Rheological Properties for Binary Blends of i-PP and Ethylene-1-hexene Copolymer

MASAYUKI YAMAGUCHI,[1] KOH-HEI NITTA,[1] HIROSHI MIYATA,[2] TOSHIRO MASUDA[3]

[1]Center for New Materials, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa, 923-12 Japan

[2]Yokkaichi Laboratory, TOSOH Corporation, 1-8 Kasumi, Yokkaichi, Mie, 510 Japan

[3]Division of Material Chemistry, Kyoto University, Sakyo-ku, Kyoto, 606-01 Japan

ABSTRACT: The dynamic viscoelastic properties for binary blends consisting of an isotactic polypropylene (i-PP) and an ethylene-1-hexene copolymer (EHR) were investigated in both solid and molten states to reveal the relation between miscibility in the molten state and the morphology in the solid state. In this study, two types of EHRs were employed: "ethylene-rich" EHR and "1-hexene-rich" EHR. The blend of i-PP and EHR of 30 mol % 1-hexene content shows a very long time relaxation due to the phase separation in the molten state. The blend film shows two separate glass-relaxation processes associated with those of the pure components. These indicate that the blend shows phase-separated morphology in the solid state as well as in the molten state. On the other hand, dynamic moduli in the molten state of the blends of i-PP and EHR of 57 mol % 1-hexene were found to be intermediate between those of individual pure components. Furthermore, the apparent activation energy of the blends is constant and is identical with those of i-PP and the EHR. The blend films show a single glass-relaxation process at the temperatures between those of the pure components, indicating that the EHR molecules are incorporated in the amorphous region of i-PP in the solid state. Accordingly, it was found that the polymer miscibility in the molten state for the i-PP/EHR blends directly affects the morphology in the solid state. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 467–474, 1997

Key words: ethylene-1-hexene copolymer; polypropylene; polymer blend; dynamic viscoelastic property; miscibility

INTRODUCTION

It is well known that immiscible polymer blends in the molten state show the long-time relaxation associated with the phase separation[1-6] and pronounced elastic properties such that storage moduli at lower-frequency regions become higher than those of the pure components. Numerous studies on rheological properties of miscible polymer blends have been extensively carried out using various polymer pairs having specific interaction. The rheological behavior[6-11] is not always simple because specific interchain interaction like hydrogen bonding leads to the reduction of the entanglement[2,7-9] and the homogeneous phase is no longer maintained during macroscopic flow.[2,12] However, systematic studies concerning the effects of miscibility on rheological properties of blends with no specific interaction are few and of another interest.

A previous article[13] demonstrated that the compatibility of isotactic polypropylene (i-PP) and rubbery ethylene-α-olefin copolymers such as ethylene-1-butene copolymers (EBR) and ethyl-

Table I Molecular Characteristics of i-PP and EHRs

Sample	α-Olefin Content (mol %)	M_n $\times 10^{-5}$	M_w $\times 10^{-5}$	M_z $\times 10^{-5}$
i-PP	—	0.74	1.36	2.19
EHR30	30.0	1.03	1.39	1.84
EHR57	57.1	1.42	1.96	2.70

ene-1-hexene copolymers (EHR) depends largely on the content of α-olefin units. The "α-olefin-rich" copolymers are miscible with the amorphous domain of i-PP, whereas i-PP and "ethylene-rich" copolymers are immiscible and form a phase-separated domain. The morphology of binary blends of i-PP and ethylene-α-olefin copolymers in the solid state will be closely related to the miscibility of the components in the molten state. Thus, the rheological properties of the blends at high temperatures are of great interest to study to control the morphology in the solid state as well as the processability. In this article, dynamic viscoelastic properties of the binary blends of i-PP and EHR are investigated in the molten state as well as in the solid state, in which an "ethylene-rich" EHR and an "1-hexene-rich" EHR are employed. The former EHR is immiscible and the later is miscible with i-PP in their amorphous domain. The relation between the morphology in the solid state and the miscibility in the molten state are discussed.

EXPERIMENTAL

Materials and Blend Preparation

Isotactic polypropylene (i-PP) and two types of EHRs were used in this study. The molecular weights of these polymers were determined by intrinsic viscosity and by gel permeation chromatography in *ortho*-dichlorobenzene. The 1-hexene content in the copolymers was determined from ^{13}C-NMR measurements.[14] Molecular characteristics of the i-PP and EHRs are given in Table I. All the samples were synthesized with a metallocene catalyst[15] and the values of M_w/M_n of all the polymers are around 1.5. Sample codes for EHRs employed in this study are as follows: EHR30 is an ethylene-1-hexene copolymer containing 30.0 mol % 1-hexene, and EHR57 is an ethylene-1-hexene copolymer containing 57.1 mol % 1-hexene.

The i-PP and an EHR were mixed in a solution

of xylene at 383 K. The compositions of the components in the i-PP/EHR57 blend were 75/25, 50/50, and 25/75 (w/w) and that in i-PP/EHR30 blend was 75/25 (w/w). The polymers were precipitated from the solution into methyl alcohol and then dried in a vacuum oven at room temperature. The blend samples were pressed in a laboratory hot press for 8 min at 473 K and at 10 MPa to prepare films to be used for the dynamic viscoelastic measurements in the solid state. The film specimens were prepared by quenching from the melts into an ice-water bath.

Measurements

Dynamic shear moduli, i.e., storage shear modulus G' and loss modulus G'', at temperatures between 353 and 523 K were measured using a cone-plate-type rheometer (Rheology Co., Ltd., MR-500) in the angular frequency range of 6.28×10^{-2} to $1.88 \times 10^1 \text{ s}^{-1}$. A dynamic mechanical analyzer (Rheology Co., Ltd., DVE V-4) was used to measure G' and G'' of EHR57 in the rubbery state at temperatures between 275 and 323 K with a sandwich-type geometry.[16] Measurements for other samples could not be extended to the plateau region because of the crystallizability of i-PP. The master curves were obtained by horizontal shifts without vertical ones. The temperature dependence of the dynamic tensile moduli, storage tensile modulus E' and loss modulus E'', were also measured for all the film specimens between 180 and 440 K at a constant frequency of 10 Hz and a heating rate of 2 K/min. Sample dimensions are length of 20 mm, width of 5 mm, and thickness of around 0.5 mm.

Density for all the film specimens was measured using a water–isopropanol density gradient column at 296 K. It was found that the densities of EHR30 and EHR57 were 854 and 857 (kg/m³) and they are almost identical with the density of amorphous polyethylene, suggesting that the copolymers are noncrystalline polyolefins. This was also confirmed by differential scanning calorimetry measurements and wide-angle X-ray diffraction analysis.

RESULTS AND DISCUSSION

Dynamic Viscoelastic Properties in the Molten State

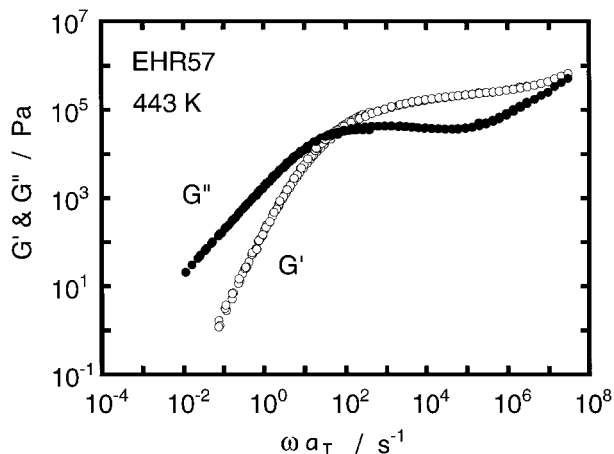Figure 1 shows the master curves of dynamic shear moduli, G' and G'', for EHR57. The refer-

Figure 1 Master curves of the storage modulus G' and the loss modulus G'' for EHR57. The reference temperature is 443 K.

ence temperature is 443 K. The curves show the terminal, rubbery plateau, and transition zones in the frequency range. We estimated the average molecular weight between the entanglement coupling by points (M_e) for EHR57, using a classical rubber elasticity theory,[16,17] as

$$M_e = \rho RT/G_N^0 \qquad (1)$$

where G_N^0 is the entanglement modulus and ρ is the density. The value of G_N^0 was determined using the following relation[16,18]:

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{a} G'' \, d \ln\omega \qquad (2)$$

where a is the upper limit before the transition zone is entered. In general, these parameters can be obtained by the integration of G'' over $\ln \omega$ encompassing the maximum of G''. In this study, the G'' vs. $\ln \omega$ curve was numerically integrated from $\ln \omega = -\infty$ to the maximum of G'', and the result was doubled. Consequently, the M_e of EHR57 was estimated to be 10000, and G_N^0, to be 2.1×10^5 Pa. The M_e of EHR57 is much higher than those of PP (M_e = 4650 [Ref. 19] or 2900 [Ref. 20]) and of PE (M_e = 1100 [Ref. 21]) and is comparable with that of poly(1-butene) (M_e = 11600 [Ref. 21]).

Figure 2(a) and (b) shows the master curves of dynamic moduli for the blends of i-PP/EHR57 and i-PP/EHR30 in the molten state. The blend ratio of both blends is 75/25 (w/w). The time–temperature superposition principle was applicable to the frequency dependence of the dynamic

moduli for both blends, indicating that the molecular aggregation state of the blend samples is stable over the entire experimental regions of frequency or temperature. The i-PP/EHR30 blend
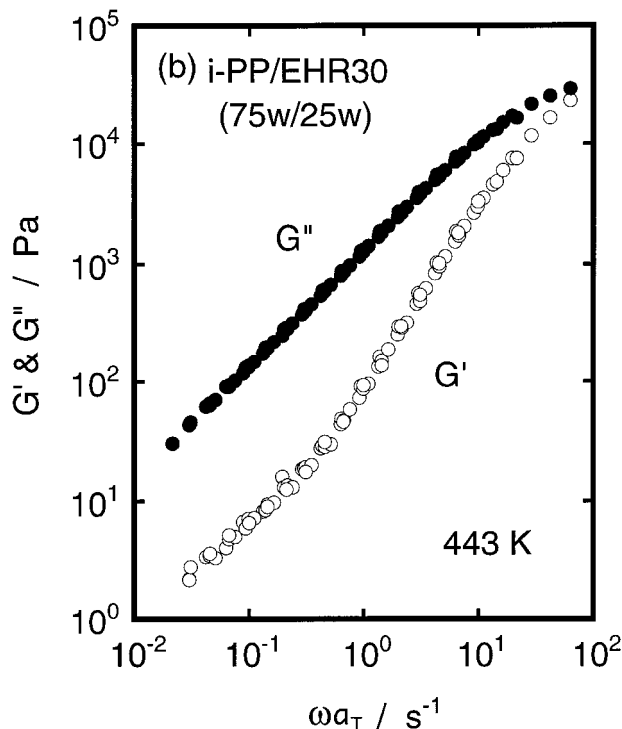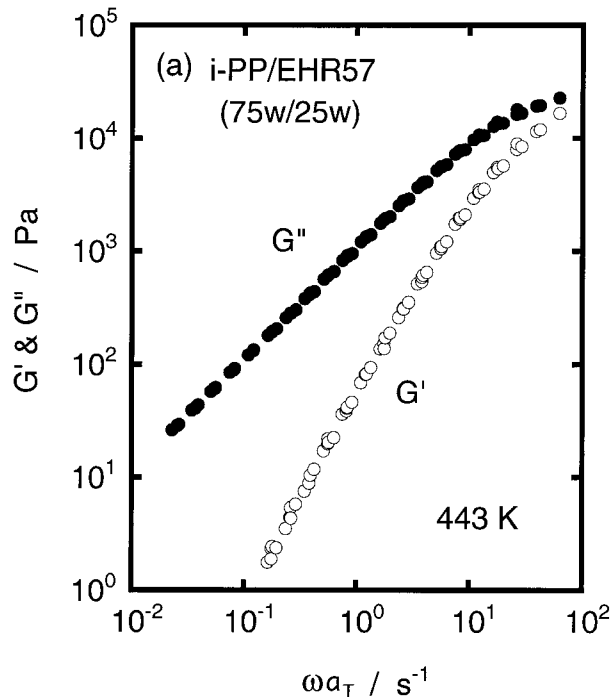

Figure 2 Master curves of the storage modulus G' and the loss modulus G'' for (a) i-PP/EHR57 (75 w/25 w) and (b) i-PP/EHR30 (75 w/25 w). The reference temperature is 443 K.
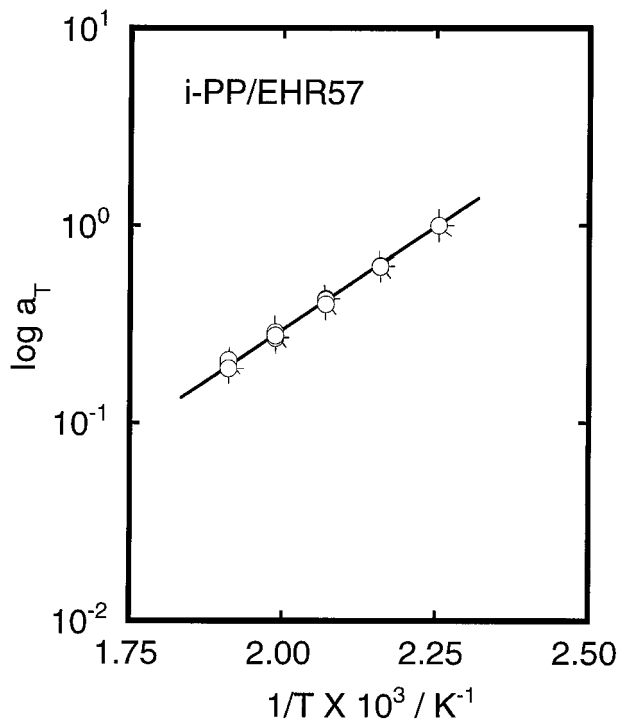
Figure 3   The logarithm of the shift factor a_T plotted against the inverse of temperature for i-PP, EHR57, and their blends: (◌) i-PP 100%; (◯) i-PP 75%; (◯-) i-PP, 50%; (◖) i-PP, 25%; (◗) EHR57 100%.

shows the "second plateau" in the G' curve at low-frequency regions, although the G' curve of the i-PP/EHR57 blend has a slope of 2.0. Furthermore, the G'' curve of the i-PP/EHR57 blend at the regions has a slope of 1.0.

The shift factor a_T is plotted against the reciprocal of absolute temperature in Figure 3. The apparent activation energy ΔH can be calculated from the slope (see Table II). The value of ΔH of i-PP was about 40 kJ/mol, which was in good agreement with the values reported previously.[20,22,23] The ΔH

of EHR57 was nearly equal to that of i-PP. Furthermore, the values of ΔH of the blends was also about 40 kJ/mol, being independent of blend composition. According to the WLF scheme,[16,24] ΔH at high temperatures can be related to the thermal expansion coefficient α so that all the samples have the same value of α. In general, thermal expansion is responsible for intermolecular anharmonicity caused by specific interaction between the neighbor molecules.[25,26] Consequently, this suggests that there is no local specific interaction between i-PP and EHR57 components.

Figure 4 compares the relaxation spectra $H(\tau)$ of the blends, which are calculated from both G' and G'' using the Tschogel equations[27]

$$H(\tau) = \frac{dG'}{d\ln\omega} - \frac{1}{2}\frac{d^2G'}{d(\ln\omega)^2}\bigg|_{1/\omega=\tau/\sqrt{2}} \tag{3}$$

and

$$H(\tau) = \frac{2}{\pi}\left[G'' - \frac{4}{3}\frac{dG''}{d\ln\omega} + \frac{1}{3}\frac{d^2G''}{d(\ln\omega)^2}\right]\bigg|_{1/\omega=\tau/\sqrt{5}} \tag{4}$$

As seen from Figure 4, the relaxation spectra determined from the master curves of G' agree very well with those determined from G''. The spectrum for the i-PP/EHR57 blend falls off rapidly with increasing τ, indicating that the longest relaxation mechanism of the blend is the entanglement slippage. The results were independent of the blend ratio, suggesting that the miscibility of i-PP/EHR57 blends are maintained at any composition. On the other hand, the spectrum for the i-PP/EHR30 blend extends for a long time, which will be associated with phase separation.[1–6]

For the miscible i-PP/EHR57 blends, G' and G'' are proportional to ω^2 and ω, respectively, in

Table II   Dynamic Viscoelastic Properties in the Terminal Zone and Apparent Activation Energy for i-PP, EHR57, and Their Blends

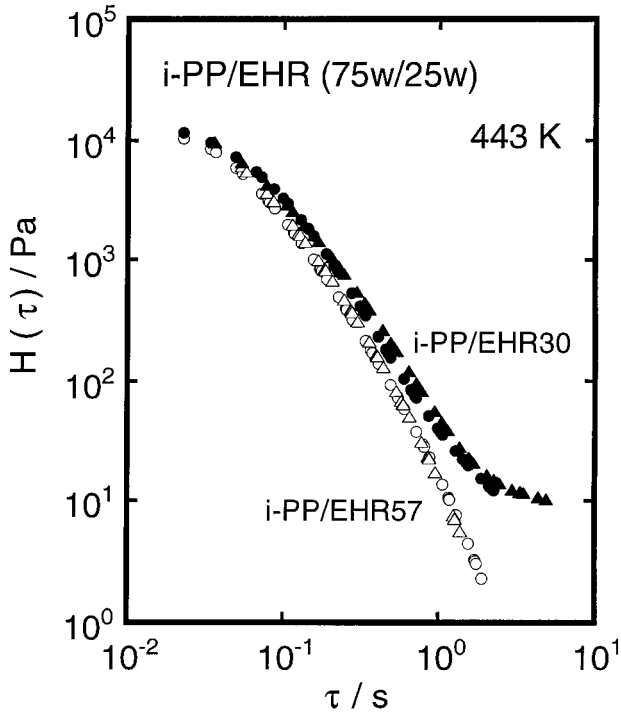| Sample	$\eta_0 \times 10^{-3}$ (Pa-s)	$J_e^0 \times 10^5$ (Pa^{-1})	$\tau_W \times 10^2$ (s)	ΔH (kJ/mol)
i-PP	0.89	4.9	4.4	40.3
i-PP/EHR57				
75/25	1.06	5.1	5.4	40.2
i-PP/EHR57				
50/50	1.27	5.5	7.0	40.6
i-PP/EHR57				
25/75	1.55	5.6	8.7	40.4
EHR57	1.88	6.2	12	40.5

Figure 4 Relaxation spectra calculated ($\bigcirc$, $\bullet$) from the storage moduli [eq. (3)] and ($\triangle$, $\blacktriangle$) from the loss moduli [eq. (4)] at 443 K for i-PP/EHR (75 w/25 w) blends.

the terminal zone. Therefore, the rheological parameters in the terminal zone, i.e., the zero-shear viscosity η_0, the steady-state compliance J_e^0, and the weight-average relaxation time τ_W, can be determined by

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega) \tag{5}$$

$$J_e^0 = \lim_{\omega \to 0} (G'/G''^2) \tag{6}$$

$$\tau_W = \eta_0 J_e^0 \tag{7}$$

Figure 5 shows the compositional dependence of η_0 and J_e^0 at 443 K. As seen from the figure, the magnitude of η_0 of EHR57 is twice larger than that of the i-PP. Furthermore, the values of η_0 of the blends are intermediate between those of the pure components and monotonously increase with increasing the EHR fraction.

It has been reported[16,28] that J_e^0 is proportional to entanglement compliance J_{eN}^0 ($= 1/G_N^0$). Furthermore, it was found that J_{eN}^0 of EHR57 is much larger than that of i-PP because M_e of EHR57 is much higher than that of i-PP. As seen from Figure 5, however, the difference in J_e^0 between i-PP and EHR57 is small. This result will be due to

the difference of their molecular weight distribution.[29-31] Assuming that J_e^0 is proportional to the 3.7 power of M_Z/M_W as in the case of polystyrene,[30] J_e^0 of monodisperse EHR57 can be calculated as 1.9×10^{-5} Pa^{-1}, which is four times larger than J_{eN}^0. If the ratio of J_e^0 to J_{eN}^0 of i-PP is identical with that of EHR57, the M_e of i-PP is estimated to be 4400, which is comparable with the value ($M_e = 4650$) reported by Plazek and Plazek.[19] The values of J_e^0 of the blends are intermediate between those of the pure components and monotonously increase with increasing EHR fraction. The values of τ_W, product of η_0 and J_e^0, of the blends are also intermediate between those of pure components. Table II summarizes the values of the parameters for the i-PP, EHR57, and their blends.

Dynamic Viscoelastic Properties in the Solid State

The temperature dependence of dynamic tensile moduli, E' and E'', for the i-PP, EHR57, and their blend films are shown in Figure 6(a) and (b). As seen from Figure 6(a), E' of the i-PP and blend films decreases with temperature and falls off sharply at the glass-transition temperature (T_g; 200–300 K) and at the melting point of i-PP (438 K). The melting point of i-PP is not affected by the blending of the EHR because the EHR molecules are not incorporated into the crystal region of i-PP as shown in Ref. 13. The magnitude of E' decreases with increasing EHR fraction. The E' of EHR57 falls off rapidly around T_g (230 K) and
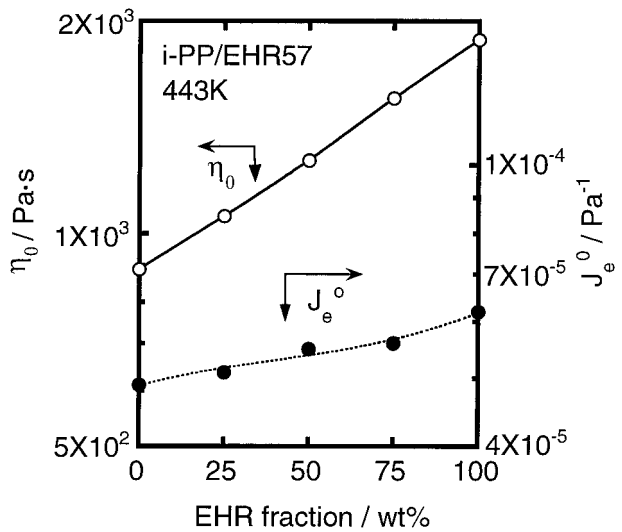

Figure 5 Compositional dependence of the zero shear viscosity η_0 and the steady-state compliance J_e^0 for the miscible i-PP/EHR57 blends at 443 K.
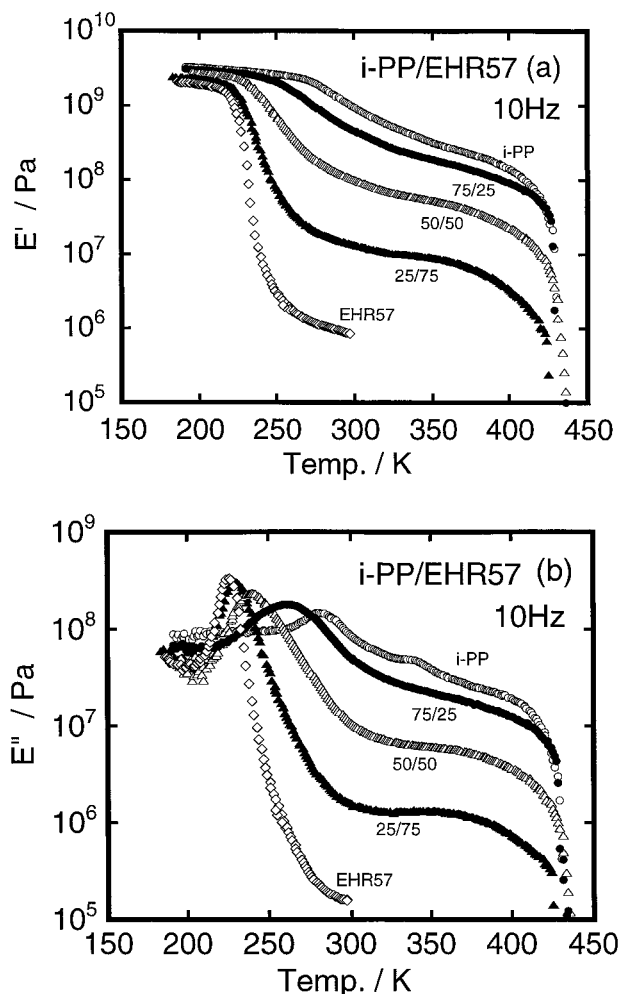
Figure 6 Temperature dependence of (a) the storage modulus E' and (b) loss modulus E'' for i-PP, EHR57, and their blend films: (○) i-PP 100%; (●) i-PP 75%; (△) i-PP 50%; (▲) i-PP 25%; (◇) EHR57 100%.

shows a rubbery plateau. As seen from Figure 6(b), a shoulder peak appears around 340 K only for the i-PP film and the magnitude of this peak is diminished by the blending of EHR57. The relaxation should be due to a transition from a semi-hexagonal (smectic) form to monoclinic α form. Similar relaxation peaks have been also observed for the compatible blend of i-PP with hydrogenated oligo(cyclopentadiene).[32] Furthermore, Figure 6(b) shows that the E'' curves of the blends show a single peak at temperatures between 200 and 300 K, being ascribed to a micro-Brownian motion of amorphous chains, i.e., a glass transition. The peak temperature decreases with increasing EHR57 fraction. The single glass-relaxation process of the i-PP/EHR57 blends demonstrates that the EHR chains are incorporated into the amorphous i-PP region in the solid state.

Several theoretical equations, evaluating the relation between T_g and composition in such a random copolymer or a miscible blend showing a single T_g, have been proposed. An example is the Fox equation[33]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{8}$$

where T_g is the glass transition temperature, T_{gi} is that of the i component, and w_i is the corresponding weight fraction. Figure 7 compares the experimental values obtained from the E'' peak, represented by open circles in the figure, and the theoretical values calculated from the Fox equation, represented by the solid line. The axis of the abscissa in the figure shows the weight fraction of EHR in amorphous parts of the blends, which was calculated from the degree of crystallinity estimated using the density. This figure shows an excellent agreement between the calculated and experimental values. This agreement suggests no specific interaction between segments.

Figure 8 shows the temperature dependence of E'' for i-PP, EHR30, and their 75/25 blend films.
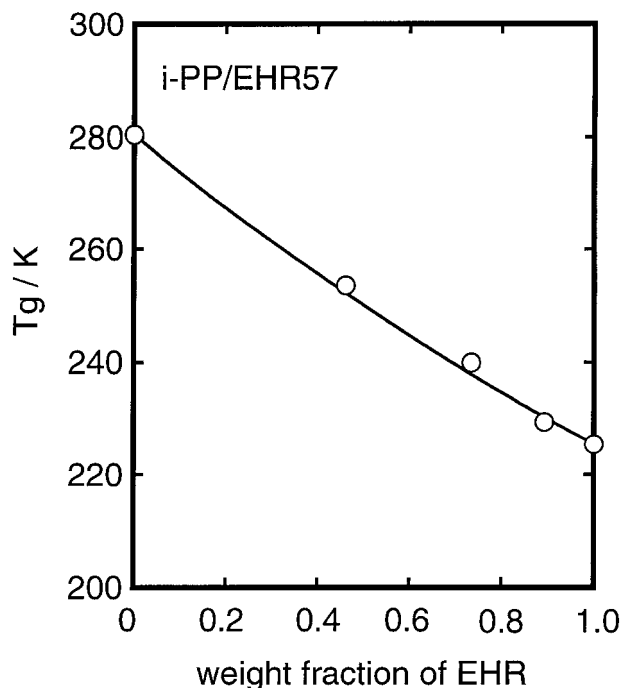

Figure 7 Comparison of calculated and experimental glass transition temperatures. The solid curve denotes the calculated values from the Fox equation and open circles represent experimental values from the E'' peak. The weight fraction of EHR represents the EHR contents of amorphous parts of the blend films.
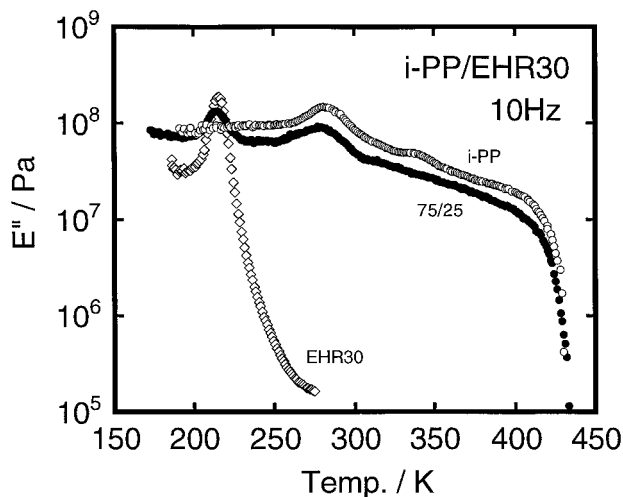
Figure 8 Temperature dependence of E'' for i-PP, EHR30, and their blend films: (○) i-PP 100%; (●) i-PP 75%; (◇) EHR 100%.

As seen from the figure, the i-PP/EHR30 blend film shows two separate peaks at 215 and at 280 K in the E'' curves. The peak in the higher-temperature region of the blend is located at the T_g of i-PP, whereas the peak in the lower-temperature region is located at the T_g of EHR30. This demonstrates that the blend of i-PP/EHR30, which is immiscible in the molten state, shows a phase separation in the solid state.

CONCLUSION

In the present study, we investigated dynamic viscoelastic properties in the melt and solid states of binary blends consisting of i-PP and ethylene-1-hexene copolymers (EHR), in which two types of EHRs, i.e., "ethylene-rich" EHR and "1-hexene-rich" EHR, were employed.

The binary blends of i-PP and the "ethylene-rich" EHR in the molten state showed a second plateau and a long-time relaxation process in the terminal zone, associated with phase separation. The blend film showed two separate glass-relaxation processes associated with those of the pure components, indicating that the blend shows phase-separated morphology in the solid state.

It was found that the dynamic moduli for the binary blends of i-PP and the "1-hexene-rich" EHR are intermediate between those of the pure components in the molten state. The time–temperature superposition principle was applicable to the frequency dependence of the dynamic moduli for the blends, suggesting that the molecular

aggregation state in the higher temperatures is stable over the entire frequency or temperature regions. The apparent activation energy of the blends is constant and is identical with those of i-PP and the EHR. The blend films showed a single glass-relaxation process between those of pure components, indicating that the "1-hexene-rich" EHR chains are incorporated into the amorphous region of i-PP in the solid state. Accordingly, it was concluded that the polymer miscibility in the molten state for the polyolefin blends directly affects the morphology in the solid state. Moreover, it is suggested that the miscible polyolefin blends have no specific molecular interaction between the components.

REFERENCES

1. D. Graebling, R. Muller, and J. F. Palierne, *Macromolecules,* **26,** 320 (1993).
2. L. A. Utracki, *Polymer Alloys and Blends,* Hanser, Munich, 1989.
3. S. Onogi, T. Masuda, and T. Matsumoto, *Trans. Soc. Rheol.,* **14,** 275 (1970).
4. T. Masuda, A. Nakajima, M. Kitamura, Y. Aoki, N. Yamauchi, and A. Yoshioka, *Pure Appl. Chem.,* **56,** 1457 (1984).
5. M. Yamaguchi and K. Suzuki, *J. Soc. Rheol. Jpn.,* **23,** 125 (1995).
6. S. Maeda and E. Kamei, *J. Soc. Rheol. Jpn.,* **22,** 145 (1994).
7. S. Wu, *J. Polym. Sci. Part B, Polym. Phys.,* **25,** 2511 (1987).
8. Y. Aoki, *Polym. J.,* **16,** 431 (1984).
9. E. Marutuscelli, C. Sellitti, and C. Silvestre, *Makromol. Chem. Rapid Commun.,* **6,** 125 (1985).
10. S. Shibasaki, E. Takatori, T. Inoue, and K. Osaki, *J. Soc. Rheol. Jpn.,* **18,** 39 (1990).
11. E. Takatori, S. Shibasaki, K. Osaki, and M. Kurata, *J. Soc. Rheol. Jpn.,* **16,** 171 (1988).
12. J. W. Teh, A. Rudin, and H. P. Schreiber, *Plast. Rubb. Proc. Appl.,* **4,** 149 (1984).
13. M. Yamaguchi, H. Miyata, and K. Nitta, *J. Appl. Polym. Sci.,* to appear.
14. E. T. Hsieh and J. C. Randall, *Macromolecules,* **15,** 353, 1402 (1982).
15. H. Miyata, M. Yamaguchi, A. Akimoto, and K. Nitta, *Polym. Prep. Jpn.,* **44,** 192 (1995).
16. J. D. Ferry, *Viscoelastic Properties of Polymers,* 3rd ed., Wiley, New York, 1980.
17. W. W. Graessley, *Adv. Polym. Sci.,* **16,** 1 (1974).
18. J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci. Part A-2,* **6,** 967 (1968).
19. D. L. Plazek and D. J. Plazek, *Macromolecules,* **16,** 1469 (1983).
20. D. S. Pearson, L. J. Fetters, L. B. Younghouse, and J. W. Mays, *Macromolecules,* **21,** 478 (1988).

21. W. W. Graessley, *Physical Properties of Polymers,* American Chemical Society, Washington, DC, 1993.

22. A. N. Dunlop and H. L. Williams, *J. Appl. Polym. Sci.,* **14,** 2753 (1970).

23. M. Fujiyama and H. Awaya, *J. Appl. Polym. Sci.,* **16,** 275 (1972).

24. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.,* **77,** 3701 (1955).

25. T. Kijima, K. Koga, K. Imada, and M. Takayanagi, *Polym. J.,* **7,** 14 (1975).

26. O. Yamamoto, *Polym. J.,* **2,** 509 (1971).

27. N. W. Tschoegl, *Rheol. Acta,* **10,** 582 (1971).

28. W. W. Graessley, *Adv. Polym. Sci.,* **16,** 1 (1974).

29. T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules,* **3,** 116 (1970).

30. T. Masuda, M. Takahashi, and S. Onogi, *Appl. Polym. Symp.,* **20,** 49 (1973).

31. N. J. Mills, *Nature,* **219,** 1249 (1968).

32. A. Cecere, R. Greco, and A. Taglialatela, *Polymer,* **33,** 1411 (1992).

33. T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).