

Compatibility of Binary Blends of Polypropylene with Ethylene- α -olefin Copolymer

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SYNOPSIS

The compatibility for binary blends of isotactic polypropylene with rubbery ethylene- α -olefin copolymers having various α -olefin contents was investigated by means of differential scanning calorimetry, X-ray analysis, transmission electron microscopy, and dynamic mechanical analysis. It was found that “ α -olefin rich” in ethylene-1-butene copolymers and in ethylene-1-hexene copolymers were miscible with amorphous polypropylene chains, when the α -olefin content is above 50 mol %. On the other hand, the blends with “ethylene rich” (above 50 mol % of the ethylene content) in ethylene-1-butene copolymers and ethylene-1-hexene copolymers showed a microheterogeneous morphology. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Isotactic polypropylene (i-PP) has been blended with various elastomers to improve the mechanical properties such as impact strength at low temperature toughness, in which ethylene-propylene rubber (EPR),¹⁻⁷ polyisobutylene,¹ and styrene/ethylene-butene/styrene triblock copolymer⁸ were widely used as the rubber component. The mechanical properties of these binary blends, however, are unsatisfactory because those blends are immiscible and/or incompatible. In the past, therefore, much attention has been focused on the improvement of morphology for the binary blends of i-PP with these elastomers. The improvement of the appropriate processing variables, the addition of ternary component and/or compatibilizer, and the copolymerization of i-PP and rubber component have been developed to improve the morphology of the binary blends.

As well known, i-PP and the ethylene-1-butene copolymers, namely linear low density polyethylene (LLDPE), are incompatible polymer pair,⁹⁻¹⁵ whereas i-PP and isotactic poly (1-butene) (PB1) are compatible pair,¹⁶⁻²² although both LLDPE and PB1 are crystalline polymers. These suggest that

the compatibility of the “ethylene rich” and “1-butene rich” copolymers with i-PP are quite different from each other. Fortunately, recent development in catalyst and new synthetic technique²³⁻²⁸ has made it possible to prepare various ethylene- α -olefin random copolymers such as ethylene-1-butene copolymers, covering nearly entire composition range from LLDPE to PB1. Thus, a rubbery α -olefin copolymers, consisting of a chain with a number of short branches, can be prepared.

In this study, we experimentally confirm the differences as described above and find a transition from immiscible state to miscible state for the binary blends of i-PP with the rubbery ethylene-1-butene copolymers (EBR) and the rubbery ethylene-1-hexene copolymers (EHR). For comparison, the compatibility for the binary blends of i-PP with EPR having a wide range of propylene contents was also examined. Finally, we discuss the effects of the species and the content of α -olefin in the copolymers on the morphology of the blends.

EXPERIMENTAL

Materials and Blend Preparation

Isotactic polypropylene used in this study was a commercial grade with 3.2 wt % ethylene. The number and weight average molecular weights and their

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Table I Characterization of Copolymers

Sample	α -Olefin Content		Molecular Weight		DSC	
	mol %	wt %	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	T_g (K)	ΔH (J/g)
EPR37	37.3	47.2	6.3	11	211	0
EPR67	66.7	75.0	9.0	14	234	0
EBR36	36.2	53.2	12	20	205	0
EBR45	45.4	62.4	12	21	210	0
EBR56	55.6	71.5	26	45	220	0
EBR62	62.0	76.5	12	24	222	0
EHR32	31.8	58.3	13	23	205	0
EHR40	39.8	66.5	15	25	208	0
EHR57	57.1	80.0	15	30	215	0

ratio were 4.2×10^4 , 2.5×10^5 , and 6.0. The EPR, EBR, and EHR copolymers with various α -olefin content, which were determined from $^{13}\text{C-NMR}$,²⁹⁻³² were synthesized with a metallocene catalyst except EPR37, which was a commercial grade (Japan Synthetic Rubber Co., Ltd., JSR EP921). All the copolymers used in this study were essentially random copolymers. The molecular weights of these copolymers were estimated by intrinsic viscosity and determined by gel permeation chromatography in ortho-dichlorobenzene. Details of the copolymers are given in Table I. The nomenclature used in this study is as follows: e.g., EPR37 is ethylene-propylene copolymer containing 37 mol % propylene.

The blends were melt mixed with a thermal stabilizer using a Rubo-plastomill (Toyoseiki) for 10 min at 473 K. The rotor rate was 60 rpm. The blend composition of the i-PP/ethylene- α -olefin copolymers was 50/50 (w/w). The i-PP and the blends were

melt pressed in a laboratory hot press at 473 K and at 10 MPa, and the ethylene- α -olefin copolymers were melt pressed at 373 K and at 10 MPa. The samples quenched at 303 K were prepared for the measurements. The thickness of the compression molded samples was adjusted to suitable thickness to suit the intended experiment.

Polymer Characterization

Differential scanning calorimetry (DSC) measurements were carried out using Perkin-Elmer calorimeter DSC-7 that was calibrated for temperature and melting enthalpy using indium as a standard. The samples of about 10 mg weight sealed in aluminum pans were used for the measurements. The heat of fusion ΔH per gram of i-PP was calculated by comparing the area of the sample and the standard. The blend samples were heated from room

Table II Physical Properties of i-PP and i-PP/Ethylene- α -olefin Copolymer Blends

Sample	T_m (K)	ΔH (J/g)	Crystallinity of PP (%)	Crystal Form	Long Period (nm)
i-PP	421	85.9	41.1	α	15
i-PP/EPR37	422	44.1	42.2	α	15
i-PP/EPR67	423	43.4	41.5	α	15
i-PP/EBR36	421	46.7	44.7	α	17
i-PP/EBR45	421	44.7	42.8	α	19
i-PP/EBR56	420	48.5	46.4	α	25
i-PP/EBR62	420	49.3	47.2	α	25
i-PP/EHR32	421	40.1	38.4	α	16
i-PP/EHR40	420	43.8	41.9	α	19
i-PP/EHR57	419	42.8	41.0	α	19

temperature to 460 K at a scanning rate of 10 K/min under a nitrogen atmosphere. The ethylene- α -olefin copolymer samples were heated from 170 to 460 K to investigate glass transition temperature in addition to the melting temperature and the heat of fusion. The weight fraction crystallinity of i-PP in the blend samples was determined from the division of the heat of fusion per gram of i-PP by that of a perfectly crystalline i-PP, 209 (J/g).³³

The morphology of the blend samples was examined with a JEOL transmission electron microscope (TEM) model JEM-2000FX. The ultrathin films were sectioned into slices after stained by ruthenium tetroxide.

The microstructure of the samples was investigated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). The WAXD and the SAXS studies were performed with Mac Science MXP18 X-ray diffractometer. Flat samples were mounted directly into the diffractometer. The WAXD experiments were carried out using CuK α radiation operating at 40 kV, 150 mA at a scanning speed of 2 degree/min over a 2θ (Bragg angle) range from 8 to 32 degree. The SAXS experiments were carried out using CuK α radiation operating at 50 kV, 300 mA. The 2θ scan data were collected at 0.01

degree step intervals in the range from 0.15 to 1.5 degree.

The measurements on the linear dynamic mechanical properties were made using a dynamic mechanical analyzer (Rheology Co., Ltd. DVE V-4) on sample specimens of the following dimensions: length 20 mm, width 5 mm, and thickness around 0.5 mm. The storage modulus (E'), the loss modulus (E''), and loss tangent ($\tan \delta$) were measured between 120 and 430 K at a constant frequency of 10 Hz and a heating rate of 2 K/min.

RESULTS AND DISCUSSION

Thermal properties of ethylene- α -olefin copolymer samples are summarized in Table I. It was confirmed from the DSC results that all the ethylene- α -olefin copolymer samples used in this study are fully amorphous and rubbery. Those of the i-PP and the blend samples are summarized in Table II. The melting temperatures of their blends are almost similar to that of the i-PP, suggesting that the thickness of lamellae is independent of blending of ethylene- α -olefin copolymers.

WAXD studies were carried out in an effort to

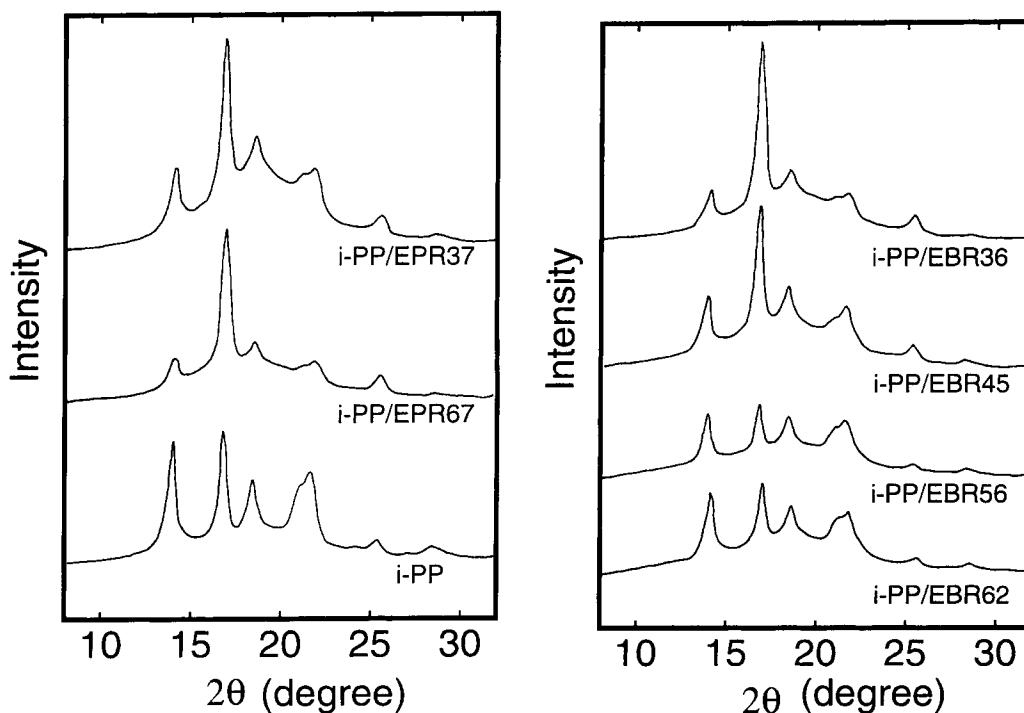


Figure 1 WAXD profiles of the i-PP and the blend samples.

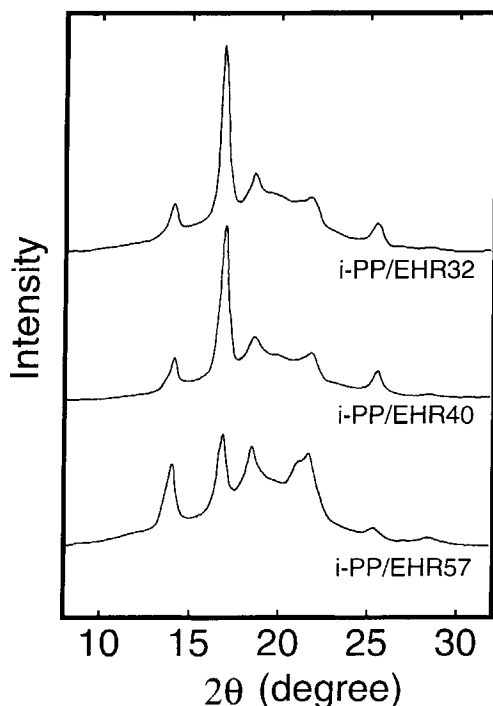


Figure 1 (Continued)

obtain much information on the crystalline level of the blend samples. The diffraction angle (2θ) curves are shown in Figure 1. The diffraction patterns have a broad amorphous background superimposed upon five sharp diffraction lines ascribed to the 110, 040,

130, 111, and 131 in addition to 041 plane in the crystal as reported previously.³⁴ The patterns of the i-PP and the blend samples show α form (monoclinic) only, because there are no line at $2\theta = 16.1^\circ$ associated with β form (hexagonal).³⁵ Furthermore, there are no measurable shifts in the positions of the lines, indicating that the blending of ethylene- α -olefin copolymer little affects the crystalline region of i-PP.

The long period, defined as the distance between the centers of two adjacent lamellae, was also examined by SAXS measurements for all samples. The SAXS results are also summarized in Table II. It was found that the long periods of i-PP/EPR37, i-PP/EPR67, i-PP/EBR36, and i-PP/EHR32 blends are comparable with that of the i-PP sample, whereas the long periods of i-PP/EBR56, i-PP/EBR62, and i-PP/EHR57 are longer than that of the i-PP sample. The increases of long periods for these blends will be due to the thickening of amorphous layers between the adjacent lamellae because the melting temperature of i-PP, reflecting the thickness of lamellae, is unchanged by blending of the ethylene- α -olefin copolymers.

Figure 2 shows the electron micrographs for the blend samples, in which i-PP rich phase is the white region and ethylene- α -olefin copolymer-rich phase is the dark region. There is apparent cocontinuous microheterogeneous morphology in i-PP/EPR37, i-PP/EPR67, i-PP/EBR36, i-PP/EBR45, i-PP/

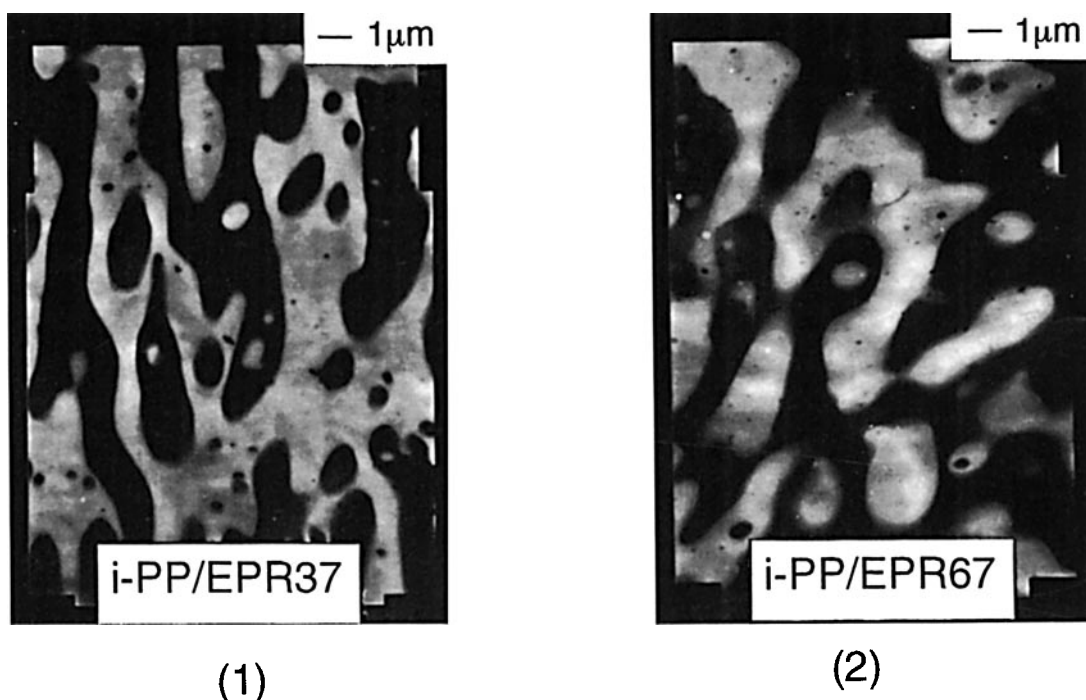
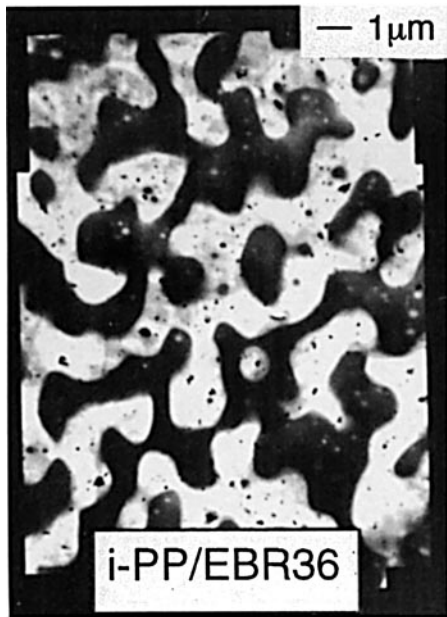
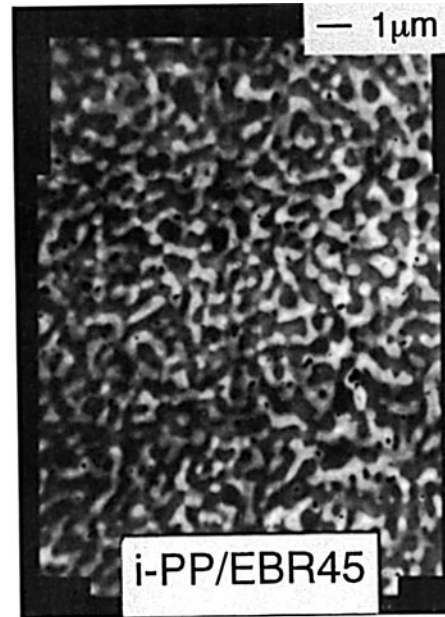


Figure 2 TEM micrographs of thin sections of a series of blends.



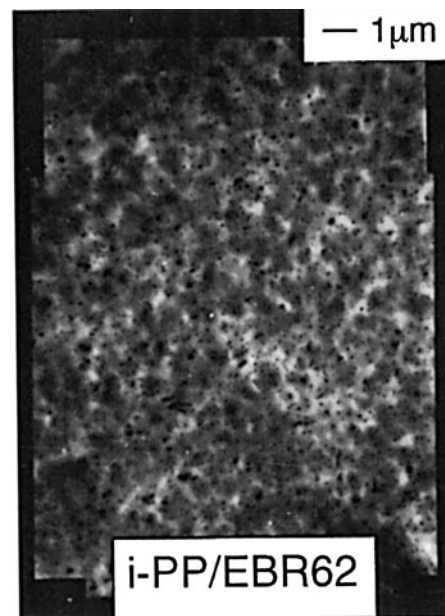
(3)



(4)



(5)

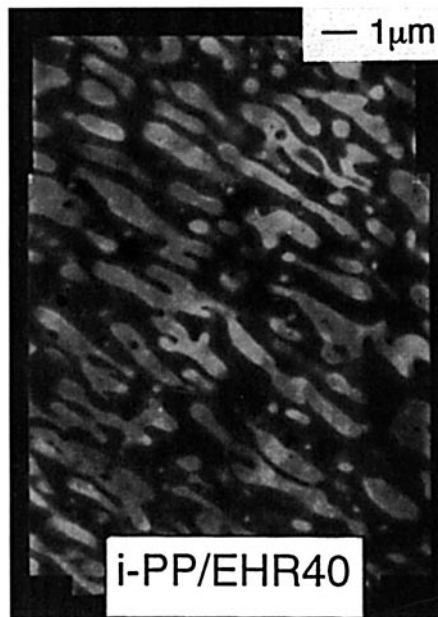


(6)

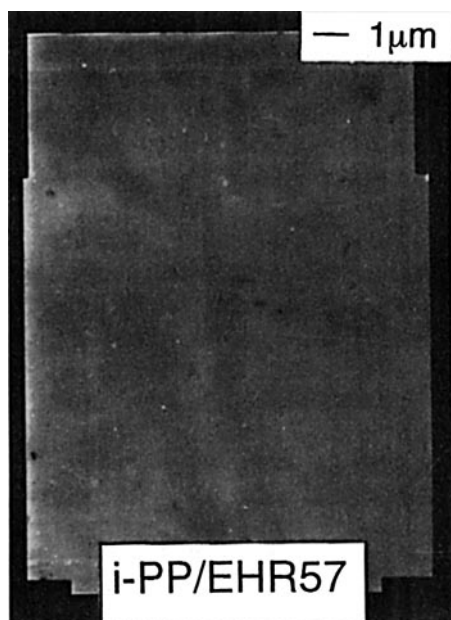
Figure 2 (Continued from the previous page)



(7)



(8)



(9)

Figure 2 (Continued from the previous page)

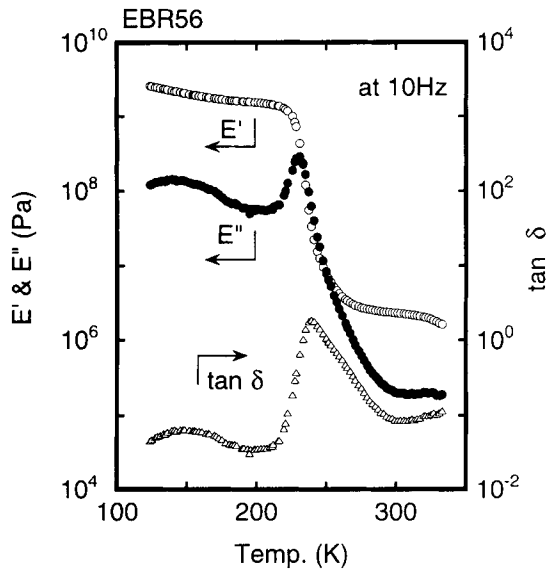


Figure 3 Variation of the mechanical storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) with temperature for the EBR56 sample.

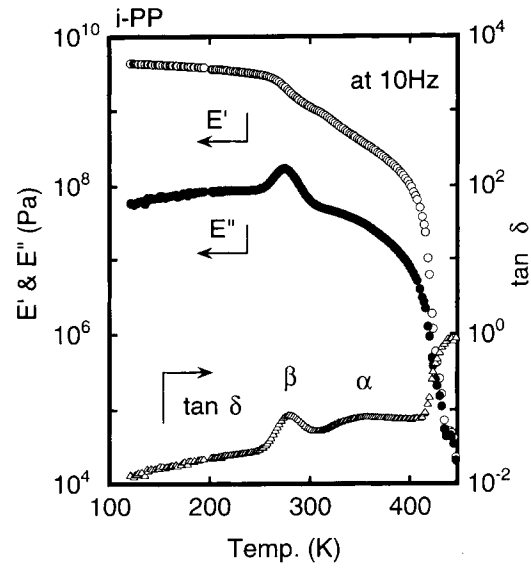


Figure 4 Variation of the mechanical storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) with temperature for the i-PP sample.

EHR32, and i-PP/EHR40 blend samples. It was found that the domain size of the copolymers in the i-PP/EBR36 blend sample is larger than that in the i-PP/EBR45 blend sample and that the domain size in the i-PP/EHR32 blend sample is larger than that

in the i-PP/EHR40 blend sample. Thus, the domain size of ethylene-1-butene or ethylene-1-hexene copolymers decreases with increasing the α -olefin content in the copolymers. On the other hand, there is fairly homogeneous morphology in the i-PP/EBR

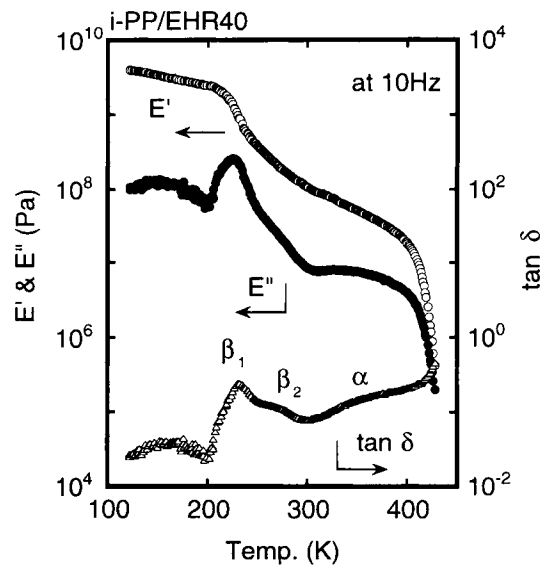
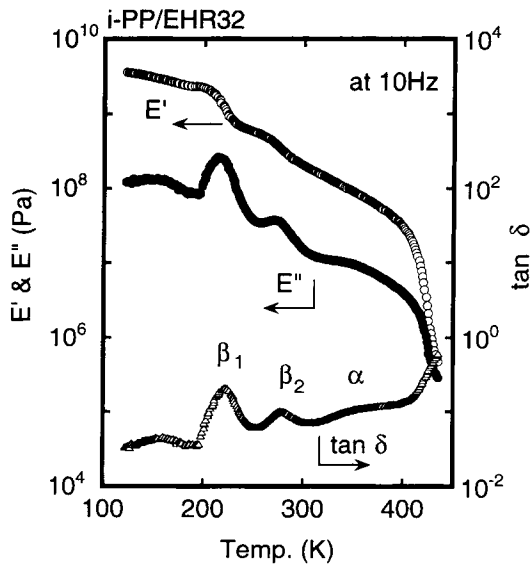


Figure 5 Variation of the mechanical storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) with temperature for the blends. (1) i-PP/EHR32, (2) i-PP/EHR40, (3) i-PP/EHR57 blend samples.

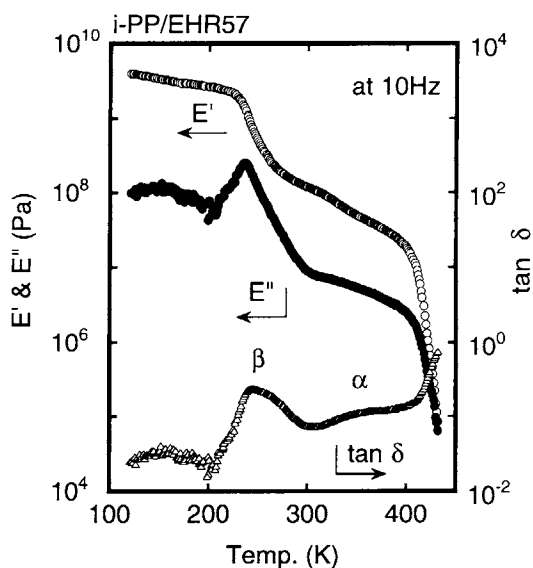


Figure 5 (Continued)

and i-PP/EHR having higher α -olefin contents such as the i-PP/EBR56, i-PP/EBR62, and i-PP/EHR57 blends.

The temperature dependence of E' , E'' , and $\tan \delta$ of EBR56 are shown in Figure 3. As seen in the figure, E' decreases moderately with temperature, and $\tan \delta$ shows two apparent dispersion peaks at temperatures between 200 and 250 K and at around 150 K. The higher dispersion is ascribed to micro-Brownian motion of amorphous chains,^{36,37} i.e. glass-rubber transition temperature (T_g). The lower dispersion is to the localized molecular relaxation,^{37,38} such as minute vibration of branch parts and chain segments. The similar behavior of dynamic mechanical properties was observed for all other ethylene- α -olefin copolymers, although the figures are not shown here. Figure 4 shows those of the i-PP sample. $\tan \delta$ shows two apparent peaks at around 320–380 K and at around 275 K. These dispersions can be assigned as α and β relaxation, respectively, from higher temperature. Numerous studies on the dynamic mechanical dispersions of i-PP have been reported.^{37,39–43} According to their results, the α -relaxation can be ascribed to intralamellar crystal reorientation process or intracrystalline chain motion; the β -relaxation corresponds to T_g in amorphous parts.

In Figure 5, three typical examples for the dynamic mechanical properties of the blend samples are shown. There is distinct difference among them in their β relaxation. In the incompatible blend samples with cocontinuous microheterogeneous

morphology, there are apparently two peaks of $\tan \delta$ in the temperature range from 200 to 300 K, which are assigned to β_1 and β_2 from the lower temperature. Furthermore, the magnitude of the β_2 relaxation decreased with decreasing the domain size. In Figures 6–8, temperature dependence of E'' around β relaxation for the i-PP, the ethylene- α -olefin copolymers, and their blend samples are shown. As seen in Figures 7(1) and 8(1), the higher relaxation peak β_2 is ascribed to the T_g of the amorphous region of the i-PP, and the lower relaxation peak β_1 is to the T_g of the ethylene- α -olefin copolymer component. For the i-PP/EBR45 and i-PP/EHR40 blend samples, however, the β_2 peak is slightly shifted to lower temperature than that of the i-PP sample, whereas the β_1 peak is slightly shifted to higher temperature than that of the ethylene- α -olefin copolymer samples. This suggests that the amorphous region of the i-PP and the ethylene- α -olefin copolymer component

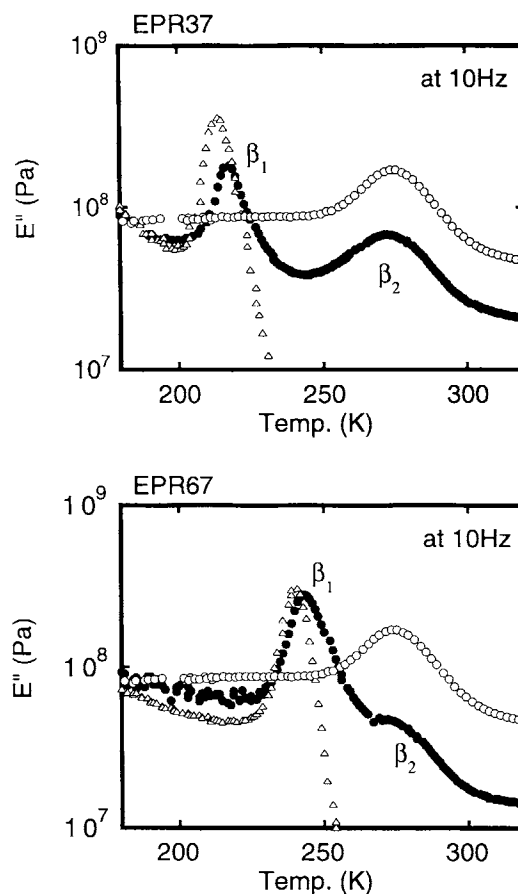


Figure 6 Variation of the mechanical loss modulus (E'') with temperature for the i-PP (O), the EPR (Δ), and their blend (\bullet).

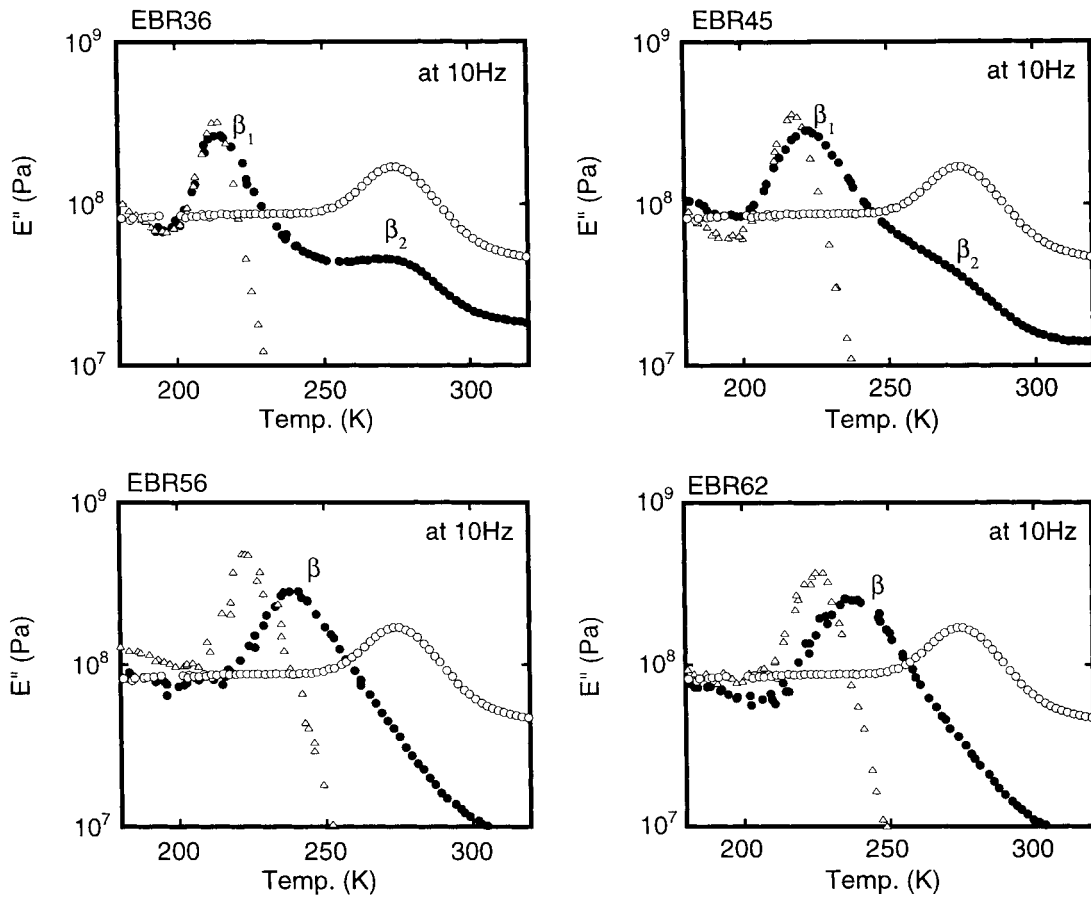


Figure 7 Variation of the mechanical loss modulus (E'') with temperature for the i-PP (○), the EBR (△), and their blend (●).

are partially dissolved in each other in the blends [see Figs. 7(2) and 8(2)]. Furthermore, for the i-PP/EPR37 and i-PP/EPR67 blend samples, only the β_1 peak is slightly shifted to higher temperature, suggesting that the i-PP component are partially dissolved in EPR phase [see Fig. 6(1,2)]. On the other hand, as seen in Figures 7(3,4) and 8(3), there is only single β dispersion between the T_g s of the pure components in the i-PP/EBR56, i-PP/EBR62, and i-PP/EHR57 blends showing the homogeneous morphology. This suggests that the ethylene- α -olefin copolymer molecules are incorporated in the amorphous region of i-PP. These results of dynamic mechanical properties are consistent with those of SAXS and DSC, i.e., the 1-butene rich EBR and the 1-hexene rich EHR are miscible with amorphous parts of i-PP; on the other hand, the ethylene rich EBR and EHR are immiscible with i-PP.

To our knowledge, there has been no report in which E'' peak around T_g appear as a single peak for binary blends of i-PP with various rubbery poly-

mers. Thus, these are very important results because the addition of such copolymers having a number of short branches (i.e. C_2 and C_4) has a potential to the drastic improvement of mechanical properties of i-PP materials.

CONCLUSION

In the present study, we investigate the compatibility for the binary blends of i-PP with rubbery ethylene- α -olefin copolymers such as EPR, EBR, and EHR. It was found that the EPR component is incompatible with i-PP component, irrespective of propylene content in a copolymer. The compatibility of i-PP/EBR and i-PP/EHR blends were quite different from that of i-PP/EPR. Although the blends of the "ethylene-rich" EBR and EHR (ethylene content is above 50 mol %) showed a microheterogeneous morphology, the " α -olefin rich" EBR and EHR (above 50 mol %) are miscible with i-PP. The EBR and the EHR were

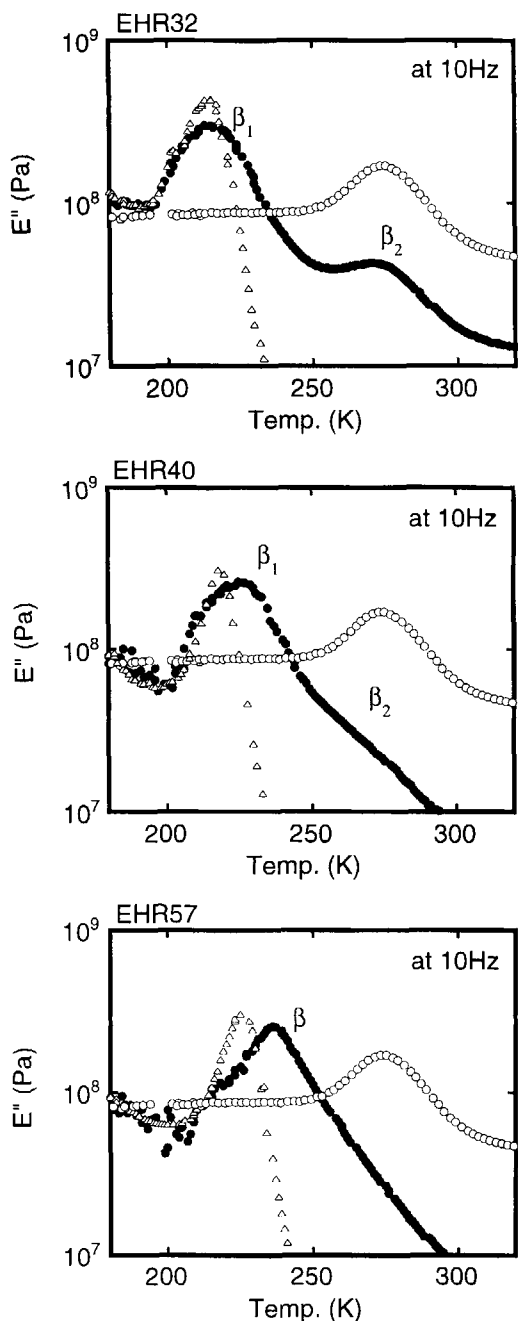


Figure 8 Variation of the mechanical loss modulus (E'') with temperature for the i-PP (O), the EHR (Δ), and their blend (\bullet).

dissolved in the amorphous region of i-PP. The result is very important because the morphology can be controlled by changing the α -olefin content in a EBR or EHR copolymer. Moreover, this suggests that the mechanical properties of i-PP can be drastically improved by changing the α -olefin content in an EBR or EHR copolymer.

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