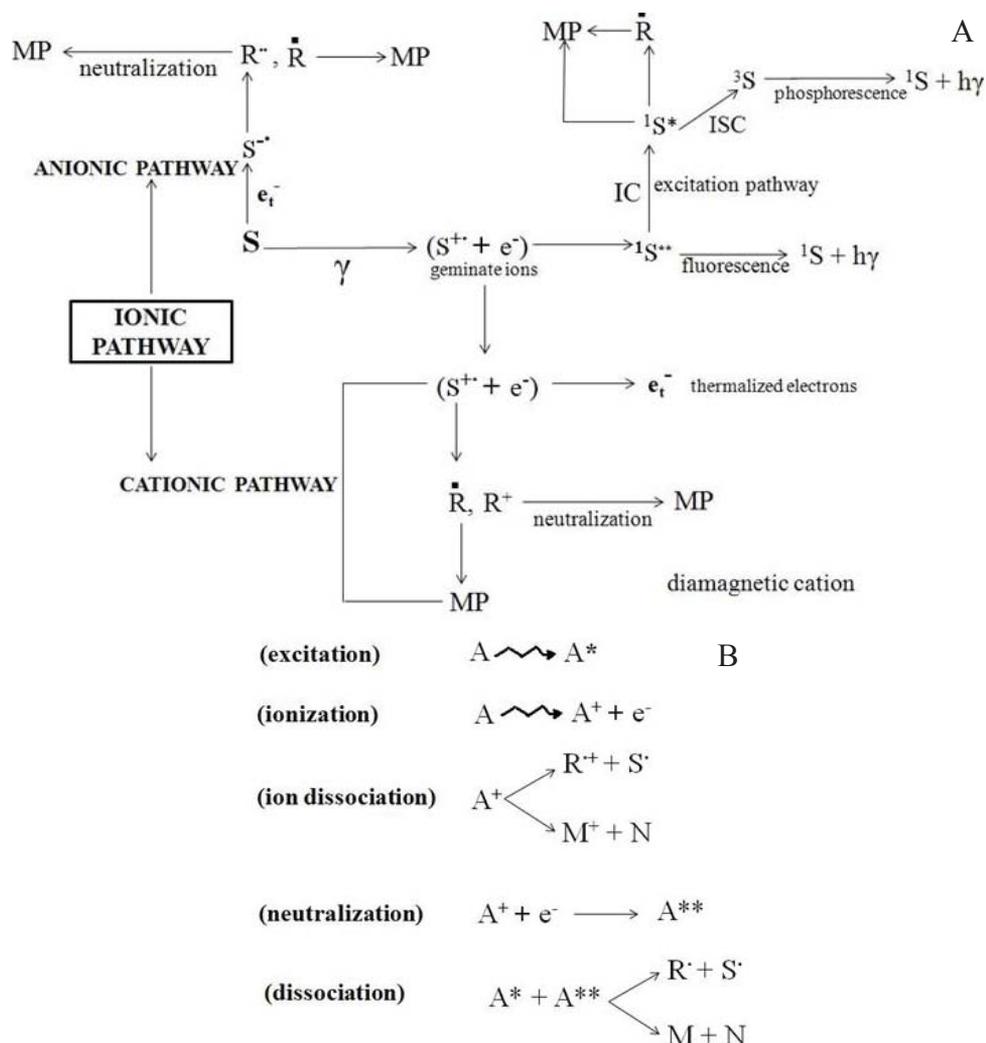


Fig.3. General radiolysis scheme (A) and primary processes in the radiolysis of organic compounds (B): R^\bullet and S^\bullet – free radicals; $S^{\bullet+}$ and $S^{\bullet-}$ – cation or anion radicals, respectively; ISC – intersystem crossing; IC – internal conversion; R^+ and R^- – diamagnetic cation or anion, respectively; MP, M and N – molecular products.

This consists of excitation radiolysis and ionic radiolysis pathways depending on the type of active species generated. The free radicals are the most important intermediates in all radiolysis processes. The excited species in condensed systems can undergo: (i) fast internal conversion (10^{-13} s) to the lowest excited levels with degradation to thermal energy of most of the electronic excitation energy, (ii) chemical reactions, (iii) return to the fundamental state of the same multiplicity with emission of radiation, (iv) fluorescence or (v) return to the fundamental state after intersystem crossing (ISC) with emission of phosphorescence radiation. The primary processes in the radiolysis of or-

ganic compounds can, in most cases, be represented by excitation, ionization, ion dissociation, neutralization and dissociation, as shown in Fig.3B.

Macromolecules are very sensitive to minute chemical changes at the appropriate places which have great influence on the morphology. A single bond altered may convert a free flowing polymer from a fluid to an elastic solid. An even smaller change may be lethal in biological systems.

The primary interactions of ionizing radiation with polymers include ionization, stabilization of electrons through generation of hot electrons, ion neutralization and free radicals formation. Free radicals are created either through chain scission or through the dissociation of the side chain (C–H(Cl)) bonds, as shown in Fig.4.

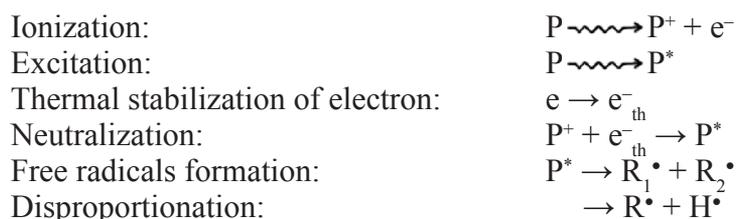


Fig.4. Primary processes occurring in polymer irradiation (P – polymer, R[•] – radical).

The irradiation of polymers, natural or synthetic, with ionizing radiation leads to the formation of reactive intermediates, free radicals, ions and atoms and molecules in excited states. These intermediates can undergo several reactions such as hydrogen abstraction, rearrangements and formation of new bonds, addition to the double bonds, chain scission, oxidation and grafting recombination (crosslinking and branching, to an extent which depends upon the polymer

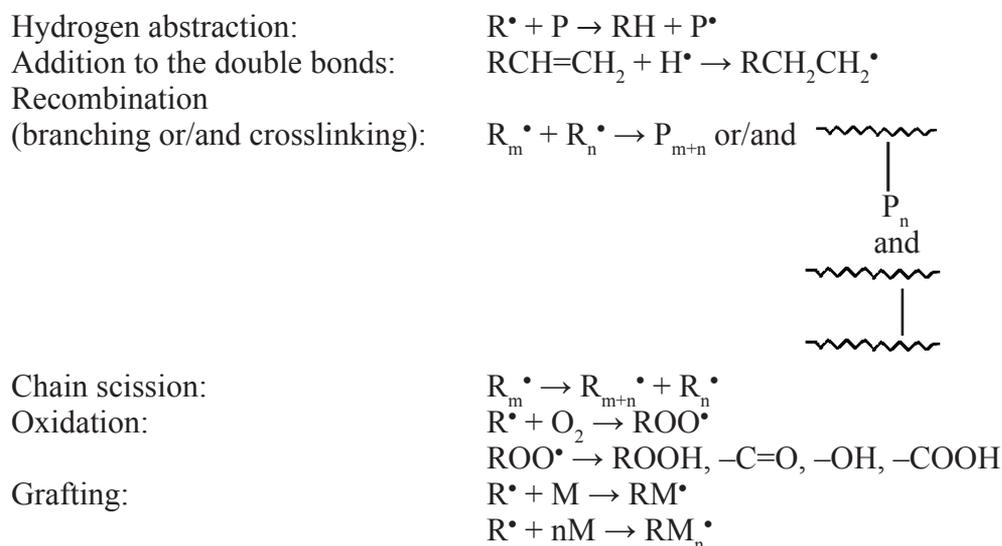


Fig.5. Secondary reactions in polymers occurring under irradiation (M – monomer).

structure), as shown in Fig.5. As a result both low molecular weight species and crosslinking occur with changes in molecular weight (decrease or increase, correspondingly). Both reactions can occur simultaneously, one of them being dominant depending on polymer structure, the presence of additives, the radiation dose and environmental conditions. Crosslinking dominates under vacuum, while chain scission may be a main reaction in presence of oxygen or air. As a consequence, radiolytic products from both a polymer and its additives are formed. As a rule, under the radiation effect on solid substances, the spatial distribution of radicals is non-uniform [5]. Sometimes it may present closely located radical pairs and/or agglomerations. Trapped radicals increase with irradiation dose.

The fundamental processes related to these reactions include:

- crosslinking – polymer chains are joined and a network is formed;
- chain scission – the molecular weight of the polymer is reduced through chain scission;
- oxidation – where the polymer molecules react with oxygen *via* peroxide radicals (oxidation and chain scission often occur simultaneously);
- long-chain branching – polymer chains are joined but a three-dimensional network is not yet formed;
- grafting – a new monomer is added onto the base polymer chain;
- polymerization – can also be initiated when monomers are irradiated;
- radiation curing (as in the case of coatings or composites) is a combination of polymerization and crosslinking.

Different polymers have different responses to radiation, especially crosslinking *vs.* chain scissioning. The same polymer such as poly(tetrafluoroethylene) can degrade by chain scission when $T < T_m$ (melting temperature of 315°C) or it crosslinks when $T > T_m$. Frequently different reactions occur simultaneously with predominance of some of them.

4. RADIATION YIELD

To quantify the radiation chemical effects of ionizing radiation, the number of molecules transformed or produced when a certain the quantity of radiation energy is absorbed should be known. The $G(X)$ value is a measure of the radiation-chemical yield. It was originally defined as the number of molecules $n(X)$, produced, destroyed or changed by radiation (consumed) to the irradiated matter by the mean energy imparted, E , usually of 100 eV of absorbed energy, as in Eq. (3):

$$G(X) = \frac{n(X)}{E} \quad (3)$$

Hence, the unit of the G-value of the International System of Units (SI) is mol/J. In the earlier literature the G-values were always given in units molecules/100 eV, but the new SI units will be used. (1 molecule/100 eV corresponds to 1.036×10^{-7} mol/J).

Table 1. G-values for crosslinking and chain scission for some common polymers.

Polymer	Crosslinking G(X)	Scission G(S)	G(S):G(X)
Low-density polyethylene	1.42	0.48	0.34
High-density polyethylene	0.96	0.19	0.20
Isotactic polypropylene	0.16-0.26	0.29-0.31	1.1-1.5
Atactic polypropylene	0.4-0.5	0.3-0.6	0.7-0.9
Poly(methyl methacrylate)	< 0.50	1.1-1.7	> 2
Poly(tetrafluoroethylene)	0.1-0.3	3.0-5.0	10
Natural rubber	1.3-3.5	0.1-0.2	0.14
Nylon-6	0.35-0.7	0.7	1.0
Nylon-6,6	0.5-0.9	0.7-2.4	1.4
Poly(vinyl acetate)	0.1-0.3	0.06	0.2
Poly(vinylidene fluoride)	0.6-1.00	0.30-0.6	0.3
Poly(methyl acrylate)	0.45-0.52	0.08	0.15
Polystyrene	0.019-0.051	0.0094-0.019	0.4
Polybutadiene	5.3	0.53	0.10
Polyisobutylene	0.05-0.5	5	> 10
Butyl rubber	< 0.5	2.9-3.7	> 6

In Table 1 lists the G-values for crosslinking, G(X), and chain scissioning, G(S), for some of the common polymeric materials irradiated at room temperature without oxygen. Materials with G(X) larger than G(S), the overall result is crosslinking, and whenever G(S) is larger than G(X), the overall result is degradation. Materials whose G(X) and G(S) values are both low are more resistant toward radiation.

Radiation effects are remarkably sensitive to molecular structure. G(S) and G(X) values vary from 0.1 to 10, as shown in Table 1. The ratio between them determines the changes in average molecular weight of polymers, as illustrated in Fig.6.

The G(X) of polyethylene (PE) is about one order of magnitude larger than that of polystyrene (PS) which demonstrates that aromatic rings exert a protective radiation effect.

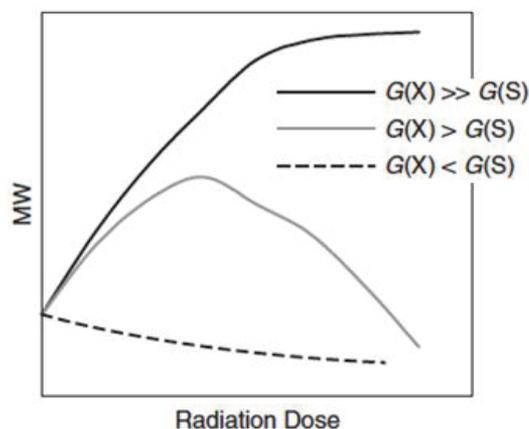


Fig.6. Relation between average molecular weight of polymers, $G(X)$ and $G(S)$ and radiation dose.

$G(X)$ and $G(S)$ also depend on irradiation conditions, such as temperature and atmosphere.

5. RADIOLYSIS PRODUCTS

Polymers used in medical devices and in primary packaging materials have been studied with respect to radiolysis products. Orthopedic implants and other medical devices that come into close contact with the human body are sterilized by either gas or high energy radiation. They are not free from the effect of ionizing radiation particularly if the process is performed in air. Food irradiation, sterilization of packaging materials for pharmaceutical or food products with ionizing irradiation can cause not only chemical and physical changes in polymer materials but also formation of some radiolysis products which can be solvent extractable or detectable by other techniques such as gas chromatography/mass spectroscopy (GC/MS), electron paramagnetic resonance (EPR), spectroscopic methods, in surrounding media [6]. Some examples are given in Table 2. The products and their concentrations are characteristic for each polymeric material. The polyolefin materials (polyethylene, PE, and polypropylene, PP) show an increase in low volatile compounds after irradiation due to an oxidative decomposition of the polymer and of additives. PE produces only traces of hydrocarbons, aldehydes, ketones, and carboxylic acids, which largely disappear within weeks. Other packaging materials, such as poly(ethylene terephthalate) (PET), polyamide (PA), and polystyrene (PS), did not significantly change their amount of solvent extractable compounds after irradiation with 25 to 44 kGy. PA-6 (nylon-6) yields pentanamide as the main

Table 2. Radiolysis products of polymers.

Name	Abbreviation	Radiolysis products	Observation	Ref.
Polyethylene	PE	Peroxy radicals on surface; chain scission, hydroperoxides, carbonyl mostly ketones, carboxylic acids, hydrocarbons (butane to nonane), acetic acid, 2-pentanone, pentanal, octane, propionic acid, 2-hexanone or 3-hexanone, hexanal, and heptanal, butanoic acid, 2-heptanone or 3-heptanone, alkyl benzenes	Gamma irradiation in air – 22 kGy	[7]
Polypropylene	PP	Hydrogen, hydroperoxides, ketones, aldehydes, alcohols and carboxylic acids. The ketones are very important in PP, but the carboxylic acids are the major products	Electron beam irradiation – 5, 10, 25 kGy	[8]
Poly(vinyl chloride)	PVC	2-ethyl-1-hexanol (100-1000 ppm), octane, 1-octene, 2-octene, 4-octene, acetic acid, 2-ethylhexyl ester; 1-octanol, heptane, 3-methylheptane, 3-heptanone, 2-ethylcyclohexanal, 4-octanone, undecane, pentylcyclopropane, 2-ethylhexanoic acid	Two months after irradiation with 22.5 kGy. Compounds results not only from polymers but also from additives	[7]
Poly(vinyl alcohol)	PVAL	Unsaturated bonds and carbonyl groups occur under irradiation; organic acids, alcohols	Gamma radiation at room temperature – 10 kGy	[9]
Poly(vinyl acetate)	PVA	Acetic acid, CO ₂ , CO, CH ₄ , H ₂	Gamma radiation at room temperature under vacuum	[10]
Ethylene-vinyl acetate copolymers	EVA	102 radiolysis compounds, unsaturated hydrocarbons, ketones, methyl derivatives	Gamma radiation at room temperature and in air presence	
Ethylene-vinyl alcohol copolymer	EVOH	Alkyl aromatics such as tert-butyl benzene and isobutyl benzene, and oxygenated aromatics such as acetophenone and 2-phenyl isopropanol; propanal, methyl ethyl ketone, 2-butanol, tert-butyl benzene, and 2-methylpropylbenzene	Electron beam irradiation – 5-50 kGy	[11]
Polystyrene	PS	Acetophenone (30-50 ppm); benzaldehyde, phenol, 1-phenylethanol (< 10 ppm), and phenylacetaldehyde	Gamma radiation in air – 25-50 kGy	[12]

Table 2. Contd.

Name	Abbreviation	Radiolysis products	Observation	Ref.
Methyl methacrylate-acrylonitrile-butadiene-styrene	MABS	Benzaldehyde, acetophenone, phenol, 1-phenylethanol, 1-phenyl-1-propanone	Gamma radiation – 22.4 kGy	[7]
Polyamide	PA-6	Pentanamide (≈ 75 ppm) and caprolactam; traces of some homologous amides	Gamma radiation in air – 25-50 kGy	[12]
Polyurethane	PU	ROOH, OH \cdot , RO \cdot ; carboxylic acids, alcohols, esters, formats	25-1000 kGy, in air	[13]
Poly(dimethylsiloxane)	Silicone, PDMS	Crosslinking, chain scission to small extent, hydrogen methane, ethane	50 kGy – noncitotoxicity	[13]
Poly(ethylene terephthalate)	PET	Formic acid, acetic acid, 1,3-dioxalane, 2-methyl-1,3-dioxolane; acetaldehyde, 1,3-dioxolane, 2-methyl-1,3-dioxolane; terephthalic acid, bis-(2-hydroxyethyl) terephthalate, dimethyl terephthalate, monohydroxyethylene terephthalate	Gamma radiation – 5, 25 and 50 kGy, at ambient temperature or an electron beam accelerator	[14]
Polysaccharides		H $_2$, CH $_4$, CO, CO $_2$ or low molecular mass substances such as water, formaldehyde, methanol, aldehydes, ketones, formic acid, acetaldehyde, methanol, acetone, ethanol, methyl formate and sugars: glucose, maltose, erythrose, ribose, mannose		[15]
Proteins	Hen egg-white lysozyme	Sulphur and carbon-centred radicals RSS \cdot ; perthyl radicals, sulphur-oxygen radicals (in presence of oxygen)	Gamma radiation – 0 to 20 kGy, in the solid state (lyophilized powder), at room temperature under three different atmospheres (air, nitrogen and oxygen)	[16]

product, plus traces of some homologous amides. The poly(vinyl chloride) (PVC) packaging material release of hydrochloric acid (HCl) during irradiation and large amounts of volatile substances were extracted from the PVC sheets. The main products of PVC and PP are fragments of additives, *i.e.* of stabilizers and phenol-type antioxidants, respectively. For consumer protection and also to meet general food packaging legislative requirements for irradiated packaging materials, it is necessary to evaluate the compositional changes in the polymers following irradiation, especially for irradiated polyolefins and PVC. Most attention should be paid to low volatile radiolysis products which are the most likely to migrate into a foodstuff or a pharmaceutical products. Under realistic polymer/food simulant contact conditions during irradiation, a large number of primary and secondary radiolysis products (hydrocarbons, aldehydes, ketones, alcohols, carboxylic acids) were produced. These compounds were detected in the food simulants after contact with all films tested, even at the lower absorbed doses of 5 and 10 kGy (approved doses for food preservation). The type and concentration of radiolysis products increases progressively with increasing dose. Volatile and non-volatile compounds produced during irradiation affected the sensory properties of potable water after contact with packaging films. Taste transfer to water was observed mainly at higher doses and was more noticeable for multilayer structures containing recycled low density polyethylene (LDPE) [17]. The main products of PS are acetophenone, benzaldehyde, phenol, 1-phenylethanol, and phenylacetaldehyde. Their concentrations are one order of magnitude below the residual styrene/styrene dimer levels [7, 18].

The radiolysis products formed during gamma-ray or electron beam radiation are generally later released. Due to rigid structure of these materials, the radiolysis products may be trapped inside the polymeric structure and be delivered later when the material enters into contact with environment that favours their release. The radiolysis products of some polyethylene irradiated at 20 kGy were evaluated 7.5 months after irradiation and it was found that the

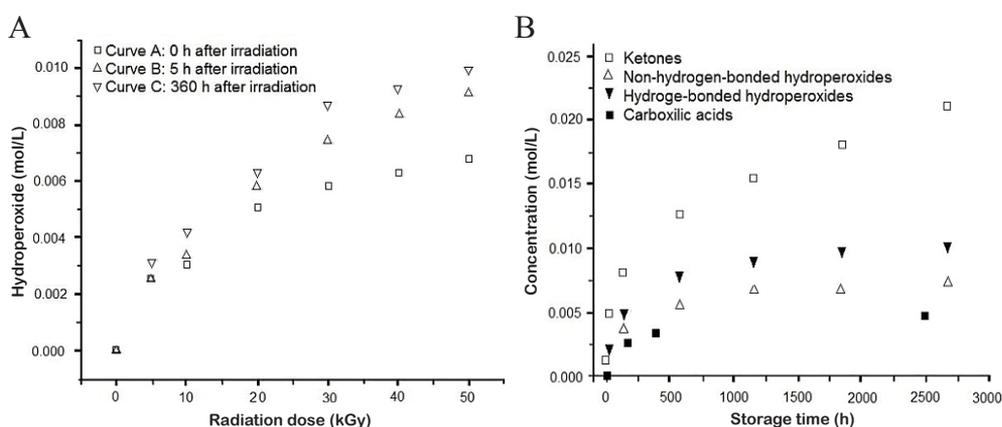


Fig.7. Variation of functional groups with radiation dose (A) and storage time of UHMWPE (B).

peroxy radicals continued to react, promoting chain scissioning, and the generation of carbonyl, of hydroperoxides and of ketones. In the radiation of ultra-high molecular weight polyethylene (UHMWPE), high concentrations and new radiolysis products were found, as shown in Fig.7.

When exposed to 25 or 50 kGy radiation doses, PS produces radiolysis products such as benzaldehyde, acetophenone (30-50 ppm), 1-phenylethanol (< 10 ppm) and phenol. Nylons evolved pentanamide (75 ppm) and caprolactam. PP generates alkyl radicals which can subsequently interact with molecular oxygen to form hydroxyl, carbonyl or carboxyl groups. These volatiles can have adverse flavour effects to irradiated food packaged in these polymers, in general in this order: LDPE > HDPE (high density polyethylene) > PS ~ PA and PET. The intensity of specific off-odors increases with the availability of oxygen in atmosphere.

The addition of the antioxidants reduces the formation of carboxylic acid derivatives in LDPE films. However, phenolic stabilizers, such as Irganox 1076, 1010 and 1330 and the arylphosphite antioxidant Irgafos 168 (in PVC, PE and PP) are susceptible to degradation under gamma irradiation. Low doses of irradiation (5 kGy) to HDPE trays can completely destruct phosphite antioxidants to their phosphate products with some covalently bonded on the polymer matrix so that they will not be found in simulants. At present, little is known about toxicity of radiolytic products from polymers and additives because of the variability of migration rates and because of the potential of polymeric entrapment of volatiles from the different polymers into food simulants [19].

6. CHANGES IN PHYSICAL AND CHEMICAL PROPERTIES

6.1. SYNTHETIC POLYMERS

Radiation is the unique source of energy which can initiate chemical reactions at any temperature, including ambient, under any pressure, in any phase (gas, liquid or solid), without use of catalysts [20]. Polymers are quite often irradiated for modification or sterilization (medical products). Therefore, the changes in their structure may be beneficial or undesirable. The application of radiation for modification of synthetic materials, mostly curing and crosslinking is a well-established technology [21].

The changes in the properties of the irradiated polymers in the solid state are:

- chemical changes:
 - crosslinking and chain scission,

- structural weakness,
- gas formation,
- double bond formation,
- oxidation,
- living radical effects after irradiation,
- effects on additives;
- physical changes:
 - changes in mechanical properties (mechanical strength, flexibility, Young's moduli, torsional resistance, *etc.*),
 - colour change,
 - changes in conductivity,
 - changes in crystallinity,
 - thermal stability and transitions.

Table 3. Linear polymers that predominantly undergo crosslinking or main-chain scissioning if irradiated with high energy radiation at room temperature in vacuum or in an oxygen-free atmosphere.

Predominant main-chain scission (average molar mass decreases)	Predominant crosslinking (average molar mass increases)
Polymethacrylates	Polyacrylates
Polymethacrylamide	Polyacrylamide
Poly(α -methacrylonitrile)	Polyacrylonitrile
Poly(α -methylstyrene)	Polystyrene
Polyisobutene	Polyethylene
Poly(tetrafluoroethylene)	Polypropylene
Poly(trifluorochloroethylene)	Polyisoprene
Poly(vinyl fluoride)	Polybutadiene
Poly(vinylidene chloride)	Polyamides
Poly(hexane-1-sulphone)	Poly(vinyl acetate)
Poly(propylene sulphide)	Poly(vinyl alcohol)
Poly(oxymethylene)	Polyvinylpyrrolidone
Polycarbonates	Polyurethanes
Poly(vinyl butyral)	Polychloroprene
Poly(phenyl vinyl ketone)	Natural rubber
Polysaccharides (cellulose, chitosan)	Polysiloxanes
Polysine, polyalanine	Copolymers of butadiene with styrene or acrylonitrile
Nucleic acids (DNA)	Copolymers of acrylonitrile with styrene

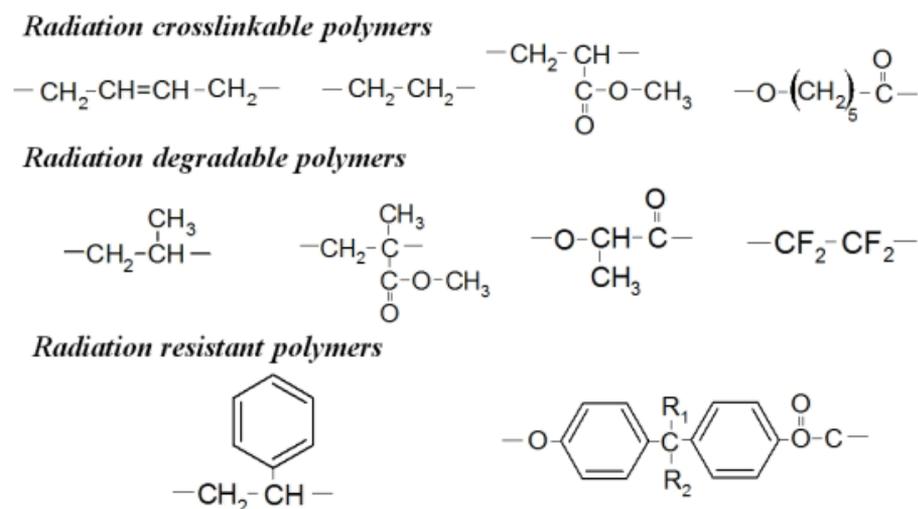


Fig.8. Examples of chemical structures of polymers with different responses to radiation.

The different responses to radiation for different polymers are related to the chemical structures of the polymers. Some examples of chemical structures that correspond to crosslinking types, degrading or scissioning types, and radiation-resistant polymers are given below. A classification of common polymers is summarized in Table 3 and the structure of some are depicted in Fig.8.

The formation of reactive oxygen species can result in the oxidation of polymer with the formation of peroxide, alcohol and carbonyl compounds. The most stable polymers are vinyl derivatives, PS and the PET with polyamides (nylons) having intermediary stability while polyolefins as the least stable polymers.

In solid state, the radicals can be found for months after irradiation. Commercial polymers often contain some additives. The effect of the additives on radiolysis is important. Radiation protecting additives have aromatic cyclic structures and reduce degradation by radiation. Plasticizers can have a similar protective role.

Mechanical properties of irradiated polymers depend on the ratio of chain scission and crosslinking and are related to molecular weight. The mechanical properties of polymers of the crosslinking type are improved upon irradiation with low absorbed doses (up to 0.1 MGy). The elastic modulus, tensile strength and hardness are increased, whereas the solubility is decreased with increasing absorbed dose. At very high absorbed doses, these polymers become hard and brittle. The polymers of the degradation type undergo deterioration of their mechanical properties even at low absorbed doses. Low doses of 5 and 10 kGy had no effect on mechanical properties such as tensile strength, elongation at break and Young's modulus. However, at 30 kGy, there was a decrease in tensile strength in HDPE, PP and a decrease in elongation at break of LDPE and a polyethylene ionomer. The mechanical properties of

neither an ethylene-vinyl acetate (EVA) nor polystyrene were affected by irradiation.

Important aromatic polymers such as polyimides and polyarylsulphones, as shown in Fig.9, are resistant to high energy radiation compared to nonaromatic polymers.

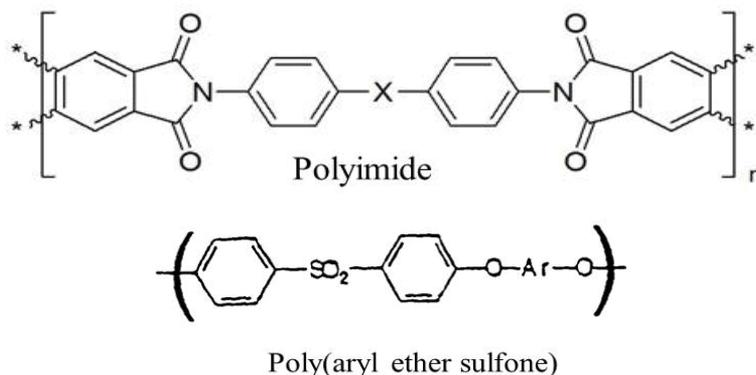


Fig.9. General chemical structure of polyimide and polysulphone.

The mechanical and electrical properties of a poly(pyromellitimide) remain satisfactory in the presence of air up to absorbed dose of 100 MGy. Most aromatic polymers proved to be radiation resistant only in the absence of oxygen. For example, the mechanical properties of polystyrene were not appreciably deteriorated when exposed in the absence of oxygen to the absorbed doses up to 10 MGy, but these properties decreased to 50% of their initial values at an absorbed dose of only 0.8 MGy in the presence of oxygen. Irradiation of pre-packaged meat and poultry should alter neither physicochemical properties of a packaging film nor result in the transfer of components or residues from packaging material to contaminate the food in contact with the plastic film. The irradiation of plastic film results in a combination of chemical crosslinking and a consequent increase of tensile strength of the film, or a fragmentation leading to a decreased strength and increased permeability of packaging films. In addition to these events, the formation of volatile radiolysis products (hydrogen, methane, HCl, *etc.*) is influenced by presence of oxygen in the irradiated products. It was reported that irradiation at 5, 10 and 30 kGy had no effect on the O₂, CO₂ permeability or water vapour transmission rates of a variety of polymers including LDPE, HDPE, PS, EVA, biaxially oriented PP and an ionomer.

Colour change can appear when the double bonds formed on irradiated polymers such as poly(methyl methacrylate) (PMMA) and PVC.

Conductivity change can increase when the double bond increased in irradiated polymers.

The overall migration into food simulants as distilled water was not affected by low irradiation doses; at 30 kGy, migration into 3% acetic acid was decreased for PP and an ionomer.

6.2. NATURAL POLYMERS

Studies of the radiolysis of biopolymers [22] serve the dual purposes of giving information on: (1) the chemical mechanisms by which radiation modifies life processes and (2) the structure-properties-application relationships in macromolecules. Irradiation effects on biopolymers result in the cleavage of chemical bonds. Because of the very complex composition of most biopolymers, many different chemical reactions are initiated and in each case a host of products are formed under the influence of high energy radiation. A variety of biopolymers composed of linear strands, including certain polysaccharides, proteins and nucleic acids undergo predominantly main-chain scission, and this is of outstanding importance in the case of deoxyribonucleic acids (DNA), because the killing of living cells correlates well with double-strand breaks.

6.2.1. Amino acids, proteins and DNA

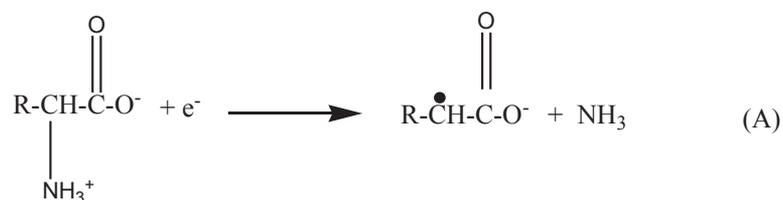
Amino acids and proteins exist as zwitterions. Under irradiation amino acids undergo by the electron capture deamination, as indicated in Fig.10A. With proteins both deamination and decarboxylation take place. For those molecules containing sulphur groups, they are cleaved by a radiolytic mechanism and hydrogen sulphide is produced as a by-product, as shown in Fig.10B.

In living cells, both direct and indirect depositions of energy are possible. Direct effects in chromatin components result in the formation of specific radical products, many of which are highly reactive. Secondary reactions of the cationic radicals are largely unknown. Indirect effects occur when energy is deposited in water or other components in a solution, and radiolysis products such as e^-_{aq} and $\bullet OH$ react with the biopolymer have been investigated, as shown in Fig.11.

Commonly DNA molecules are tightly associated with 8 to 12 water molecules per nucleotide forming a primary solvation shell which increases the radiation-induced damage to DNA by ~50%. When the water molecules are ionized, an entire transfer to DNA can occur and electrons ejected from water molecules can be scavenged by DNA molecules. The events due to the direct effect are single- and double-strand breaks, crosslinking, base release, and lesions in bases and sugar moieties. Hydrogen bonds between the two strands of the double helix are broken. A large number of radiolysis products results. From base damage the following products have been identified: 5-hydroxy-5,6-dihydrothymine, 5,6-dihydrothymine, 5-hydroxyuracil, 5,6-dihydroxyuracil, 5-hydroxycytosine, 2-hydroxyadenine, 8-hydroxyadenine, 7-hydro-8-oxo-guanine, 2,6-diamino-4-oxo-5-formamidopyrimidine, 4,6-diamino-5-formamidopyrimidine.

Studies carried out half a century ago showed that this process is effective in inactivating enzymes. Replacing $\bullet OH$ to the less reactive inorganic radical anion $\bullet Br_2^-$ has been done. It is then possible to determine the role of tyrosine

AMINOACIDS



PROTEINS

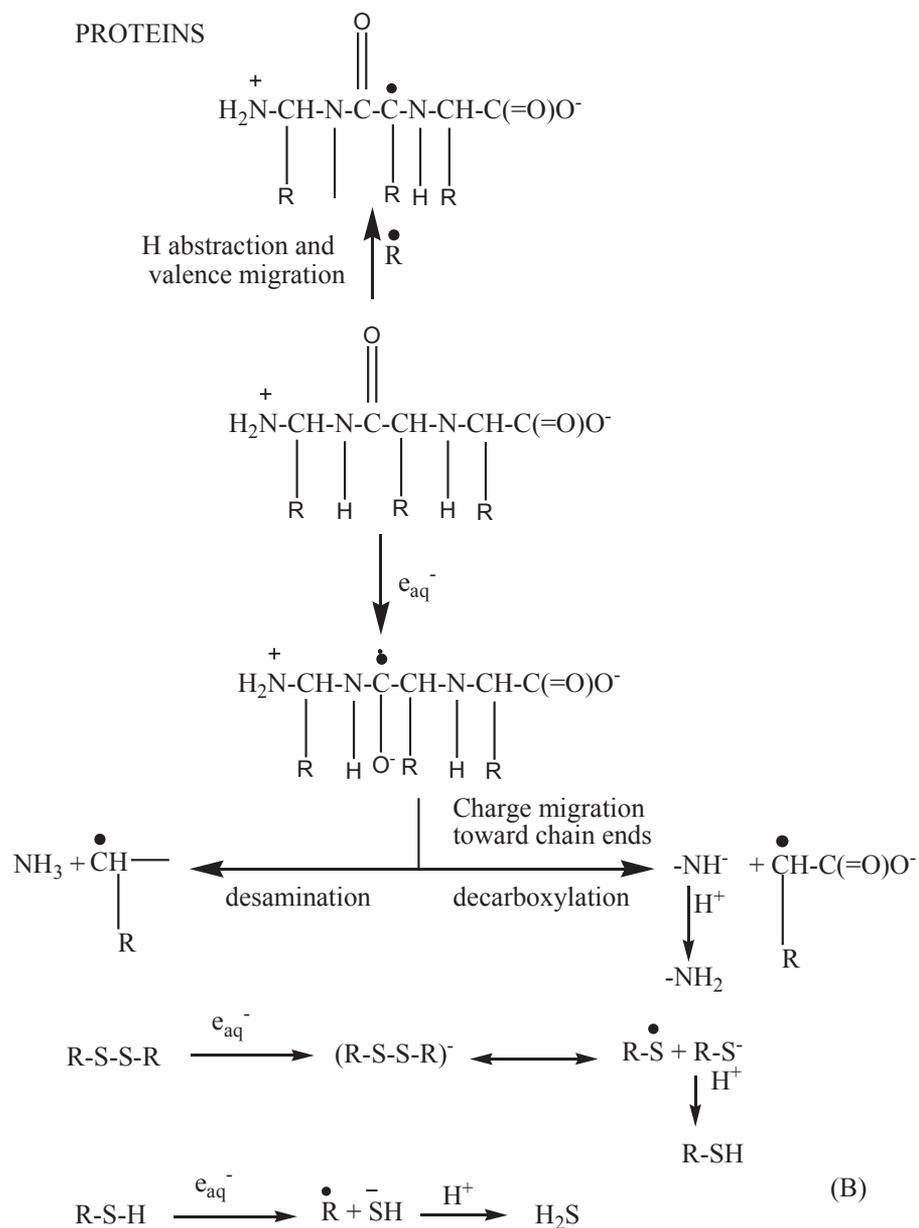


Fig.10. Radiolytic mechanism of amino acids (A) and proteins (B).

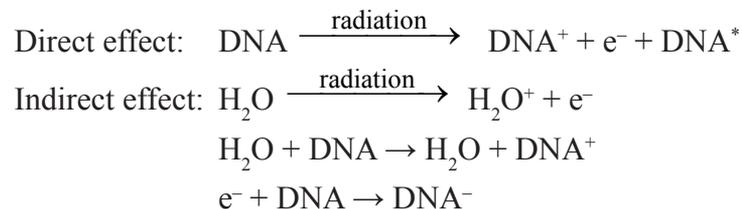


Fig.11. Radiolytic mechanism of DNA.

in functional and structural integrity of several proteinase inhibitors. Both e^-_{aq} and $-\text{OR}$ react rapidly with DNA, but only $\bullet\text{OH}$ initiates reactions which damage DNA. Radiolysis of double-stranded DNA leads to an increase in optical absorption. The $\bullet\text{OH}$ is believed to attack the deoxyribose moiety, causing strand

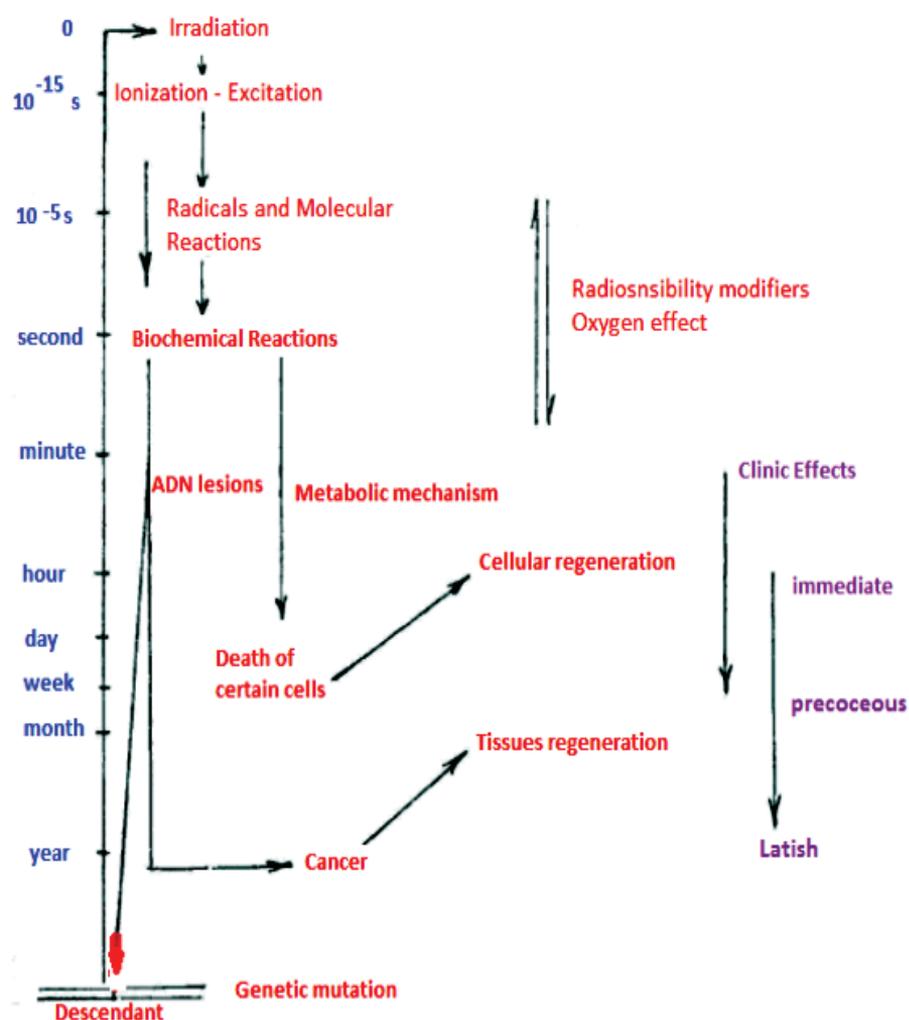


Fig.12. Schematic representation of phenomena launched by ionizing radiations in biological molecules/organisms.

breaks and partial denaturation, thus reducing the hypochromic effect. After the DNA is partially denatured, or single-stranded, $\bullet\text{OH}$ attacks the bases also. Three kinds of strand breaks have been observed: (i) immediate, (ii) those appearing post irradiation, and (iii) those appearing on post-irradiation treatment with alkali. Radiolysis of chromatin results in DNA strand breaks, base damage, and protein-DNA crosslinks. Yields for strand breaks and base damage are lower in chromatin than in purified DNA, and lower still in intact cells [23].

In living organisms, this denaturation of the biological molecules without adequate protection over a long period of exposure could have deleterious effects on health, as illustrated in Fig.12.

6.2.2. Polysaccharides

Irradiation of polysaccharides in the solid state induces the radical formation in molecular chains as a result of the direct action of radiation [24]. Here mainly two events take place: (1) direct energy transfers to the macromolecule to produce macroradicals and (2) the generation of primary radicals due to the presence of water (moisture). The course of the degradation of carbohydrates in the solid state is illustrated in Fig.13. The main effects are fragmentation, hydrolysis and rearrangement leading to low molecular weight products. When polysaccharides such as starch, cellulose, chitosan, amylose and dextran are subjected to high energy radiation, a vast number of products is formed, such

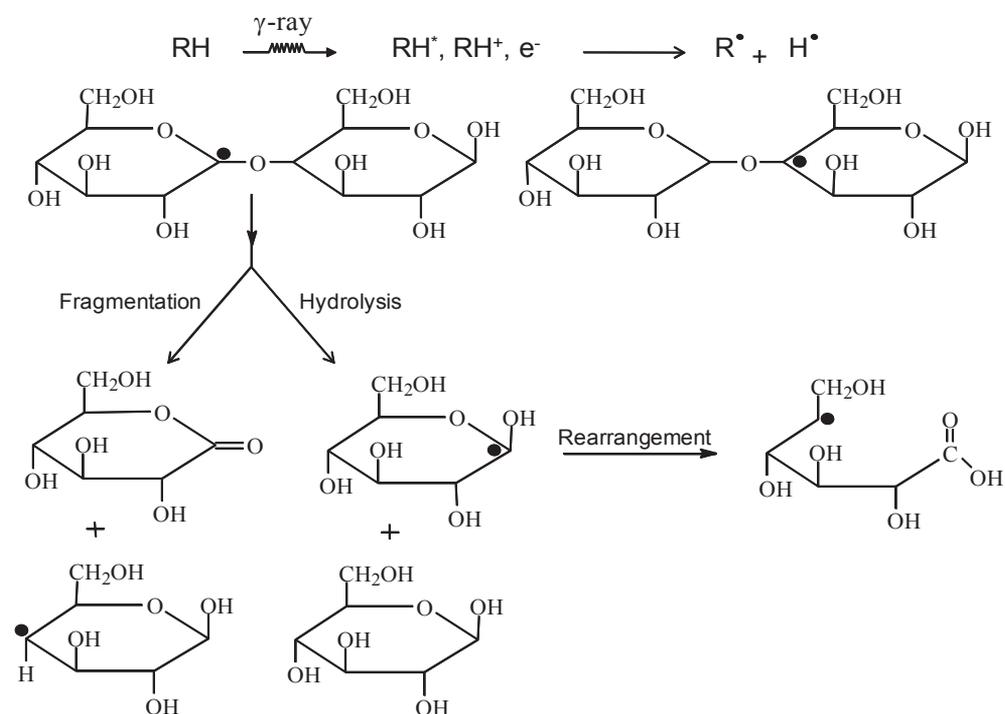


Fig.13. Events in solid state radiation of carbohydrates.

as gaseous H_2 , CH_4 , CO , CO_2 and low molecular mass substances such as water, formaldehyde, methanol, aldehydes, ketones and sugars. The remaining polymer contains carbonyl, carboxyl, and aldehyde groups. The average molecular molar mass is reduced because of the predominant main-chain scissioning through cleavage of the C–O–C glycoside bond between base units. When high energy radiation is directly absorbed by polysaccharides, electronically excited moieties, radical cations and electron are generated. Free radical processes play an important role, while the radical cations generated are rapidly transformed to free radicals by deprotonation.

During the solid state radiolysis of polysaccharides, scissioning of the glycosidic bond, analogous to the reactions shown in Fig.13, is the dominant process which eventually leads to a decrease in the molecular weight of the macromolecules. Degradation and the resulting changes in average molecular weight products are often quantified as radiation yields of degradation $G(s)$. Moisture content strongly influences the reaction pathways and yields. The radiolysis of water contributes to this. The yields of radicals are significantly higher than in dry polysaccharide so the contribution of indirect effect may be greater than based on percent of moisture, and also due to the effect of water molecules on the dry matrix structure and polymer chain mobility [25].

6.3. COMPLEX MATERIALS

Complex materials, including multilayer laminated and coextruded ones, are very useful because they combine a number of desirable properties which no single of material possesses. Most are based on polyolefin, PS, PET, PA, EVA, and other synthetic or natural polymers. The effect of gamma irradiation

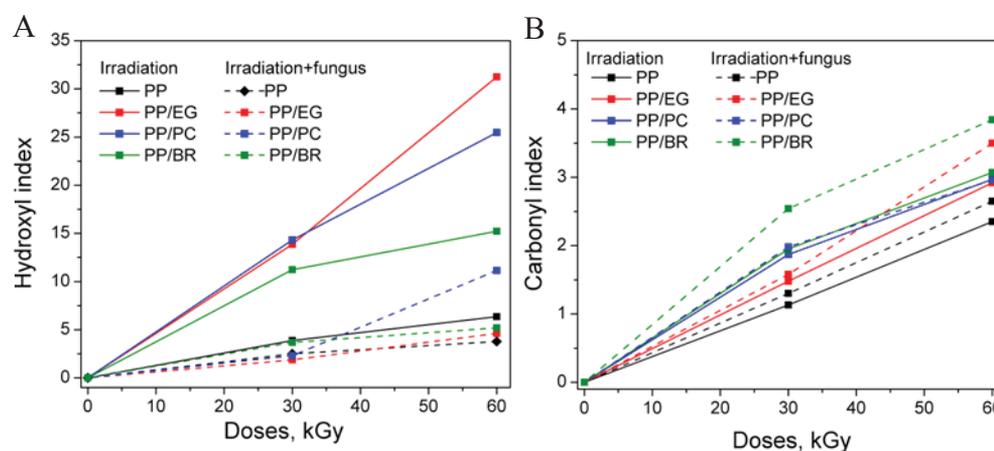


Fig.14. Variation of (A) hydroxyl and (B) carbonyl indexes of gamma-irradiated PP and PP/biomass composites compared with those of 7 weeks fungal degradation of the PP/biomass samples. (Adapted from Ref. [26]).

on PP biocomposites (*Eucalyptus globulus*, pine cones, and *Brassica rapa*) has been studied by Parparita *et al.* [26]. The biomass lignin content acts as an antioxidant and has a stabilization effect against gamma irradiation degradation. For the materials studied, gamma irradiation promoted the biodegradability under the action of the *Bjerkandera adusta* fungus [27]. Removing a protective layer of relatively inert polyolefin, increased the effects of absorbed dose which leads to increase of oxygen containing functional groups, as illustrated in Fig. 14. In this manner, an eco-friendly method for improving integration of some “undegradable” materials in natural cycles could be improved.

7. RADIATION PROTECTION

Measures to fully protect polymers against radiation exposure do not exist. The stabilization of polymeric materials against high energy radiation may be achieved through the use of antioxidants, ultraviolet and heat stabilizers, which, in turn, also undergo degradation. Radiolysis products could originate more from additive decomposition than from the originating polymers themselves.

Protective agents added to the polymers in small amounts are effective only to a limited extent and function *via* different mechanisms. They can act mainly as antioxidants by preventing radiation-induced oxidative chain reactions or more generally as free radicals scavengers. Other additives may act as energy absorbers in accepting electronic excitation energy transferred from a polymer. In this manner, agents that operate protectively are aromatic compounds, including polymers with aromatic constituents or fillers (inorganic materials or carbon black). Electronic excitation energy transported to or directly absorbed by aromatic rings is delocalized due to the π -electron-based resonant structure of the aromatic ring, and thus converted to heat by collision with neighbouring groups or molecules. Hence, bond rupture is much less likely in the case on nonaromatic compounds.

8. CONCLUSIONS

Study of the radiation chemistry of solid organic materials is important for many applications, as in the medical, pharmaceutical, and food preservation fields because the effects of radiation exposure can be beneficial or deleterious. Limits should be based on known effects. Much greater effort is needed in this direction.

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