A Rheology Study of High-Energy Radiolysis of a Semicrystalline Ethylene-Propylene Copolymer Containing DOP Mobilizer

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ABSTRACT: The radiolysis of a poly(ethylene-co-propylene), Elpro grade P 750 J, marketed by Thai Polypropylene Co. Ltd. for the manufacture of medical goods, was investigated at ambient temperature and melt rheology measured. The roles of calcium stearate, blended with the Elpro as a processing aid, and dioctyl phthalate (DOP), added in various amounts as a radical scavenger, were assessed. Following radiolysis, G' and the viscosity of the polymer melts at 453 K both decreased with increasing radiation dose, even when the mobilizer was present. The results indicated that although the DOP did scavenge radicals, it did not protect the polymer from net chain scission in a low-dose regimen. The value of $(G_S - 4G_X)$ was approximately $0.6 - 0.7$. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3437–3441, 2006

Key words: poly(propylene); irradiation; degradation; stabilization; rheology

INTRODUCTION

Polypropylene and copolymers of ethylene and propylene have been widely used in the manufacture of medical goods[1] such as syringes and catheters. Medical products sometimes require sterilization before use, and this has most often been carried out by autoclaving or by processing under ethylene oxide gas. However, these methods have some inherent disadvantages for the sterilization of polymeric materials.[2] For example, autoclaving can lead to oxidation of the polymer, and ethylene oxide gas is a known carcinogen and can be retained in the polymer matrix. Therefore, radiation sterilization is becoming the preferred method of sterilization of polymeric medical devices.

Radiolysis of polymers can result in oxidation and yellowing of the polymer if the process is carried out in air, so radiation sterilization is usually carried out in an inert atmosphere. However, even in an inert atmosphere, chain scission and crosslinking reactions occur, which change the mechanical properties of the polymer. In addition, long-lived radicals can remain trapped in the crystalline regions after radiolysis, and these can affect the long-term shelf-life of any sterilized products. To eliminate or reduce these side effects of radiation sterilization, radiation stabilizers are added to the polymer. Some radiation stabilizers used in polyolefins are low-molecular-weight aliphatic compounds. They are mobile in the polymer matrix, so they can scavenge polymeric radicals by proton transfer processes before other chemical reactions can occur in the polymer, such as double-bond formation or postirradiation oxidation and subsequent chain scission. These types of stabilizers are called mobilizers.[3] One mobilizer that has been investigated as a stabilizer for polyolefins is dioctylphthalate (DOP), which is a liquid at ambient temperature.

There have been many previous studies of the radiolysis of polypropylene (PP) and its copolymers with ethylene (PE/PP). These studies have been extensively reviewed in the past, most recently by Hill and Whittaker.[4] Both PP and PE/PP undergo crosslinking on radiolysis under vacuum or in an inert atmosphere. For example, PP was reported[4] to have a gel dose of approximately 15 MGy. However, for radiolysis to the low doses required for sterilization, 25 kGy, PP has been reported to undergo degradation even in an inert atmosphere.[1,5] The origin of the observed degradation at low dose has been variously attributed to the pres-

ence of adventitious oxygen or other impurities,[6] to the low concentration of double bonds formed at low doses,[7] to weak links,[8] or to the fact that $G(X) < G(S) < 4G(X)$.[9] The values of $G(S)$ and $G(X)$ reported by different studies vary significantly for PP,[8] probably because of variation in crystallinity level, crystallite size, and crystallite quality. O'Donnell and Whittaker[10] showed that as the level of crystallinity increased, the value of $G(X)$ decreased for a series of PE/PP copolymers, which they interpreted as indicating that crosslinking occurred principally in the amorphous regions of the polymers.

O'Donnell and Whittaker[10] reported a study of radical formation for low-dose irradiation of polyethylene, polypropylene, and poly(ethylene-co-propylene). They measured the radical yields at 77 K for the two homopolymers and two amorphous copolymers that contained 0.23 and 0.36 mole fractions of propylene. They found that the radical yields for PE and PP were in the range 2.7–3.7 and 2.4–2.6, respectively, depending on the crystallinity, and for the two amorphous copolymers were 2.2 and 2.3 for $F_{PP} = 0.23$ and 0.36, respectively. O'Donnell and Whittaker also measured the yields for the formation of hydrogen and methane and reported G values of 2.6 and 0.08 and 1.8 and 0.11, respectively for the two copolymers, indicating a much higher probability for scission of carbon hydrogen bonds than for scission of the methyl side chain in the propylene units.

We recently reported[11] a study of radical formation at low radiation doses and 77 K in a commercial PE/PP copolymer, Elpro, marketed for the manufacture of medical goods. Elpro is principally composed of PP and has only a small ethylene content, approximately 1%. We found that at 77 K the radical yields, $G(R)$, were 3.0 and 3.2 for Elpro and Elpro, respectively, containing 0.08 phr of calcium stearate processing aid. On incorporation of the DOP stabilizer, lower G values, ranging from 1.6 to 1.4, were obtained for samples with 0.5 and 2.5 phr of DOP, respectively. Thus DOP reduced the radical content of the polymers following radiolysis at 77 K. Annealing the irradiated Elpro containing DOP to ambient temperature resulted in a loss of almost all the radicals formed at 77 K.

The molecular weight changes in PP following low-dose irradiation have been monitored by osmometry, light scattering, solution viscosity, and melt rheology.[12] These studies were consistent, with $G(S)$ being slightly greater than $G(X)$ but less than $4G(X)$, so that the weight-average molecular weight, M_W, would become infinite at high doses.[9] Marans and Zapas[13] reported that the melt viscosity of PP decreased on radiolysis at low doses. They also found that the dependence of the melt viscosity on shear rate was smaller for the irradiated polymer, which could be accounted for by either crosslinking or a narrowing of the molecular-weight distribution. However, for $G(X) < G(S) < 4G(X)$, the molecular-weight distribution would broaden on radiolysis. Safranj et al.[14] also reported that the melt viscosity of a PP grade used for manufacture of medical syringes decreased on radiolysis to sterilization doses.

Thus, although the natures of the radicals formed on the radiolysis of PP and PE/PP with and without stabilizer present have been studied, much less is known about the changes in other properties and about the roles of stabilizers in the sterilization dose range, 0–50 kGy. This is notwithstanding that sterilization of the polymers used in the manufacture of medical products requires irradiation only to low doses, generally about 25 kGy.

Therefore, in the present study we examined the changes in the melt rheology of Elpro and Elpro stabilized with DOP following radiolysis over the range of 0–50 kGy under vacuum at ambient temperature. The effect of the DOP on the scission and crosslinking processes occurring in irradiated Elpro was assessed.

EXPERIMENTAL

Materials

Poly(ethylene-co-propylene), Elpro grade P 750 J, was obtained from Thai Polypropylene Co. Ltd. (Bangkok, Thailand) and had an MFI of 12. It was used without further purification. The copolymer was blended in a Brabender blender at 160°C with 0.08 phr of calcium stearate as a lubricant and with various amounts of DOP mobilizer in the range 0.5–2.5 phr. The calcium stearate was obtained from Reidel-de-Haen, and the DOP was obtained from Aldrich. After blending, the copolymer samples were pressed into $150 \times 120 \times 1$ mm sheets in a hot press at 160°C (433 K).

Studies of melt rheology

Polymer samples for the study were cut from the pressed sheets in the form of 8-mm diameter discs and placed in Pyrex tubes for evacuation. The tubes were evacuated ($<10^{-2}$ Pa) for 12–24 h to remove all oxygen and then sealed under vacuum. The samples were irradiated at ambient temperature using ^{60}Co gamma radiation (Nordian Gammacell-220) at a dose rate of 3.5 kGy/h to doses in the range of 0–50 kGy. After irradiation, the tubes were allowed to stand to allow the radicals to decay, then they were opened, and the rheological measurements made immediately.

A Rheometrics rheometer was used to measure the storage and loss moduli and the shear viscosity of the molten polymers at 453 K using both dynamic and steady shear experiments. The conditions for measurement were: frequency of 0–100 s^{-1} and gap between the parallel plates of 0.5 mm.
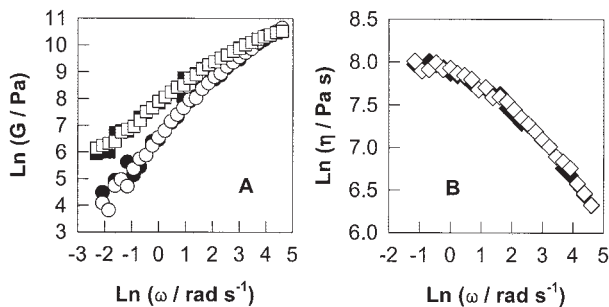
Figure 1 Rheological properties of Elpro at 453 K before irradiation plotted versus shear rate (ω). Results were obtained under dynamic shear. (A) Moduli G', $\bigcirc$; G'', $\square$. (B) Shear viscosity, $\blacklozenge$. Open symbols indicate the first measurement, closed symbols the second measurement.

RESULTS AND DISCUSSION

Studies on Elpro

Figure 1(a) shows the experimental data for the storage modulus, G', and loss modulus, G'', of Elpro as a function of the shear rate, ω, at 453 K obtained from a dynamic shear experiment. Figure 1(a) demonstrates the excellent reproducibility of the data. In Figure 1(b) the corresponding data for the shear viscosity, η, as a function of the shear rate is shown, and once again the agreement between the measurements is excellent. From Figure 1(a,b), it can be seen that G'' was greater than G' at low shear rates, as expected, for a molten polymer, and the crossover point for the storage and loss moduli curves at 453 K was at 60 rad/s. The zero shear viscosity at 453 K obtained from the dynamic shear experiments was 3.0×10^3 Pa s. The same value for the limiting viscosity of Elpro at 453 K was obtained from steady shear measurements (see Fig. 2).

The effect of irradiation of Elpro on G' and G'' is demonstrated in Figure 3(a,b), respectively. For the irradiated samples, both G' and G'' decreased over the range of shear rates as the dose increased, but the changes over the dose range of 0–25 kGy were greater than those observed over the range of 25–50 kGy. Figure 2 shows that after radiolysis the shear viscosity of the Elpro also dropped with increasing dose. The lowering of the values of the two moduli and the limiting shear viscosity with increasing dose were consistent with scission of polymer chains and a decrease in the molecular weight of the Elpro. These observations were consistent with those reported by Marans and Zapas[13] and Lugao et al.[7] for radiolysis of PP.

Studies with added mobilizer

When calcium stearate and DOP mobilizer were added to Elpro, G' decreased at 453 K, and the difference increased as the DOP concentration increased, as
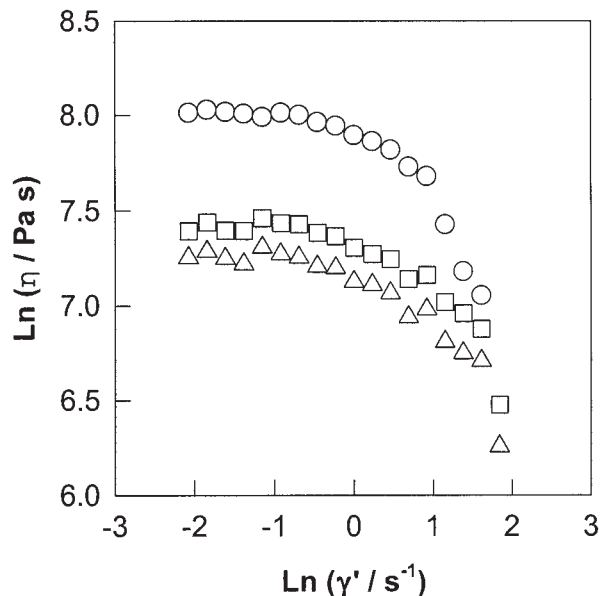

Figure 2 Shear viscosity of irradiated Elpro at 453 K versus shear rate (γ'). Results were obtained under steady shear. Dose: $\bigcirc$, 0 kGy; $\square$, 25 kGy; $\triangle$, 50 kGy.

shown in Figure 4(a). This was consistent with expectations when the low-molecular-weight calcium stearate and DOP were added to the Elpro. The steady shear viscosity of the melt also changed with the addition of the calcium stearate and DOP, as shown in Figure 4(b), but there was no consistent trend in the changes observed with increasing concentration of the DOP.

When the blends of Elpro, calcium stearate, and DOP were subjected to irradiation, both the storage modulus and the melt viscosity of the molten blends, determined from dynamic shear and steady shear experiments, respectively, decreased with increasing dose, as was observed for Elpro. The results are summarized in Figure 5(a,b), where the storage modulus at a shear rate of 3.16 rad/s and the viscosity at zero shear are plotted versus dose for each polymer blend.
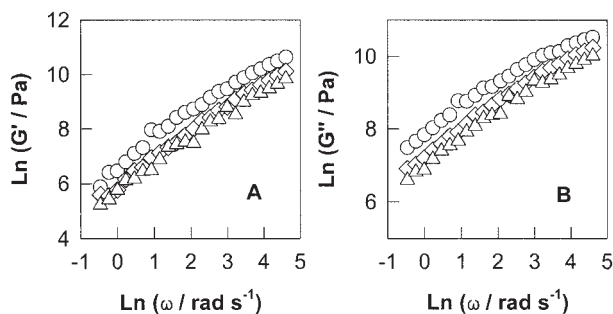

Figure 3 Rheological properties of Elpro at 453 K after irradiation plotted versus shear rate (ω). Results were obtained under dynamic shear. (A) G', (B) G''. Dose: $\bigcirc$, 0 kGy; $\blacklozenge$, 25 kGy; $\triangle$, 50 kGy.
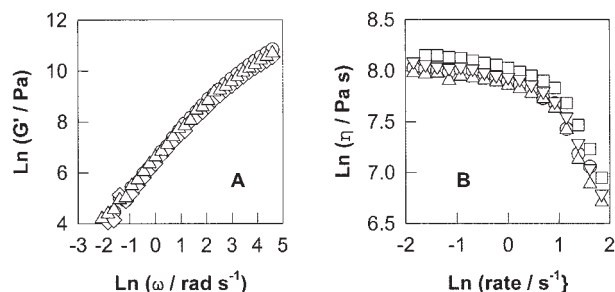
Figure 4 Rheological properties of Elpro plus DOP at 453 K before irradiation plotted versus shear rate (ω). Results were obtained under dynamic shear. (A) G', (B) η. DOP: ○, 0 phr; □, 0.5 phr; △, 1.5 phr; ▽, 2.5 phr.

A shear rate of 3.16 rad/s was chosen for the plot in Figure 5(a) because this value falls in the middle of the range of shear rates investigated. Although the values of G' and η decreased with increasing radiation dose, the size of the change did not appear to be systematically dependent on DOP content. The results show that DOP did not protect the Elpro against radiation-caused damage to the rheological properties of the polymer.

For a polymer with the most probable molecular weight distribution, the relationship between the weight-average molecular weight, M_w, and the absorbed dose is given by[15]

$$\left(\frac{(M_w)_{D=0}}{(M_w)_D}\right) = 1 + 0.519 \times 10^{-4} (M_w)_{D=0} \times (G_s - 4G_x)D$$

where G_S and G_X are the yields of chain scission and crosslinking, respectively (with molecular weight expressed in kg/mol), and D is the absorbed dose (in kGy).

The dependence of the zero shear viscosity of a polymer melt, η_0, on the molecular weight of the polymer, M, can be expressed through the empirical relationship[16]
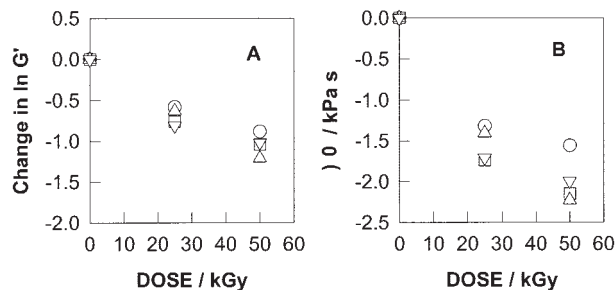

Figure 5 Changes in G' (obtained from dynamic shear experiments) and zero shear viscosity (obtained from steady shear experiments) after irradiation plotted against dose. DOP: ○, 0 phr; □, 0.5 phr; △, 1.5 phr; ▽, 2.5 phr.
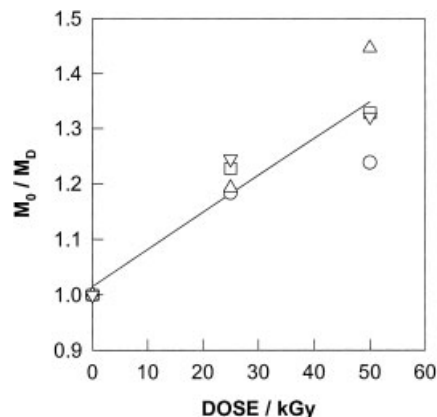

Figure 6 Plot of the molecular weight ratio versus dose. DOP: ○, 0 phr; □, 0.5 phr;, △, 1.5 phr; ▽, 2.5 phr.

$$\eta_0 = kM^{3.4}$$

so that,

$$\left(\frac{(\eta_0)_{D=0}}{(\eta_0)_D}\right)^{0.29} = \left(\frac{(M_w)_{D=0}}{(M_w)_D}\right)$$

Thus, a plot of the ratio of the initial M_w to that for Elpro after dose D (obtained from the ratio of the zero shear viscosities using the equation above) versus dose should be linear. And if the initial molecular weight of the polymer is known, the value of ($G_S - 4G_X$) can be calculated from the slope of the plot.

Such a plot is shown in Figure 6. There is some scatter in the plot, but it is approximately linear with no apparent dependence of the slope on the DOP content of the Elpro blends. The slope of the plot in Figure 6 obtained by regression analysis was 6.7 × 10^{-3} kGy^{-1}. Although the initial molecular weight of the Elpro was not measured, PP with an MFI of 12 would be expected to have a weight-average molecular weight of approximately 250–300 kg/mol.[17] For this initial molecular weight, the value of ($G_S - 4G_X$) for Elpro would be approximately 0.6–0.7 in the low-absorbed-dose regimen. This indicates that Elpro underwent overall net scission, with a reasonably high G value for the scission process.

We previously reported[11] that the incorporation of DOP into Elpro to a level of 2.5 phr only decreased the percentage of crystallinity slightly, but the G value for radical formation in the polymer decreased by approximately 50%. The present study of melt viscosity along with the previous study indicate that DOP acts as a radical scavenger in the polymer but that the scavenging process principally occurs subsequent to chain scission. This observation is supported by tensile property measurements and solubility studies[18] on irradiated samples, which also indicated that Elpro

degrades on radiolysis to low doses even with DOP present.

If the crosslinking of PP did occur through a grafting reaction of radicals at or near the ends of scissioned chains with other polymer radicals or reactive functional groups, as suggested by Lugao et al.,[7] then the scavenging of radicals in the amorphous regions of Elpro by DOP would serve to interfere with this crosslinking process. However, little effect of DOP on $(G_S - 4G_X)$ was observed over the range of doses studied.

CONCLUSIONS

On radiolysis of Elpro up to 50 kGy, G', G', and the zero shear melt viscosity of the polymer at 453 K all decreased in value, consistent with chain scission for the polymer. Analysis of the changes that occurred in melt viscosity yielded an estimated $(G_S - 4G_X)$ of 0.6–0.7. A comparison of the results of this study with those from a previous study of radical formation suggests that DOP does act as a radical scavenger for Elpro but that the transfer of the polymer radicals to DOP takes place following chain scission reactions. Thus, DOP does not act to protect the Elpro from molecular-weight degradation during radiolysis in the low-dose regimen.

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