Packaging of irradiated foods

Current progress in evaluation of materials and techniques is summed up by a Federal Government researcher. Indicated are new commercial programs of interest to all packagers

By John J. Killoran

The expansion of food-irradiation research from its small beginnings in the 1950s has been accompanied by an ever-increasing emphasis on packaging. Finding the right packaging material for irradiated products has been a primary concern of investigators. Transfer of the irradiation process from the laboratory to the industrial plant will involve even more complex investigations, including studies of packaging design based on research into package integrity.

In this article, some recent data on the response of packaging materials to irradiation are discussed. In addition, the impact on packaging of industrial-scale irradiation processing will be considered, because much remains to be done before the packaging problem can be regarded as solved. Food & Drug Administration approval of canned, irradiated bacon indicates that food radiation is on the way to commercial acceptance, but it is also clear that we shall need to know more about what happens when other packaged products undergo irradiation. In this regard, it is interesting to see what is already known.

▸ *Possible hazards.* "Safe for use after radiation" is a primary criterion for packaging materials proposed for use in radiation preservation of foods. When packaging materials are in contact with food, the possibility always exists that certain extractives may contaminate the food. To this end, studies using food-stimulating solvents and selected packaging materials and an appropriate radiation dose have been performed to determine the amount and nature of extractives for comparison with non-irradiated controls. Some packaging materials with prior food approval show amounts of extractives not significantly different, whether irradiated or non-irradiated. They can be termed safe. But if inconclusive data are derived from extractive studies or if the packaging materials have not been granted prior approval, safety must be established by appropriate animal-feeding studies (1) (numbers in parentheses identify References appended).

▸ *Approved materials.* For pasteurization, in which the radiation dose does not exceed 1.0 megarad, the FDA has approved use of nitrocellulose-coated cellophane, glassine, ethylene alkene-1 copolymer, wax-coated paperboard, polypropylene, rubber hydrochloride, polystyrene, polyvinylidene chloride-vinyl chloride, vinylidene chloride copolymer-coated cellophane and nylon films for gamma-irradiated foods (2).

For sterilization, the first packaging material cleared for radiation packaging at an absorption dose of up to 6.0 megarad is vegetable parchment used as a wrap for canned bacon, sterilized by gamma or X-ray (2).

On July 13, 1965, FDA published a "Notice of Filing" for four films—polyethylene, polyethylene terephthalate, polyvinyl chloride-vinyl acetate and nylon 6—for use in radiation sterilizing processing of packaged foods. Information needed for acceptance filing of other films—polystyrene and polyvinylidene chloride-vinyl chloride—has been submitted to FDA.

▸ *Induced radioactivity.* When a food package is irradiated at certain energy levels, the possibility exists that radioactivity will be induced in some atoms of the packaging material. If measurable radioactivity is induced, the packaging material is not safe. It has been shown that no measurable activity is induced by cobalt-60 or cesium-137 or by electrons up to 10 MeV, in normally present elements (3).

In a recent study at Natick, induced radioisotope activity was not found in four films—polyethylene, polyethylene terephthalate, polyvinyl chloride-vinyl acetate and nylon 6—irradiated to 5.6 megarads with cobalt-60. No consistent or significant differences were

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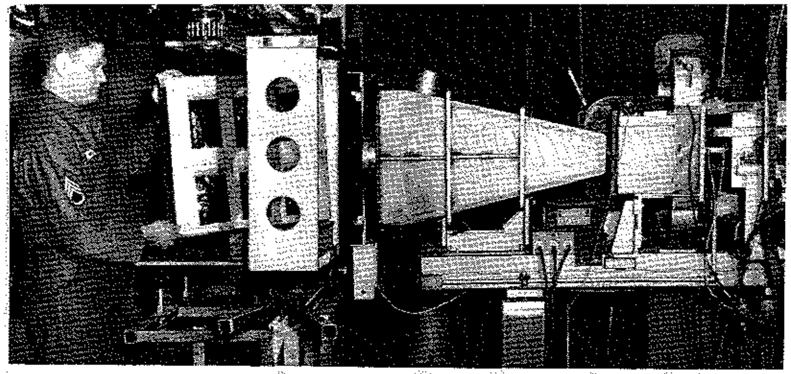

Figure 1. *Flexible packages of a meat product, contained in a fibre case, are positioned for high-energy radiation treatment at Natick laboratory.*

found between control or irradiated samples when analyzed for beta-emitting and gamma-emitting isotopes. Continuing research is being performed with regard to the dose and energy of radiation.

▶ *Chemical effect of radiation on materials.* Radiant energy in the form of heat or light can have a deleterious effect on packaging materials. One example is the effect of heat and ultraviolet light in degrading polyvinyl chloride. Therefore, it is expected that other forms of radiant energy could promote chemical changes in packaging materials.

It is known that radiation forms ions and free radicals in plastics. The end result varies with the particular plastic and the conditions of radiation. In some cases crosslinking is observed; in others, chain scission, formation of unsaturated bonds, hydrogen and other gases and, where the irradiation is conducted in the presence of air, oxidation may occur. The net result is governed, however, by the predominant reaction that, in turn, depends on the film's chemical structure.

These changes have a profound effect. With crosslinking, there is a marked increase in molecular weight and a conversion of the molecule from a linear and two-dimensional structure to a three-dimensional configuration. Principally, this results in an increase of tensile and flexural strengths and of the softening point. There is a corresponding decrease in elongation, crystallinity and solubility. Conversely, shortening of the polymeric chain (through scission) results in a loss of such properties as tensile and flexural strengths. The formation of unsaturated, conjugated, double bonds introduces off-color. The most serious aspect is a susceptibility to oxidation and chain scission. Formation of gases within the plastic will result in increased porosity either during irradiation or subsequent exposure to heat. The gases may also lead to development of unpleasant odors and flavors.

Relative stability of various polymeric materials being investigated as candidates for packaged irradiation-sterilized foods is shown in Table I.

Flexible materials, as a whole, are fairly resistant to radiation—except for cellulosics, which are the least radiation resistant of common packaging materials. Nevertheless, only slight changes in the physical properties of cellulose-type packaging materials occur at radiation doses up to 6.0 megarad.

Seaman (4) has reported that irradiation of cellulose with high-voltage cathode rays caused reduction in crystallinity, and simultaneous depolymerization of the cellulose chain and extensive decomposition of glucose units at doses above 100 megarads. The apparent ratio of number of glucose units destroyed to number of depolymerizations is 5 to 1. Charlesby (5) used Seaman's data to verify a derived theoretical relationship between intrinsic viscosity and radiation dose. The calculated and observed decomposition data for cellulose are compared in Table II.

It is estimated from these data that 6 megarads of ionizing radiation will fracture less than 1.0% of the bonds between monomer units in the cellulose molecule. It appears likely that, for each chain fracture, one glucosyl unit is destroyed. The 1, 4-acetal bond must be the chief site of scission; because if this bond remained intact, it would be necessary to break particular pairs of ring bonds to achieve scission.

Polystyrene has remarkable radiation resistance. At doses of about 100 megarad, in the absence of air, the polystyrene molecule undergoes crosslinking with the evolution of hydrogen gas. In the presence of air, some surface oxidation and chain scission has been observed (6). But the stability of polystyrene to radiation-induced changes is illustrated by the total energy —3,000 to 5,000 electron volts—required to produce one crosslink (7). One explanation for this is the presence of the benzene ring, the resonance energy of which is known to stabilize the compound. Each polystyrene molecule contains as many as 3,000 benzene rings, which increases the stability (7).

Mass spectrometric analysis of gaseous products evolved by exposure of polystyrene to 5.6 megarad (cobalt-60 gamma radiation) showed that polystyrene evolved fewer products than such other materials as polyethylene, polyethylene terephthalate, polyvinylidene chloride and polymonochlorotrifluoroethylene.

Exposure of polyethylene terephthalate (polyester) film to cobalt-60 gamma radiation of 5.6 megarad produced only a few products, the major one being carbon dioxide. Hydrogen and saturated hydrocarbons, both in tiny amounts, were noted. Krasnavsky (8) conducted a study to determine the effects of cobalt-60 gamma radiation of 6.0 megarad on six classes of plastic films. Polyethylene terephthalate was found to be highly radiation resistant. Stability was judged on total moles of gas evolved per gram of specimen exposed to radiation.

Polyethylene terephthalate was listed as number two in order of stability, the polyamide from meta-xylylenediamine and adipic acid being the most radiation resistant. The presence of a phenyl group enhances the stability of polyesters and polyamides.

Radiation stability of polyamides from: (1) hexamethylenediamine and adipic acid (Nylon 66), (2) the 11-aminoundecanoic acid (Nylon 11) and (3) metaxylylenediamine and adipic acid (MXD-6) were subjected to cobalt-60 gamma radiation at dosages of 6, 36 and 60 megarad. Mass spectrometric analysis of the three polyamides irradiated at 6 megarads showed that total number of moles of gas evolved per gram of film were less than 5 micromoles for each polyamide. The order of decreasing stability was polyamide MXD-6, nylon 11, and nylon 66. This shows polyamides to be remarkably radiation resistant, placing them in the class of polystyrene and polyesters (7).

It is of much interest that the materials most stable to irradiation appear to be those that contain a phenyl group and/or an amide linkage. The added amide linkage seems to increase the stability of polymers containing a phenyl group, a fact attributed to the ionic character of the amide linkage.

Gamma radiation of polyethylene at 6.0 megarads produces hydrogen (about 90%) and carbon dioxide, carbon monoxide and, in the case of low-density polymer, such light hydrocarbons as propane and ethane. The oxides may result from oxidation of the polyethylene prior to radiation. The production of hydrocarbons by the low-density material was attributed to cleavage of short-chain branches (11).

If the amount of hydrogen produced is subtracted from the total weight of each polyethylene, it will be found that, on the basis of total products evolved, the polyethylenes rank immediately behind the most radiation-resistant polystyrenes, polyesters and polyamides. The evolution of hydrogen from polyethylene results in crosslinked structures with improved properties. Tripp and Crowley have shown that small changes in tensile strength, elongation, greaseproofness, water-vapor transmission rate, oxygen permeability and film sealability occur when polyethylene is radiated at 6.0 megarad or less (9). Wright reported that the main effects of electron radiation on the properties of high-density polyethylene were to decrease its melt index and to increase its resistance to environmental stress cracking. Density and softening point were changed only slightly. Ultimate tensile strength and impact strength increased with radiation, but doses of about 25 megarad were required to cause a noteworthy change in these properties (10).

Extractive data were performed by Hazelton Laboratories (11) on seven commercially available plastic laminates with low-, medium- and high-density polyethylenes on the food-contacting sides. Evaluation of the laminates was the same as that used in the AEC radiation pasteurization study on extractives for FDA regulation 121.2543. Samples of the laminates were irradiated with cobalt-60 at 6.0 megarads with three food-simulating solvents (water, acetic acid, and n-heptane). Radiation caused no significant change in chloroform extractives for seven packaging structures.

No satisfactory fundamental study of radiation behavior of polyvinyl chloride and vinyl chloride-vinyl acetate copolymers has been made. The work reported, so far, has been of a practical nature and, consequently, there is no information as to the mechanism and energy requirements of reactions leading to cross-linking and scission. The technical literature indicates that halogen-containing polymers—polyvinyl chloride, polyvinylidene chloride copolymers and vinyl chloride-vinyl acetate copolymers—liberate traces of hydrochloric acid at radiation dosages of about 100 megarad.

Nitta (12) studied the radiation chemical process at various temperatures in polyvinyl chloride by means of electron-spin resonance and measurement of gas evolution. Gas yield vs. temperature of reaction showed that at 10 deg. C., hydrochloric acid gas was produced in small amounts at a radiation dose of 20 megarad. In packaged irradiated foods with PVC as the food-contacting film, the acid produced by radiation will be neutralized by the buffering action of the food to form traces of chloride salts. These salts are present in foods normally, particularly in meat.

Atchison (13) performed an investigation of the free radicals in unplasticized polyvinyl chloride at 5.9 to 7.3 megarad at room temperature in the absence of air. Spectrophotometric data indicated that conjugated double bonds were introduced into the polymer molecule as a result of radiation.

Impact of radiation on packaging

It is not yet possible to assess the full impact of radiation preservation on packaging, but it is worthy of note that research is being oriented increasingly toward commercial application. This is evident in a recent review by Wierbicki and Killoran (14). The goal has been flexible containers capable of providing protection during rough handling and storage.

Since this goal requires a rugged, dependable container, initial efforts were concentrated on the metal can. As a package for radiation-processed foods, however, its physical, chemical and protective characteristics have had to be evaluated anew, including the

Table I: Order of stability of plastic films to Gamma radiation

Below 1 micro-mole/gm.	1 to 5 micro-moles/gm.	5 to 10 micro-moles/gm.	10 to 20 micro-moles/gm.	Over 50 micro-moles/gm.
Polyamide: meta-xylylene-diamine and adipic acid	Nylon 11	Polyvinylidene chloride	Polyethylene (high density)	Polyacetal
Polyester: polyethylene terephthalate	Nylon 66		Polyethylene (low density)	
Polymonochlorotrifluoro-ethylene	Polycarbonate		Polypropylene	
Polystyrene				
Rubber hydrochloride				

Criterion: evolution of gaseous products at 6 megarad (10^{-6} mm. Hg.).

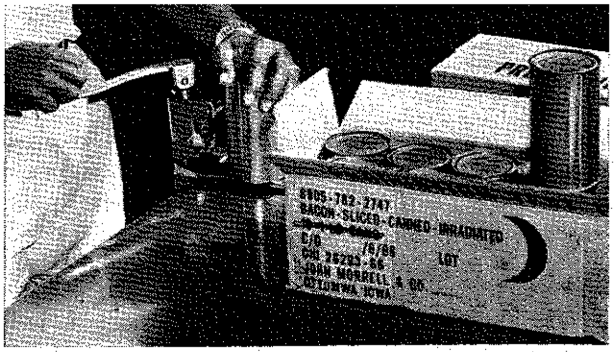

Figure 2. *Irradiated bacon in cans, approved for use by FDA, was packed in a recent test for consumption by the military.*

effect of radiation on tin coatings, internal enamels and seal compounds. A tinplate container with various enamels of epoxy phenolic, polybutadiene or oleoresinous-types compounds (15) and such can-sealing compounds as unvulcanized butadiene rubber, butadiene-acrylonitrile rubber, natural rubber or neoprene (16) was determined to be an efficient package for radiation-sterilized foods. Recently, under a contract with the Army, 30,000 lbs. of bacon were packaged by a commercial source in 1-lb. metal containers and irradiated at 4.5 to 5.6 megarads at the Brookhaven National Laboratory. This production test represents the first effort to procure a food sterilized by irradiation on a commercial scale. The bacon will be consumed by the Army and Air Force in the United States.

Foods—whether frozen, irradiated or heat-processed—have very similar packaging requirements, all related to the integrity of a flexible package. These requirements concern sealability, durability, extractives, microbial and insect penetration, shelf life and acceptance (17). Behavior under radiation has already been discussed. To be considered now is behavior under field conditions.

One of the major objectives of the Department of the Army's program for radiation preservation of foods is development of flexible containers to replace metal cans. Initial effort was devoted to screening numerous commercially available plastic films to determine both their protective qualities and resistance to radiation. Not a single commercially available film that could meet all requirements was found (18).

Recognizing a need for more basic information, Continental Can Co., under contract to the Department of the Army, evaluated three newly developed packaging materials for food compatability, low-temperature resistance and resistance to microbial and insect penetration. As a result, a flexible laminate incorporating nylon 11 as the food-contacting film was recommended for single-service packaging of ham, chicken and bacon. This material was the only one that maintained adequate seal and bond strengths and retained its laminated structure in various test environments for 12 months. All three packaging materials maintained their integrity during shipping vibration tests and resisted penetration by boring insects (19).

Five commercially available plastic laminates were screened for in-package radiation-sterilization processing of bacon, ham, and pork. One plastic laminate was transparent and had medium-density polyethylene in contact with food. The other four laminates had either paper or Mylar on the outside, aluminum foil as an oxygen barrier in the middle and/or low-density polyethylene, medium-density polyethylene, high-density polyethylene or polyvinyl chloride as the food-contact surface. All samples were packed under vacuum. Control samples were: (1) irradiated meat products in metal containers stored at 23 deg. C. and 50% RH and (2) non-irradiated meat products in metal containers and pouches stored at —20 deg. C. Test samples were meat products packaged in flexible pouches, irradiated at 4.5 to 5.6 megarads (cobalt-60 radiation) and stored at 23 deg. C. and 50% RH for 12 months.

The evaluation phase of the investigation included observations for odor, leakage and color changes and determination of physical-property changes in flexible pouches. Each meat product was subjected to organoleptic and chemical testing. At the end of six months, four of the flexible-packaging materials were removed from the study because of off-odor and/or off-color that developed in the meat products. Swelling of these pouches was not observed. However, there were pinholes, delamination and loss of vacuum. One laminate, containing medium-density polyethylene as the food-contacting material, was found satisfactory for packaging meat products and for storage over a one-year period. Small changes in physical properties of such pouches did not affect their functional performance.

Preference scores, obtained from an organoleptic evaluation, indicated that the products were acceptable. Storage time had no pronounced effect on organoleptic acceptability (18).

Low-temperature irradiation

Irradiation at cryogenic temperatures can maintain superior quality in such flesh products as beef, ham, pork and chicken. Texture, color and flavor of these products are greatly improved. To date, low-temperature irradiation has been the only means found to assure consistently palatable items of beef. Radiation has been performed at temperatures as low as —180 deg. C. More recently, it has been shown that the lowest temperature need not exceed —80 deg. C. (20).

Questions are posed as to whether metal cans and flexible packaging materials will perform satisfactorily at these low temperatures. What is the effect of temperature on interior enamels and end-sealing compounds? Does the combination of radiation and low temperature promote "tin-rot" in metal cans? Hundreds of metal cans containing various meat products have been irradiated at —180 deg. C. using liquid nitrogen as a coolant. Some failures have occurred because of nitrogen pickup (as indicated by headspace-gas analysis) which causes swelling of the cans.

In pack tests of beef and ham, flexible-laminate pouches of 0.5-mil Mylar (outside), 0.5-mil aluminum foil (center) and 2-mil food-contacting films, such as nylon 11 and medium-density polyethylene, have performed satisfactorily when subjected to electron and cobalt-60 irradiation (4.5 megarads) at temperatures as low as —80 deg. C. Swelling, leakage and delamination were not observed in any of the pouches tested. Preference scores, obtained from organoleptic evaluation, indicated that beef and ham irradiated at —80 deg. C. with cobalt-60 and electrons were equally acceptable. The obvious advantage of low-temperature radiation was noted in the improved texture, and decreased off-odor and radiation flavor, in both beef and ham. Flexible pouches positioned for irradiation are shown in Figure 1.

In the recent production test of 30,000 lbs. of irradiated bacon, 12 tinplate cans (303 by 509) of bacon were placed in a fibreboard box as shown in Figure 2. Seven boxes, stacked one above the other, were gamma irradiated at one time. The advantage of packing the cans prior to irradiation is obvious. However, the effect of radiation on fibreboard containers could be a problem. Laboratory screening tests of fibreboard components (V2s, V3s and V3c) have shown that a radiation dose of 6.0 megarads caused some loss in the protective characteristics of these materials. For example, Mullen burst strength of the three fibreboard materials tested in the dry state were reduced by 19%, 22% and 28%.

Conclusion

Research is continuing to establish the safety of flexible packages for irradiated foods. Correlation data between the "laboratory package-integrity test method" and actual field usage on a military obstacle course will be obtained. Flexible packages are ideal for electron irradiation.

At the present time, there is no generally accepted method that can be used to indicate whether a food package has been irradiated and how much radiation has been applied. The packaging material, itself, appears to offer an ideal indicator through such physical or chemical changes as thermoluminescence.

The U. S. Atomic Energy Commission and the U. S. Department of Commerce have agreed to join in a cooperative program with industry to construct and operate a pilot-plant irradiation facility for processing meat and poultry products. The U. S. Department of Defense will support the facility for at least three years by procuring a minimum of 300,000 lbs. annually of the acceptable shelf-stable foods. The procurement will relate to products—both food and packaging—cleared by FDA and USDA and will be used by the military. Initially, the foods will be packaged in metal cans; subsequently, in flexible packages cleared by FDA.

Table II: Decomposition data for irradiated cellulose (wood pulp)

Radiation dose, Roentgen*	10^6	10^7	10^8
Calculated decomposition, %	0.16	1.6	16
Observed decomposition, %	—	5	17

*Note: at 800 kv, absorbed dose is 0.93 rad/Roentgen.

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