

Chapter 35

Stability of Polypropylene to Gamma Irradiation

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Irradiation of polypropylene in air leads to severe oxidative degradation, discoloration, and eventually embrittlement. The mechanisms involved have been examined and methods of stabilization have been explored in this study. Although this work has concentrated on radiation effects on polypropylene, the methods for stabilization are applicable to other polymers.

Ionizing radiation is rapidly becoming the preferred method for sterilizing medical products. Unlike gaseous sterilization, radiation eliminates chemical residuals and the need to quarantine large volumes of product. As a general rule, substantial degradation occurs during the radiation sterilization of a plastic product, and special grades of plastic must be employed to prevent excess degradation.

The need for materials that will withstand ionizing radiation during sterilization of medical products has increased dramatically due to regulatory problems associated with ethylene oxide residuals found after ethylene oxide sterilization. As a consequence, the need for better stabilization packages that can tolerate a sterilizing dose of 25 kGy has increased along with the requirement to understand the mechanism of why a plastic embrittles or discolors during irradiation. A guideline to selecting plastics for use in medical products is given in (1) and will not be repeated in this chapter. However, polypropylene which readily degrades during irradiation will be used as a mechanistic example along with experimental results to support the theory of polymer stabilization by different approaches.

In order to stabilize polypropylene to high energy radiation, solutions to the problems of post irradiation embrittlement, discoloration and thermal instability must be found. Radiation results in degradation of the polymer by direct energy transfer, subsequent autooxidative reaction kinetics and thermal degradation due to processing temperatures, gamma and electron local heating, and post irradiation high temperature storage. Control of radical reaction kinetics is dependent on the polymer morphology, in general, and specifically on the degree of crystallinity, molecular weight distribution and main chain mobility. Control of both autooxidation

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and heat-initiated oxidation require the addition of free radical scavengers, peroxide decomposers, and other stabilizers to the polymer formulation. The necessary condition for use of resulting formulations is that the stabilizer provides the desired characteristics yet does not discolor the polymer. Since the radiation induced radicals and peroxides formed in solid polymers are long lived, the potential for chain cleavage remains for years following irradiation. The stabilizer system must therefore remain active for storage not only at room temperature but also at high temperatures which may be encountered in warehouses in hot climates.

Materials and Methods

The details of the experimental procedures employed for most data presented are given in the respective references. Where unpublished results appear, ESR data were recorded at 9.25 GHZ and 3303.5G using a Varian E-Line Century Series Electron Spin Resonance Spectrometer. Spin concentration measurements were calculated from the double integration of spectra obtained on a 200G sweep width at a power level of 2 mW, a modulation amplitude of 4.0G, a time constant of 0.5 second, and a sweep time of 2 min.

Mechanical property measurements on test bars or molded syringes were carried out on a conventional Instron (Model 1122). In the case of post irradiation time studies, the samples were allowed to age at room temperature. The samples were irradiated with ^{60}Co at a 10 kGy/hr dose rate in an AECL Gammabeam 150 at ambient conditions.

Discussion and Background

Semicrystalline polymers such as polypropylene are nonhomogeneous. To a first approximation, however, polypropylene becomes a two-phase system consisting of amorphous and crystalline domains including a discontinuity at the crystal interface. The degree of crystallinity ranges from 0.35 to 0.65 with spherulite diameters of 0.1 - 300 microns. The densities in the two phases are $\rho_a = 0.854 \text{ g/cm}^3$ and $\rho_c = 0.946 \text{ g/cm}^3$ (2). During irradiation, energy is deposited uniformly and radicals are formed throughout the polymer in both the amorphous and crystalline domains. Different chemistry can result from energy deposition in the two regions since oxygen, stabilizers, and specific active radical species are excluded from the crystalline phase.

As a result, the local chemical reaction rates will be different from the average which results in a distribution of rate constants and activation energies in the different phases and at the crystal interface. The reaction kinetics will take three forms: those for polymer radicals alone, oxidation reactions and stabilizer reactions. All three forms of radical reactions are tied to the kinetics of molecular motion in solid polymers. (2,3)

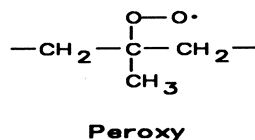
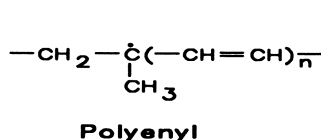
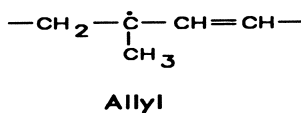
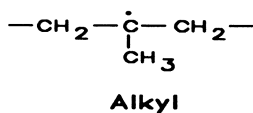
Finally, the energy deposited in the polymer system results in an equally complex initiation of chemical changes to the additives employed in the polymer. Often, a particular additive cannot be used due to the detrimental effects brought about by direct radiation modifications.

Color Formation. Pure polypropylene when irradiated in air from 10 to 100 kGy does not discolor. However, a characteristic yellow discoloration occurs in this dose range in most commercial grade polypropylenes. The formation of color is due primarily to the presence of phenolic additives which are included in the formulation to inhibit oxidation of alkyl and peroxy radicals formed during irradiation or exposure to high temperature.

Phenolic antioxidants are generally trisubstituted phenols which generate stable phenoxyl radicals upon oxidation. The phenoxyl radicals formed can dimerize, disproportionate or continue to react with other polymer radicals (4). Reactions with polymer peroxy radicals result in the formation of peroxycyclohexadienones and quinonoid compounds, such as quinone methide and spiroquinolide ether. These conjugated structures absorb in the visible region of the spectrum and discolor the polypropylene. For applications where color is the primary concern and the polymer does not see a significant temperature cycle, phenolics can either be removed or added at very low concentrations. Also, consideration should be given to additives which do not discolor but still behave as primary radical scavengers or peroxide decomposers, such as dilaurylthiodipropionate (DLTDP). Most translucent medical products such as syringes and bottles would fall into this category of non-discoloring products.

Radical Reactions. Since energy is deposited uniformly throughout the polymer, radicals are formed inside the crystalline lattice as well as in the amorphous regions. The form of the radicals, however, is different. The main radical species formed in polypropylene during irradiation in vacuum and air are listed in Table I (5,6,7). The respective ESR spectra are shown in Figure 1.

Table I
Radical Species Formed During Irradiation
of Polypropylene



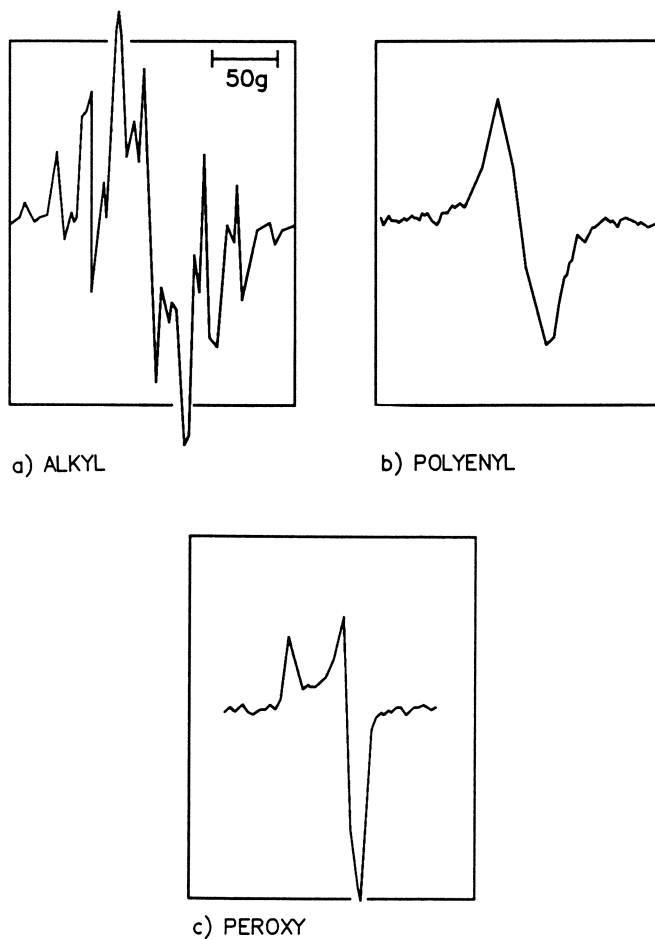


Figure 1. ESR spectra of polypropylene radical species.

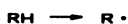
The alkyl radical is the dominant species formed during irradiation in both the crystalline and amorphous domains. When the sample is maintained under vacuum, the radicals slowly convert to the allylic species and eventually to the more resonant stabilized polyenyl radical. These radicals must be located at the crystalline interface since radicals containing double bonds would be excluded from the crystal lattice structure resulting in a defect (8). This fact has been substantiated by the rapid oxidation of the polyenyl radical formed in vacuum when exposed to air as illustrated in Figure 2 (6). Since oxygen is restricted from the crystal, it follows that chain transfer mechanisms must dominate for the radicals to move to the crystal surface and react with oxygen. Otherwise more evidence of alkyl radicals should be present in the ESR spectrum which is not the case. The polyenyl radical would then have to be at the interface in order to react with oxygen forming the dominant peroxy radical observed at longer times by ESR. In a similar manner, alkyl radicals formed in the amorphous phase will also rapidly oxidize to peroxy radicals. These oxidative reactions are dependent on oxygen diffusion and are discussed in more detail in the references. (2,3,9)

A list of the various radical reactions occurring with polymer radicals, oxygen and stabilizer appears in Table II (8,10-13). Various aspects of these reactions and their extent determine the severity of the degradative reactions before an additive or termination reaction disrupts the kinetic chain and reduces the degradation of the polymer.

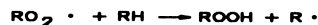
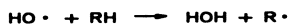
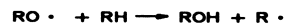
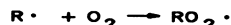
Table II

Radiation Induced Polymer/Stabilizer Radical Reactions

Initiation



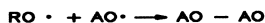
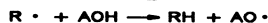
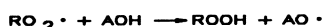
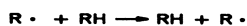
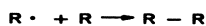
Polymer Radical Oxidative Reactions



Radical Reactions During Irradiation



Termination Reactions



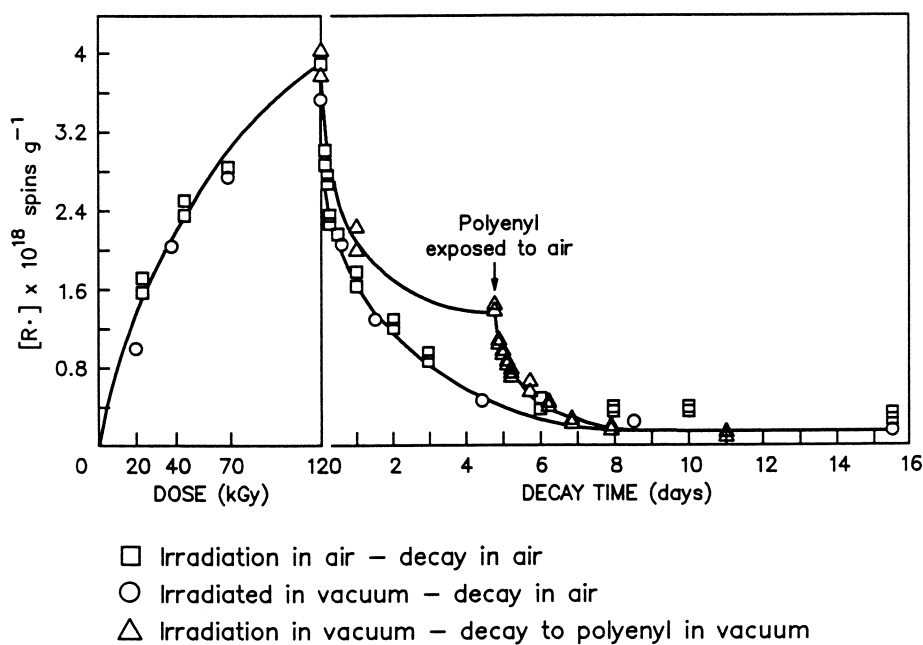


Figure 2. Radical buildup and decay of gamma-irradiated polypropylene.

Polymer Morphology. The preparation of molded parts from the melt will modify the morphology of polypropylene. Various aspects of the semicrystalline morphology are equally important to the control of polymer degradation. For instance, it has been shown in the literature that the degree of crystallinity increases in the first step of heat treatment with the rate of the increase dependent on the initial sample crystallinity (2). In addition, the oxidation rate of semicrystalline polymers depends on the degree of crystallinity (2,14). Adams (7) has shown that the molecular weight distribution varies with time exposure to temperature. Control of polymer morphology is of primary significance to direct radiation effects on polymers and subsequent degradation.

Primary radical termination may occur by chain segmental motion, hydrogen atom transfer or oxidative propagation. Consider the following equations from Table II:



These termination and transfer reactions are important to the stabilization of polymers. It is generally assumed that equation 2 dominates because physical chain motion is too slow a process for measurable rates of chain termination (3). From studies of gamma-irradiated polypropylene in vacuum, it has been shown that chain termination can be effectively enhanced by the addition of mobilizing additives to the polymer such as mineral oil. (15,16) As illustrated in Figure 3 for the same % crystallinity, the addition of mobilizing additive increases the chain termination constant by a factor of four. This result has been further substantiated by studying the effect of degree of crystallinity on the reaction rate of equation 1 as illustrated in Figure 4. These data illustrate that the low percent crystallinity samples yield a higher termination rate constant which is further enhanced in the mobilized samples (17).

During irradiation in air where oxygen is present, peroxy radicals are easily formed as follows:



The reaction rate of equation 3 is much more rapid than for main chain radical termination given in equation 1 due to ease of oxygen diffusion to the radical site. However, the effect of enhancing main chain termination by addition of mobilizing additives is a significant and a measurable factor as shown in Figure 5. Although the mobilizer increases oxygen diffusion, it is less an effect than the increase in the main chain radical termination reaction, which is greatly aided by the additional segmental chain mobility. As a consequence, the addition of mobilizer confers additional radiation stability to the polymeric system depending mainly on the level of mobilizer added.

The peroxy radicals formed during radiation lead to the formation of peroxides as follows:

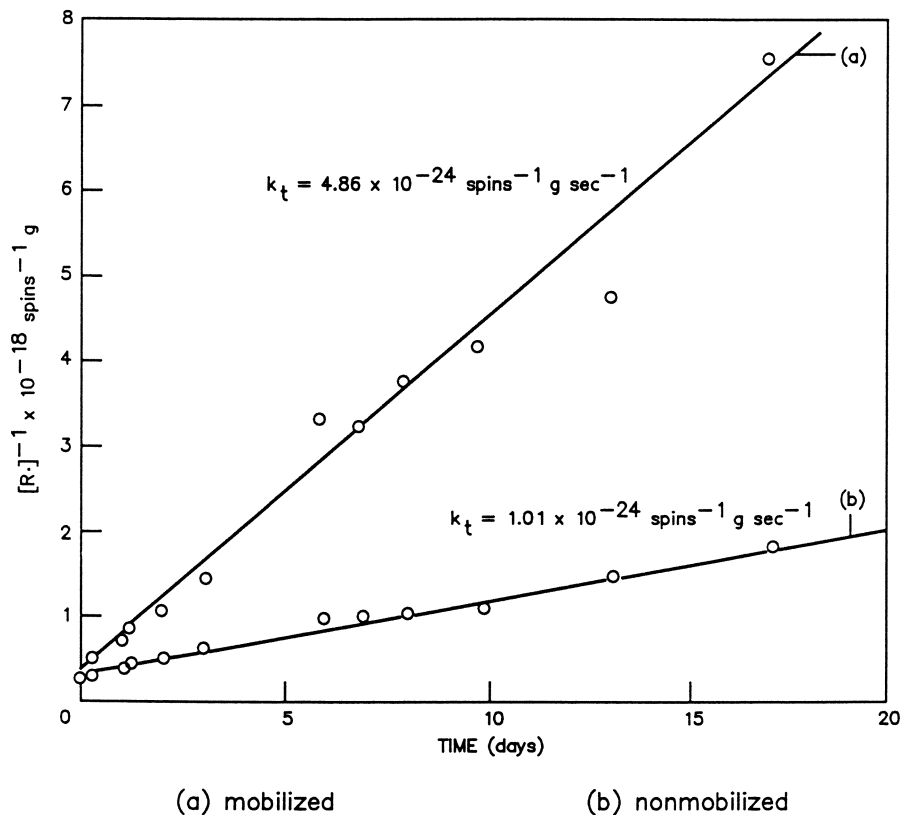


Figure 3. Second order termination rates in vacuum (48% crystalline homopolymer).

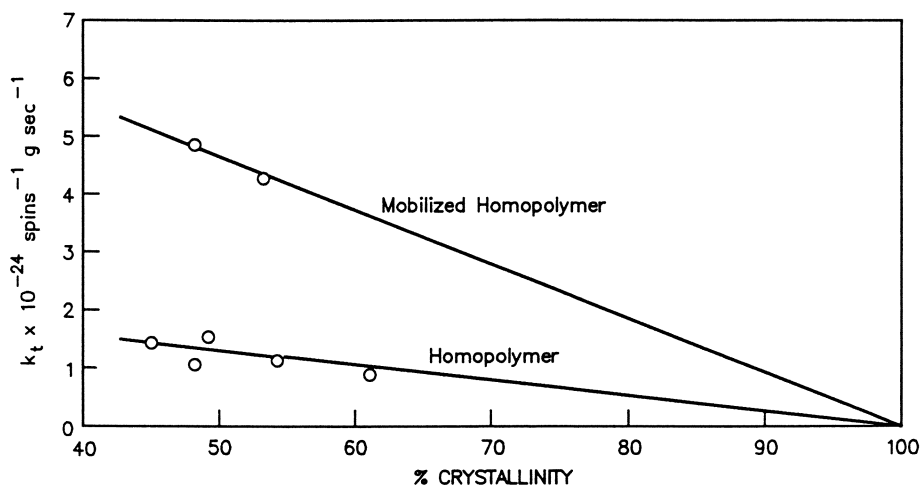
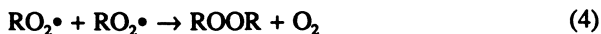


Figure 4. Dependence of second order termination rate on percent crystallinity of gamma irradiated polypropylene.



The peroxides remain in the polymer for long periods of time and upon dissociation result in chain scissions. The effect is continued embrittlement as a function of long term aging as illustrated in Figure 6 (17). It follows that increased mobility alone will not totally stabilize the polymer. As a consequence, inhibitor or aromatic stabilizer molecules, e.g., AOH, should be available in the polymer to suppress primary and oxidized polymer radicals.



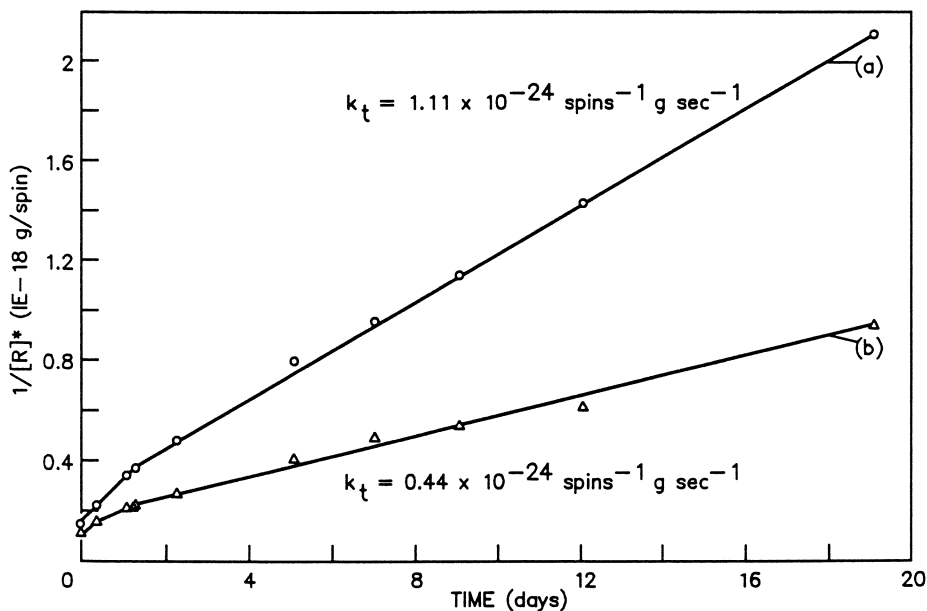
Primary radical scavengers and other stabilizers are a necessary addition to stable formulations.

Primary Methods of Polymer Stabilization

Mobilized Polymer. As discussed above, the addition of mobilizer increases main chain radical termination significantly reducing polymer chain autoxidation. The effect of the overall reduction in polymer embrittlement by the addition of the mobilizer is shown graphically in Figure 7. The angle at break of a syringe flange is plotted as a function of time up to 12 months storage. It is evident that the mobilized sample does not embrittle significantly even after 20 kGy and aging for nine months. On the other hand, the non mobilized sample starts to embrittle immediately. The increased stability of the mobilized sample is brought about mainly by the reduction in radical sites for main chain oxidative degradation.

Molecular Weight Distribution. A severely radiation embrittled polypropylene object will regain its original strength if remolded. The explanation for the renewed strength in this case resides in the fact that new tie molecules are formed between crystallites, upon remolding. An immediate conclusion is that the bulk strength of the polymer is dependent on the number of tie molecules between crystallites and not the average chain length. Any factor which increases the number of tie molecules should, in principle, increase the radiation stability of the semi-crystalline polymer.

In polypropylene with narrow molecular weight distribution, the chain lengths are more uniform and nearer to the mean value than polypropylene with broad molecular weight distributions. As a consequence, more load bearing chains or tie molecules are present in the amorphous phase between crystallites in the polypropylene with narrow molecular weight distributions than in broad molecular weight distribution, of the same melt flow. This fact results in better maintenance



(a) mobilized

(b) nonmobilized

Figure 5. Second order termination rates in air (48% crystalline homopolymer).

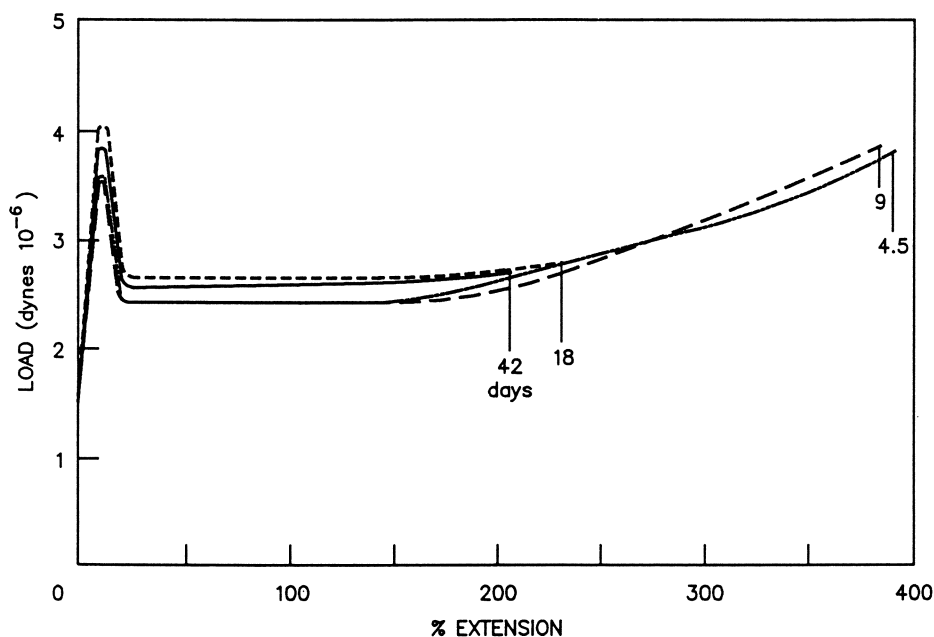
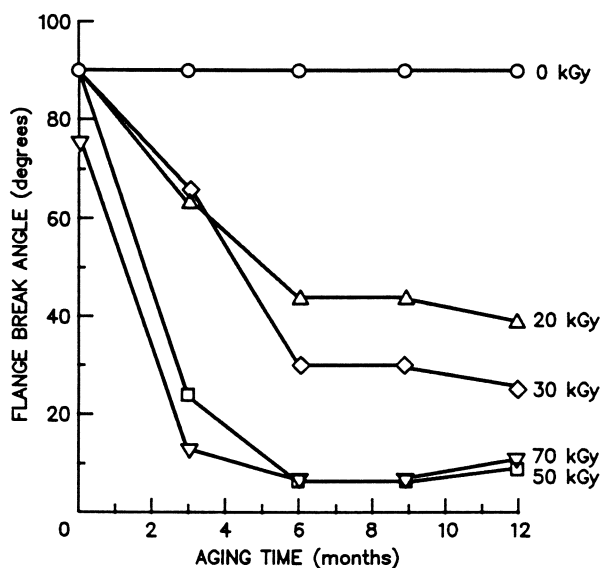
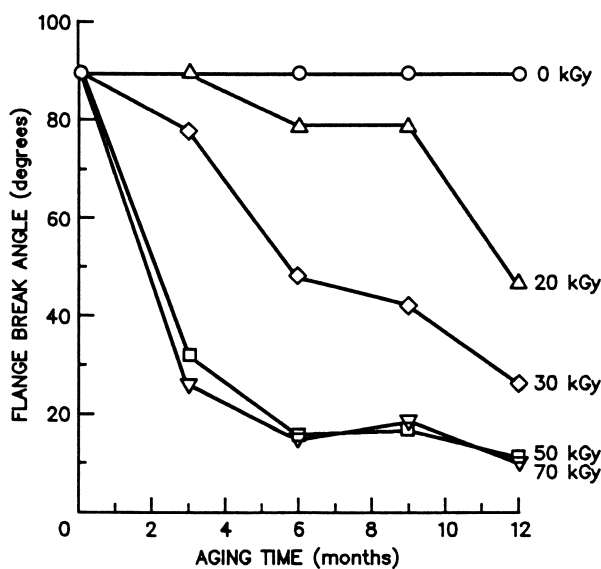


Figure 6. Embrittlement of irradiated polypropylene test bars as a function of aging time.

In Radiation Effects on Polymers; Clough, Roger L., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 1991.



(a) nonmobilized



(b) mobilized

Figure 7. Improvement in radiation stability with mobilized homopolymer at ambient conditions.

of mechanical properties after irradiation, as illustrated in Figure 8, particularly when coupled with the beneficial effects of the mobilizing additive discussed above (18).

Antioxidants and Stabilizers. Polyolefins are sensitive to thermally induced oxidative degradation even without irradiation. The use of stabilizers becomes even more important to radiation stable formulations due to the molding, processing, and storage at high temperature. Stabilizers shown to be beneficial to both thermal and UV stability include phenolic antioxidants (19-21), hindered piperidine derivatives (22-24), sulfur (25), and phosphorous containing compounds (26,27).

Radical scavenging activity of various stabilizers was studied individually and in various combinations as a function of temperature (28,29). The combination of hindered phenol and piperidine yielded the highest activity and demonstrated the best thermal stability. The combination of DLTDP to these same compounds significantly reduces both the activity and thermal stability. These data were substantiated by aging studies of the mechanical properties of irradiated polypropylene (28,30).

The beneficial effect of adding a primary radical scavenger to molded syringe barrels is demonstrated in Figure 9. Narrow distribution formulations containing a primary radical scavenger are compared with and without the addition of a mobilizer. It is clear that the mobilizer enhances the radical scavenging activity and yields a polypropylene stable to irradiation effects, up to a dose of 70 kGy after 12 months aging.

In order to be effective, the stabilizer must be both soluble and mobile in the polymer. The semicrystalline morphology excludes the stabilizers from the crystalline phase, therefore concentrating them in the amorphous regions. Experimental data indicates that the limiting step for inhibited oxidation is the molecular diffusion of the stabilizer. The addition of the mobilizer facilitates the diffusion of these large stabilizer molecules and thus enhances the reaction rates and resulting stabilization of the polymer (3).

Conclusions and Future Trends

From the data discussed here, several methods have been identified that are effective for the stabilization of polypropylene. Maintaining the lowest practical degree of crystallinity is important. Homopolymers with narrow molecular weight distribution are preferable. The inclusion of mobilizing additives reduces polymer oxidative degradation by facilitating both main chain termination and additive diffusion rates. To achieve maximum autooxidative inhibition and thermal stability with minimal discoloration, a primary radical scavenger should be included in the formulation. The combination of these various factors in a given formulation yields a high probability of successful stabilization of polypropylene to radiation degradation.

In this context, polypropylene has been used as an example, but all the theory and mechanisms would apply to any organic material.

The economic advantages of radiation sterilization will fuel the growth of this general form of sterilization in the future for both gamma and e-beam. Gamma will continue to be the primary source for sterilization due to the outstanding penetration characteristics of this form of radiation compared to electron irradiation.

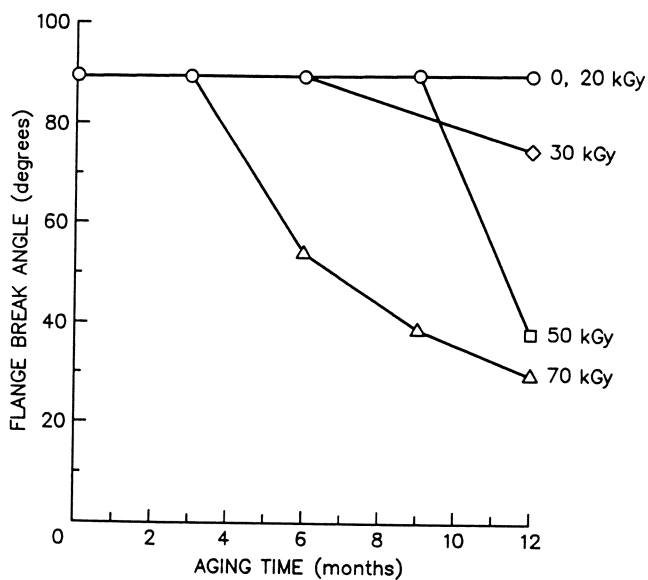


Figure 8. Narrow molecular weight distribution homopolymer with mobilizing additive at ambient conditions.

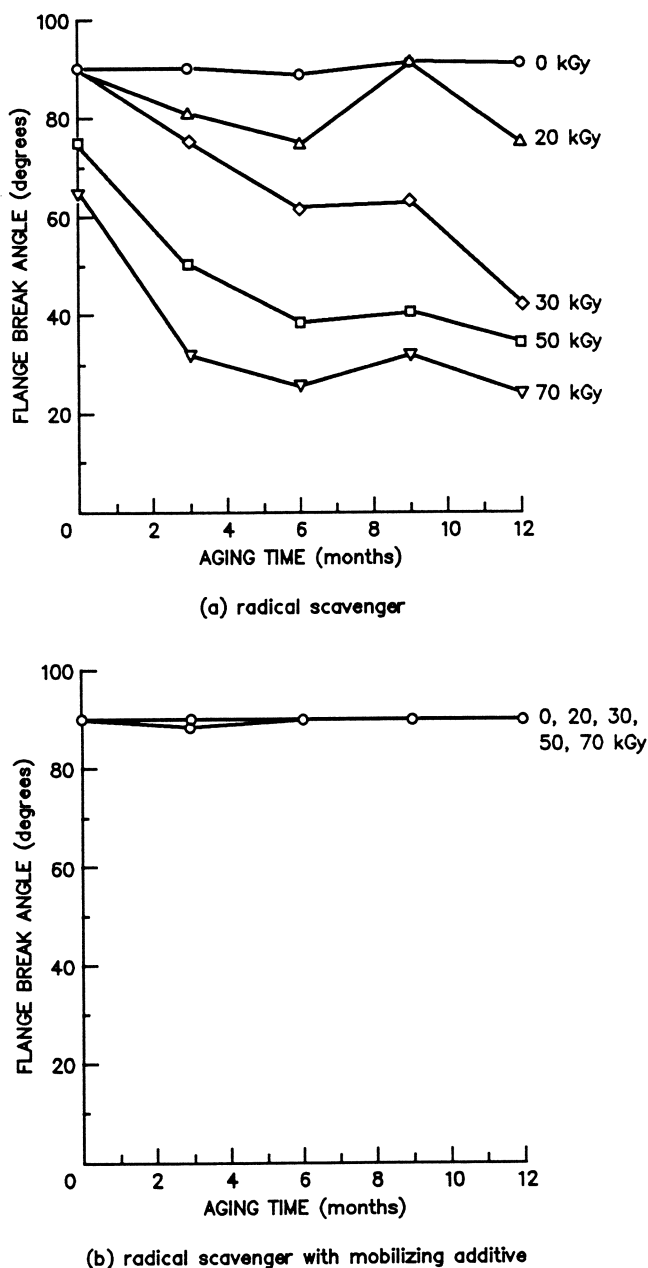


Figure 9. Enhanced radiation stability with addition of a radical scavenger to the polypropylene formulation at ambient conditions.

The future will require continued improvements in materials especially in the polyolefin class which readily degrade during irradiation if not properly stabilized. It is anticipated that better stabilizing systems could be developed.

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