

Chapter 15

**Chemical Changes in Food Packaging
Resulting from Ionizing Irradiation****Donald W. Thayer****Eastern Regional Research Center, U.S. Department of Agriculture,
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Recent approvals of food irradiation processes by the U.S. Food and Drug Administration have led to a search for packaging approved for use with ionizing radiation. Though 13 packaging materials were approved several years ago as food contactants for gamma irradiation up to 10 kGy at refrigeration temperatures and 4 packaging materials were approved for up to 60 kGy at cryogenic temperatures, no currently used packaging is approved for irradiated foods. Extensive research was conducted by the U.S. Army and others on the suitability of both flexible packaging and metal cans for packaging irradiated foods. The results of the studies of packaging for irradiated foods will be described and discussed in context of currently used packaging materials for non-irradiated meats and poultry.

There have been several recent approvals for the use of ionizing radiation treatments of food products and it is anticipated that more will be forthcoming for the use of ionizing radiation treatments to eliminate food-borne pathogens in (and incidentally to increase shelf life of) meats and poultry. Though several materials are approved as food contactants for gamma irradiation up to a maximum dose of 10 kGy by the Food and Drug Administration, the existing regulation (1) was written in the late 1960's to provide packaging materials for the planned irradiation of bacon by the U.S. Army. Only films were included in the regulation; no multilayer materials were included. Furthermore, only gamma radiation sources were included in the regulation. Today, stretch or shrink packaging using bags or trays with overwrap is most commonly used for meat and poultry. The packaging films usually used for poultry have a high moisture barrier and a low oxygen barrier. The packaging films used for red meat usually have both high moisture and high oxygen barriers. Frequently the required

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properties for packaging materials for both poultry and red meats are best achieved using multilayer films. It is in the latter that a problem may exist.

The purpose of this manuscript is to review the extensive research conducted by the U.S. Army and others on the suitability of both flexible packaging and metal cans for packaging irradiated foods. The results of the studies of packaging for irradiated foods will be described and discussed in context of currently used packaging materials for non-irradiated meats and poultry.

Packaging Materials Approved for Irradiated Foods

The regulation (1) states that the following materials may be safely subjected to gamma radiation doses up to 10 kGy incidental to the radiation treatment and processing of prepackaged foods: 1) wax-coated paperboard, 2) vegetable parchments, 3) nitrocellulose-coated cellophane, 4) vinylidene chloride copolymer-coated cellophane, 5) glassine paper, 6) polyolefin film, 7) polyethylene film, 8) polyethylene terephthalate film, 9) polystyrene film, 10) rubber hydrochloride film, 11) vinylidene chloride-vinyl chloride copolymer film, 12) nylon 6 film, 13) nylon 11 film, and 14) vinyl chloride-vinyl acetate copolymer film. In the regulation the coated cellophanes are treated as a single class. The regulation (1) also lists the approval of Kraft paper as a container for flour with a dose not exceeding 0.5 kGy. Vegetable parchments, polyethylene film, polyethylene terephthalate film, nylon 6 film, and vinyl chloride-vinyl acetate copolymer film are approved for use in radiation processing of prepackaged foods at a dose not to exceed 60 kGy of gamma or X-radiation. The regulation (1) must be consulted for details on the materials approved. Neither laminated packaging materials nor the use of electron irradiation are included in the regulation.

Radiation Effects on Individual Packaging Materials

General Radiation Chemistry of Polymers. Ionizing radiation has two major effects on polymers: crosslinking and scission of the polymer chains (2). Both reactions may occur simultaneously and the predominating reaction dictates whether the polymer is degraded or if it increases in molecular weight as well as undergoing changes in its physical properties (2-5). The scission reactions may also result in the production of hydrogen gas, hydrocarbons, carboxylic acids, and changes in extractives from the various polymers. Ionizing radiation can be effectively used to modify the properties of polymers and improve their packaging properties (6-8). The properties of ionizing radiation may, however, generate long-lived free radicals (9) in the packaging materials which could conceivably contribute to subsequent reactions in the packaging material or presumably even in the food. The tests that must be applied to a food packaging product include some that would not be applied to polymers intended for use in medical applications. The physical tests that must be applied however are similar and several common

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tests applied to polymers intended for medical applications were described by Landfield (10).

Acrylic Plastics

The acrylic resins are polymers of acrylic or methacrylic esters and are readily polymerized, either as homopolymers or copolymers, with many other monomers (11). Polyacrylic esters, polyacrylic acid, polyacrylamide, butadiene-acrylonitrile copolymers, and styrene-acrylonitrile copolymers were listed by Bovey (2) as being among the polymers in which crosslinking rather than degradation would be the predominant reaction. Polymethyl methacrylate, polymethacrylic acid, and polymethacrylamide, on the other hand, were listed as among those polymers in which the predominant reaction with ionizing radiation would be degradation (2). Landfield (10) indicated that acrylonitrile-butadiene-styrene was stable for a single dose of 25 kGy. The regulation (1) includes coatings for polyolefin film or polyethylene terephthalate comprising a vinylidene chloride copolymer containing a minimum of 85% vinylidene chloride with acrylic acid, acrylonitrile, methyl acrylate, and methyl acrylate for radiation doses not to exceed 10 kGy. The flexible multilayer packaging used by the US Army for studies of irradiation sterilized beef and poultry products contained an ethylene-acrylic acid copolymer between the inside polyethylene layer and the aluminum foil central layer (12).

Cellulose and Cellulose Derived Products

Wax-coated paperboard is approved, as mentioned above, for use up to a radiation dose of 10 kGy (1). Ionizing radiation results in reduction of the crystallinity and depolymerization of the cellulose chain (13). Wierbicki and Killoran (14) reported that essentially no water, acetic acid, or n-heptane solubles were produced from vegetable parchment (KVP Sutherland Paper Co.) after ionizing radiation doses of 60 kGy. Killoran (13) reported over two-fold reductions in the intrinsic viscosity of fiberboard and bleached sulfite paperboard after a radiation dose of 30 kGy. The tensile strength and tear resistance of the bleached sulfite paperboard was reduced by 19% and 7% in the machine and cross directions, respectively (13). Both electron and gamma irradiation of fiberboard resulted in decreased bursting strength. The changes observed in these cellulosic products upon irradiation were to be expected in that a large body of evidence exists documenting the degradation of cellulose by ionizing radiation (2). Bovey (2) cites studies from as early as 1929 that paper becomes brittle and crumbly and gives off hydrogen, carbon dioxide, and carbon monoxide when exposed to cathode rays. Glegg and Kertesz (15) describe the results of 60 kr to 2,300 kr doses on cellulose in which there was both an immediate and a delayed decrease in the intrinsic viscosity of the cellulose. Predominate chain scission occurs in the substituted as well as in the unsubstituted cellulose chain (2).

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Vegetable parchment and nitrocellulose coated cellophane were included in the same petition to the food and Drug Administration from the Atomic Energy Commission (16). Zehnder (17) concluded that derivatives of cellulose, such as cellophane, are not suitable for packaging goods that are to be subjected to irradiation treatments.

Epoxy Plastics

These groups of thermo- or nonthermo- plastics contain epoxy groups and are usually as coatings or adhesives (18). The laminated packaging material used by the U.S. Army for packaging of electron sterilized beef and poultry products contained an epoxy modified polyester as the adhesive between the outside nylon 6 layer and middle aluminum foil layer (12).

Ethylene-Vinyl Acetate

Patients exist for crosslinking of ethylene-vinyl acetate copolymers (19-21), and Chapiro (22) discusses in detail the radiation induced polymerization of vinyl acetate and a radiation induced copolymer graft of vinyl acetate-cellulose diacetate.

Glass

Most glasses are discolored when exposed to ionizing radiation and turn brown (23).

Ionomers

No information was located concerning the reaction or lack of reaction of Surlyn A or any other ionomer with ionizing radiation.

Nylon

Nylon is the generic name for long-chain polyamides and as mentioned above, nylon 6 and nylon 11 are included in the list of films approved for irradiation of prepackaged foods (1). Eighteen commercially available flexible films were evaluated for the packaging of radiopasteurized fishery products by Tinker et al. (25). The criteria used to evaluate the films were the organoleptic qualities of the products and the seal efficiency and resistance to bacterial penetration of the films. Using these criteria, polyethylene, polypropylene, saran coated cellophane, cellophane, and nylon 6 were considered unsatisfactory. Nylon-11, saran-coated nylon-11, polyolefin-coated polyester, polyethylene-coated polyester, laminated paper-aluminum-polyolefin-coated polyester, laminated aluminum-paper-polyolefin coated-polyester, laminated saran-polyethylene nylon, and saran-coated polystyrene lids and trays were considered to be excellent for packaging radiopas-

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teurized (2.5 kGy, sources ^{60}Co , temperature and dose rate not stated) fish for a refrigerated shelf life of one month. Bovey (2) reviewed the radiation chemistry of nylon up to 1958. The evidence indicated that crosslinking was the predominate reaction and that the elastic modulus and tensile strength increased while elongation and impact strength decreased (2). Key in 1968 (26) concluded that nylon 11 was superior to two laminated packaging materials for the packaging of irradiated fish. Essentially no changes were found in the nylon 11 up to doses of 160 kGy (26).

Polycarbonates

Two studies report results obtained with laminates in which polycarbonate was the food contacting layer (13, 14). Though neither study discussed the polycarbonate film in any detail, the results would seem to indicate that there were no marked changes in extractives (14) nor in tensile, burst, or seal strength (13) of the laminates.

Polyesters

Bovey (2) reviews several studies of the effects of ionizing radiation on polyesters stating that polyethylene terephthalate has received the greatest attention. Bovey (2) did not feel that the data conclusively indicated that scission predominated. Chapiro (22) concluded in his review that data existed conclusively demonstrating that polyethylene terephthalate was crosslinked by ionizing irradiation. Killoran (13) investigated the properties of polyethylene terephthalate following either electron or gamma radiation doses of approximately 64 kGy. No radiation-induced extractives were found in water, acetic acid, or n-heptane. No significant effect was detected of irradiation on the tensile strength, burst strength, or tear resistance of this polyester. Cooper and Salunkhe (27) concluded that mylar bags were superior to polyethylene bags for packaging of irradiated bing cherries.

Polyethylene: General Radiation Chemistry

The radiation chemistry of polyethylene has been extensively investigated (2) and the predominate reaction is usually crosslinking. The petitions for the use of polyethylene were filed in 1964 by the Atomic Energy Commission for doses up to 10 kGy (16) and by the U.S. Army for doses up to 60 kGy in 1967 (24). Radiation-induced crosslinking can be used to extensively modify the properties of polyethylene for shrink wrapping (7) or for greatly increased heat stability (2). Polyethylene reacts to radiation by at first becoming increasingly insoluble due to the crosslinking and with greater doses changes in color finally to ruby red (28). Physical properties including flexibility and oxygen transmissibility may be altered (28).

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Polyethylene Film: Extractives

Killoran (13) investigated the extractives from medium density polyethylene irradiated in the presence of food-simulating solvents. When either distilled water or acetic acid was used as the food-simulating solvents, no identifiable changes were produced in total extractives or chloroform-soluble extractives by a radiation dose of approximately 60 kGy from either gamma or electron radiation sources. The gamma radiation temperature was 23-65°C, and the 10 MeV electron radiation temperature was 25-40°C. The dose rates were 8 Gy/sec and 2×10^7 Gy/sec for gamma (^{60}Co) and electron beam, respectively. Minimal change occurred in the extractive from gamma irradiated medium density polyethylene in the presence of n-heptane from that of the control. Less n-heptane extractive was obtained from electron irradiated polyethylene than from the control. The irradiation produced no chloroform-soluble residues from the polyethylene in water or acetic acid, and the n-heptane soluble residue was identical to that from the control.

Polyethylene Film: Radiation Induced Volatiles

Killoran (13) reported that electron irradiation of low-density and high-density polyethylene at average radiation doses of 10, 60, and 120 kGy produced hydrogen, methane, hydrocarbons, and carbon dioxide. The quantities of volatiles increased with increasing radiation dose; almost 3 times the total amount of hydrocarbons were produced by a radiation dose of 60 kGy as opposed to a dose of 10 kGy from the low-density polyethylene. Some ninety hydrocarbons were identified which ranged in molecular weight from 16(CH_4) to 184($\text{C}_{13}\text{H}_{28}$). Almost twice the amount of hydrocarbons were produced from the low as opposed to the high-density polyethylene.

In a much more recent series of studies, Azuma et al. (29-30) identified the odor-producing volatiles from electron beam and gamma irradiation sterilization of low density polyethylene films. Azuma et al. (29), using contemporary gas chromatographic and gas chromatographic-mass spectroscopic techniques, identified the volatile compounds produced from six types of low-density polyethylene films by a dose of 20 kGy from a 2.5 MV electron beam. Aliphatic hydrocarbons accounted for approximately 35% of the total peak area with saturated hydrocarbons up to C_{13} predominating. Four aldehydes (C_2 - C_5) and six ketones (C_4 - C_8) accounted for approximately 26% of the total peak area. Five carboxylic acids (C_2 - C_5) accounted for 18% of the peak area, and small amounts of alcohols, toluene, and phenol were identified. The odor from a mixture of the identified components in the same volume ratio as their peak areas resembled that of the off-odor of the irradiated polyethylene. Azuma et al. (30) studied the effects of film variety on the amounts of carboxylic acids produced by electron irradiation of polyethylene film. Nine types of low-density polyethylene were examined after a radiation dose of 20 kGy; and acetic, propionic, n-butyric, and n-valeric acids were quantitated. The predominate product (40 to 75% of total carboxylic acid) was

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acetic acid followed by propionic acid (30). The addition of butylated hydroxytoluene to the film reduced the total amounts of carboxylic acids that were formed. It should be noted that the total amounts of the four carboxylic acids produced by the irradiation of the films ranged from 1.83 $\mu\text{g/g}$ to 15.7 $\mu\text{g/g}$. Azuma et al. (31) extended their studies to include the effects of the conditions of electron beam irradiation and a comparison of electron-beam to gamma-irradiation on the production of volatiles for irradiated polyethylene film. At an irradiation dose of 20 kGy (2.5 MeV e^- , beam current 250 μA), Azuma et al. (31) noted that the formation of carbonyl compounds increased several fold as the oxygen content was increased from zero to five percent. Hydrocarbon formation was not noticeably affected by the oxygen content. The production of both carbonyls and hydrocarbons during electron irradiation of the polyethylene film could be lowered dramatically by irradiation at temperatures below polyethylene's glass transition temperature of about -78°C . The amount of carboxylic acids that were formed by a radiation dose of 20 kGy from 2.5 MeV e^- at a beam current of 250 μA were relatively constant at temperatures above 0°C but decreased to 35% at -75°C and to 16% at -196°C . Azuma et al. (31) discovered that there was a sharp increase in the production of carboxylic acids from polyethylene when the energy was increased from 1.5 to 2.0 MeV. Unfortunately from the viewpoint of this reviewer, the investigators did not extend their study up to a level of 10 MeV, which would be required for the irradiation of many foods. They also did not state the other irradiation conditions, e.g., temperature, or atmosphere. It was noted that lower beam currents, i.e., 125 μA , increased the formation of carboxylic acids (31). The formation of carboxylic acids almost doubled when the polyethylene received a dose of 20 kGy from ^{60}Co rather than from the 2.5 MeV electron beam source. Unfortunately, the authors did not indicate the dose rate or temperature of the gamma irradiation treatment. Azuma et al. (31) interpreted these results as being due to dose rate. With gamma radiation, the probability of crosslinking would be low because of a low concentration of primary radicals and a high relative availability of oxygen. With electron beam radiation, the recombination of the primary radicals, rather than their oxidation would be more favored because of their much higher relative concentration (31).

Polyethylene-Radiation Induced Crosslinking

The effects of ionizing radiation on crosslinking of polyethylenes and grafting of polyethylene and polypropylene to other materials has been the subject of many studies (6). Generally these studies appear to have limited application to our consideration of the effects of ionizing radiation on materials used for packaging of foods; but nevertheless, these studies do provide a strong theoretical background and may, as well, provide the basis for radiation-stable materials suitable for packaging foods that are to be subjected to irradiation treatments. This field has moved with such rapidity that Baird and Joonase (32) listed a bibliography of

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500 patents related to radiation crosslinking of polymers in 1982. Godlewska et al. (33) described the use of ionizing irradiation to increase dramatically the impact resistance of polyethylene films intended for use in packaging foods. Azuma et al. (30) described the effects of incorporating an antioxidant into low-density polyethylene on the subsequent generation of carboxylic acids from the film during irradiation. Gal et al. (34) described the effects of three antioxidants on the radiation crosslinking efficiency of low-density polyethylene. All three antioxidants that were investigated decreased the amount of crosslinking at a given dose. Schlein et al. (35) obtained a patent for the addition of 2,2'-methylene-bis(4-ethyl-6-t-butyl) alcohol to polyethylene, which was reported to stabilize it so that there was no odor formation at sterilization doses for meats (20-40 kGy).

Polypropylene

Bovey considered the predominant reaction of ionizing radiation with polypropylene to be that of crosslinking (2). Chapiro (22) discussed the nature of the crosslinking reactions. Tinker et al. (25) considered polypropylene to be unsuitable for the packaging of radiopasteurized fish because the gas permeability rate was too high. Varsanyi and Farkas (36) concluded that non-oriented polypropylene film was suitable at dose levels of less than 8.0 kGy, did not suffer significant alteration of either chemical or physical properties, and was suitable for packaging of radiopasteurized meats. The radiation-crosslinking of polypropylene to improve its heat resistance and tensile strength was described by Benderly and Bernstein (37).

Polystyrene

Bovey reviewed several studies on the effects of ionizing radiation on polystyrene concluding that the predominant reaction was crosslinking (2). Very little gas was formed during the crosslinking. Kline (38) reported the results of studies of radiation on the dynamic mechanical properties of styrene concluding that crosslinking took place but no changes in the dynamic mechanical properties were detected. Chapiro (22) provided an extensive review of the effects of ionizing radiation on polystyrene. Tinker et al. (25) reported polystyrene lids and trays to be good to excellent for the packaging of radiopasteurized fish.

Polytetrafluoroethylene

Polytetrafluoroethylene, though almost chemically inert, is degraded by ionizing radiation. It loses mechanical strength and CF_4 is evolved (2).

Polyvinyl Chloride

Bovey (2), in reviewing the existing studies as of 1958, indicated that vinyl chloride polymers were on the border line between

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predominant formation of crosslinks and/or scission reactions. Several studies were cited as indicative of degradation, including the evolution of hydrogen chloride, darkening, reduction in tensile strength, and hardness. Some reports, however, cited by Bovey (2) indicated that crosslinking was taking place under some circumstances. Chapiro (22) reported in 1962 that his research indicated that irradiation in air caused a steady degradation of the polymer, but that irradiation in vacuo led to only minor changes at doses as high as 83 kGy. Yegorova et al. (39) reported that radiation crosslinking predominated in the case of the ethylene copolymer containing 15 mole % vinyl chloride. The tensile strength was reported to rise with increasing dose. Haesen et al. (40) reported that gamma irradiation stimulated the formation of a heptane soluble, nonvolatile Sn compound with a high migration tendency from organo-tin compounds added to poly(vinyl chloride) for stabilization properties.

Other Plastic Films

Killoran (13) tested eight plastic films for water, acetic acid, and n-heptane extractives following either gamma or electron radiation to an average dose of 63 or 67 kGy, respectively. Polyethylene-polyisobutylene blend, plasticized polyvinyl chloride, polyethylene terephthalate and polystyrene had minimal net changes in water or acetic acid extractives. Four other gamma-irradiated films, polyiminocaproyl, polyiminoundecyl, poly(vinyl chloride-vinyl acetate), and poly(vinylidene chloride-vinyl chloride) had increased water and acetic acid extractives after irradiation. There were minimal changes in n-heptane extractives after gamma- and electron-irradiation of polyiminocaproyl and polyethylene terephthalate. Increased amounts of n-heptane extractives were obtained from gamma- or electron-irradiated films of polyethylene polyisobutylene blend, plasticized polyvinylchloride, poly(vinylidene chloride-vinyl chloride) and polystyrene than from non-irradiated controls. Gamma-irradiated films of polyethylene, and polyiminoundecyl and electron-irradiated poly(vinyl chloride-vinyl acetate) also had increased n-heptane extractives. There were minimal changes in n-heptane extractives after gamma-irradiation of poly(vinyl chloride-vinyl acetate), and electron-irradiation of polyiminoundecyl. Electron-irradiated medium-density polyethylene had less extractive than the non-irradiated control. The author attributed the differences in extractives to the relative stability of the films to crosslinking and/or degradation by either the gamma radiation or electron radiation. Killoran (13) concluded that the radiation stability, based on the total amounts of volatiles produced by electron irradiation of each film, was polyiminocaproyl > high-density polyethylene > poly(vinylidene chloride-vinyl chloride) > low-density polyethylene. The abrasion resistance of low-density polyethylene and polyiminocaproyl increased with increasing radiation dose (13).

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Laminated-Packaging

Keay (26) examined the effects of gamma radiation up to a dose of 160 kGy from spent fuel elements (no temperature, atmosphere, or dose rate was stated) on pouches of nylon 11, pouches of laminated polypropylene (0.002 inch thick)-medium density polyethylene (0.002 inch thick) bonded with an unspecified adhesive, and laminated pouches of 0.002 inch medium-density polyethylene and (0.0005 inch) polypropylene bonded with an unspecified adhesive. The evaluations included development of color or change in transparency, loss of slip, brittleness, delamination, infrared spectral examination, gas chromatographic examination, and a taste panel examination of cod fillets stored in the vacuum sealed irradiated pouches at 2°C for 5 days. The fish fillets themselves were not irradiated. They were evaluated for raw odor taint and then steam cooked and tested for odor and flavor taint. The nylon 11 was essentially unaffected by the radiation treatments through a dose range of 80 kGy. Both of the laminates, however, had dose-related increases in odor though only the polypropylene-polyethylene pouches had a loss of slip with increasing dose. Both laminates were discolored by the radiation. The polypropylene-polyethylene pouches had a four-fold increase in total volatiles after a radiation dose of 80 kGy and strongly tainted the raw but not the cooked fish fillets (26).

Killoran et al. (41) investigated the use of five commercially available plastic laminates for the packaging of bacon, ham, or pork, which was to be irradiated at 3°C to a dose of 45 to 56 kGy at a dose rate of 53 krads per min using a ⁶⁰Co radiation source. The evaluation included observations for odor, leakage, color changes, and determination of the physical changes in the pouches. The following packaging materials were evaluated: Film A: 0.5 mil 50 A Mylar/0.5 mil Al foil/2 mil poly(vinyl chloride); Film B: 30 lb paper/0.35 mil Al foil/2 mil Scotchpak 20A5; Film C: 30 lb paper/0.35 mil Al foil/1 mil Marlex TR-515; Film D: 0.3 mil Al foil/30 lb paper/2 mil Scotchpak 20A5; and Film E: 4.5 mil transparent Scotchpak 45A27. The last named component was in each case the food-contacting film. Only film B proved satisfactory for packaging of the three meat products over a one-year period.

Packaging Studies of Shelf-stable Meat and Poultry

The most comprehensive published studies of the effects of ionizing radiation on packaging materials were conducted at the U.S. Army Laboratories, Natick, Massachusetts to develop packaging materials suitable for use in packaging irradiated foods intended to have a two year shelf life at room temperature. Large scale studies of the wholesomeness of radiation treated (to commercial sterility) poultry and beef products were conducted. The products used for these studies received radiation doses in excess of 40 kGy at an average temperature of $-25 \pm 15^\circ\text{C}$ and the studies were conducted on such a scale as to provide realistic testing of the packaging materials. In the most recent study, 135,405 kg of broiler chicken meat was processed and packed either in cans or in flexible

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packages depending on the treatment it was to receive (42-44). The details of the processing of the chicken were reported by Wierbicki (44).

Tinplate Cans

The chicken that was to be sterilized by gamma radiation was vacuum packed in 404 x 309 mm epoxy-phenolic- enamel lined cans (42-44). The cans were constructed of 80 to 90 weight, No. 25 tinplate, coated with epoxy-phenolic enamel (44). The lids were sealed with a blend of cured and uncured isobutylene-isoprene copolymer (43-45). Killoran et al. (45) had evaluated the tinplate can with certain enamels and end-sealing compounds and found it to be suitable for packaging meat and poultry products that were to be irradiated to a dose of 70 kGy at -60°C.

Flexible Packaging.

The chicken that was to be sterilized by electron beam was packed in flexible packages 165 mm x 208 mm and fabricated with 0.025 mm polyiminocaproyl (nylon 6) as the outside layer, 0.0090 mm aluminum foil as the middle layer, and 0.062 mm polyethylene terephthalate-medium density polyethylene as the food contacting layer (42-44). The actual food contactant was the medium density polyethylene layer. The reliability of this flexible packaging material was extensively tested during the packaging of the beef described above (12). Under conditions that would have been similar to commercial use, only 140 of 441,470 pouches containing beef were defective after the vacuum sealing operation for a defect rate of 0.03%. The bond strength of the pouches increased approximately 3 fold during the irradiation process and did not deteriorate during storage for 24 months (12). The burst strength of the pouch also increased during the irradiation process from 1.9×10^5 Pa to 2.4×10^5 Pa (12).

The food-containing layer in the pouches used for packaging the chicken was extensively tested for possible production of extractives during irradiation by Killoran (43). Standard food simulating solvents were used: water, acetic acid (pH 3.5), and n-heptane. The film was formed into pouches that would hold 160 g of food and had an exposed surface area of 290.3 cm² per pouch. Five pouches were used for each sample. The pouches with food-simulating solvent were sealed in an atmosphere of nitrogen, cooled to -40°C, and irradiated with 10 MeV electrons at a dose rate of 2×10^7 to 5×10^7 kGy/sec, to a total dose of 47 to 71 kGy. The initial temperature, as previously mentioned, was -40°C and rose to -18°C during the irradiation. After thawing the pouches were stored at 50°C. Under these conditions of irradiation, the total water extractives were 0.54 mg/pouch and 0.33 mg/pouch when not irradiated. When the equilibrium values for the extractives in pH 3.5 acetic acid were corrected for that formed in the acetic acid when irradiated, (1.17 mg/pouch) the irradiated samples had 0.26 mg/pouch and the non-irradiated

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0.40 mg/pouch. In a similar manner, when the equilibrium extractives for n-heptane were corrected for radiation induced extractives in the heptane (1.35 mg/pouch), 0.57 mg/pouch and 0.76 mg/pouch were found in the irradiated and the non-irradiated samples, respectively. The grease-like material extracted from the pouch by n-heptane was not part of the adhesive between layers, which was a cured polyester-epoxy system. It was identified by UV, IR, and mass spectra as a low molecular weight polyethylene.

Conclusion

Data exists on the reactions of ionizing radiation with a number of polymer and copolymer films. Some of these films such as polyethylene, polystyrene, and polyethylene terephthalate appear to be very well suited for use as packaging materials for foods which are to be subjected to ionizing radiation. But even these materials do react with ionizing radiation and it should be remembered that the regulation (1) was written from data submitted in the early 1960s. Modern analytical technology should be applied to the analysis of volatiles and extractives. Few laminated films have been extensively investigated and none have been approved for use in packaging foods which are to be irradiated. The use of ionizing radiation to improve the characteristics of films opens the question as to what subsequent additional reactions might take place if such films were used to package foods which were to be irradiated. Fortunately, the extensive use of radiation cross-linking by industry should provide the knowledge to select the proper films for formation of laminated packaging materials to provide safe and reliable materials for use in packaging foods which are to be irradiated. It is possible that satisfactory packaging films could be produced by co-extrusion of polymers which have been previously approved avoiding the necessity of seeking a new approval from the Food and Drug Administration. The approvals already granted for irradiation of foods and the potential for additional approvals should generate a considerable market for packaging materials cleared for use with ionizing radiation. Abbreviations used: Gray(Gy) - A radiation dose of 1 Gy involves the absorption of 1 J of energy per kilogram of matter. 1 Gy = 100 rad. 1 kGy = 1000 rad. Rep(r) - Roentgen equivalent physical. An absorbed dose of ionizing radiation equivalent to 93 ergs/g; 1 Gy = 107.5 rep, 1 million electron volts (MeV).

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