Mechanical Properties and Morphology of Crosslinked PP/PE Blends and PP/PE/Propylene–Ethylene Copolymer Blends

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Synopsis

Blending is an effective method for improving polymer properties. However, the problem of phase separation often occurs due to incompatibility of homopolymers, which deteriorates the physical properties of polyblends. In this study, isotactic polypropylene was blended with low-density polyethylene. Crosslinking agent and copolymers of propylene and ethylene (either random copolymer or block copolymer) were added to improve the interfacial adhesion of PP/LDPE blends. The tensile strength, heat deflection temperature, and impact strength of these modified PP/PE blends were investigated. The microstructures of polyblends have been studied to interpret the mechanical behavior through dynamic viscoelasticity, wide-angle X-ray diffraction, differential scanning calorimetry, picnometry, and scanning electron microscopy. The properties of crosslinked PP/PE blends were determined by the content of crosslinking agent and processing method. For the material blended by roll, a 2% concentration of peroxide corresponded to a maximum tensile strength and minimum impact strength. However, the mechanical strength of those products blended by extrusion monotonously decreased with increasing peroxide content because of serious degradation. The interfacial adhesion of PP/PE blends could be enhanced by adding random or block copolymer of propylene and ethylene, and the impact strength as well as ductility were greatly improved. Experimental data showed that the impact strength of PP/LDPE/random copolymer ternary blend could reach as high as 33.3 kg · cm/cm; however, its rigidity and tensile strength were inferior to those of PP/LDPE/block copolymer blend.

INTRODUCTION

Polyblends can be made through several techniques, such as mechanical blending, solution blending, latex blending, and copolymerization reaction. Among these the mechanical blending is most widely used in industry because of its easy operation and high capacity for production.[1] The properties of polyblends are determined by the intrinsic properties of homopolymers, processing methods, and compatibility of homopolymers. Most polymers are only partially compatible with others. There exists the problem of phase separation in polyblends and the mechanical properties of polyblends are badly influenced. So the improvement of interfacial adhesion is very important in the study of polyblends. With regard to the PP/PE blends,[1-7] much of the research paid attention to the PP/HDPE blends, few to PP/LDPE blends.[2,7,8] In 1973, Robertson and Paul[6] investigated the tensile properties of both PP/LDPE and PP/HDPE blends, and found that PP and PE are incompatible. In 1981, Brewis et al.[2] studied the interfacial adhesion of PP/PE blends. In 1982, Starkweather[7] found that propylene–ethylene

random copolymer could act as an interfacial adhesive for PP/PE blends. Recently, authors[3] have studied the mechanical properties, dynamic viscoelasticity, crystallinity, and morphology for both PP/HDPE and PP/LDPE blends. In this work, we focus on investigating the interfacial adhesion of PP and LDPE phases by adding crosslinking agent or copolymers to PP/LDPE blends. The impact strength of PP/LDPE/copolymer blends was found to be greatly increased.

EXPERIMENTAL

Materials. (1) isotactic PP, melting index = 5.0 g/10 min; (2) LDPE, melting index = 3.0 g/10 min; (3) HDPE, melting index = 6.5 g/10 min; (4) ethylene–propylene block copolymer, melting index = 2.0 g/10 min, 6–10% ethylene; (5) ethylene–propylene random copolymer (EPR), 60% ethylene; (6) 2.5-dimethyl-2, 5-di(t-butylperoxy)hexyne-3 (crosslinking agent). The composition of polyblends studied in this work are listed in (Table I).

Extrusion Blending. The polyblends (either PP/LDPE/copolymer blends or crosslinked PP/LDPE blends) are made continuously through an extruder with screw speed of 60 rpm and torque of 5–6 mkp. The temperatures of six zones in extruder are 210°C, 215°C, 215°C, 215°C, 210°C, and 210°C, respectively. The pressure of die head is 800–850 kg/cm². The extrudate is cooled in water at room temperature, cut into pellets, and then dried for 2 h at 80°C.

Injection Molding. The test specimens for the measurements of tensile strength, impact strength, and heat deflection temperature are made through an injection molding machine with screw diameter of 30 mm, screw speed of 100 rpm, temperature of 220°C at hopper and nozzle, temperature of 50°C at mold, and injection pressure of 976 kg/cm². The period of time for injecting, cooling, and ejecting stages are 10, 36, and 1.5 s, respectively.

Compression Molding. The test specimens for the measurements of dynamic viscoelasticity and X-ray diffraction are made through a hot press. The specimens are preheated for 10 min, pressed for 5 min under 190°C and 23 kg/cm², and then cooled in water at room temperature.

Roll-Blending-Compression Molding. The crosslinked PP/LDPE blends are also made through hot rolls with a speed of 20 rpm and temperature of 170°C. The materials are blended for 30 min. Then the test specimens for the measurements of tensile strength, heat deflection temperature, and impact strength are made through a hot press. The specimens are preheated for 20 min, pressed for 10 min under 180°C, and 46 kg/cm², and then cooled in water at room temperature.

Tensile Strength Test. The measurements are done at room temperature according to the testing method of ASTM D 638. The speed of crosshead of Instron instrument is kept at 5 cm/min.

Heat Deflection Temperature Test. The measurements are done under a pressure of 1820 kPa and heating rate of 120°C/h according to the testing method of ASTM D 648.

Impact Strength Test. According to the testing method of ASTM D 256, the measurements are done through an Izod-type impact tester, with impact rate of 3.35 m/s at room temperature.

TABLE I
Composition of PP/PE Blends

Sample	PP	HDPE	LDPE	wt % Random copolymer	Block copolymer	Peroxide	Blending
PP100	100	—	—	—	—	—	Extrusion
PH 75	75	25	—	—	—	—	Extrusion
PH 50	50	50	—	—	—	—	Extrusion
PH 25	25	75	—	—	—	—	Extrusion
PH 00	0	100	—	—	—	—	Extrusion
PL 75	75	—	25	—	—	—	Extrusion
PL 50	50	—	50	—	—	—	Extrusion
PL 00	0	—	100	—	—	—	Extrusion
PLR	70	—	20	10	—	—	Extrusion
PLB	70	—	20	—	10	—	Extrusion
CE 00	85.00	—	15.00	—	—	1.0	Extrusion
CE 10	84.15	—	14.85	—	—	1.0	Extrusion
CE 20	83.30	—	14.70	—	—	2.0	Extrusion
CR 00	85.00	—	15.00	—	—	0.0	Roll
CR 10	84.15	—	14.85	—	—	1.0	Roll
CR 20	83.30	—	14.70	—	—	2.0	Roll

Dynamic Viscoelasticity Test. The specimens with size of 4.0 cm × 0.3 cm × 0.02 cm are tested through a Rheovibron DDII-C machine, in which the frequency of oscillation is 3.5 Hz, testing temperature ranges from −150°C to 120°C, and the heating rate is 1.5–2.0°C/min.

Morphology. The morphology of fracture surfaces of impact specimens are examined through a scanning electron microscope.

Thermal Analysis. The melting temperature and heat of fusion of polyblends are measured through DSC. The heating rate is 10 K/min and the temperature ranges from 320 K to 470 K.

Density Measurement. The densities of polyblends are measured at 27°C by using a picnometer.

X-Ray Diffraction. The scanning rate is 4°C/min and 2θ ranges from 5° to 60°.

Intrinsic Viscosity. The intrinsic viscosity of crosslinked PP/LDPE blends in decalin is determined by using an Ostwald–Fenske capillary viscometer at 135°C.

RESULTS AND DISCUSSION

Crosslinked PP/LDPE Blends

Crosslinking agent (peroxide) is added to the PP/LDPE blends to enhance the interfacial adhesion between PP and LDPE phases, and to improve the mechanical strength of PP/LDPE blends. However, degradation apparently occurs in some cases.

Mechanical Properties

PP, LDPE, and peroxide (crosslinking agent) are blended through two methods: roll blending and extrusion blending. The tensile modulus and yield strength of these crosslinked PP/LDPE blends are shown in Figure 1. The polyblends through extrusion blending have lower modulus and strength with increasing peroxide concentration. But the polyblends through roll blending have maximum modulus and strength at 2 wt % peroxide concentration. Apparently, the mechanical properties of polyblends are highly influenced by the processing method. For the polyblends made by roll blending, when a small amount of peroxide is added to PP/LDPE blends, crosslinking reaction may occur only slightly not enough to destroy the crystallinity of PP/LDPE blends, so that the molecular chain is stiffer. But when peroxide concentration is higher, the crystallinity of polyblends decreases, which results in the decrease of strength and modulus of polyblends. As for the polyblends through extrusion blending, the degradation reaction becomes important at high shear and high temperature, so the strength of polyblends is deteriorated. Figure 2 shows the tensile yield elongation of polyblends as a function of peroxide concentration. There is a minimum point around 1–2 wt % peroxide on both curves. Figure 3 shows the impact strength of polyblends as a function of peroxide concentration. The polyblends from roll blending have higher impact strength than those from extrusion blending. Both curves show minimum impact strengths at 2 wt % peroxide. There are many factors which affect the
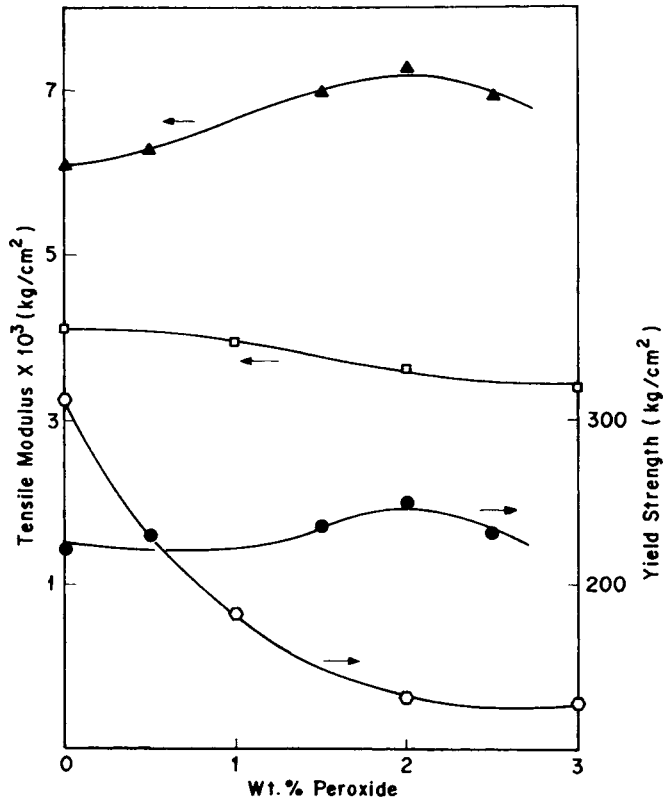
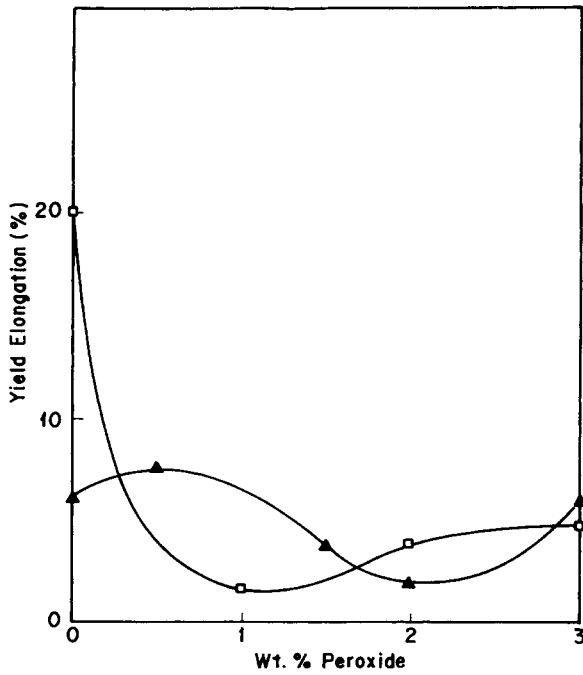Fig. 1.   Tensile modulus and yield strength as a function of peroxide concentration; (□, ○) CE; (▲, ●) CR.

Fig. 2.   Tensile yield elongation as a function of peroxide concentration: (▲) CR; (□) CE.

impact strength of polyblends, such as interfacial adhesion, crystallinity, chain flexibility, molecular weight, etc. The results obtained (Fig. 3) may be a combination of all factors mentioned above.

Intrinsic Viscosity

Figure 4 shows the intrinsic viscosity of crosslinked PP/LDPE blends as a function of peroxide concentration. With increasing peroxide concentration, the intrinsic viscosity (hence, molecular weight) decreases, especially in the extrusion blending case. That means crosslinking reaction and degradation reaction simultaneously happen among molecular chains. For the extrusion blending case, the degradation reaction is more serious.

Dynamic Viscoelasticity

Figures 5–8 show the temperature dependence of loss tangent, storage modulus, and loss modulus of crosslinked PP/LDPE blends as a function of peroxide concentration. For the polyblends through roll blending, the dynamic viscoelasticity remains almost the same when the peroxide concentration is lower than 2 wt %. But as peroxide concentration goes beyond 2 wt %, the tan δ peak increases greatly, and the amorphous region increases largely. The tan δ peak and loss modulus peak shift to higher temperature, and the storage modulus decreases because of the hindrance of molecular chain movement by crosslinking reaction. For the polyblends through extrusion blending, the large increase in both tan δ peak and loss
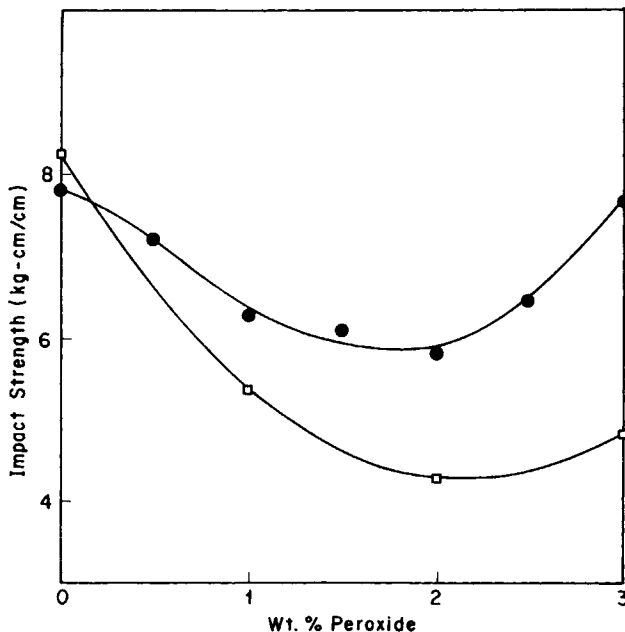

Fig. 3. Impact strength as a function of peroxide concentration: (●) CR; (□) CE.
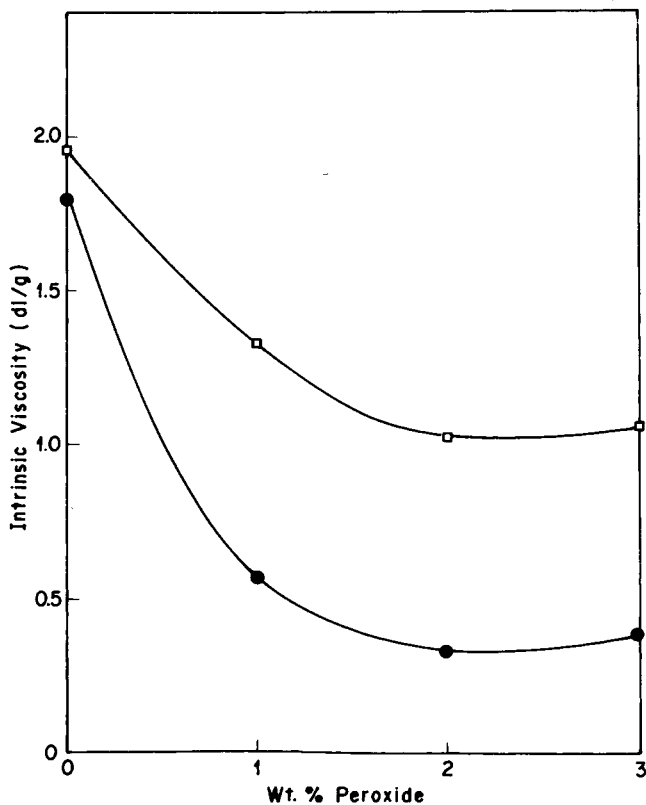
Fig. 4. Intrinsic viscosity of crosslinked PP/LDPE blends as a function of peroxide concentration: (□) CR; (●) CE.
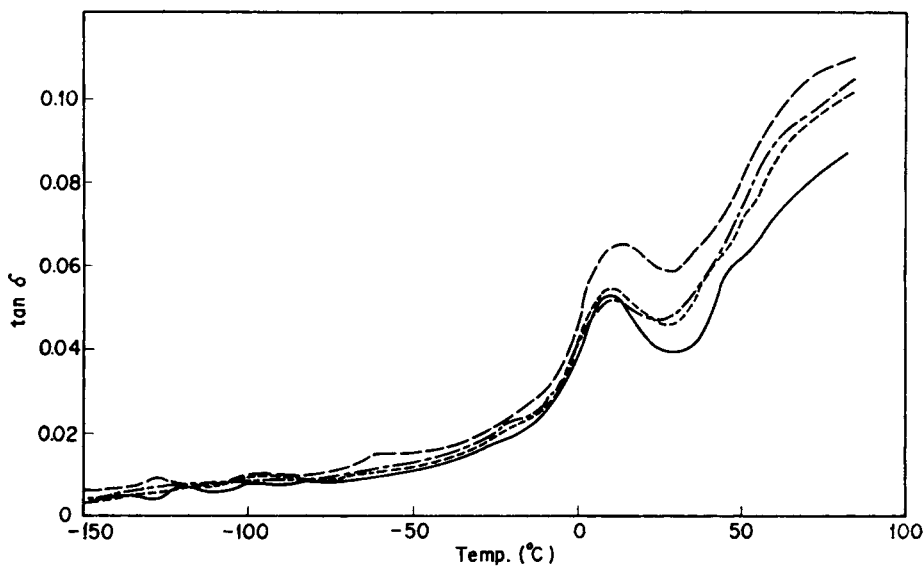

Fig. 5. Temperature dependence of loss tangent as a function of peroxide concentration (blending by roll): (—) CR 00; (---) CR10; (————) CR 20; (---) CR 25.
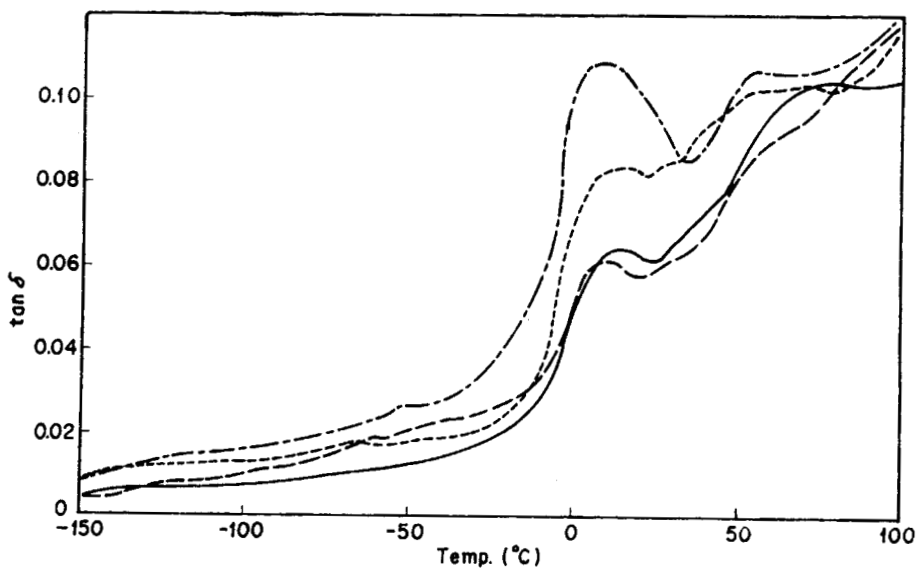
Fig. 6. Temperature dependence of loss tangent as a function of peroxide concentration (blending by extruder): (---) CE 00; (—) CE 10; (-·-) CE 20; (— — —) CE 30.
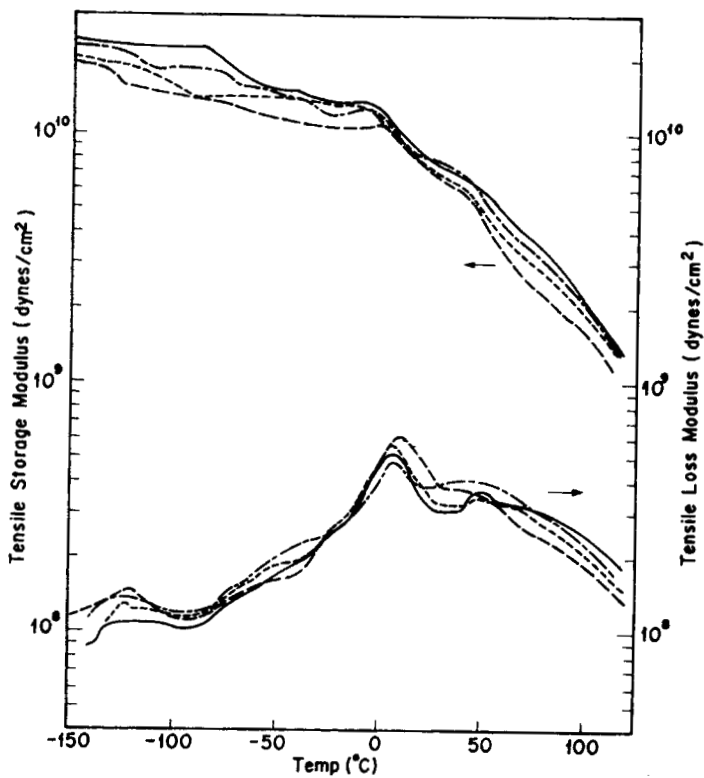

Fig. 7. Semilogarithmic plots of tensile storage and loss modulus vs. temperature for cross-linked PP/LDPE blends (blending by roll): (—) CR 00; (-·-) CR 10; (— — —) CR 20; (---) CR 25.
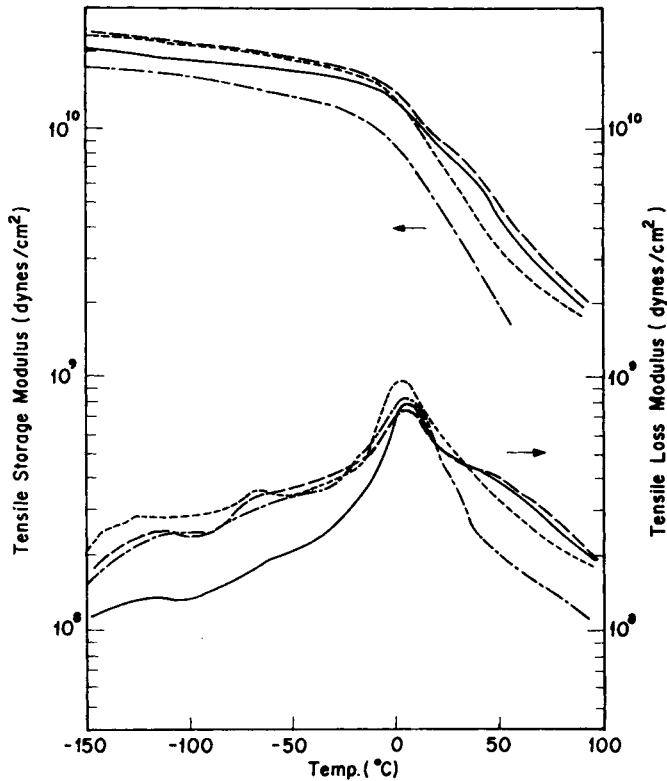
Fig. 8. Semilogarithmic plots of tensile storage and loss modulus vs. temperature for cross-linked PP/LDPE blends (blending by extruder): (---) CE 00; (—) CE 10; (---) CE 20; (————) CE 30.

modulus peak, and the large decrease in storage modulus are obviously seen (Figs. 6 and 8) when peroxide concentration is higher than 2 wt %. These results are due more to the effect of degradation reaction.

Crystallinity

Figures 9 and 10 show the X-ray diffractogram of crosslinked PP/LDPE blends. For the extrusion blending case, all the curves are similar. The absorption strength decreases with increasing the peroxide content. However, for the roll blending case, there appears a new peak around 17° (2θ) when the peroxide concentration is 1 or 2 wt %. The absorption strengths of all peaks also vary with peroxide concentration. The structure of polyblends has been changed, and a new crystalline region forms. When the peroxide concentration is 3 wt %, the new peak disappears. Figures 11 and 12 show the DSC thermogram for crosslinked PP/LDPE blends. The T_m peaks for both LDPE and PP in polyblends are around 110°C and 165°C, respectively. Table II shows the detailed results from DSC measurements. The T_m decreases with increasing peroxide content in the extrusion blending case because of degradation. The variation of T_m in the roll blending case with the peroxide content is smaller and random. There is a new T_m peak
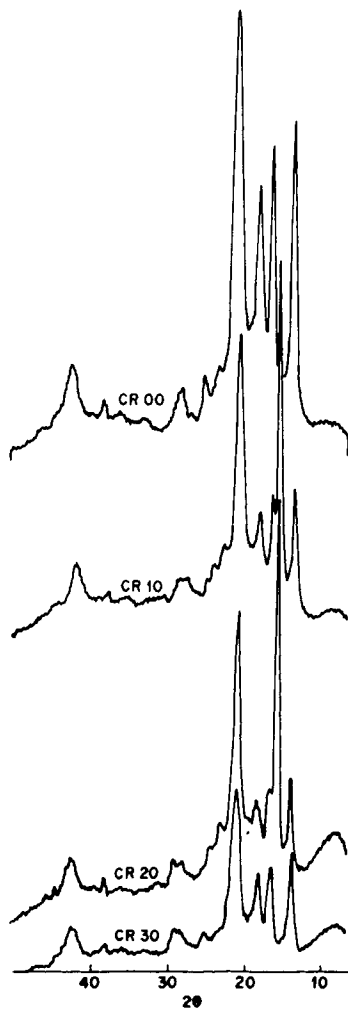
Fig. 9.   X-ray diffractogram of crosslinked PP/LDPE blends (blending by roll).

found around 175°C, corresponding to the new crystalline region, which conforms with the results found in the x-ray diffractogram, Table II and Figure 13 show the crystallinity of polyblends obtained from the measurements of density and DSC. For the extrusion blending case, the crystallinity decreases with increasing peroxide content. For the roll blending case, the crystallinity increases first, and then decreases with increasing peroxide content.

Morphology

Figure 14 shows the scanning electron micrographs of fracture surfaces obtained from impact specimens of crosslinked PP/LDPE blends. Two phases are clearly seen (Figure 14(a)), but the interface becomes obscure with increasing peroxide content [Figs. 14(b)–(e)], implying that the interfacial wettability between PP and LDPE has been enhanced by crosslinking.
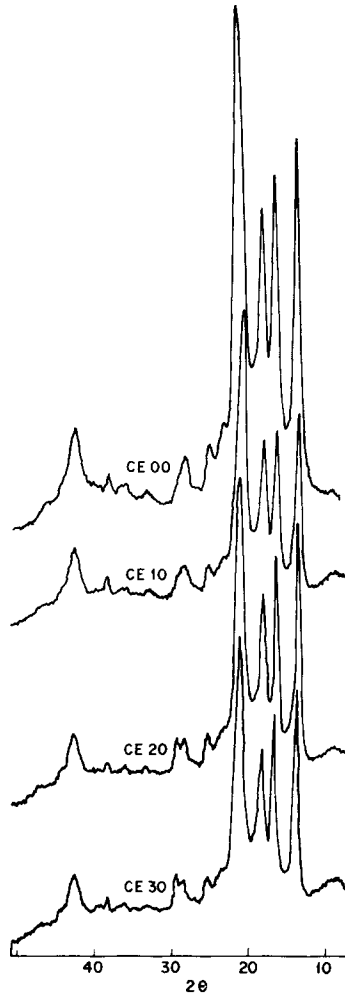
Fig. 10. X-ray diffractogram of crosslinked PP/LDPE blends (blending by extruder).

PP/LDPE/Copolymer Blends

Mechanical Properties

Table III shows the comparison of mechanical properties among ternary blends, homopolymer, and binary blends.[3] The impact strength and elongation of ternary blends are much higher than those of binary blends or homopolymer. The impact strength of PLR reaches as high as six times the impact strength of PP; the tensile modulus decreases about 20%. The impact strength of PLB reaches three times the impact strength of PP, while the tensile modulus decreases only about 10%. From this result, it follows that the interfacial adhesion between PP and LDPE has been largely improved by adding their copolymers.
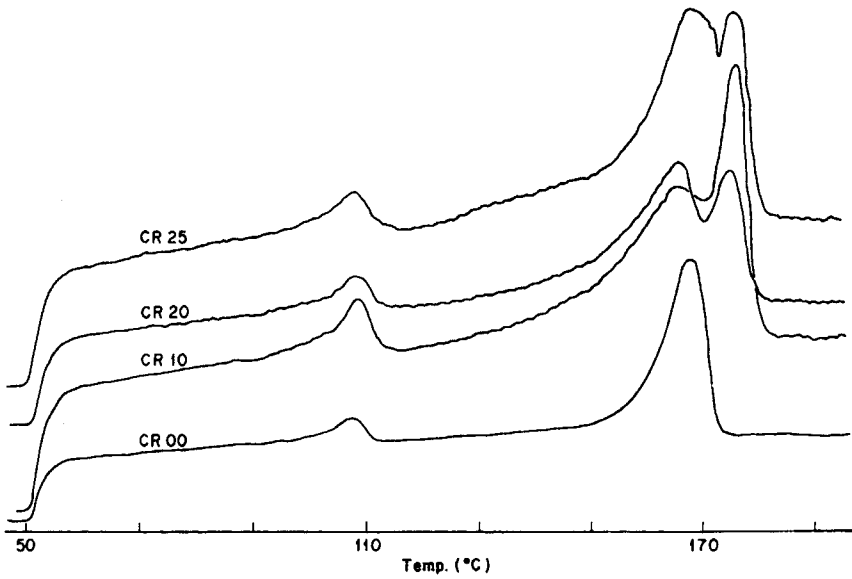
Fig. 11.   DSC thermogram for crosslinked PP/LDPE blends (blending by roll).

Dynamic Visoelasticity

Figures 15 and 16 show the temperature dependence of loss tangent, storage modulus, and loss modulus for PLR and PLB ternary blends. The three peaks at $-123°C$, $-35°C$, and $10°C$ for PLR blends stand for the
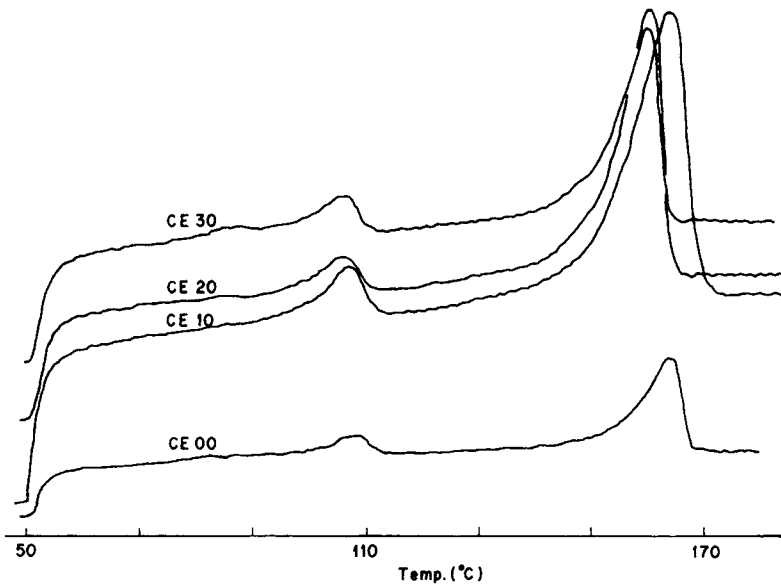

Fig. 12.   DSC thermogram for crosslinked PP/LDPE blends (blending by extruder).

TABLE II
Melting Point, Heat of Fusion, and Crystallinity of Crosslinked PP/LDEP Blends from
Density and DSC Measurements

Sample	Density (g/mL)	$(T_m)_{PE}$ (°C)	$(T_m)_{PP}$ (°C)	$(T_m)_C^{*a}$ (°C)	ΔH_f (cal/g)	Fractional crystallinity	
						From densities	From ΔH_f
CR 00	0.888	108.0	167.8	—	22.9	0.400	0.437
CR 10	0.902	109.3	166.0	176.1	24.7	0.547	0.471
CR 20	0.908	109.0	165.1	174.7	23.2	0.609	0.443
CR 25	—	108.8	168.9	175.9	20.4	—	0.389
CR 30	0.901	—	—	—	—	0.537	—
CE 00	0.891	109.4	165.5	—	19.5	0.432	0.372
CE 10	0.887	108.9	165.1	—	18.5	0.400	0.353
CE 20	0.889	106.1	160.4	—	18.7	0.411	0.357
CE 30	0.877	106.1	159.8	—	18.2	0.281	0.347

a $(T_m)_C^*$ is obtained from the third peak of DSC curve (see Fig. 11).

transition peaks of LDPE, EPR, and PP, respectively. There are only two peaks, corresponding to PP and LDPE phases, found in figures for PLB blends.
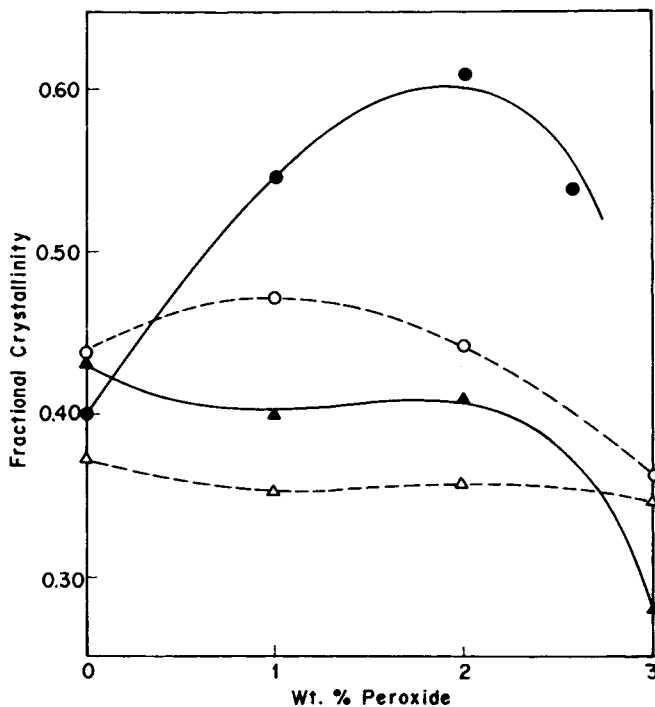

Fig. 13.   The effect of peroxide concentration on fractional crystallinity for crosslinked PP/LDPE blends: (—) calculated from densities; (---) DSC measurement; (○, ●) CR; (△, ▲) CE.
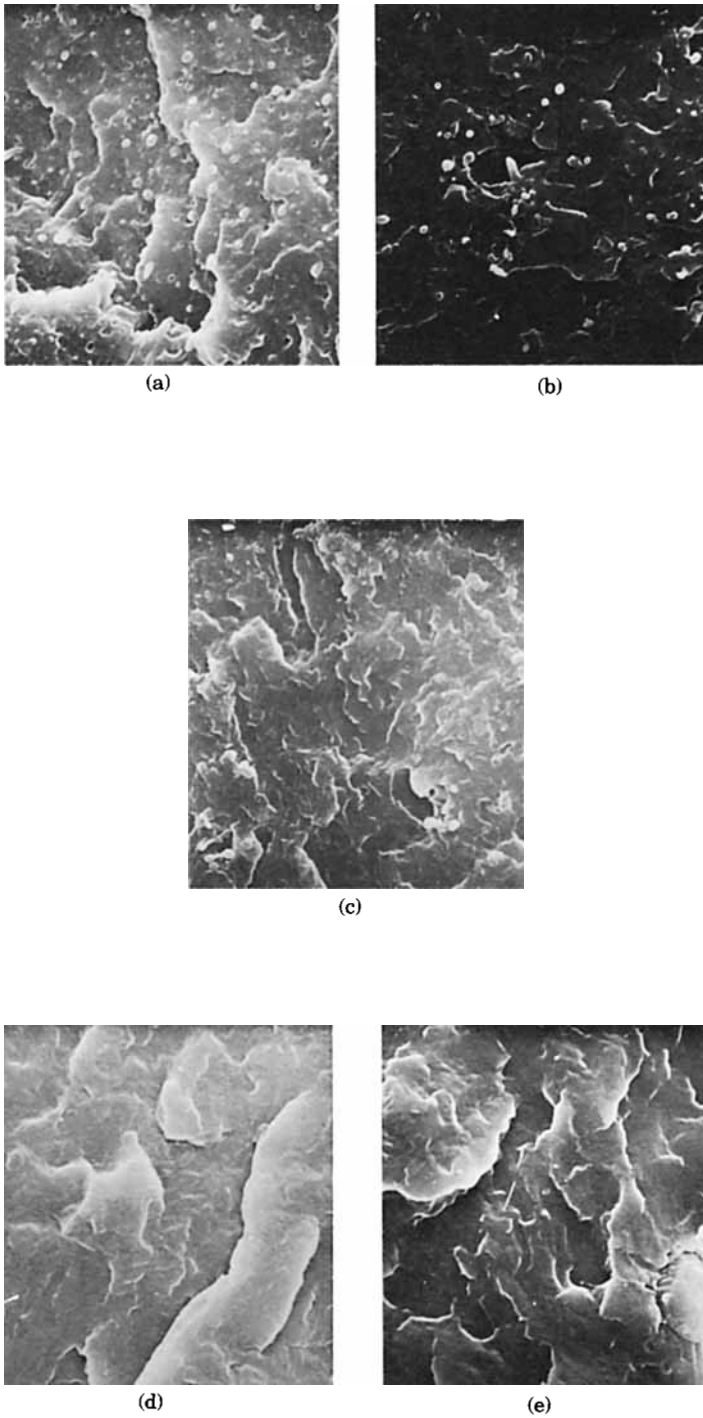
Fig. 14.   Scanning electron micrographs of fracture surfaces obtained from impact speci-
mens of crosslinked PP/LDPE blends: (a) CE 00; (b) CE 10; (c) CE 30; (d) CR 25; (e) CR 10.

TABLE III
Comparison of Mechanical Properties among Ternary Blends, Homopolymer,
and Binary Blends

Sample	IS (kg · cm/cm)	Modulus (kg/cm²)	Yield TS (kg/cm²)	Yield el. (%)	Nominal break TS (kg/cm²)	Break el. (%)
PLR	33.3	3730	254	27	183	280
PLB	16.2	4000	337	24	202	230
PL100	5.5	4660	375	20	202	150
PH 85	5.1	5020	383	17	181	100
PH 75	5.2	4810	374	17	161	—
PL 85	5.7	4000	326	19	154	120
PL 75	6.1	3560	300	20	124	110

Morphology

Figure 17 shows the scanning electron micrographs of fracture surfaces obtained from impact specimens of PLR and PLB blends. The dispersed particles are much smaller than those in binary blends,[3] and are uniformly distributed over continuous phase, and are able to absorb high impact energy. So both PLR and PLB blends have higher impact strength. The random copolymer acts as a cosolvent,[7] while the block copolymer acts as an emulsifier[8] for PP and LDPE. The interfacial adhesion between PP and LDPE phases is effectively enhanced by adding any of these copolymers. Also the distribution between two phases becomes more uniform.
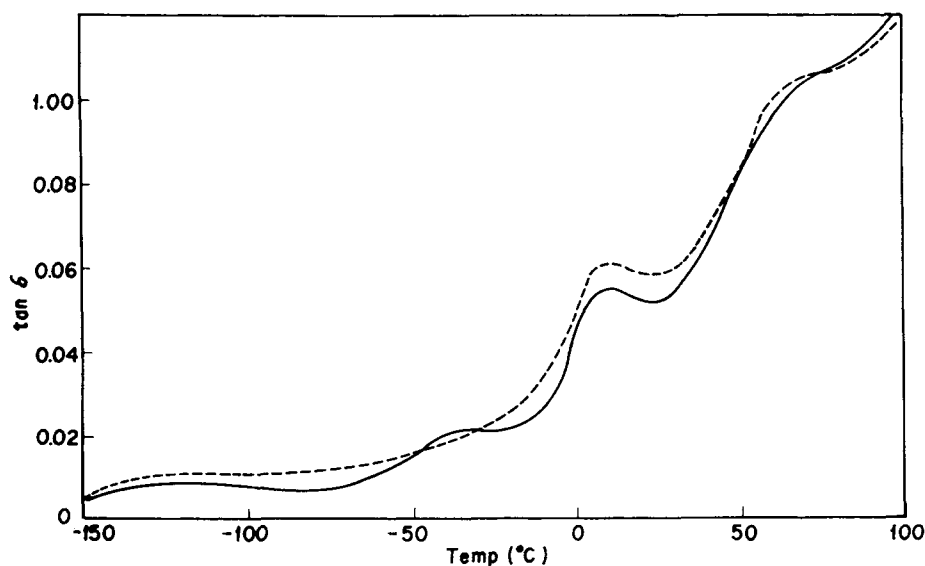

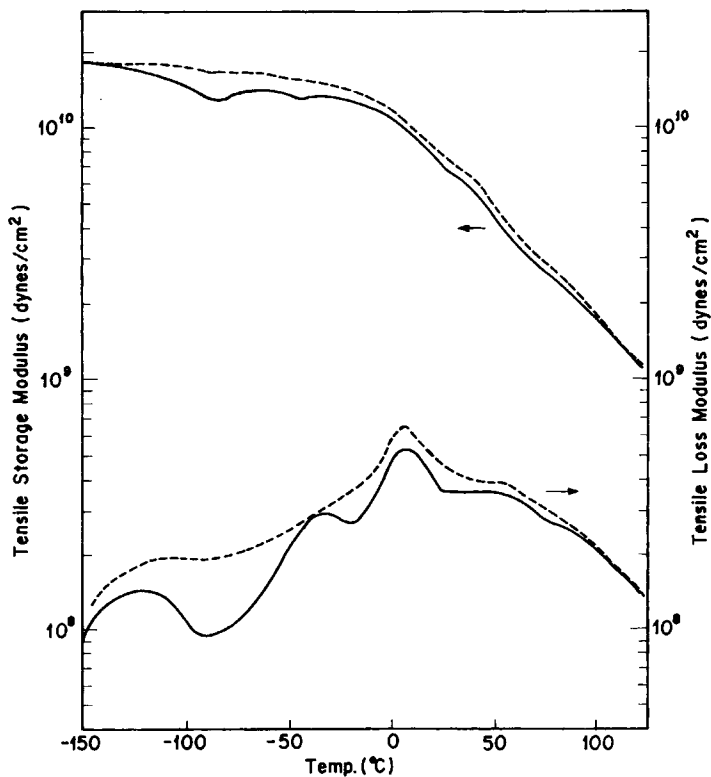Fig. 15. Temperature dependence of loss tangent for PP/LDPE/copolymer ternary blends: (—) PLR; (---) PLB.

Fig. 16. Semilogrithmic plots of tensile storage and loss modulus vs. temperature for PP/ LDPE/copolymer ternary blends: (—)PLR; (---) PLB.
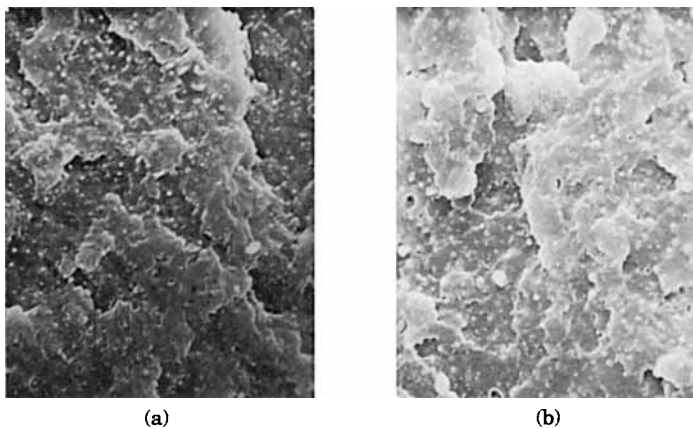

(a)   (b)

Fig. 17. Scanning electron micrographs of fracture surfaces obtained from impact speci- mens of PP/LDPE/copolymer ternary blends: (a) PLR; (b) PLB.

CONCLUSION

The mechanical properties of crosslinked PP/LDPE blends have not been improved as expected. Although the interfacial adhesion between PP and LDPE phases may have been enchanced by crosslinking reaction, the overall properties of crosslinked PP/LDPE blends are influenced by several other factors, such as processing method, crystallinity, chain flexibility, and morphology of polyblends. The addition of random copolymer or block copolymer of propylene–ethylene to the PP/LDPE blends can effectively improve the interfacial adhesion. So ternary blends with high impact strength can be obtained. The impact strength of PLR blends is as high as 33.3 kg · cm/cm, while the impact strength of PLB blends is as high as 16.2 kg · cm/cm, and their tensile strengths remain relatively high.

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