LDPE/PP Blends Modified by Peroxide and Radiation Induced Reactions

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SYNOPSIS

LDPE/PP polyblends, modified through either peroxide initiated reactions or irradiation, were characterized in terms of rheological and mechanical properties and microstructure. In the presence of peroxide, or through irradiation LDPE crosslinks, PP degrades. Data were obtained at two peroxide concentration levels (0.1 and 1% by weight) and two radiation doses (30 and 100 kGy). The results show that in peroxide modification, the degradation of PP prevails over the crosslinking of LDPE. However, the effect of irradiation on LDPE (crosslinking) is predominant over that of PP (degradation). The irradiation process tends to yield improved mechanical properties vs. peroxide modification for the PP-rich blends. In addition, the melt viscosity and elasticity of the irradiated PP-rich blends are higher than those of the peroxide-reacted blends at a given level of PP content and frequencies between 10 and 100 rad/s. Attempts were made to relate the shape of the rheological curves and the mechanical properties of the blends to the observed changes in their microstructure.
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INTRODUCTION

To obtain a broad spectrum of controlled rheological and mechanical properties of polyolefin blends, various methods have been attempted, such as the use of block or graft copolymers,[1] modification through peroxide,[2-5] and irradiation.[6-10] High energy radiation is widely used in the polymer industry[11]; radiation can create free radicals from organic substances conveniently at room temperature, and thereby initiate free radical reactions that often lead to crosslinking or degradation.[12] Recently, peroxide-initiated radical reactions were applied by the authors onto LDPE/PP blends to enhance dispersive mixing of the components by modifying their rheological properties.[13,14]

This article will attempt to compare the structure and some properties of LDPE/PP blends, prepared in a corotating twin screw extruder, and modified by: (a) reaction with peroxide during melt mixing, and (b) by postextrusion high energy electron beam radiation in the solid state.

EXPERIMENTAL

Materials

The blend components were unstabilized PP (Profax 6501, Himont) and LDPE (DYNH-1, Union Carbide), with similar viscoelastic characteristics, with viscosity and storage modulus ratios not exceeding 3 : 1, as indicated in Table I. The peroxide used was 2,5-dimethyl-2,5-bis-(t-butylperoxy) hexane (Lupersol 101, Atochem North America), with a reported half-life of 68.5 s in dodecane dilute solution at 180°C. A phenolic antioxidant (Cyanox 2246, American Cynamid Co.) was added after reaction for stabilization of the melt during the rheological characterization.

Sample Preparation

Compounding/Reactive Extrusion

Unmodified blends, containing 25% or 75% by wt LDPE, were prepared in a 30 mm corotating twin

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Table I   Characteristics of Blend Components

	Polypropylene	Low Density Polyethylene
Grade	Profax 6501	DYNH-1
Manufacturer	Himont	Union Carbide
Melt Flow Rate (230°C, 2.16 kg)	1.9	6.6
Complex Viscosity, η^* (Pa.s, T = 180°C)		
0.1 rad/s	25,990	11,380
100 rad/s	895	519
Storage Modulus, G' (Pa, T = 180°C)		
0.1 rad/s	1,034	390
100 rad/s	78,860	41,090

* Both resins are unstabilized.

screw extruder (W & P ZSK-30), operating at 100 rpm and barrel temperature settings of 180°C. Peroxide modified blends were also prepared under the same conditions by first mixing the blend components and then pumping a solution of 0.1 or 1 wt % initiator in cyclohexane downstream. Vacuum was applied to remove reaction by-products and residual solvent. The extrudates were pelletized and dried prior to characterization and injection molding.

Injection Molding

The unreacted and peroxide reacted samples were molded in a 40 ton Van Dorn injection molding machine, equipped with an ASTM specimen mold. Injection pressure was 55.2 MPa, barrel temperatures were set at 205°C, and mold temperature was kept at 38°C.

Modification by Radiation

The source of electrons was the I-10/1 electron accelerator, designed and manufactured by the Atomic Energy of Canada Limited.[16,17] This machine delivers 10 MeV electrons in a pulsed beam (4 μs, up to 300 pulses/s), at a dose rate of 1.5 MGy/h.

Injection molded unmodified blends were placed in a plastic bag and were irradiated under a nitrogen atmosphere. Thirty and 100 kGy of radiation doses were selected to modify the samples. These radiation doses were considered to be equivalent to 0.1 and 1 wt % peroxide, respectively, on the basis of the amount of the resulting gel fractions in polyethylene. If PE alone were irradiated, the gel fraction would be about 30% and 70%, respectively, at the doses chosen. In fact, the experimentally determined gel fraction at 1 wt % peroxide in PE was reported to

be about 67%.[15] The irradiated samples were placed in an oven at 70°C, while still under nitrogen for 2 h to remove any unreacted radicals.

Characterization

The rheological behavior of the blends and their components were determined by employing a Rheometrics Mechanical Spectrometer (RMS-800), with a 25 mm diameter parallel plate arrangement at 180°C, under a nitrogen heating environment. The dynamic experiments were conducted in the linear viscoelastic range of strain at the frequency range of 0.1 to 100 rad/s.

The JEOL JSM-840 Scanning Electron Microscope (SEM) was employed to examine the morphology of blend samples fractured cryogenically. The samples were kept for over 2 h in liquid nitrogen prior to fracture. The fracture surfaces were sputtered with gold-palladium for 20 s at 30 mA and then were examined in the microscope using 15 kV.

Tensile properties of the injection-molded samples were measured at room temperature using a Tinius Olsen Locap Universal Testing machine, according to the ASTM Method D638, at a crosshead speed of 5 cm/min.

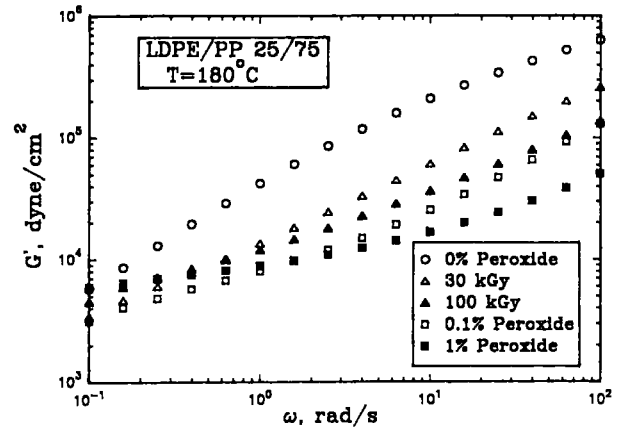## RESULTS AND DISCUSSION

Rheological Behavior

The frequency dependent complex viscosity curves of the unmodified LDPE/PP 25/75 blends, and those modified through peroxide reaction and irradiation, are compared in Figure 1. Without modification, the blend shows a typical non-Newtonian
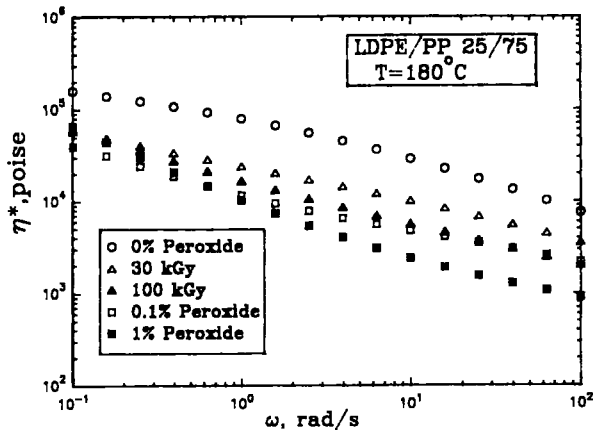
Figure 1 Complex viscosity, $\eta^*(\omega)$ of the LDPE/PP 25/75 blends without and with modification through peroxide (0.1 and 1 wt % peroxide) and irradiation (30 and 100 kGy).

Figure 2 Storage Moduli, $G'(\omega)$ of the LDPE/PP 25/75 blends without and with modification through peroxide (0.1 and 1 wt % peroxide) and irradiation (30 and 100 kGy).

flow behavior and high viscosity. Due to the degradation of the PP component, the complex viscosities, $\eta^*(\omega)$, of the blend decrease with increasing radiation dose and peroxide concentration. The viscosities of the irradiated blends show higher values than those of the peroxide-reacted blends in the examined frequency range. At moderate modification conditions, that is, at 30 kGy and 0.1 wt % peroxide, the viscosity behavior of the blends indicates that the response of the system is governed by the degraded PP, which is the major component. However, the complex viscosities of the irradiated and peroxide-reacted blends at 100 kGy and at 1 wt % peroxide show a particularly interesting behavior. The viscosity of both blends exhibit an "upturn" with decreasing frequency, contrary to the expected pseudoplastic behavior that is typically exhibited by the viscosity of the unmodified blend. This observation indicates that these modified blends behave, in the frequency range examined, as typical "suspensions" of solid particles in a Newtonian matrix. The particles are the crosslinked or branched LDPE domains, embedded in the highly degraded, low viscosity, and almost Newtonian PP matrix.[13]

The storage modulus curves, $G'(\omega)$, of the LDPE/PP 25/75 blends are shown in Figure 2. The response of the unmodified blend is both expected and typical; the modulus decreases with decreasing frequency. At low frequencies, the response of the high molecular weight fraction of the sample is predominant. With the 1% peroxide-modified blend, it is observed that the decrease of the modulus, $G'(\omega)$, with decreasing frequency, is much smaller. Ac-

tually, a plateau is almost obtained at low frequencies. This is attributed to the presence of the highly branched or crosslinked LDPE minor phase, both in this and the other modified samples, which exhibit similar behavior.

Morphology and Mechanical Properties

Figure 3 shows a microphotograph of the unmodified LDPE/PP 25/75 blends. The domain size varies from 0.5 to 1 μm. The similarities in the rheological properties of the blend components, being the most

Figure 3 Scanning electron microscopy (SEM) microphotograph of the LDPE/PP 25/75 blends prior to modification ($\times$10,000).
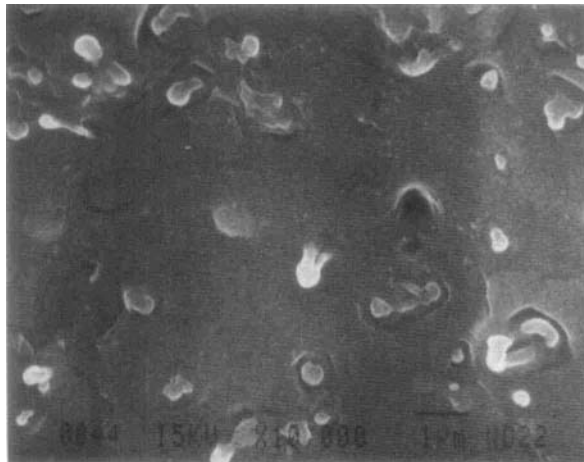
Figure 4 Scanning electron microscopy (SEM) microphotograph of the LDPE/PP 25/75 blends modified by 0.1 wt % peroxide (×10,000).

Figure 6 Scanning electron microscopy (SEM) microphotograph of the LDPE/PP 25/75 blends modified by 1 wt % peroxide (×10,000).

favorable condition for dispersive mixing, are apparently responsible for the fine and uniform morphology of the blends.

As the peroxide reaction takes place during melt mixing, the LDPE phase eventually becomes crosslinked, while the PP matrix becomes weak and/or brittle, due to the degradation reaction. The micrographs of the corresponding blend composition (LDPE/PP 25/75), at 0.1 wt % of peroxide and 30 kGy of irradiation dose, are shown in Figures 4 and 5, respectively. The domain size of those modified, dispersed LDPE phases is ranging from 0.5 μm to 1
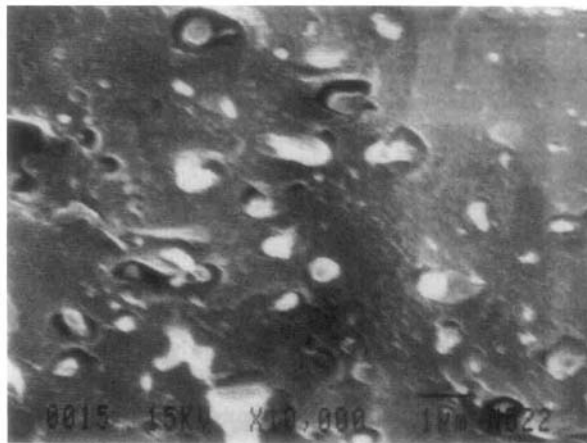
μm. Fracture surfaces indicate some plastic deformation in the vicinity of a slightly stretched-out LDPE phase. Figure 6 shows the morphology of the highly reacted blend system with 1 wt % peroxide. It is important to note that the dispersed LDPE maintains its domain size, as in the unreacted blends. This suggests that coalescence of the LDPE phase does not take place. Motion coalescence could be expected, as the matrix viscosity decreases, due to the peroxide degradation reaction. Thus, it seems that the morphology is stabilized by the crosslinking reaction of the LDPE phase; crosslinked particles are unlikely to coalescence. It should be noted that

Figure 5 Scanning electron microscopy (SEM) microphotograph of the LDPE/PP 25/75 blends modified by 30 kGy irradiation (×10,000).

Figure 7 Scanning electron microscopy (SEM) microphotograph of the LDPE/PP 25/75 blends modified by 100 kGy irradiation (×10,000).

it would be difficult to mix components with such high viscosity and elasticity ratios in conventional mixing equipment, and to produce the observed fine morphologies.

The possibility of graft copolymer formation by the peroxide-initiated reaction cannot be excluded, although attempts to confirm it were not successful.[15] If graft copolymers were formed, they would tend to reduce the dispersed domain size. But this formation is difficult, because of the weak stresses generated by the low viscosity matrix, and the crosslinking of the dispersed phase. Similarly, graft copolymer at the interface would tend to improve, in general, the mechanical properties. However, this effect could be masked by the anticipated poor mechanical properties of the highly degraded matrix.

The morphology of the LDPE/PP 25/75 blends, irradiated with 100 kGy, is shown in Figure 7. The dispersed domain size of this blend is similar to that of the unmodified blend, that is, about 0.5–1 μm. The microphotograph indicates that the dispersed phase can be stabilized by the radiation process without size changes. Similar attempts to stabilize

a crosslinkable dispersed morphology, by employing irradiation, have been reported in earlier publications.[18,19]

The elongation at yield, ε_y, and the yield stress, σ_y, of unmodified and modified blends at two different compositions, are shown in Figures 8(a) and (b). Overall, the yield properties of the irradiated PP-rich blends slightly improve vs. the unmodified ones, whereas those of the peroxide-modified blends decrease with increasing peroxide concentration. For LDPE-rich blends, yield properties show improvement with increasing peroxide concentrations and radiation doses. Yield properties of the peroxide-reacted blends at the LDPE-rich composition are slightly better than those of the irradiated blends.

The elongation at break, ε_b, and the tensile stress at break, σ_b, of the above blends are shown in Figures 9(a) and (b). The elongation at break of modified blends, at the compositions shown in this article, decrease with increasing peroxide concentrations and irradiation doses; this may be due to the fact that PP becomes brittle and weak due to the degradation reaction. The tensile stress at break, σ_b,
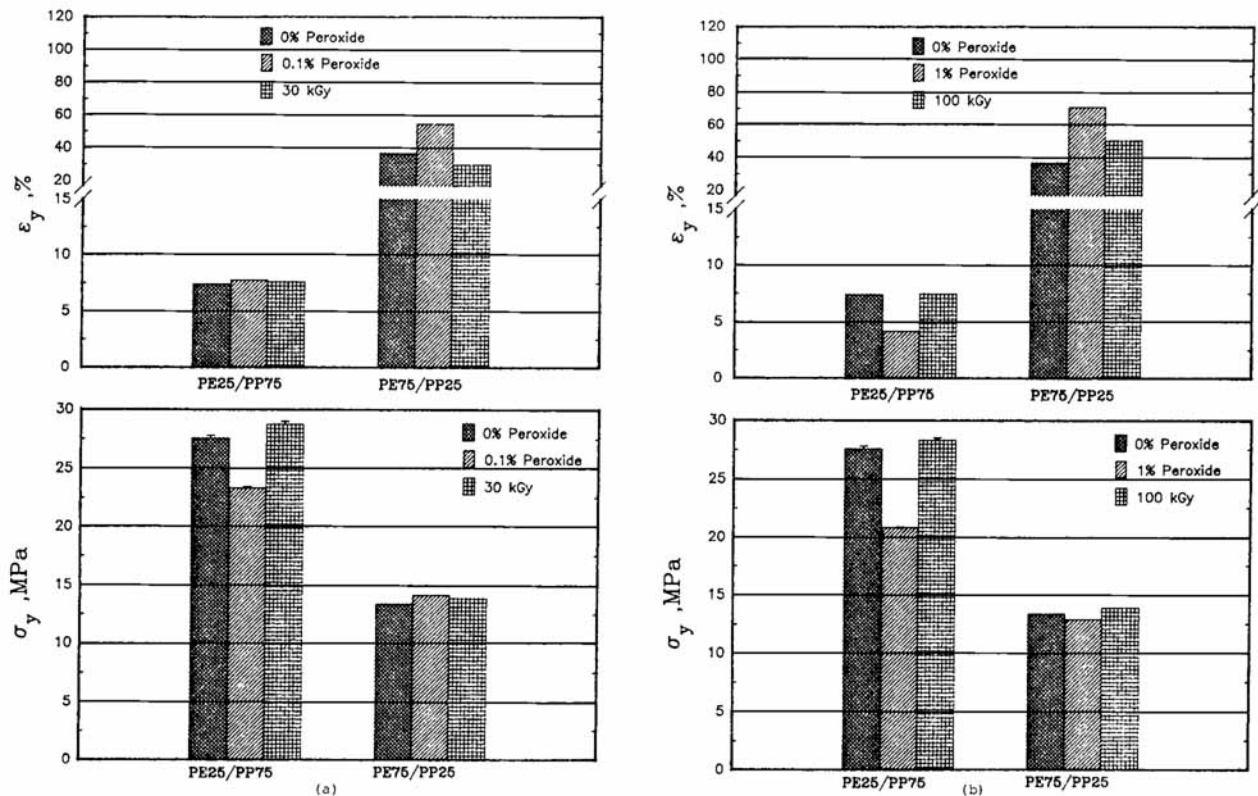
Figure 8   Elongation at yield, ε_y, and yield stress, σ_y, of the unmodified and the modified blends through peroxide. (a) 0.1 wt % peroxide and 30 kGy irradiation, (b) 1 wt % peroxide and 100 kGy irradiation.
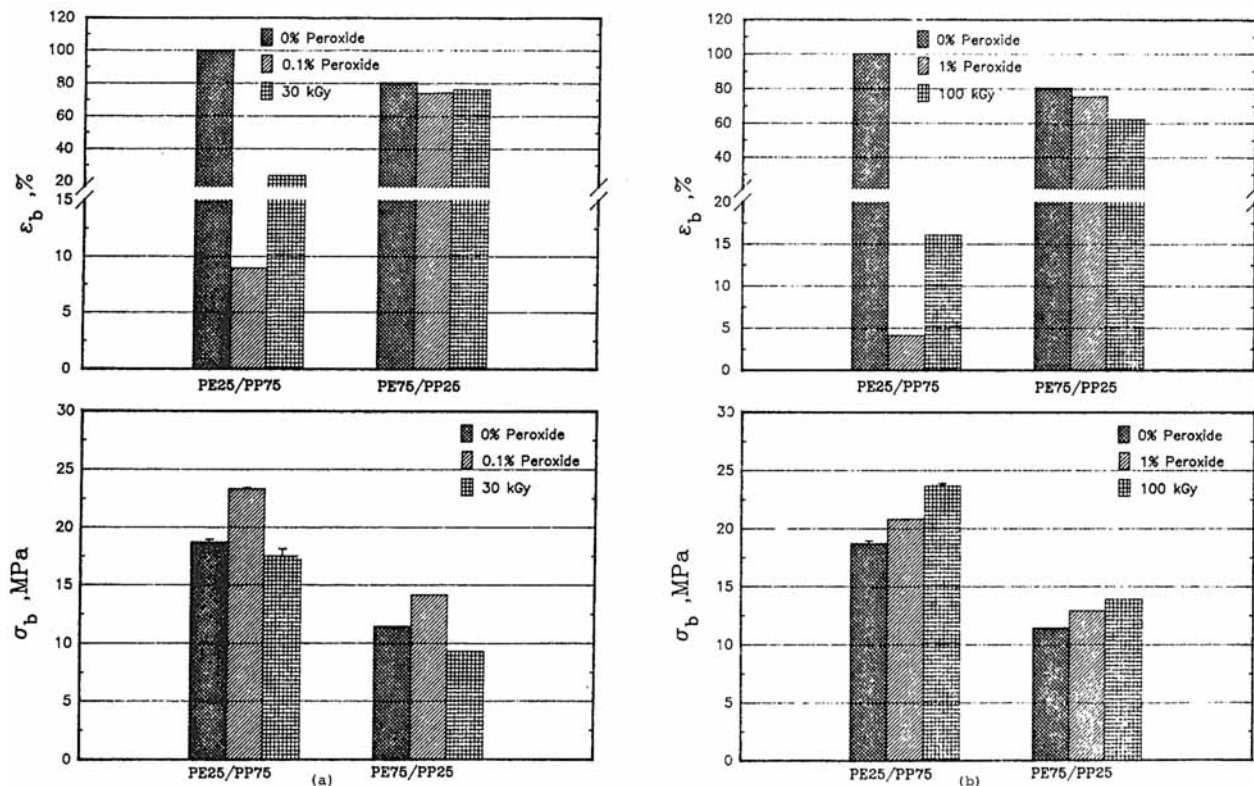
Figure 9 Elongation at break, ε_b, and tensile stress at break, σ_b, of the unmodified and the modified blends through peroxide. (a) 0.1 wt % peroxide and 30 kGy irradiation, (b) 1 wt % peroxide and 100 kGy irradiation.

however, shows improvement at both the highly reacted and irradiated blends. The tensile stress at break, σ_b, of the irradiated blends at 100 kGy, is higher than that of the peroxide reacted blends at 1 wt %.

CONCLUSIONS

In a manner similar to the peroxide modification, irradiation leads to simultaneous crosslinking and degradation of the LDPE and PP, respectively. The rheological results indicate that the degradation of PP prevails over the crosslinking of LDPE during the peroxide modification, while, during irradiation, the effect on LDPE is predominant over that on PP. The fine and uniform morphology of the unmodified blends, resulting from the similarities in the "original" rheological properties of the blend components, is preserved and is stabilized both by the peroxide reaction and irradiation processes. Due to its lesser

destructive effect on the PP phase, the irradiation process tends to yield improved mechanical properties, as compared to the peroxide modification for the PP-rich blends.

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