The Effects of Radiation Sterilization on Plastics

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INTRODUCTION

THERE ARE many different kinds of atomic radiations, but they may be classified into two basic groups: neutral particle radiation and charged particle radiation. The interaction of neutral particles with matter generally yields energetic charged particles, so the observed radiation effects of both types of particle are similar even though the original radiation may have been neutral. For sterilization purposes the radiations of practical importance are high-energy electrons, which are negatively charged, and gamma rays which can be regarded as electromagnetic radiation and neutral. Although both radiations give rise to essentially similar effects, there are important differences in their behavior. The distance to which particles penetrate matter depends largely on their type and whether they are charged or not and only slightly on their energy. Gamma rays possess a much greater penetration ability than do high-energy electrons. As considerably greater dose rates can be achieved from electron sources than with gamma rays from ^{60}Co decay, however, the sterilizing time is correspondingly shortened. In the remainder of this discussion the term *radiation* will be used to mean both high-energy electrons and gamma rays except where an explicit distinction is made.

No induced radioactivity arises in materials irradiated with ^{60}Co gamma radiation or with electrons of energies up to 5 Mev.

GENERAL INTERACTION WITH MATTER

Radiation with energies below 5 Mev affects primarily the electrons of matter on which it impinges. Collisions with nuclei can be ignored. The charged particle gradually loses energy passing through the absorbing material, the energy being dissipated by excitation or ionization of the atoms or molecules concerned. The subsequent alterations in molecular structure govern the changes in physical and chemical properties of the material. As they are not necessarily deleterious these changes are referred to as radiation effects rather than radiation damage.

The processes of excitation and ionization of an organic molecule leads to one or more of a number of effects. Gas evolution, polymerization, crosslinking, degradation and double-bond formation have all been observed, and all lead directly to changes in physical properties. These effects are relevant too to the results of irradiating polymers. A polymer may undergo chain scission, the molecules being broken into smaller fragments, or crosslinking may take place with the formation of larger molecules. Very low molecular weight fragments, i.e., gases, and unsaturation are important side results of these reactions.

Polymers preferentially crosslink or degrade depending on their chemical structures. Conflicting results have been found with a few materials, but a general empirical conclusion for polymers with carbon chains is that crosslinking occurs if each carbon carries at least one hydrogen atom, whereas if a tetra substituted carbon is present scission takes place. Both crosslinking and degradation may occur in the same polymer simultaneously, although usually one process predominates. This explains why, for example, both gas evolution and increases of molecular weight may be observed together.

STERILIZATION DOSE

For the purposes of this assessment it is assumed that the dose required for radiation sterilization is 5 Mrad. This adequately covers the range of doses that are used or proposed and allows some latitude for inexactness in application. The effects of higher doses are included as well because of possible repeated sterilization. For practical purposes it can be assumed that effects of resterilization are cumulative and additive.

EFFECTS ON PLASTIC PROPERTIES

GENERAL

Plastics are synthetic organic materials of high molecular weight which at some stage in their production are capable of being shaped and subsequently capable of retaining that shape. The polymer molecules are made up of a large variable number of repeating monomer units and may be straight or branched, either randomly or regularly. The arrangement of molecules may also be random or regular, giving zones of low or high crystallinity. Virtually all plastics contain small amounts of other ingredients to confer to each particular technical properties, and in a few cases these amounts approach 30 % by weight. These ingredients are normally simple chemicals of low molecular weight.

All plastics are affected by ionizing radiation; the only variables are the type of effect and the size of dose necessary to produce it. Not only do they behave as other organic substances but, owing to their high molecular weight, drastic changes in the physical properties of plastics may be exhibited as a result of only minor chemical modifications. As the chemical reactions are taking place in a solid medium, and an ill-defined one too, it is difficult to predict behavior on a theoretical basis. Certain additives have a protective action and can reduce the effect of radiation on plastics. These may either be energy absorbers or chemical reactants which combine with radiation-produced free radicals. The atmosphere in which irradiation takes place often modifies the effects. In particular, differences are usually observed between the behavior in the presence or absence of oxygen. Findings, however, are not consistent; with some plastics degradation is enhanced in the presence of air, whereas for others it is reduced. Thin specimens are likely to be more affected because oxygen is freely available; with bulky items the oxidation process, except at very low dose rates, will be diffusion-controlled. Post-irradiation effects have been also noted, presumably because of the persistence of free radicals in the material following exposure to radiation.

The observed effects on plastics properties are varied but, most importantly, involve mechanical characteristics. Polymerization and crosslinking increase the molecular weight and therefore lower the mobility of molecules and reduce creep. This may raise the tensile strength, depending on the normal mechanism of tensile breaking, and does increase the hardness and brittleness. Impact strength usually decreases or remains relatively unchanged. Radiation-induced degradation, on the other hand, by lowering the molecular weight, detracts from

most of the valuable properties associated with plastics. Tensile, impact, and shear strengths all are reduced and so is the elongation at break. Often embrittlement occurs even though the material may have become somewhat softer. Crystallinity can increase in polymers that undergo scission, there being less restraint on the shortened molecules, causing a rise in density.

An obvious effect of radiation on many plastics is the development of color; in some cases the material will become opaque after prolonged exposure. Most materials turn yellow or brown, but the dose at which discoloration becomes noticeable varies widely. The extent and amount of color development may vary on storage after irradiation, either increasing or diminishing with time, and are usually affected by the presence of oxygen.

Much of the literature dealing with the effects of radiation on plastics is concerned with mechanisms especially under extreme exposures. The behavior at sterilizing doses has in many cases to be determined by interpolation. Information presented here has been gathered from a number of general sources (7, 12, 13, 23), but specific further references are quoted where appropriate.

OLEFINE POLYMERS

Polyethylene Both low- and high-density forms of polyethylene are resistant to single-dose radiation sterilization and can withstand, without substantial change in mechanical properties, doses up to at least 100 Mrad (23).

Polyethylene in general crosslinks on irradiation, although there is a chain scission mechanism as well (5). The average molecular weight increases and the crystallinity decreases. The effect on mechanical properties is complex; e.g., the tensile strength first increases with dose up to about 10 Mrad, then decreases slowly, returning to its original value at 100–150 Mrad. The elastic modulus behaves in an opposite manner, first falling then rising again. Impact strength begins to fall at 70 Mrad, reaching zero at 500 Mrad (9). Gas permeability changes are small (17), there being no alteration at 10 Mrad and about 50% reduction after 100 Mrad (16).

As would be expected radiation brings about a reduction in solubility. Even after only a 5 Mrad dose the solubility in xylene at 25 C is reduced to half that of unirradiated material.

Polypropylene Polypropylene is readily affected by radiation and is

borderline in stability to single-dose sterilization. Thus it is one of the more interesting materials for consideration especially as its combination of mechanical properties make polypropylene useful for many biomedical applications (20).

Both chain scission and crosslinking result from irradiating polypropylene although, in the presence of air, oxidative degradation is an important effect as well. The rate of diffusion of oxygen into the material may be rate controlling. Items irradiated at high dose rates, such as can be achieved by electron beams, may therefore show much less damage than those treated at low dose rates. Crosslinking is evidently the major factor at low doses because the impact strength suffers an immediate fall followed by a slow decay over a period of months. Even after 2.5 Mrad the impact strength can decrease eventually by more than 50 %. Discoloration also occurs in polypropylene, often a noticeable yellow after single-dose sterilization, which although aesthetically objectionable may be masked by the incorporation of a trace of blue pigment.

Because of the radiation sensitivity of polypropylene the small differences between the products of different manufacturers and indeed the various formulations on each manufacturer's range can be important. The changes referred to do not necessarily go together; thus a grade which discolors severely does not always embrittle nearly so much in comparison. The purity of the polymer, the stabilizers used (19), the fabrication process, and the shape of the final article all are relevant to suitability for radiation sterilization. The onset of brittleness, e.g., is much less severe with simple moulded shapes than for the more complex ones such as hypodermic syringe barrels where there is some locked-in strain.

Currently, therefore, some polypropylene items can satisfactorily withstand a radiation sterilization dose; others are not yet good enough. It is essential to evaluate performance after storage and not merely immediately following exposure.

Poly(4-methyl pentene) Little information is available, although radiation effects could be predicted as similar to those in polypropylene. In fact poly(4-methyl pentene) seems to be rather more resistant and can be regarded as unaffected by a single sterilization dose although unsuitable for repeated exposure.

Copolymers Both ethylene-vinyl acetate copolymer and ethylene ethyl acrylate copolymer are satisfactory for radiation sterilization.

Indeed, the latter has been found more resistant than polyethylene itself (21).

STYRENE POLYMERS

Polystyrene This is the most radiation-stable of the common moulding plastics, and large doses are required to bring about significant effects. The aromatic rings in the structure appear to provide a protective action towards radiation effects, and the plastic is largely unaffected up to doses of 500 Mrad. The so-called high-impact polystyrene is somewhat less stable towards radiation, but nevertheless is still among the more resistant of plastics.

Styrene-acrylonitrile Styrene-acrylonitrile copolymers (SAN) are not as resistant to radiation as polystyrene itself, but are still fairly stable (21) and well able to resist a number of sterilization doses.

ACRYLIC POLYMERS

Poly(methylmethacrylate) Poly(methylmethacrylate) can satisfactorily withstand a single radiation sterilization dose both in the high molecular weight cast sheet form and as a moulded item. It is not, however, suitable for repeated doses. The effect of radiation is degradation both in the ester side chains and in the main chain of the molecule. Hence mechanical strength is affected, the tensile strength, e.g., being lowered by 50 % at about 20 Mrad and thereafter decreasing rapidly. The material eventually becomes brittle and cracks may appear.

A yellow discoloration develops in poly(methylmethacrylate) during radiation doses as low as 0.5 Mrad and the optical transmittance falls by one-third at 5 Mrad (24). This coloring tends to fade following subsequent storage in air although no postirradiation recovery seems to occur in mechanical properties. Certain additives can give a degree of protection against the degradation of poly(methylmethacrylate) (3).

VINYL POLYMERS

Poly(vinyl chloride) Poly(vinyl chloride) is suitable for single-dose radiation sterilization both in its unplasticized and plasticized forms. The mechanical properties begin to show some change above 15 Mrad so that repeated dosing is not advisable.

In general the polymer crosslinks in the absence of air and degrades if oxygen is available. Thus degradation may be observed upon irradiation of thin films but is confined to the surface of thicker articles. Poly(vinyl chloride) discolors at quite low doses, 2 to 3 Mrad, the shade

and intensity of color varying with the presence of different plasticizers and stabilizers. It is interesting that, in contrast to the behavior of poly(methylmethacrylate), the discoloration of poly(vinyl chloride) intensifies upon subsequent storage. The inclusion of sodium stearate is reported to be effective in reducing discoloration, whereas the use of organotin stabilizers promotes color development (26). These tin stabilizers also seem to inhibit crosslinking.

Differences have been noted between the effects of radiation on unplasticized and plasticized poly(vinyl chloride) and also between compositions containing different plasticizers. However, the differences are slight and probably not significant in a consideration of sterilization although one study (11) has shown a relatively good resistance to radiation in material plasticized with DOP, presumably dioctyl phthalate.

A more important effect is the liberation of hydrochloric acid with the corresponding production of unsaturation. The effect is reduced by the stabilizers always present in commercial compositions but some hydrochloric acid is available for further reaction. The subsequent sterilization by ethylene oxide of poly(vinyl chloride) previously treated by radiation has been reported to cause formation of the toxic agent ethylene chlorhydrin (14). Such resterilization should therefore be avoided (4).

Vinyl chloride copolymers Copolymers appear to be less resistant to radiation than poly(vinyl chloride) itself and to undergo degradation rather than crosslinking. Vinyl chloride/vinyl acetate copolymer, for example, shows a threshold effect at 1.4 Mrad (10) and could not be regarded as suitable for radiation sterilization.

Poly(vinylidene chloride) This too is less stable than the vinyl chloride polymer. The mechanical properties start to be affected at 4 Mrad (10), hence, although it may just withstand radiation sterilization, this procedure is not recommended.

FLUORINATED POLYMERS

Poly(tetrafluoroethylene) In contrast to its resistance to heat and to chemical attack poly(tetrafluoroethylene) is extremely sensitive to radiation. Effects on tensile strength have been observed at doses as low as 0.1 Mrad although there is much less damage in the complete absence of oxygen (25). This plastic is therefore quite unsuited to radiation sterilization.

Others Poly(chlorotrifluoroethylene) and fluorinated ethylene/propylene copolymer are both more resistant to radiation effects than poly(tetrafluoroethylene). Only limited data are available on these products, by they can probably withstand one-dose sterilization without undue change.

POLYAMIDES

No great difference has been noted in the effect of radiation on various types of polyamide: nylon 66 and nylon 6. All are suitable for sterilization although not for many repeat doses. Polyamides crosslink and lose crystallinity upon irradiation causing a slow increase in tensile strength but a much more rapid drop in impact strength. The latter characteristic falls to half its initial value after a dose of about 20 Mrad. Films and fibers are more affected mechanically than thick mouldings possibly because the loss of strength arising from the reduction in crystallinity is more important for thin section material than the accompanying increase in strength caused by crosslinking. Also the presence of oxygen substantially increases the effects of radiation, and such changes will in practice be more important for thin section material.

POLY(ETHYLENE TEREPHTHALATE)

Poly(ethylene terephthalate) is suitable for radiation sterilization whether in film or fiber form. Mechanically it can withstand at least 100 Mrad although discoloration occurs at lower doses. Crosslinking is the major effect of radiation but radiation-induced oxidation can be important too in the presence of air.

CELLULOSE ESTERS

Cellulose acetate is relatively unaffected by radiation doses up to 10 Mrad and may therefore be sterilized by this means. The tensile strength is reduced by 50 % at about 40 Mrad (10). Other esters such as the propionate, the acetate-butyrate, and the nitrate behave similarly. Cellulose itself undergoes scission under the influence of radiation more rapidly than its esters and ethers.

THERMOSETS

Phenol formaldehyde and urea formaldehyde are both reasonably stable towards radiation and suitable for irradiation sterilization. PF is the more resistant of the two resins being largely unaffected at 100 Mrad, but color changes may occur below this. Cellulose fillers such as wood

flour and paper are relatively more affected by radiation and generally lower the resistance of the resins containing them.

Epoxy resins are very stable and usually satisfactory up to 500 Mrad. In the form of thin films or coatings they are, however, more susceptible to radiation degradation in air. Comparisons of epoxy resins cured with different reagents show that aromatic amines give products that are much more resistant to radiation than those prepared with aliphatic curing agents (2).

Polyester resins have good stability too, being resistant up to around 100 Mrad, and may indeed be cured using radiation (23).

MISCELLANEOUS PLASTICS

Acetals Polyformaldehyde and acetal copolymers are sensitive to radiation and cannot be recommended as suitable for sterilization. Of the two the copolymer has somewhat better resistance (18) but radiation above about 1 Mrad brings about unacceptable changes.

Polycarbonate Polycarbonate can satisfactorily be given a single-dose sterilization exposure (22) but tends to become brittle much above 2.5 Mrad.

Acrylonitrile-Butadiene-Styrene ABS is much less resistant than the styrene-acrylonitrile (SAN) materials (21) but nevertheless is sufficiently stable to be suitable for a single sterilization dose.

Poly(phenylene oxide) Modified PPO is reported to exhibit good radiation resistance (21).

Some important properties are summarized in Table 1.

EFFECTS ON OTHER MATERIALS

To complete this survey some very brief information is included to indicate the radiation stability of selected other materials for quick reference and also to put the behavior of plastics into context.

RUBBERS

Conventional rubber compounds exhibit about a 50-fold variation in their resistance to deterioration in tensile strength and ultimate elongation brought about by radiation. Damage is reduced in the absence of oxygen, but is greatly accelerated if irradiation takes place under conditions of stress. Table 2 shows the general effect of radiation on

Table 1 Summary of relative resistance of plastics to radiation

Plastic	*Resistance to radiation*	*Suitability for sterilization*	
		One dose	*Several doses*
Polyethylene (HD and LD)	Good	Yes	Yes
Polypropylene	Fair	Borderline	No
Poly(4-methylpentene)	Fair	Yes	No
Ethylene/vinyl acetate	Good	Yes	Yes
Polystyrene	Excellent	Yes	Yes
SAN	Good	Yes	Yes
Poly(methylmethacrylate)	Fair	Yes	No
Poly(vinyl chloride)	Fair	Yes	No
Poly(vinylidene chloride)	Poor	No	No
Poly(tetrafluoroethylene)	Very Poor	No	No
Polyamides	Fair	Yes	No
Poly(ethylene terephthalate)	Good	Yes	Yes
Cellulose acetate	Fair	Yes	No
Phenol formaldehyde	Good	Yes	Yes
Urea formaldehyde	Good	Yes	Yes
Epoxy resins	Excellent	Yes	Yes
Acetal copolymers	Poor	No	No
Polycarbonate	Fair	Yes	No
ABS	Fair	Yes	No
Poly(phenylene oxide)	Good	Yes	Yes

Table 2 General effect of radiation on types of rubber in unstressed state

Material	*Comments*
Polyurethane rubber	Excellent stability up to 500 Mrad
Natural rubber	Good stability up to 100 Mrad
Butadiene styrene rubber (SBR)	Good stability up to 100 Mrad
Nitrile rubber	Good stability up to 100 Mrad
Silicone rubber	Poly(dimethylsiloxanes) stable up to 10 Mrad and methylphenyl silicones rather more stable
Neoprene rubber	Stable up to 10 Mrad
Butyl rubber	Unstable above 1 Mrad

various types of rubber (23) in an unstressed state, although stability can be influenced by the nature of antioxidants and fillers present.

TEXTILES AND FIBERS

Owing to differences in assessing radiation effects and relating changes in fiber characteristics to those of the resultant textiles there is some

conflict in the literature about radiation tolerance. A suggested maximum exposure level for common fibers (8) is:

Polyester fibers Acrylic fibers	50 Mrad
Wool Viscose Rayon Silk Cellulose acetate	20 Mrad
Nylon Cotton	1 Mrad

Work on the sterilization of sutures (6), however, showed a reduction in breaking strength of cotton surgical sutures of only 15–20 % because of radiation and demonstrated that radiosterilization was an acceptable procedure. Absorbable gut sutures and nonabsorbable sutures of silk, polyester and nylon are not affected in tensile strength by 2.5 Mrad (15).

ADHESIVES AND CEMENTS

Adhesives and cements behave upon irradiation in a manner generally similar to the plastics or reinforced plastics on which they are based. Structural adhesives such as the epoxy and phenolic resins and polystyrene systems (1) have excellent radiation resistance which is further improved when inorganic fillers are present. The glass fiber in reinforced resins, e.g., provides substantial further protection. Vinyl type adhesives —a common one is polyvinyl acetate—have moderate radiation resistance which is adequate for single-dose sterilization. Pressure-sensitive adhesives undergo oxidative breakdown readily and are not recommended for sterilization by radiation (23).

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