# PACKAGING OF IRRADIATED FOOD

Foods deteriorate as a result of physiological changes, activities of enzymes and attack by insect pests and micro-organisms during post-harvest storage. Insect infestation and microbial activity are by far the most important factors that affect food spoilage. Among the newly emerging methods of food preservation, food irradiation is an effective method to inactivate micro-organism and destroy insect pests. Unlike other preservation techniques that often tend to produce unacceptable changes in the quality of food, radiation processing does not bring about serious organoleptic changes, as it is a cold process. Extensive studies have demonstrated that such food are toxicologically safe and nutritionally wholesome.

In 1980, a Joint FAO/IAEA/WHO Expert Committee on the Wholesomeness of Irradiated Food concluded that the irradiation of any food commodity up to an overall average dose of 10 kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems<sup>[1]</sup>. Since then, irradiated food has been given access to markets. In United States, new approvals for ground beef and fresh fruits and vegetables were granted<sup>[2]</sup>. Australia and New Zealand amended their food standards for use of irradiation for quarantine treatment of tropical fruits<sup>[3]</sup>. Food irradiation has also been approved in India and a number of commodities have been cleared under The Prevention of Food Adulteration Act 1954 rules (Table 1).

Food irradiation thus offers a proven and unique option to address the problems of food security, safety and trade issues.

## **Food Irradiation**

Food irradiation is the use of ionizing radiation to increase food storage life, reduce post harvest food losses, and eliminate food borne pathogens. Ionizing radiation used in food preservation include gamma rays, X-rays with energies of 5 MeV or less and high-energy electrons of 10 MeV or less. Gamma rays and X-rays are high-energy (short wavelength) electromagnetic radiation consisting of photons of energy transmitted in the form of wave motion. Gamma ray source for food processing applications are the radio-nuclides, cobalt-60 or caesium-137, while X-rays are produced by using electron beam machine. Heating a tungsten element and accelerating the emitted electrons inside an evacuated chamber at high voltage produces high-energy electrons. Photons and high-energy electrons unlike other forms of radiation such as microwave, infrared and ultraviolet radiation have sufficient energy to cause ionization of atoms (of low atomic number e.g. carbon, hydrogen, oxygen), while passing through a medium containing them. Ionization is the creation of positive and negative ions by removal of orbital electrons from an atom. Formation of charged ions caused by absorption of energy of ionizing radiation in the medium, results in chemical and biological effects. In the energy ranges used for food irradiation, both photons and highenergy electrons produce the same chemical and biological effects.

The International Commission on Radiation Units has defined the quantity of energy absorbed when ionizing radiation traverses through a medium as 'the mean energy imparted to the matter in a volume element divided by the mass of the matter in that volume element'. Thus, the

TABLE 1
Clearances for Radiation Processed Foods

Food Item	Radiation Dose (kGy*)		D	
rood item	Minimum	Maximum	Purpose	
Onions	0.03	0.09	Sprout inhibition	
Potatoes	0.06	0.15	Sprout inhibition	
Shallots(small onions), garlic, ginger	0.03	0.15	Sprout inhibition	
Rice, semolina (suji or rawa), atta ( wheat flour) and maida (refined wheat flour)	0.25	1.0	Insect disinfestation	
Pulses	0.25	1.0	Insect disinfestation	
Dried sea-foods	0.25	1.0	Insect disinfestation	
Resins, dried figs and dates	0.25	0.75	Insect disinfestation	
Mango	0.25	0.75	Shelf-life extension and quarantine treatment for export trade	
Meat and meat products including chicken	2.5	4.0	Shelf-life extension and pathogen control.	
Spices	6.0	14.0	Microbial decontamination	
Fresh sea-foods	1.0	3.0	Shelf-life extension	
Frozen sea-foods	4.0	6.0	Microbial pathogen control	

 $Gray(Gy=1\,Joule/kg\,,1kilogray\,(kGy=1000Gy))$ 

absorbed dose has the units of energy per unit mass and in SI system has been given the special unit Gray (Gy) defined as 1 joule per kilogram (1J/kg). Old unit is rad, defined as 100 erg/g, officially discontinued in 1986 (1Gy =  $100 \text{ rad} = 6.25 \times 10^{18} \text{ eV/kg}$ ).

<sup>\*</sup>kilogray (kGy) is SI unit of energy absorbed by food from ionizing radiation

Food is usually irradiated with an absorbed dose of 0-10 kGy. Higher absorbed dose (25 kGy) may be needed for sterilization of food. "Typical" dose rates are 1-10 kGy per hour for cobalt-60 gamma-source and several thousand kGy per second for electron accelerators.

The main purposes of irradiation processing of food and the recommended dose ranges are listed in Table 2.

TABLE 2
Main Purposes of Food Irradiation and Recommended Dose Ranges

Purpose	Food	Effect of Radiation	Approx. Dose Range (kGy)
Extend storage life	Vegetables such as potatoes, onions, garlic	Inhibition of sprouting	0.05-0.15
	Fruit	Delay ripening	0.2-1.0
Prevent post-harvest losses	Cereals, flour, fresh and dried fruit, other products liable to insect infestation	Destruction of insects	0.15-1.0
Extend shelf-life	Chilled Meat, poultry, fish, ready meals	Reduction of micro-organisms that cause spoilage	0.5-3.0
Prevent food-borne illness	Meat, poultry, fish	Destruction of various parasites	0.03-6.0
	Meat, poultry ,fish	Destruction of pathogenic bacteria Eg. Salmonella, Listeria, Campylobacter	3.0-7.0
Minimize contamination of food to which ingredients are added	Spices and other dried food ingredients	Reduction in numbers of micro-organisms	5.0-10.0
Shorten food drying and cooking items	Dehydrated vegetables and fruits, legumes	De-polymerization of pectin, cellulose and starch	3.0-10.0
Sterilization to produce shelf-stable products	Meat, poultry, ready meals	Destruction of micro-organisms, including spore-formers	up to 50

## Role of Packaging in Food Irradiation

Food once irradiated, can be prone to re-contamination unless appropriately packed. Therefore, if radiation treatment is intended to control microbiological spoilage or insect infestation, prepackaging becomes an integral part of the process. Technical functions of packaging are well known. These include prevention of moisture uptake or loss, maintenance of an atmosphere other than air, protection from mechanical damage or simply keeping the food clean.

Since packaging materials are also exposed to radiation during the treatment, these materials must also satisfy additional requirements such as resistance to radiation with respect to its functional properties. In addition, it should not transmit toxic substances into food nor impart any off odour to the products. Of the several packaging materials currently available such as cellulose, glass, metals and organic polymers, plastics offer unique advantages over the use of conventional rigid containers from the point of view of flexibility, low cost, light weight and low weight to volume ratio. Increasingly, packaging materials for use in aseptic processing lines in the food, pharmaceutical and cosmetic industry are now being sterilized by ionizing radiation.

The packaging requirements of a particular food are significantly influenced by the desired objective of the radiation treatment. Packaging materials used for irradiated food are broadly classified into two categories<sup>[4]</sup> depending on the type of radiation treatments.

- Processes requiring doses less than 10 kGy, such as extension of shelf-life of food.
- Processes requiring doses from 10-60 kGy, for storing such items as meat and poultry for long periods without refrigeration.

This provides a logical division of the packaging requirements and the behavior of packaging materials in relation to the desired objective of the radiation treatment. In case of insect proof packages, radiation treatment should not result in loss of quality of the packaging material with respect to their ability to protect against invading (those that enter through existing openings) and penetrating (those that perforate the packaging material to gain entrance) insects<sup>[5]</sup>.

#### **Plastic Packaging Materials**

Polymers such as polyethylene, polypropylene, poly vinyl chloride, polystyrene, polyethylene terepthalate and polyamide are some of the most common plastic packaging materials presently available. They all contain additives that vary in nature and quantity for obtaining certain useful properties. No single flexible material has all the chemical, physical and protective characteristics necessary for meeting the requirements of packaging radiation-processed food. Therefore, flexible packages, which tend to be multi-layer films with different barrier properties, have been developed to meet modern packaging needs. Requirements of flexible packages with respect to food irradiation are:

- Must be easily heat sealed
- Must withstand the irradiation processing at temperatures up to 40°C without cracking, de-lamination, or losing seal strength
- Must withstand shipment hazards
- Must protect the contents from microbial or other contamination

- Must provide an oxygen and moisture barrier
- Must be inert to the package contents

Radiation-induced changes in the physical properties of a packaging material should not impair its function. Radiolytic degradation products should neither be toxic nor affect the sensory qualities of the packed product. Global migration values should not be increased after irradiation. Effect of ionizing radiation on these materials has been extensively studied. Permeability of plastic films is generally not affected by food irradiation doses. Deterioration of mechanical properties, which may occur with certain polymers, can usually be controlled with adequate stabilizers; and changes in infrared and UV/VIS spectra are also slight at doses prescribed for food processing. Comparatively, little is however known on the effect of irradiation on multi-layer packages. Studies have been conducted, using food-simulating solvents (water, acetic acid and n-heptane). Selected packaging films are exposed to appropriate radiation dose, to determine the amount as well as the nature of extractives when compared with non-irradiated controls. If the amount of extractives obtained from irradiated and non-irradiated films is not significantly different, then the film is termed as safe; otherwise the safety of the film must be established through acceptable protocols. On the basis of these results, a few polymeric films have been approved for radiation processing (Table 3).

#### Effect of Gamma Irradiation on Plastics

Fundamental chemical changes that are caused in polymers by ionizing radiation are:

- Simultaneous scission and cross-linking of the polymeric chains, their net effect determining the changes in physical properties
- Formation of gases and low molecular weight radiolysis products
- Formation of unsaturated bonds

In the presence of oxygen, oxidative chain scission and oxidation of the polymer leads to formation of peroxide, alcohol and carbonyl functions. CO, CO<sub>2</sub> and various oxygen-containing low molecular weight compounds are also formed. Free radicals formed during irradiation and trapped in the polymer may also result in post-irradiation "aging" of the polymer.

It may be noted that the extent of radiation-induced changes depend on the chemical structure of the polymer, on the composition (additives) and processing history of the plastic and on the irradiation conditions (temperature, presence of oxygen, dose, dose rate).

Effect of gamma radiation on packaging materials can be broadly classified into physical effects and chemical effects. Physical effects comprise of changes in crystallinity, permeability, changes in surface structures and post irradiation aging effects. Chemical effects include evolution of gases and volatile radiolysis products, global migration of radiolytic products of the polymer and additives and degradation of antioxidant and their radiolytic products.

#### **Physical Effects**

Permeability is a measure of the ease with which gases or vapours can penetrate through the polymer materials. It is, therefore, a major consideration in the selection of a polymeric material

 $TABLE~3~^{\tiny{[22]}}$  Food Packaging Materials Authorized Nationally for Irradiation of Pre-packaged Food

Materials Approved in the United States	Maximum Dose (kGy)	Approval Date				
Ethylene-vinyl acetate co-polymer	30	February 1989				
Nylon 11 [polyamide-11]	10	March 1968				
Nylon 6 [polyamide-6]	60	June 1967				
Polyethylene film	60	June 1967				
Polyethylene terepthalate film	10	March 1968				
Polyethylene terepthalate film	60	June 1967				
Polyolefin film	10	March 1965				
Polystyrene film	10	August 1964				
Rubber hydrochloride film	10	August 1964				
Vinyl chloride-vinyl acetate co-polymer film	60	June 1967				
Vinylidene chloride-vinyl chloride co-polymer film	10	August 1964				
Fiberboard, wax-coated (boxes)	10	August 1964				
Glassine paper	10	August 1964				
Kraft paper	0.5	July 1967				
Nitrocellulose-coated cellophane	10	August 1964				
Vegetable parchment	60	March 1965				
Vinylidene chloride co-polymer-coated cellophane	10	June 1965				
Materials Approved in Canada						
Ethylene –vinyl acetate coextruded (bags,films)		July 1988				
Fiberboard, wax–coated (boxes)		June 1989				
Polyolefin (low density, as middle layer or sealant layer)		June 1989				
Polyolefin (high density, as middle layer or sealant layer)		June 1989				
Polystyrene foam trays (Styron 685D)		June 1989				
Materials Approved in the United Kingdom						
Cardboard kegs						
Hessian sacks						
Multiple paper sacks						
Polypropylene sacks						

for food packaging. Investigation using different packaging films, permeating gases and analytical techniques have demonstrated, that there is no alteration in the permeability even after exposure to doses upto  $1000 \text{ kGy}^{[6,7]}$ .

There are no significant changes in crystallinity and shrinkage in commonly used packaging materials such as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene, polyethylene terephthalate (PET), poly vinyl chloride and poly vinylidene chloride in the dose range of 0-8 kGy <sup>[6,7]</sup>.

In many polymers, the extent of unsaturation increases with irradiation. Visible (VIS), Ultraviolet (UV) and Infrared (IR) absorption methods are generally used to study unsaturation. At doses applied in food irradiation, no significant changes in the IR and UV/VIS spectrum of most of the commonly available polymers could be detected in comparison to the control samples<sup>[6, 7]</sup>.

Mechanical properties of polyethylene (LDPE and HDPE), polypropylene, polystyrene, polyester, PET, polyamides and laminates such as polyester-polyethylene and polyethylene aluminum-polyester-polyethylene were unaffected up to a dose of 10 kGy. Using suitable stabilizers, changes in mechanical properties of certain polymers e.g. polyethylene can be minimized when subjected to higher doses of radiation<sup>[6,7]</sup>.

Free radicals and ions are formed during irradiation. These highly reactive species are trapped in the polymer matrix and are responsible for the colour changes in irradiated polymers. Electron Spin Resonance (ESR) measurements are widely applied for the detection of free radicals. No measurable ESR signals upto a dose of 20 kGy were observed in polyethylene, polystyrene and cellophane both in nitrogen atmosphere and in air, while polypropylene showed both alkyl and peroxy radicals indicative of degradation in abundance. Post irradiation aging effects were observed with some polymers e.g. polypropylene. This could be the result of trapped radicals in crystalline regions of polymers where they are inaccessible to oxygen<sup>[6, 7]</sup>.

Studies<sup>[8]</sup> carried out on the effect of radiation on polymeric films both single such as polypropylene, low density polyethylene (LDPE), polyester (PET) and laminates (BOPP/LDPE, PET/LDPE, Pet/L

Grunewald and Berger<sup>[9]</sup> found that the heat sealability of two laminates (aluminium foil/HDPE and polyester/LDPE) irradiated with 10 kGy remained good, whereas after 50 kGy the seals could relatively easily be re-opened. No brittleness or de-lamination and no impairment of barrier or sealing properties were observed in polyester-polyethylene and polypropylene laminates and polyamide films at absorbed doses of 10-160 kGy. In another study<sup>[10]</sup>, changes in tensile, burst and seal strengths were unaffected in five laminates (PET as outer layer and aluminum foil as middle layer and either PET, HDPE, HDPE-polyisobutylene blend, polyamide-6 or polycarbonate as inner (food contacting) layer) when exposed to gamma irradiation at a dose of 60 kGy.

#### **Chemical Effects**

Most important modifications observed in irradiated polymers are radiation-induced crosslinking and degradation. For vinyl polymers, where each carbon atom of the main chain carries atleast one hydrogen atom, the polymer crosslinks<sup>[8]</sup>. Presence of tetra substituted carbon atom in the chain, on the other hand, causes a strain in the molecule by steric repulsion effects. Multiple bond scissions and primary rearrangement processes thus result in stabilization of the fragment preventing restoration by recombination<sup>[8]</sup>. Plastic films containing a phenyl group and/or an amide linkage are the most radiation resistant, as these groups, due to their increased resonance energy, are known to stabilize the polymer. Thus, high radiation stability of polyester, polystyrene and polyamide is possibly due to the requirement of high energy to form crosslinks<sup>[4]</sup>.

#### **Evolution of Gases and Volatile Radiolysis Products**

Studies on evolution of gases during radiation treatment have been extensively covered in literature<sup>[6]</sup>. Main products formed during irradiation under vacuum are hydrogen and methane (and HCl for chlorine containing compounds). In the presence of oxygen, significant amounts of carbon dioxide, carbon monoxide and increased quantities of hydrogen, methane and hydrocarbons were noted. Nature and amount of gases formed are dependent on the formulation of the plastics. Since most of these studies pertain to doses beyond 100 kGy, it is practically impossible to extrapolate to the normal food irradiation doses. Based on evolution of gases, Kransnansky and Parker[11] established the radiation stability of five classes of plastic films irradiated by gamma radiation (60 kGy) in vacuum at 25°C as polyethylene terephthalate > polystyrene > polyiminoundecyl > poly(vinylidene chloride-vinyl chloride) > polyethylene. In another study, based on the same criteria, Angelini<sup>[12]</sup> showed that the order of radiation stability of four films subjected to electron radiation between 0.9-13.2 kGy were polyaminocaproyl > HDP > poly (vinylidine chloride-vinyl chloride) > LDP. Although several other quantitative data on gaseous radiolysis products from plastic food packaging materials have been published, the studies were inconsistent.

Volatile radiolysis products have been investigated by GC/MS after thermal desorption and concentration [13]. The compounds identified in irradiated polymers include predominantly hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids. These compounds were found to increase with increase in absorbed dose. Killoran[10] has reported formation of hydrocarbons in LDPE, HDPE and polyamide and of chlorinated hydrocarbons in a vinylidine chloride-vinyl chloride copolymer during irradiation under vacuum. Rojas de Gante and Pascat<sup>[14]</sup> have reported that the total amount of volatiles formed was greater for polypropylene than for LDPE. The polypropylene giving more branched isomers, while LDPE more linear products. The amount of carboxylic acids formed were found to depend on the processing history of the film and on the presence of additives. The antioxidant butylhydroxytoluene very effectively reduces the formation of carboxylic acid. Electron irradiation was found to produce smaller amounts of volatiles than gamma irradiation as a result of variation in dose rate between the two processes. Although several other investigations<sup>[6]</sup> have also shown the formation of gaseous and volatile radiolysis products in various irradiated polymers, the data obtained does not provide a clear picture regarding the quantity of radiolytic products formed at food irradiation doses. It may, therefore, safely be assumed that effects of radiation processing on production of the above volatiles are insignificant at doses relevant to food irradiation since minute quantities of these constituents are produced even at high doses.

## **Degradation of Antioxidant**

Major antioxidants added to plastics during processing are the phenol antioxidants Irganox 1076 (octadecyl-3-[3,5- di-t-butyl-4-hydroxyl] propionate) and Irganox 1010 (pentaerythritoltetrakis-3-[3,5-di-t-butyl-4-hydroxy-phenyl] propionate) the aryl phosphite antioxidant, Irgafos 168 (tris-[2,4-di-t-butylphenyl] phosphite) and the hindered amine, 2,2,6,6-tetramethyl-4-piperidyl sebacate. Stabilizers such as organotin stabilizers (eg. dibutyltin bis[iso-octylthioglycollate] and dibutyltin bis [iso-octylmaleate]), n-butyl stearate and stearyl alcohol are the other additives commonly used.

Bourges et al.<sup>[15]</sup> have characterized the two major degradation products of Irganox 1010 and 1076 as 2,4-di-t-butyl phenol and 2,6-di-t-butyl-1,4-benzoquinone in polypropylenes. A triaryl phosphate namely tris-(2,4-di-t-butylphenol) phosphate was shown to be the oxidation product of Irgafos 168 by Allen et al.<sup>[16]</sup>. The workers also observed that the structure of transformation product of Irganox 1076 and 1330 was largely the same for irradiation and thermal oxidation with the exception that irradiation led to dealkylated structures that have lost t-butyl groups.

Sterically hindered phenols and aryl phosphite antioxidants are gradually destroyed with increasing absorbed doses; the effect of gamma irradiation and electron beam being comparable in magnitude. Bourges et al.<sup>[15]</sup> reported a higher rate of degradation of Irgafos 168 (85-90%) compared to Irganox 1010 and 1076 (50-60%) present in LDPE and polypropylene when subjected to electron irradiation at a dose of 10 kGy. When incorporated into HDPE, the rate of degradation was found to be still lower than LDPE. These antioxidants are covalently bound atleast to some extent to the polymer, resulting in reduced taint transfer at food irradiation doses<sup>[17]</sup>. At doses greater than 30 kGy, rapid conversion of organotin stabilizers to monobutyl tin species and tin chloride by dealkylation is noted when incorporated in PVC. Extent of degradation is dependent on the processing history of the samples and the initial concentration of the stabilizer<sup>[18]</sup>.

## Global Migration of Radiolytic Products of Polymers and Additives

When packaging materials are in contact with food, possibility exists that certain compounds produced as a result of irradiation may contaminate the food. Determination of migrants in heterogeneous food material is a difficult and time-consuming task. To this end, the studies using food-simulant solvents, selected packaging materials and the appropriate radiation dose and storage conditions have been performed to determine the amount and nature of extractives for comparison with non-irradiated controls. Water, alcohol, acetic acid and heptane are normally used as simulants.

Studies on global migration pattern of various polymers such as LDPE, polypropylene, polyamide-6, polyamide-11, poly(vinylchloride-vinylacetate) and poly(vinylidene chloride-vinyl chloride) and PET showed that gamma irradiation caused no significant extractability of these materials compared to their non-irradiated counterpart<sup>[7]</sup>.

A decrease in migration of sterically hindered phenol antioxidants (Butyl hydroxy toluene, BHT and Irganox 1076) from LDPE, HDPE and polypropylene into fatty food simulants like iso-octane was noted by Figge and Freytag<sup>[19]</sup>. Gamma and electron irradiation was found to give similar effects<sup>[18]</sup>. Migration of various additives (BHT, Irganox1076, n-butyl stearate, octyltin iso-octylthioglycollate and steryl alcohol) from polystyrene and rigid PVC films were demonstrated to be practically unaffected by irradiation<sup>[19]</sup>. Increased migration of tin from poly vinyl chloride (PVC) into heptane resulting from the degradation of organotin stabilizers during gamma irradiation (0-100 kGy) was observed by Haesen et al.<sup>[20]</sup>. The concentration of the migrated tin depends on the processing history of the sample, being smaller for extruded rigid PVC than pressed rigid PVC.

Bourges et al.[15] studied the relationship between degradation of antioxidant in bi-oriented polypropylene film stabilized with hindered phenol (Irganox 1010 and phosphite Irgafos 168) and the migration of their degraded products into food simulant (distilled water, 3% acetic acid and 15% ethanol). Electron irradiation at 2, 5, and 10 kGy did not result in detection of degradation products of these antioxidants in these simulants. Allen et al.[21] on the other hand reported significant migration of the degradation products of antioxidant at doses above 10 kGy. Thus at doses less than 10 kGy migration of degradation products may not be of much significance. Despite the importance of laminates in modern packaging, information on global migration or formation of volatile products during radiation treatment of these multi-layered structures is almost nonexistent. In one such study<sup>[22]</sup>, no significant change in extractability into simulants such as water, acetic acid (pH 3.5), acetate buffer (pH 3.5), phosphate buffer (pH 6.2) and heptane could be noted up to six months of storage in six laminated pouches irradiated to a dose of 60 kGy. Recent work<sup>[23]</sup> on the effect of gamma irradiation (7.5 kGy) on the migration of additives in newly developed laminate consisting of LDPE/Nylon/Ethylene acrylic acid (EAA, food contact layer) have however revealed the migration of several plasticizers such as phthalates and toluene sulfonamides into water used as simulant.

# **Application of Plastics in Food Irradiation**

The above discussions have revealed that the functional properties and protective characteristics of packaging materials used in radiation processing are not adversely affected by the doses applied. While the physical properties of most of the polymers are not influenced at the doses used in food irradiation, low molecular weight radiolysis products and extractable substances produced, are normally in minute amounts and hence should not alter the sensory qualities of the irradiated products or compromise its safety. It is generally found that polyethylene, polystyrene and PET are well suited for use as packaging materials for food which are subjected to ionizing radiation. Gamma irradiation at 5-50 kGy did not significantly effect migration of non-volatiles in PET and hence has been found to be suitable for pre-packed irradiated food.

Based on their findings, various researchers have suggested several packaging materials for use in radiation processing of food. Flexible materials such as Nylon 11, saron coated nylon, polyolefins-coated polyester, laminated paper/aluminium/polyethylene have found to be suitable for packaging of radurized fish and poultry products, while laminates of

cellophane/saran/polyethylene and polyvinylidine chloride/polyester/polyethylene have been employed for vacuum packing of radurized meat<sup>[4]</sup>. Most satisfactory flexible package for radappertized ham, bacon, fish and chicken consists of three-ply laminate made up of 0.0127 mm Mylar A (outside), 0.0127 mm aluminium foil (middle) and one of the several types (a) 0.0762 mm Nylon-11 or (b) 0.0762 mm HDPE modified with isobutylene or (c) 0.0635 mm polyethylene coated polyester<sup>[4]</sup>. The general performance of these materials has been found to be satisfactory when evaluated for food compatibility, resistance to low temperature handling, radiation-induced changes, microbial and insect penetration, absence of potentially toxic substances and overall integrity and suitability for both electron and gamma irradiation.

Killoran<sup>[24]</sup> has recommended a laminate consisting of 3 layers [polyamide-6 (0.25mm, outer layer), 0.009 mm aluminium foil (middle layer) and 0.062 mm PET-medium density polyethylene (food contacting layer)] for packaging of chicken and beef sterilized by electron beam. This material did not deteriorate during storage up to 24 months. Bond strength and burst strength increased during radiation treatment and had lower extractives than the non-irradiated control samples.

Suitability of flexible packaging materials for pre-packaging of irradiated food was also reported by Agarwal et al<sup>[25]</sup> and their recommendations are listed in Table 4. Several of these packaging materials are currently being used for food irradiation.

Studies with 5 different multi-layer pouches used successfully for radiation sterilization of food showed that the release of chemical substances into water, acetic acid, and n-heptane after irradiation to 71 kGy of ionizing energy was insignificant. Also insignificant release of chemicals from the adhesive used to bond the layers of the pouches was observed. The irradiation treatment improved the bonding of the layers and the seal strength of the pouches. The reliability of the flexible multi-layer pouches for sterilizing, shipping, and storing beef, chicken, ham and pork was tested in an experiment using 725,000 pouches. The rejection rate due to defective pouches by the end of 2 years was 0.03% higher than that for the metal cans, but still acceptable.

# Packaging of Food Irradiated for Insect Disinfestation

Retail marketing of pre-packaged spices, cereals, pulses and their products such as wheat flour (atta), semolina (sooji or rawa), besan in consumer packs made of plastic films have shown phenomenal growth in recent years. Insect infestation is the major problem during marketing of these products. Irradiation of doses of 0.25 to 1 kGy can kill or prevent the development of insect eggs, larvae, and pupae into adults. Adult insects, if present, are rendered sterile and further reproduction is prevented. The feeding ability of larvae and/or adults is also reduced considerably followed by death and, therefore, reduction in damage expressed as weight loss and maintaining the initial quality is an advantage of radiation disinfestation.

After irradiation to eliminate internal infestation, packaged products must be protected from external insects that could subsequently be encountered in shipping, storage, transportation and marketing systems until the time the package is opened by the consumer. Flexible films may vary in their resistance to insect penetration depending on the type of the

 ${\bf TABLE~4^{~[25]}}$  Suitability of Flexible Packaging Materials for Pre-Packaging of Irradiated Foods

Packaging Material	Packaging Requirements	Applications	Radiation Dose in kGy	Shelf-life at 20-34° C
Polyethylene (0.076 to 0.127 mm)	Impermeability to bacteria	Radurized fish	1.0-5.0	3-4 weeks <sup>a</sup>
		Cooked and irradiated eggs	1.0	15-20 days
	High WVTR <sup>b</sup> & gas transmission rate	Irradiated fruits	0.15-0.35	10-20 days
Polyethylene (0.165 mm)	Good physical strength and low WVTR	Disinfestation of sundried fish & Bombay duck laminate	0.5-1.0	4-6 months
		Disinfestation of wheat flour & samolina (Rava)	0.3-0.5	4-6 months
	Impermeability to bacteria & low WVTR	Irradiated unleavened chappaties	1.0	6 months
		Heat & radiation treated leavened bread	0.5-1.0	1.5-2 months
Polyethylene (0.038 to 0.076 mm) 300 MST cellophane	Impermeability to bacteria, low water vapour and gas transmission rates	Cooked and irradiated shrimps	1.0	1-1.5 months
Paper/ polyethylene/ aluminium foil/ polyethylene	Impermeability to bacteria and sunlight. Very low gas and vapour transmission rates	Dehydro- irradiated fish	2.5-5.0	3-6 months
		Cooked & irradiated mutton	2.5	4-6 months

a = Storage temperature of  $0-4^{\circ}C$ 

b = Water vapour tranmission rate(WVTR). It may be noted that water vapour and gas transmission rates of polyethylene are increased by punching the film.

polymer and film thickness. Polycarbonate, polyester, polypropylene and hard (unplasticized) poly vinyl chloride films have been found to be resistant to insect penetration. In storage tests of irradiated pulses, polyester/polypropylene, and polyester/polyethylene laminates were more resistant to penetration by four species of insects than were polyethylene, cellophane or paper. The most resistant packaging material was polyester/polyethylene laminate. Biaxally oriented polypropylene/polyethylene laminates (BOPP 25 $\mu$ /LDPE 40 $\mu$ ) provided good protection from penetrating insects in radiation disinfested basmati rice and rava in consumer packs.

For bulk packaged irradiated pulses and oil seeds, jute bags lined with polyethylene (0.1mm) and treated with permithrin (80-100 mg/m²) on the outer layer provided full protection from infesting insects for 8 months of storage, whereas PVC bags and polyethylene lined jute bags provided better protection from reinfestation than did the standard jute bags. Irradiated tobacco leaves were effectively protected from reinfestation when packed in PVC or PE bags in 10 kg cartons. Irradiated coffee beans packed in woven polypropylene bags or permethrin treated polypropylene bags also remained almost free from insect for 10 months. Dates irradiated and packed in PE wrapped cartons remained free of insects for 7 months while the cellophane wrapped cartons were heavily infested.

Spice powders and spice mixtures packed in BOPP or laminates of polyester and polyethylene or metalized polyester have been found to retain the natural aroma and at the same time provide good protection from reinfestation.

#### **Packaging of Irradiated Fresh Fruits and Vegetables**

There are no special requirements for packaging of fresh fruits and vegetables irradiated for delay of ripening or inhibition of sprouting. These fresh commodities remained metabolically active and respiring and, therefore, the package should be permeable to oxygen,  $CO_2$  and ethylene and at the same time provide barrier to water vapour to reduce water loss and shrinkage of the produce. All flexible plastic films conventionally used are suitable. If irradiation is combined with modified atmosphere, films suitable for such purposes or active packaging with ethylene and oxygen scavenging systems can be used.

# Packaging of Food of Animal Origin Irradiated at Sub-sterilizing Doses

Irradiation treatment at the end of the processing line can reduce the population of spoilage bacteria, termed as "radurization", with consequent increase in the shelf-life of these products under refrigeration. Also, irradiation at appropriate dosages can inactivate, or kill non-spore forming pathogenic bacteria and parasites (termed as "radicidation"), which cause common intestinal infection and other food borne diseases. It is important that the treated products are protected from subsequent contamination by suitable packaging.

Because sterility is not the objective of processing food with doses of ionizing energy below 10 kilograys, single-layer plastic packaging generally suffice for such uses. Films thinner than  $25\mu$  have too many imperfections to be suitable. Films 25 to  $75\mu$  thick are proof against microorganisms, but creasing will damage such films sufficiently to make them unsatisfactory. Thicker films appear to be satisfactory.

Flexible packages for radiation pasteurized (radurized) haddock fillets were found to be satisfactory when made from the following films:

- Saran-coated nylon 11
- Nylon 11
- Polyolefin-coated polyester semi-rigid polystyrene
- Paper-aluminium-polyolefine-coated polyester
- Nylon-saran-coated polyethylene
- Aluminium-coated nylon 11
- Aluminium-paper-polyolefin-coated polyester
- Polyethylene-coated nylon, and
- Nylon-saran-Polyethylene

Films of polyethylene and polypropylene were not found to be satisfactory. For radurized fresh meat, fish and poultry, the following oxygen-permeable films are among those that are satisfactory:

- Poly vinyl chloride (fresh meat wrap)
- Cellophane (fresh meat type), and
- Polyethylene (high oxygen permeability type)

Among oxygen-impermeable films satisfactory for use with meat are:

- Polyvinylidene chloride (saran)
- Laminate of polyvinylidene chloride with polyester and polyethylene, or with nylon.

Packages made from polyethylene films of 75-165 $\mu$  thickness were found to be satisfactory for several Indian fish varieties, meat and poultry irradiated for shelf-life enhancement and microbial safety.

Use of double packaging systems that provide anaerobic conditions during most of the storage period and aerobic conditions only in the later part during retail display was found to be effective for controlling dis-colouration in irradiated retail cuts of meat. Individual cuts were packaged in oxygen permeable poly vinyl chloride and subsequently the individually wrapped packages were bulk over-wrapped with an oxygen impermeable films or vacuum packaged employing a laminate of polyester, poly vinyl chloride and polyethylene. This procedure was found to retain the pristine red colour fresh beef during display for retail sale.

Vacuum and modified atmosphere pre-packaging instead of the standard aerobic packaging has been found to enhance products sensory quality without compromising the product safety. Both vacuum, and high  $\mathrm{CO}_2$  modified atmosphere packaging without oxygen can be successfully combined with radiation pasteurization to extend life of chilled/refrigerated fresh meat through delay of microbial spoilage while avoiding undesirable oxidative changes.

#### **Packaging of Radiation Sterilized Food**

The principal objective of radiation sterilization termed as "radappertization" is to obtain food that will keep fresh without refrigeration. In this process, the food is heated to 70 - 80°C to inactivate autolytic enzymes, vacuum packed in sealed metal cans or sealed flexible packages, frozen to a temperature of -40°C and exposed to controlled amount of ionizing energy at -40°C  $\pm$ 5°C. The processed products can subsequently be stored without refrigeration. The dose of ionizing energy must be good enough to activate the spores of the clostridium botulinum bacteria and to assure to spoilage of biological origin as long as the food is not recontaminated by failure of the sealed container. As compared to heat sterilized food, radiation sterilized food have better sensorial attributes as overcooking is avoided.

Single-layer plastic packaging films do not provide adequate protection to radiation sterilized food from microbial recontamination, insect penetration, and deleterious effects of light, oxygen, moisture, and rough handling during long-term storage without refrigeration. So far the most satisfactory flexible packaging material for radiation-sterilized food is a three-ply laminate comprising 25µ nylon 6 (outside), 9µ aluminium foil (middle) and 62µ intermolecularly bonded polyethylene terephthalate medium-density polyethylene. Polyethylene is the food- contacting layer. This lamination appears to be the best, based on the criteria that the films are not changed adversely (a) in their protective characteristics (e.g. heat stability, permeability, etc); (b) by radiation-induced changes in the food; and (c) causing transmission of toxic or potentially toxic substances to the food (ICGFI, 1992). A 4 layer laminated flexible pouch made of nylon/aluminium foil/polyester/VLDPE has been found to be suitable for several radiation sterilized meat and poultry products of exceptionally high quality, which have been produced on a semi-commercial basis for the last 7 to 8 years in South Africa.

#### **Future Work**

There is a need to increase the number of polymers available for food irradiation. Most of the packaging materials currently approved are several decades old and outdated. Food irradiation has just recently received impetus after red meat irradiation was approved by US FDA, and by clearances of several items elsewhere including India. Approved food-packaging materials for food irradiation are limited. This has prompted manufacturers to submit several proposals for new packaging materials for use during irradiation of prepackaged food. Additional information on formation of radiolytic compounds must be granted for many new polymers crucial for optimal food packaging.

Some of the recent developments include studies<sup>[26]</sup> on radiation resistance of Ethylene Vinyl Alcohol (EVOH), a prominent barrier material used in multi-laminate packaging structures. Results have shown that EVOH does not produce unsafe levels of radiolytic products in prepacked food up to a dose of 10 kGy. All compounds produced during irradiation were of GRAS status. Use of corn zein films (a biodegradable food packaging material) for packaging irradiated food has demonstrated that at moderate doses up to 20 kGy increased cross-linking of polymer matrix occurs<sup>[27]</sup>. These materials may thus be used in future with suitable modifications for radiation processing of food. EVOH; nylon 616T; nylon 6,6; nylon 6,66; and inomers and anhydride grafted polyethylenes have been recommended in recent years as the most important polymers needed for smooth introduction of commercial irradiation for packaged meat<sup>[28]</sup>.

Thus, newer plastic materials capable of being used both at low as well as sterilization doses need to be further developed that will enable introduction of irradiated food at a greater pace in the market.

#### Conclusion

Irradition of food is one of the most effective way of food preservation to inactivate microorganisms and destroy insect pests. Effective irradiation treatment on food is associated with an effective packaging material, which performs all the technical functions of packaging along with resistance to raditions. Though several packaging materials like glass, cellulose, metals and organic polymers are available for this purpose, plastics offer unique advantages over the conventionally used rigid containers in terms of flexibility, low cost, light weight, and low weight to volume ratio. Multi-laminate packaging structure of polymers like nylon, EVOOH, PVC, cellophane, PE and Polyester are used as a prominent barrier material in packaging of irradiated food.

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