Chapter 20

APPLICATION OF RADIATION TECHNOLOGY TO FOOD PACKAGING

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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.

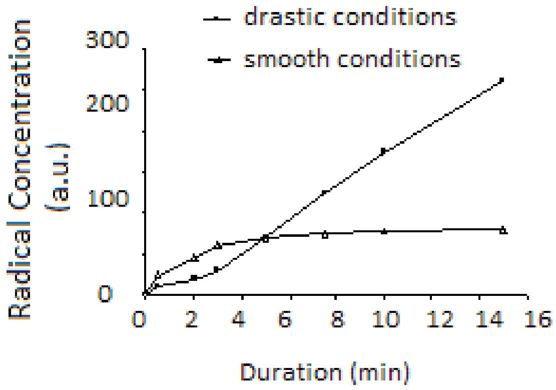

Fig.1. Radical concentration *vs.* N_2 plasma treatment duration of polypropylene. (Adapted from Ref. [11]).

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

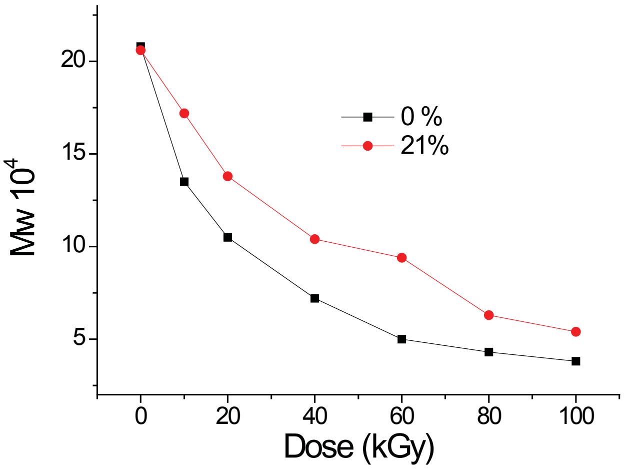

Fig.2. The change of weight-average molecular weight of carrageenans with different water contents as a function of irradiation dose. (Adapted from Ref. [37]).

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].

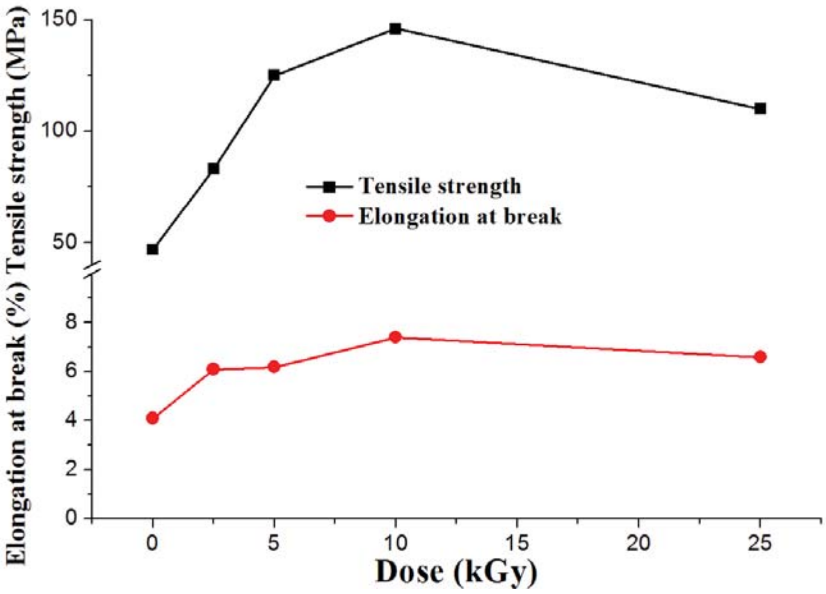

Fig.4. Effect of gamma radiation on the tensile strength and elongation at break of alginate films containing 5% NCC. (Adapted from Ref. [50]).

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].

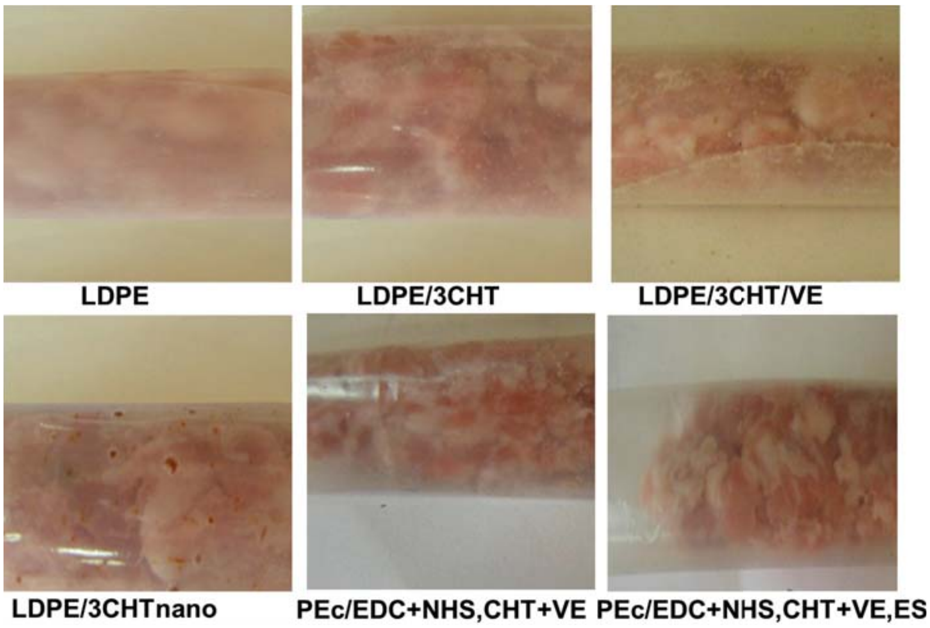

Fig.5. Microscopically aspects of the minced poultry cuts packed in films of LDPE grafted chitosan (CHT) after plasma activation, containing vitamin E (VE) and coated by electrospinning technique (ES). (Adapted from Refs. [53, 54]).

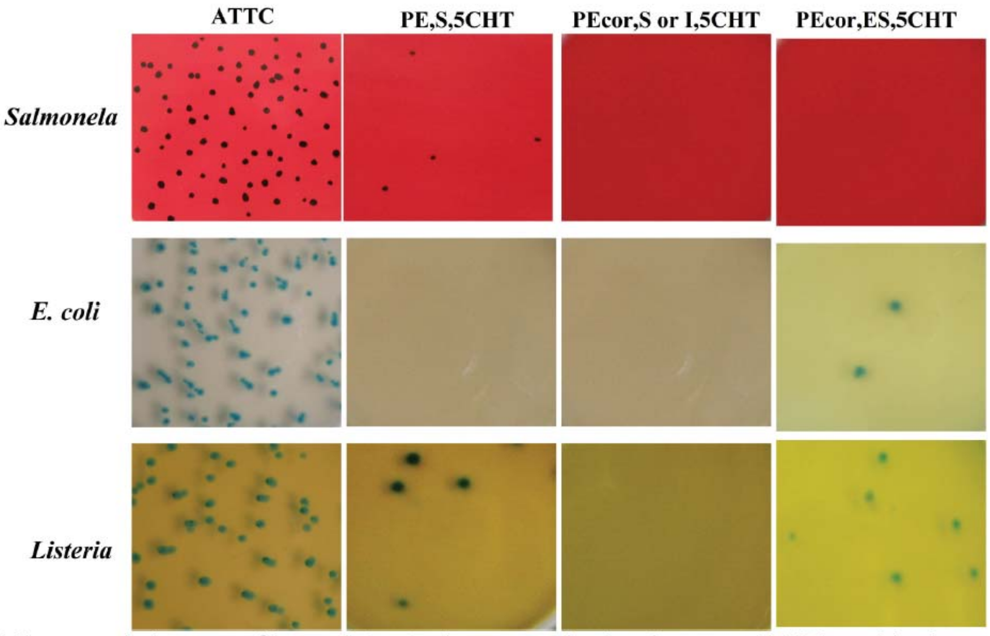

Fig.6. Microscopic images of bacterial colonies grown in the absence (ATCC) and in the presence of PE films coated with chitosan (CHT) by spreading (S) or electrospinning (ES) technique. (Adapted from Refs. [53, 54]).

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

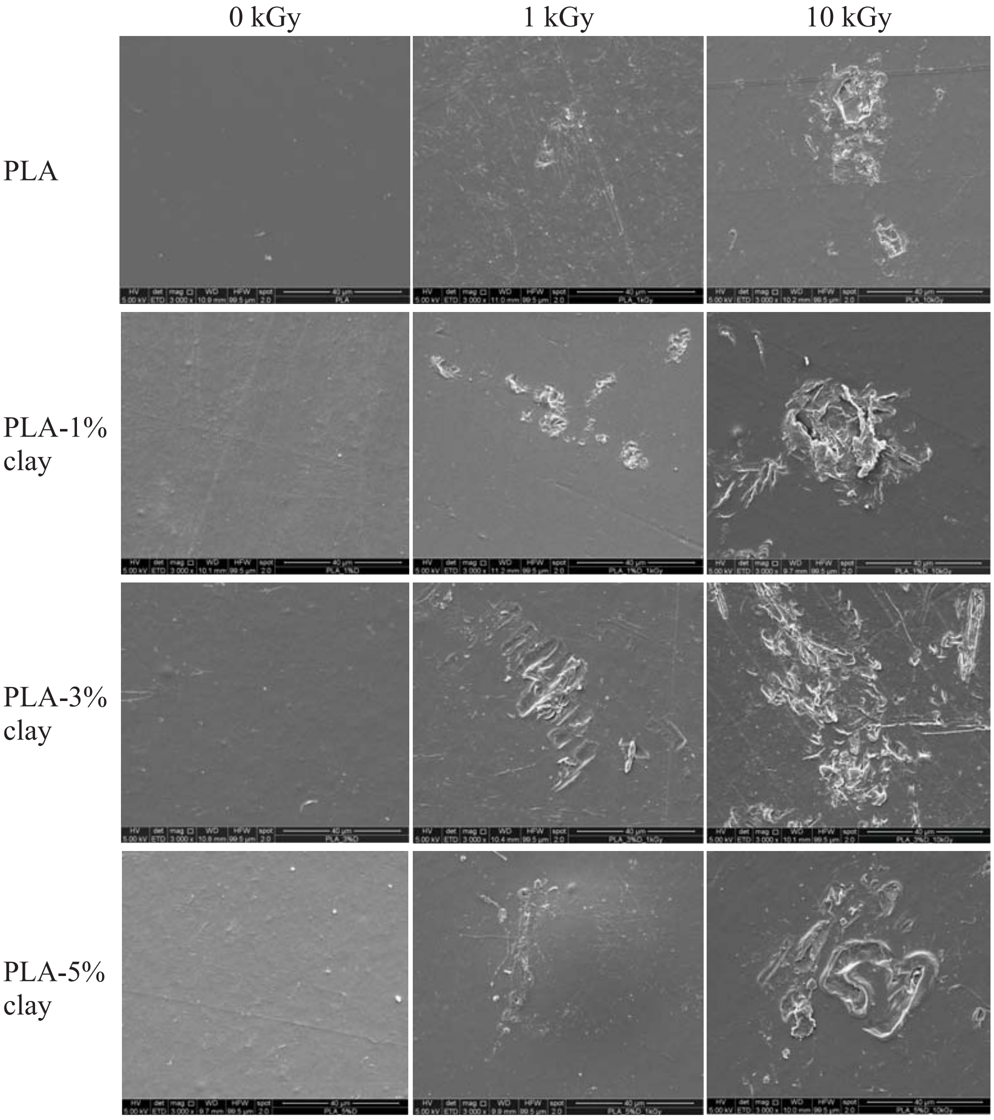

Fig.7. SEM (3000x magnification) of film surfaces of nanocomposites of PLA at 1, 3 and 5% by weight of clay irradiated at 1 and 10 kGy [55].

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.

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