γ-Ray-Induced Degradation in Ethylene–Propylene Copolymer

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SYNOPSIS

The stabilization of polypropylene-disposable medical syringes against the γ-ray-induced degradation has been the subject of active research during the last decade due to the large-scale use of γ-irradiation for sterilization purposes. Ethylene–propylene (EP) copolymers have been suggested as suitable alternatives to polypropylene for these purposes. In this article, we investigated the effect of irradiation dose and postirradiation time on the melt index and mechanical properties of an EP copolymer. We also determined the chemical changes occurring during irradiation and storage using IR spectroscopy and have made an attempt to co-relate the changes in chemical structure to the changes in mechanical properties and melt index measurements. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High-energy radiations like γ-rays and accelerated electron beams induce main-chain scission and/or crosslinking in polymeric materials.[1-4] The chemical reactions induced by these radiations in the solid state affect the physical properties of polymers to various extents. During the last decade, much interest was generated in the radiation sterilization of medical supplies like disposable syringes made of polypropylene.[5-8]

Polypropylene, when subjected to irradiation using γ-rays, primarily undergoes chain scission, leading to a drastic decrease in mechanical strength and aesthetic values.[9] Ethylene–propylene (EP) copolymers, on the other hand, are supposed to overcome these shortcomings.[10,11] In this article, we report the effect of γ-radiation on the physical and mechanical properties of an EP copolymer. The extent of the decrease in the mechanical properties was monitored with respect to the irradiation dose. The changes in the chemical structure was monitored using infrared (IR) spectroscopy. The effect of the irradiation dose and postirradiation time on the melt index (MI) is also reported.

EXPERIMENTAL

The EP copolymer (Grade APD133), with low ethylene content (2–4%), was procured from Shell Chemicals, Australia. The sheets and films were prepared by compression molding between two aluminum foils placed in a mold at 200°C. The aluminum foils were immediately quenched in cold running water. The test specimens were then irradiated in air, at room temperature, in a γ-chamber (GC-900) with a Co-60 source. The irradiation dose was varied by varying the irradiation time. The dosimetry of the γ-chamber was done using Fricke's dosimetry (ASTM E 1026). The dose rate was determined to be 0.218 Mrad/h.

Melt Index Measurements

The melt index (MI) measurements were done on melt flow index tester according to ASTM D 1238. The EP copolymer granules were irradiated in air at room temperature, with mixing at regular intervals. The granules were irradiated for doses between 0 and 7 Mrad. The MI was measured at 230°C with a standard load of 2.16 kg. The MI was determined with respect to irradiation dose and postirradiation time.
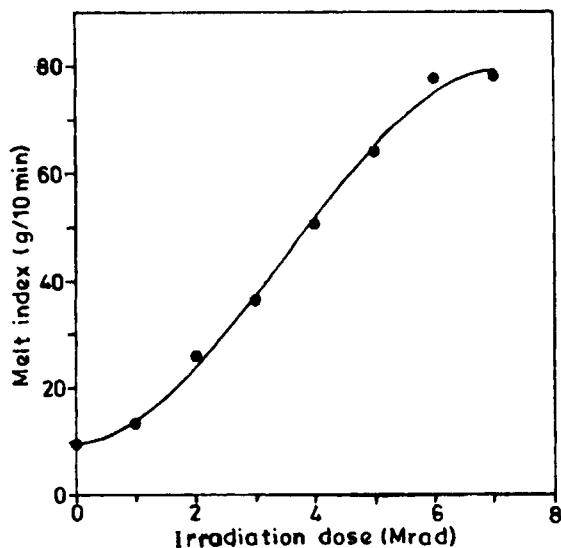
Figure 1   Plot of MI vs. irradiation dose.

Infrared Spectroscopy

The compression-molded films were 0.09 mm thick. The IR spectra of the neat film samples were measured on a Perkin-Elmer 681 IR spectrophotometer at room temperature. The variation in the absorbance at 3380 and 1710 cm^{-1} with postirradiation time was measured.

Mechanical Properties

The sheets prepared were of 0.70 mm thickness. The dumbbell-shaped specimens were cut from the sheets and irradiated. The samples were allowed to condition at room temperature in air for 7 days before testing. The mechanical properties were determined on an Instron UTM 1195 at room temperature. The full scale load was 20 kg and the crosshead speed was 200 mm/min.

RESULTS AND DISCUSSION

Figure 1 is a plot of the MI of the irradiated copolymer immediately after irradiation against the irradiation dose. The curve is fitted with a third-order polynomial. It is observed that the MI of the unirradiated copolymer, which is 9.5 g/10 min initially, increases to 78 g/10 min upon irradiation at 7 Mrad. The polymer on irradiation undergoes degradation primarily by main-chain scission, leading to a decrease in the molecular weight.[3,12] The MI is a function of molecular weight and molecular weight distribution.[13]

During irradiation, polymers undergo both crosslinking and chain scission, but based on the ratio of radiochemical reaction yield (G value) for the crosslinking to that of chain scission, either chain scission or crosslinking predominates. In the case of iPP irradiated in vacuum, it is observed that the G value for the chain scission reaction is higher than that for crosslinking. Hence, the chain scission reaction predominates. The presence of air or oxygen accentuates the oxidative degradation.[14]

The increase in the MI with irradiation dose indicates that the chain scission is occurring during the irradiation of the EP copolymer. The chain scission leads to a decrease in molecular weight and the random nature of the chain scission will increase the molecular weight distribution, resulting in the increase in the MI.

It is also observed that at higher doses the rate of increase in the melt index is lower. At higher doses, a large number of macroradicals are generated, thereby increasing the statistical probability of their becoming quenched by association. This would limit the widening of the molecular weight distribution.

Figure 2 is a plot of MI vs. postirradiation time at different irradiation doses. It is observed that the MI increases with increase in the postirradiation time at all doses. It is also observed that the increase in the MI with postirradiation time is higher in the case of 7 Mrad-irradiated samples. The macroradicals generated upon irradiation undergo oxidative degradation in the presence of oxygen from the air,
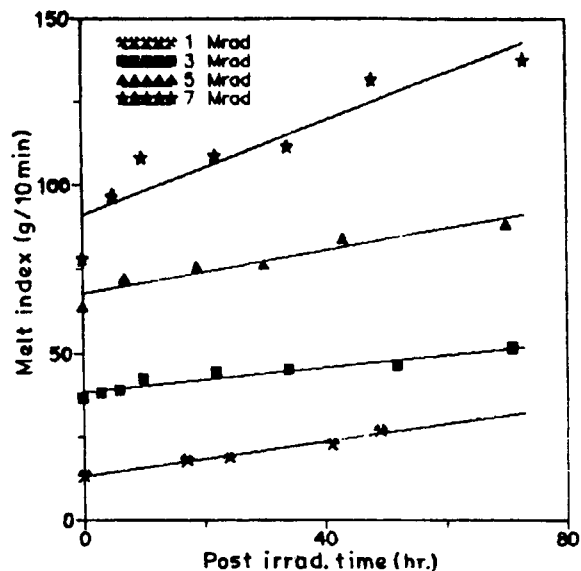

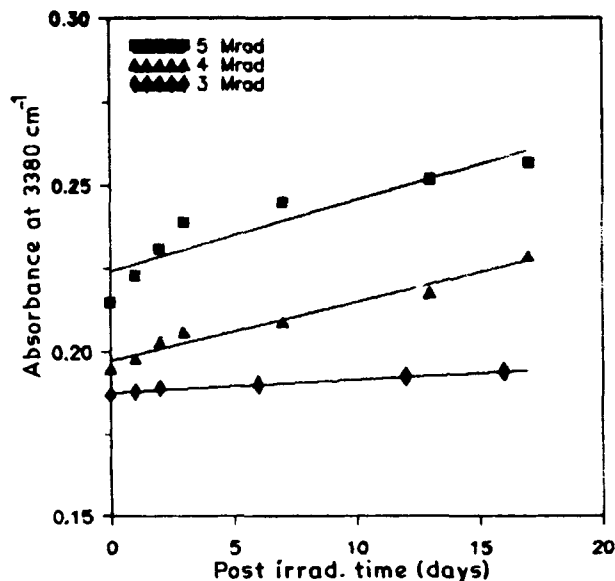**Figure 2**   Plot of MI at various doses vs. postirradiation time.

Figure 3 Plot of absorbance at 3380 cm⁻¹ at various doses vs. postirradiation time.

Figure 4 Plot of absorbance at 1710 cm⁻¹ at various doses vs. postirradiation time.

leading to a greater widening of the molecular weight distribution.

Figure 3 is a plot of the IR absorbance at 3380 cm⁻¹ against postirradiation time at different doses. This absorbance corresponds to the O — H stretch in a hydroperoxide system.[15] It is seen that the absorbance immediately after irradiation is higher in the case of the 5 Mrad-irradiated sample as compared to the 3 Mrad-irradiated sample. This indicates the formation of the hydroperoxide group during the irradiation process, on account of the reaction of the macroradicals with the diffused oxygen present in the sample. It is also observed that the absorbance increases with the postirradiation time for all doses. The rate of increase of absorbance with respect to the postirradiation time is higher for higher doses, indicating the increased presence of macroradicals.

Figure 4 is a plot of the IR absorbance at 1710 cm⁻¹ vs. postirradiation time for different doses. This absorbance is due to the presence of a nonconjugated carbonyl group (C=O).[16] The absorbance at lower doses increases slightly with the postirradiation time. However, at higher doses, the increase in absorbance is higher. The absorbance immediately after irradiation at higher doses is found to be higher.

Figure 5 is plot of % retention of elongation against the irradiation dose. The unirradiated EP copolymer showed an elongation of 770%. There is a small change in the elongation up to 3 Mrad, but
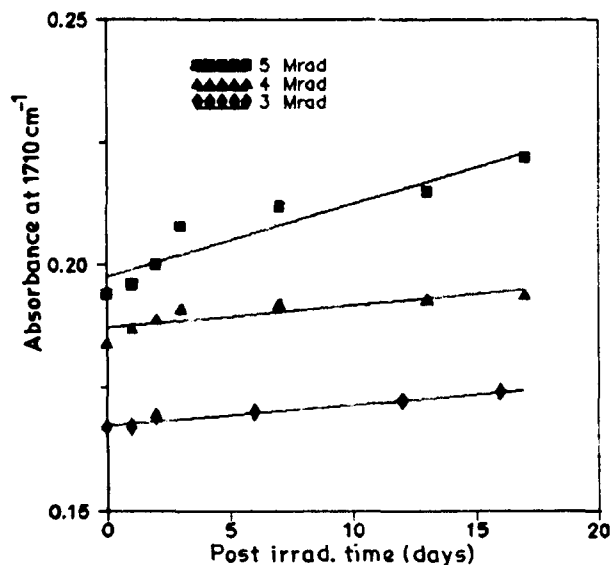
beyond it, there is a sudden drop in elongation and it is negligible at 5 Mrad.

Figure 6 is a plot of % retention of tensile strength at break and yield against the irradiation dose. The unirradiated EP copolymer had a tensile strength at yield and break of 28 and 30 MPa, respectively. The tensile at yield shows a negligible change between 0 and 5 Mrad irradiation, whereas the tensile at break shows a small decrease at 1 Mrad, which remains constant up to 3 Mrad. At 4 Mrad, there is a rapid decrease and the % retention of the tensile strength reaches a minimum. However, at 5 Mrad,
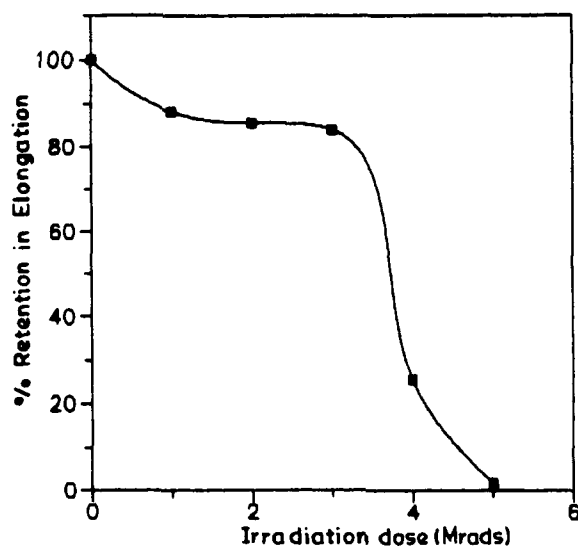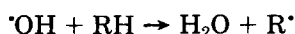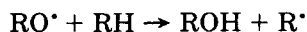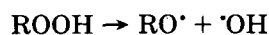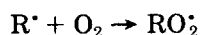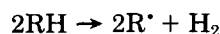

Figure 5 Plot of % retention in elongation vs. irradiation dose.

as the elongation is small, the tensile at break cannot be calculated from the stress–strain curve.

The tensile at yield is more of a plastic deformation aspect of mechanical strength, which is less affected by irradiation, as it is well known that the effect of irradiation is predominantly observed in the elastic amorphous domains in the case of semicrystalline polymers like polyethylene and polypropylene. The tensile at break, on the other hand, has a substantial contribution from the elastic deformation of the amorphous domains in the polymer. The elastic deformation is dependant on the degree of crosslinking and/or degradation.

Polypropylene on irradiation with γ-rays undergoes chain scission initiated by the loss of a proton which generates macroradicals as shown below. These macroradicals react with atmospheric oxygen, leading to formation of peroxy radicals.[17,18] These peroxy radicals abstract a proton from the polymer and form hydroperoxides[14]:

$$2RH \rightarrow 2R^{\bullet} + H_2$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$${}^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet}$$

$$ROOH, ROO^{\bullet}, R^{\bullet} \rightarrow$$

$$SCISSION\ OR\ CROSSLINKING$$

$$2ROO^{\bullet} \rightarrow ROOR + O_2$$

During the irradiation, the formation of these hydroperoxides leads to increase in the absorbance at $3380\ cm^{-1}$. These hydroperoxides further decompose to carbonyl compounds, increasing the absorbance at $1710\ cm^{-1}$—hence, the observed increase in the rate of absorbance with respect to the postirradiation time at higher doses. The decrease in the molecular weight and the randomness of the chain-scission reactions lead to an increase in the MI and a decrease in the mechanical strength.

Hegacy et al.[19] observed no change in the tensile strength at break and a slight increase in the elongation at low doses. We have not observed these, probably due to the lower dose rates resulting in higher irradiation times. The higher irradiation time would lead to substantial degradation by reaction with atmospheric oxygen diffusing into the sample during the irradiation itself.
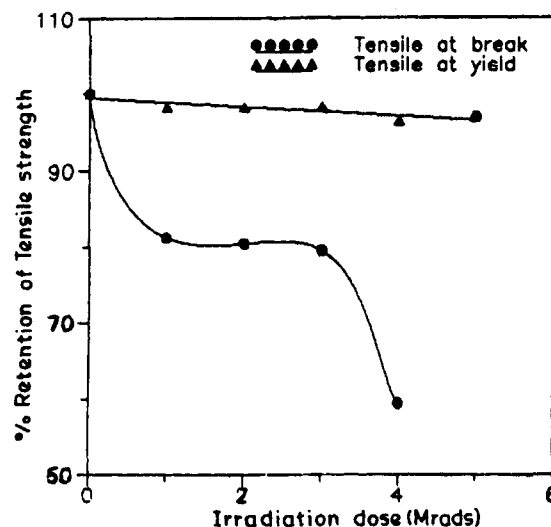

Figure 6 Plot of % retention of tensile strength at yield and break vs. irradiation dose.

CONCLUSIONS

The MI can be used as a technique to monitor the extent of degradation in a polymer caused by γ-ray irradiation. The IR absorption shows the formation of both hydroperoxide as well as carbonyl groups. The mechanical properties show that the EP copolymer undergoes substantial degradation beyond 3 Mrad irradiation.

The authors are further interested in quantifying the extent of γ-radiation-induced degradation in EP copolymers by monitoring the changes in UV absorbance, yellowness index, X-ray diffraction, and thermal transitions. The quantification of the hydroperoxide and carbonyl formation from IR data will lead to the comparison of the rates of hydroperoxide formation and its conversion to carbonyl groups. It is also felt that the study of the mechanical properties with respect to postirradiation time at different doses would be important vis-à-vis the application of these copolymers as molding materials for γ-radiation-sterilizable disposable syringes.

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