γ-Ray-Induced Degradation: A Comparative Study for Homo- and Copolymers of Polypropylene

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ABSTRACT: Disposable medical supplies are currently made of polypropylene, which are conveniently sterilized by exposure to γ-rays. However, the homopolymers (HP) and random copolymer (CP) of polypropylene, when exposed to high-energy γ-irradiation, undergo oxidative degradation and loss in mechanical properties. In the current article, a comparative study of the effect of γ-irradiation at different irradiation doses and the postirradiation oxidation on both the polymers is reported. The loss in mechanical properties was monitored by the bend angle and tensile measurements. The yellowness index measurements were carried out as a function of the irradiation dose and postirradiation storage time. The changes in the molecular weight (MW) and molecular weight distribution (MWD) were monitored using melt index (MI) measurements. The changes in chemical structure was determined using infrared spectroscopy. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2715–2720, 1997

INTRODUCTION

There is a growing demand for disposable medical supplies globally in view of body fluid transmitted diseases like HIV and AIDS. Disposable supplies ensure complete sterilization and eliminate the possibility of cross contamination by reuse. In the past decade, sterilization using ionizing radiation like γ-rays has gained much importance. Radiation sterilization leaves no carcinogenic residues and is foolproof, as the sterilization occurs after the packaging. However, a serious drawback of this method of sterilization is that the ionizing radiation tends to degrade the commonly used base polymers like polypropylene (PP) and poly-(vinyl chloride) (PVC).[1,2] The degradation of the polymers results in yellowing and loss of mechanical strength. The yellowing, although not a serious drawback, results in a loss of aesthetic appeal in the sterilized product.

We studied the effect of γ-ray irradiation on homopolypropylene (HP) and random copolypropylene (CP). The degradation was monitored by bend angle and yellowness index measurements. The bend angle measurement data are important in the case of γ-radiation-sterilized disposable PP syringes, as the bend fracture of the grip tabs on either side of the syringe barrel, during use, is a dominant failure mode.[3] PP was characterized for changes in the molecular weight distribution, due to exposure to γ-rays, by melt index measurements.[4] The mechanical properties of the irradiated PP were determined as a function of the irradiation dose and postirradiation storage time. The extent of oxidation, due to inclusion of the atmospheric oxygen in the macromolecular chains during the irradiation and the subsequent postirradiation storage, was monitored by infrared spectroscopy.

EXPERIMENTAL

Materials

The commercial homopolypropylene (HP) was procured from IPCL, Vadodara, India. The ran-

Table I Material Specifications

Type	Grade	MI (g/10 min)	Density[a] (g/mL)	Melting Point (°C)
HP	M0030	9.5	0.8936	165
CP	APD133	10.0	0.9012	143

[a] Measured by flotation technique at 30°C.[5]

dom copolypropylene (CP), with a low ethylene content (2–4%), was procured from Shell Chemicals, Australia. The material details are shown in Table I.

Sample Preparation

The sheets (150 × 150 × 0.7 mm) and films (150 × 150 × 0.09 mm) were prepared from the selected PP granules by compression molding between two aluminum foils placed in a mild steel mold. The molding was done at 200°C for 2 min. The aluminum foils were then immediately quenched in cold running water.

Sample Irradiation

The γ-irradiation of the test specimens was carried out in a gamma ray chamber GC-900 fitted with a Co-60 source. The dose rate was determined by standard Fricke's dosimetery (ASTM E1026) and was found to be 0.218 Mrad/h. The test specimens were irradiated in air at room temperature. The irradiation dose was varied by varying the irradiation time. In the case of postirradiation study, the test specimens were allowed to age in air after irradiation at room temperature for various periods of time prior to the testing.

Bend Angle Measurements

The bend angle measurements were carried out on injection-molded test strips of dimensions (80 × 10 × 1.5 mm). The tests were carried out at room temperature on an instrumented hinge system which was driven by an Instron tensile testing machine UTM 1195 with a crosshead speed of 20 mm/min, as described by Carlsson et al.[3] The test strips were forced to bend around the 1.5 mm diameter hinge pin. Bend angles from 0° to 140° could be achieved in this system. The bend angle data are an average of three readings at 1 cm spaced points about the midpoint of the injection-molded strip.

Yellowness Index Measurements

The yellowness index of the γ-irradiated samples as a function of irradiation dose and postirradiation storage time was determined in accordance with ASTM D1925 by reflectance measurements using a CS-3 Chroma sensor colorimeter (Datacolour International). The sample of dimensions (25 × 25 × 0.7 mm) were used. The instrument is designed to directly give yellowness index values on the basis of CIE standard illumination.

Melt Index Measurements

The HP and CP granules were γ-irradiated between 0–7 Mrad with mixing at regular intervals to ensure uniform irradiation of the granules. The melt index readings were taken on a melt index (MI) tester at 230°C with 2.16 kg load according ASTM D1238. The MI was determined with respect to postirradiation storage time at each irradiation dose. The results given in the following section are the average of five readings.
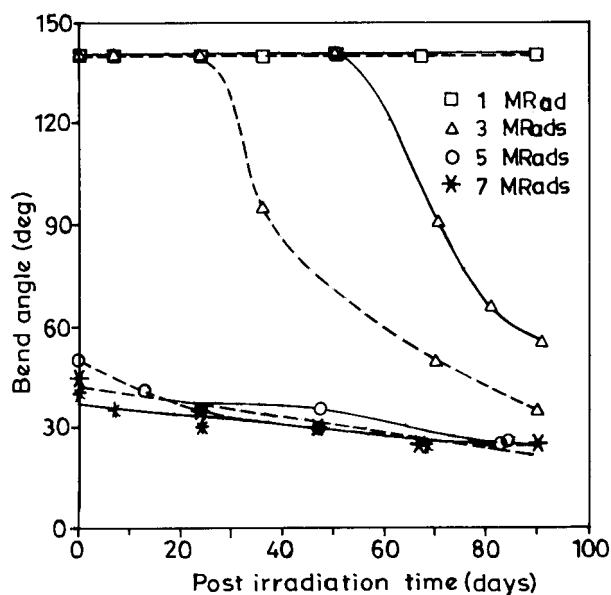

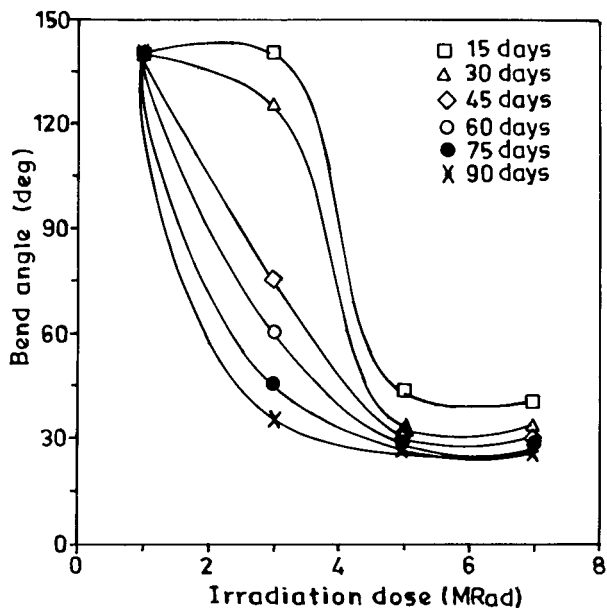**Figure 1** Plot of bend angle at various irradiation doses against postirradiation time: (---) HP; (——) CP.

Figure 2 Plot of bend angle at different postirradiation times against irradiation dose for HP.

Mechanical Properties

The mechanical properties of the γ-irradiated samples were determined as a function of irradiation dose and postirradiation storage time on an Instron UTM 1195 according to ASTM D638 at a crosshead speed of 60 mm/min. The results given in these sections are an average of four readings. The maximum variation within the readings is ±3%.

Infrared Spectroscopy

The infrared (IR) spectra of the γ-irradiated film samples (10 × 30 × 0.09 mm) were measured between 4000 and 600 cm^{-1} on a Perkin-Elmer 681 IR spectrophotometer at room temperature. The variation in the IR absorbance at 3380 and 1710 cm^{-1} at different irradiation doses and with respect to postirradiation time was monitored.

RESULTS AND DISCUSSION

The bend angle measurements of irradiated PP are very important, as the data can be directly linked to the dominant failure mode of γ-ray-sterilized disposable PP syringes. Disposable syringes made of PP, sterilized by γ-irradiation, usually fail due to the breaking of the grip tabs on the syringe side due to bending when the drug is dispensed.[3]

Figure 1 is a plot of the bend angle against the

postirradiation storage time at different irradiation doses for the HP and CP, respectively. It is observed that the 1 Mrad irradiated PP shows no change in the bend angle with postirradiation time. However, in the case of the 3 Mrad irradiated samples, the bend angle shows a decrease with an increase in the postirradiation storage time. The decrease in the bend angle is higher in the case of the HP. The oxidative degradation of the PP leads to embrittlement, resulting in a decrease in the bend angle. The oxidative degradation occurs at the crystal lamallae interface and is higher in the case of more crystalline samples.[6] However, in the case of 5 and 7 Mrad irradiation doses, both the HP and CP show a drastic decrease in bend angle immediately after irradiation, indicating substantial degradation.

Figures 2 and 3 are plots of the bend angle against the irradiation dose at different postirradiation times for the HP and CP, respectively. These plots are important as they give an indication of the shelf life of the irradiated syringe at a particular irradiation/sterilization dose using half the maximum bend angle value as the deciding criteria. The decrease in the bend angle with respect to the irradiation dose at different postirradiation times is greater in the case of the HP as compared to the CP.

Figures 4 and 5 are plots of the yellowness index against the postirradiation time at different irradiation doses for the HP and CP, respectively. The yellowness index increases with increase in
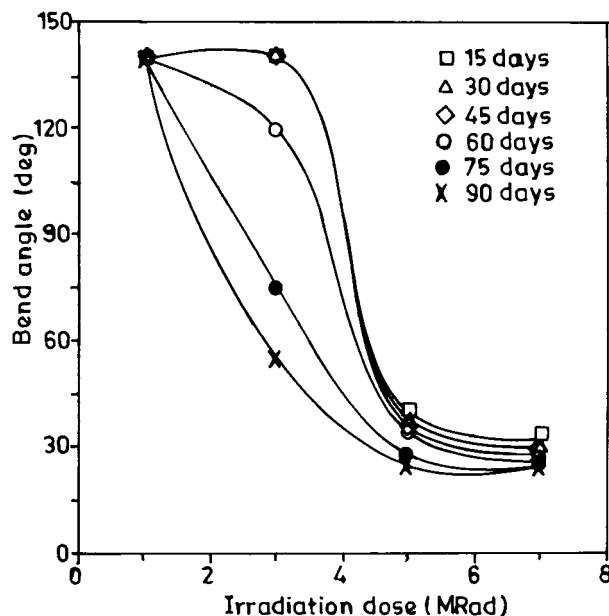

Figure 3 Plot of bend angle at different postirradiation times against irradiation dose for CP.
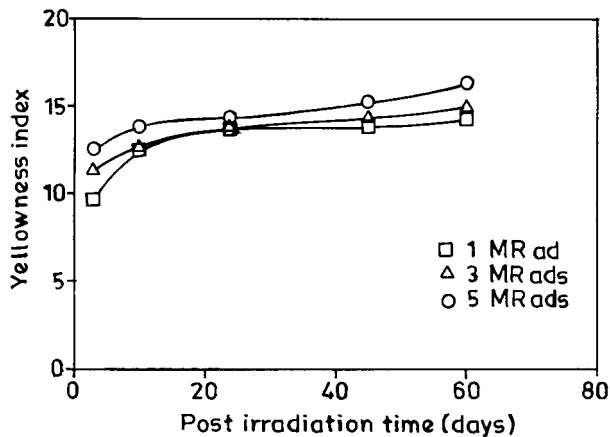
Figure 4 Plot of yellowness indexes at various irradiation doses against postirradiation time for HP.

Figure 6 Plot of percent increase in MI against irradiation dose (Mrad): (---) HP; (——) CP.

the postirradiation time at all irradiation doses. It is also observed that the yellowness index at a 1 Mrad irradiation dose is lower in the case of the CP. The yellowness in irradiated PP is due to the formation of chromophoric groups like carbonyl and hydroperoxide.[7] The formation of these groups is higher in case of the HP as observed in Figures 10 and 11.

Figure 6 is a plot of the percent increase in the MI immediately after irradiation against the irradiation dose for the HP and CP. The MI of unirradiated HP and CP is 10.0 and 9.5 g/10 min, respectively. The MI increases with irradiation dose in the case of both polymers. At 7 Mrad, the MI of the HP increases to 144 g/10 min and that of the CP increases to 78 g/10 min. It is seen that, for the HP, there is a sudden increase in the MI beyond 3 Mrad irradiation dose, whereas the increase in MI is more gradual in the case of the CP.
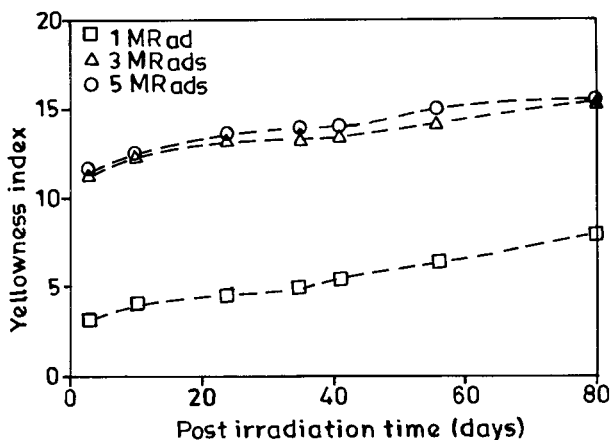
At higher irradiation doses, the rate of increase in MI decreases. This can be attributed to the fact that, at higher doses, a large number of macroradicals are generated, thereby increasing the statistical probability of their becoming quenched by association. This would limit the widening of the molecular weight distribution.[4]

The MI is a function of molecular weight and molecular weight distribution.[8] The increase in MI with irradiation dose indicates that chain scis-
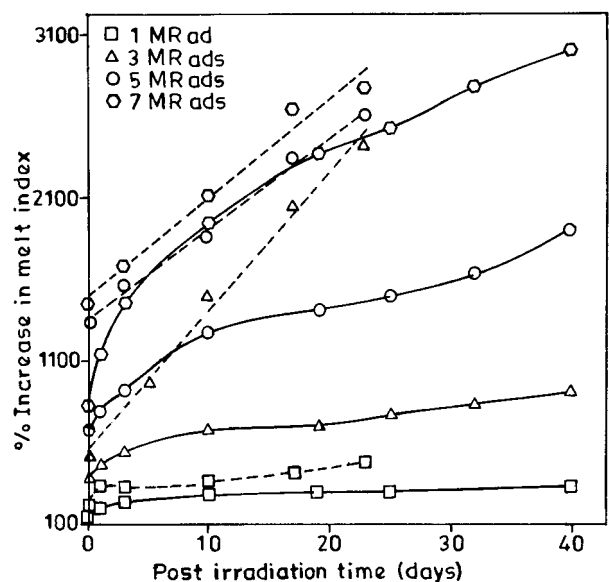

Figure 5 Plot of yellowness indexes at various irradiation doses against postirradiation time for CP.

Figure 7 Plot of percent increase in MI against postirradiation time (days): (---) HP; (——) CP.

Figure 8 Plot of percent retention in elongation against postirradiation time (days): (---) HP; (——) CP.

Figure 10 Plot of absorbance at 3380 cm⁻¹ against postirradiation time (days): (---) HP; (——) CP.

sion is occurring during irradiation. Chain scission leads to a decrease in molecular weight. The random nature of chain scissions induced by γ-irradiation leads to an increase in molecular weight distribution, resulting in an increase in the MI.[4] The presence of ethylene units in the CP limits the widening of the molecular weight distribution by forming crosslinks, thus restricting the increase in the MI.
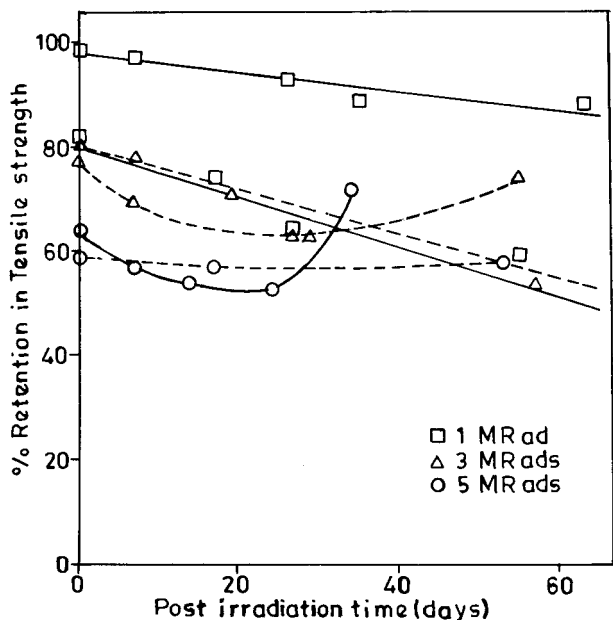
Figure 7 is a plot of the percent increase in the MI with respect to postirradiation time at different irradiation doses for the HP and CP. It is observed that in the case of both polymers, there is an increase in MI with respect to the irradiation dose and postirradiation time. The increase in the MI with respect to the irradiation dose and postirradiation storage time is marginal at 1 Mrad, but becomes more pronounced at higher doses. However, the HP exhibits a much greater increase in the MI at 3 Mrad as compared to the CP.

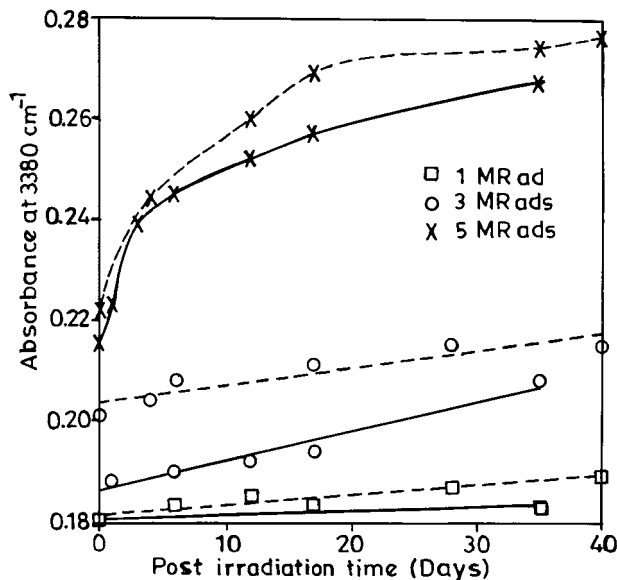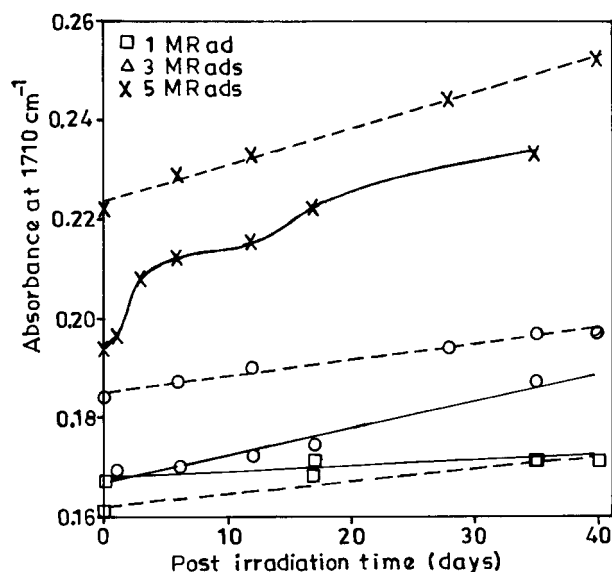**Figure 9** Plot of percent retention in TSB against postirradiation time (days): (--) HP; (——) CP.

Figure 11 Plot of absorbance at 1710 cm⁻¹ against postirradiation time (days): (---) HP; (——) CP.

Figure 8 is a plot of percent retention in elongation against the postirradiation time at different irradiation doses. The unirradiated HP and CP show 690 and 770% elongation, respectively. The decrease in the percent elongation at 1 Mrad is small in the case of both polymers. At higher doses, the rate of decrease in the percent elongation in the case of the CP increases with the postirradiation time, but in the case of the HP, there is drastic reduction in percent elongation immediately after γ-irradiation.

Figure 9 is a plot of percent retention in tensile strength at break (TSB) against postirradiation time at different doses. The TSB for the unirradiated HP and CP are 40 and 38 MPa, respectively. The TSB decreases with increase in the irradiation dose in the case of both polymers. The decrease is greater in the case of the HP. However, at 3 and 5 Mrad irradiation, the TSB shows an increase at higher postirradiation storage time.

The oxidative degradation-induced embrittlement at higher doses results in zero yield stresses and a higher modulus. This results in the higher TSB and lower elongation. The decrease in the TSB at lower irradiation doses is due to the plasticization by the lower molecular weight fragments formed by main-chain scission.[3]

Figure 10 is a plot of the absorbance at 3380 cm^{-1} against the postirradiation storage time at different irradiation doses. The absorbance at 3380 cm^{-1} corresponds to an O—H stretch in a hydroperoxide system.[9] Figure 11 is a plot of the absorbance at 1710 cm^{-1} against the postirradiation storage time at different irradiation doses. This absorbance is due to the formation of a nonconjugated carbonyl group.[10]

It is observed in both figures that the absorbance increases with increase in the irradiation dose and postirradiation storage time. However, the rate of increase in the absorbance is higher in the case of the HP. The rate of increase in the absorbance is higher at higher doses for both the polymers.

The irradiation of PP results in the formation of macroradicals at the crystal lamellae interface, which react with atmospheric oxygen to form chromophoric hydroperoxides groups. The formation of these groups results in the absorption at 3380 cm^{-1}. The rearrangement of the hydroperoxides results in the formation of strongly chromophoric carbonyl groups which absorb at 1710 cm^{-1}.

CONCLUSIONS

It is established that the bend angle data can be correlated to the dominant failure mode of γ-ray-sterilized disposable PP syringes and can be used as a tool for performance evaluation. The CP is more resistant to γ-ray-induced mechanical damage and retains the mechanical properties at the sterilization dose of 3 Mrad over longer periods of postirradiation storage as compared to the HP. The CP, however, does not show any significant improvement in the resistance to yellowing due to γ-ray sterilization. The CP also exhibits a greater resistance to degradation occurring during the poststerilization storage.

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