Rheological and Thermal Properties of Binary Blends of Polypropylene and Poly(ethylene-*co*-1-octene)

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ABSTRACT: Dynamic viscoelastic properties of binary blends consisting of an isotactic polypropylene (i-PP) and ethylene-1-octene copolymer (PEE) were investigated to reveal the relation between miscibility in the molten state and the morphology in the solid state. In this study, PEE with 24 wt % of 1-octene was employed. The PEE/PP blend with high PEE contents showed two separate glass-relaxation processes associated with those of the pure components. These findings indicate that the blend presents a two-phase morphology in the solid state as well as in the molten state. The PEE/PP blend with low PEE content showed a single glass-relaxation process, indicating that PEE molecules were probably incorporated in the amorphous region of i-PP in the solid state. The DMTA analysis showed that the blends with low PEE contents presented only one dispersion peak, indicating a certain degree of miscibility between the components of these blends. These results are in accordance with the results of the rheological analysis. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1634–1639, 2001

Key words: polypropylene; poly(ethylene-co-1-octene); blends; rheological properties; thermal properties

INTRODUCTION

Polypropylene-based materials are increasingly attractive because of their low cost, processability, and good balance of properties. In recent years, metallocene ethylene–octene copolymers have started displacing EPR and EPDM as impact modifiers for PP.[1,2] These new polymers are of great interest commercially, and make possible the systematic study of the effects of various molecular characteristics on rheological behavior.[3]

It is well know that as polymer melts are viscoelastic materials, both viscosity and elasticity should be measured. These characteristics are obtained from the viscoelastic spectrum. The resultant data produce master curves, and generate retardation and relaxation spectra.[4]

The immiscible polymer blends in the molten state show a long-time relaxation associated with the phase separation and pronounced elastic properties, such that storage moduli at lower frequency regions are higher than those of the pure

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Table I Characteristics of Polymer Samples

Material	PP	PEE
Manufacturer	POLIBRASIL RESINAS/Brasil	DOW CHEMICAL/USA
Designation	KM 6100	EG 8100
Density at 23°C $(g/cm^3)^a$	0.917	0.887
Melt index (g/10 min)[b]	2.1	2.0
M_w[c]	427900	152950
M_w/M_n[c]	9.2	2.0
Zero-shear viscosity $(Pa \cdot s)^d$	5830	5553

[a] Measured in IMA laboratory by ASTM D792; [b]measured in CENPES/PETROBRÁS laboratory by ASTM D1238; [c]measured in Nitriflex laboratory by ASTM D 1646; [d]measured in DEMA/UFSCar laboratory.

components.[5–7] Numerous studies related to rheological properties of miscible polymer blends have been extensively carried out using various polymer pairs having specific interactions. The rheological behavior is not always simple, because specific interchain interactions like hidrogen bonding lead to the reduction of the entanglement, and the homogeneous phase is no longer maintained during macroscopic flow.[6–8]

The main goal of the present work is to invesigate the miscibility degree of polypropylene (PP) and ethylene/1-octene copolymer (PEE) blends, with different PEE contents, with the aid of rheological measurements and thermal analysis.

EXPERIMENTAL

Materials and Blend Preparation

Commercially available grades of the following polymers—polypropylene (PP) and ethylene/1-octene copolymer (PEE)—were used. The material specifications are listed in Table I.

A Wortex single-screw extruder, model H210, was used to prepare by melt blending the PEE/PP blends, containing different weight percents of

Table II PEE/PP Compositions

Elastomer (PEE) (wt %)	Sample PEE/PP
0	A′
5	A
20	B
50	C
80	D
100	E

PEE. Table II shows the material compositions prepared in the extruder.

The screw speed was set at 80 rpm, and the temperature profile in the extruder from the feed to the metering zone was set at 220°C.

Rheological Measurements

Dynamic shear moduli, i.e., storage shear modulus, G' and loss modulus, G'', at 220°C, were measured using a cone plate-type rheometer (Rheometrics Dynamic Stress rheometer, SR 200) in the angular frequency range of 0.01 to 100 rad/s.

Thermal Analysis

A dynamic mechanical analyzer (DMTA MK III) was used to measure G', G'', and tan δ of PEE,
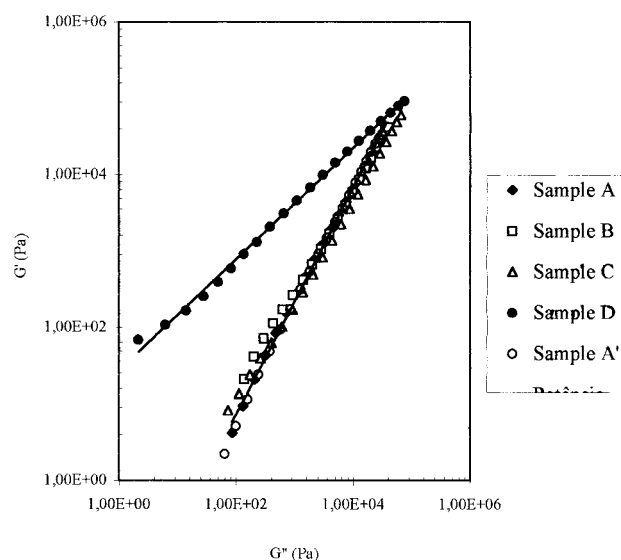

Figure 1 Master curves for G' vs. G'' plots for (a) A; (b) B; (c) C, and (d) D at 220°C.
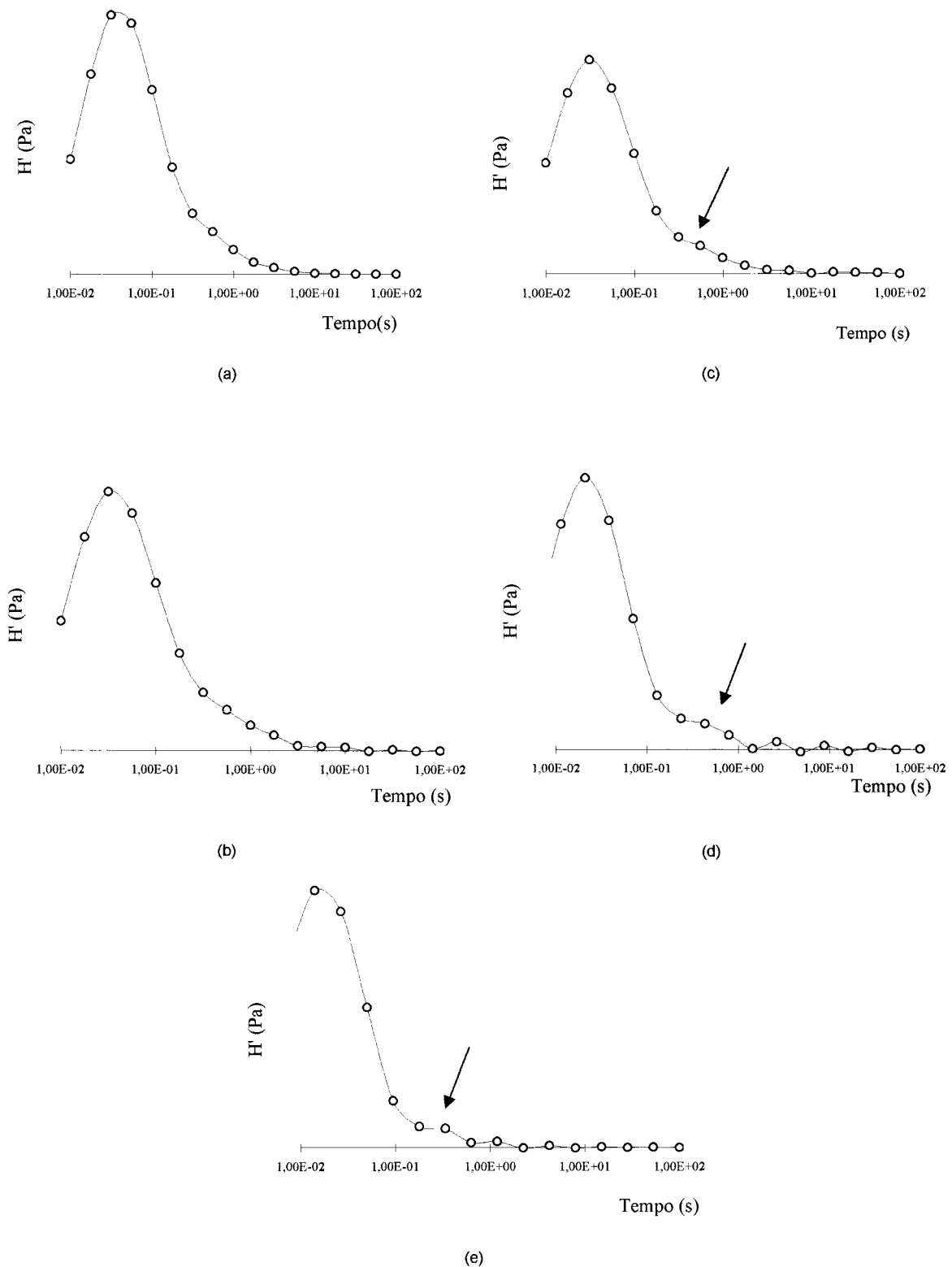
Figure 2   Relaxation spectra calculated from the storage moduli G' at 220°C for (a) sample A′; (b) sample B; (c) sample C; (d) sample D; (e) sample E.

PP, and PEE/PP blends at temperatures between −60 and 70°C at a constant frequency of 1 Hz and a heating rate of 1°C/min^{-1}. The samples specimens have the following dimensions: length 24 mm, width 9 mm, and thickness around 2.0 mm.

RESULTS AND DISCUSSION

Dynamic Viscoelastic Properties in the Molten State

The development of theories and experimental techniques that may be useful for determining polymer–polymer miscibility has been the primary focus in polymer blend research. Criteria for rheological compatibility of PEE/PP blends have been suggested by Han.[9] The criteria proposed make use of plots of storage modulus (G') against loss modulus (G''). Miscible blends tend to present plots that yield correlations that are independent of blend composition, but dependent upon blend composition in the case of incompatible blend systems. Figure 1 shows the G' vs. G'' plots for PEE/PP blends.

The results show a dependency of G' on G'', indicating that blends with higher PEE contents tend to be immiscible. The PEE/PP systems with low PEE content (sample A) presented a correlation similar to that of the pure polymer (sample A′). This result suggests that in blends with low PEE content (up to 5 wt %), an interdiffusion of the polymer chains across the phase boundaries should occur, resulting in enhancement of the component interaction. This behavior was already reported previously.[10] Figure 1 also shows that PEE/PP system presents a lower correlation between G' and G'', indicating that the loss modulus (G'') increases in relation to the storage modulus (G'). This behavior may be attributed to the fact that with PEE addition, materials with higher energy dissipation are produced.

Figure 2 compares the relaxation spectra $H(\tau)$ of the PEE, PP, and PEE/PP blends, which are calculated from the eq. (1).[11]
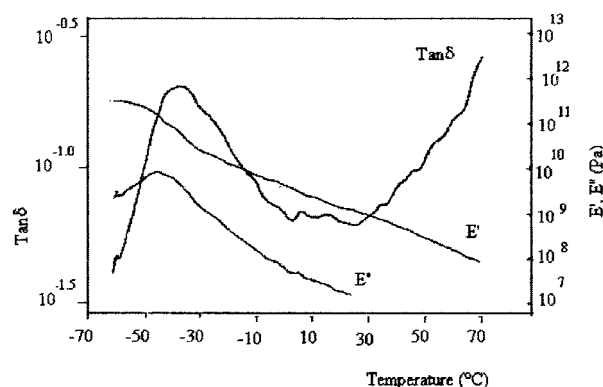
$$G'(\omega) = \sum_{1+1}^{M} H_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \qquad (1)$$

where H_i is the relaxation spectrum, ω is the frequency, and λ is the relaxation time.

As seen in Figure 2, the spectrum for PEE/PP blends with low PEE content (sample A, 5 wt % f
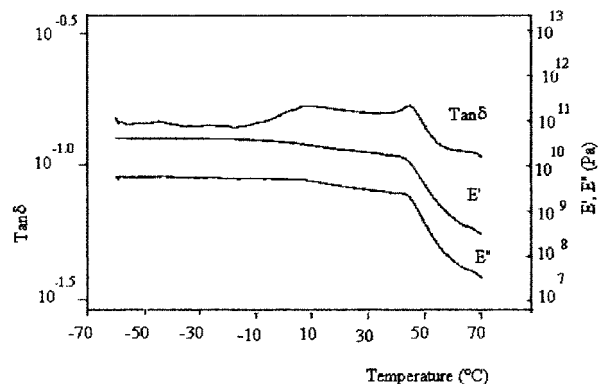
(a)

(b)

Figure 3 Values of E', E'', and tan δ of (a) PP, (b) PEE.

PEE) is similar to the spectrum of sample A′ (PP), i.e., the spectrum falls off rapidly with increasing τ, indicating that the longest relaxation mechanism of the blend is the entanglement slippage. According to Yamaguchi and coworkers,[11] this behavior suggests that blends with low PEE contents present a certain degree of miscibility. The spectrum of the blends with high PEE contents is extended for a long time, which may be associated with phase separation occurrence.

Dynamic Mechanical Properties

The temperature dependence of E', E'', and tan δ of PEE and PP are shown in Figure 3. As seen in the figure, E' of PEE and PP decreases moderately with temperature, and PP tan δ shows two apparent dispersion peaks at temperatures
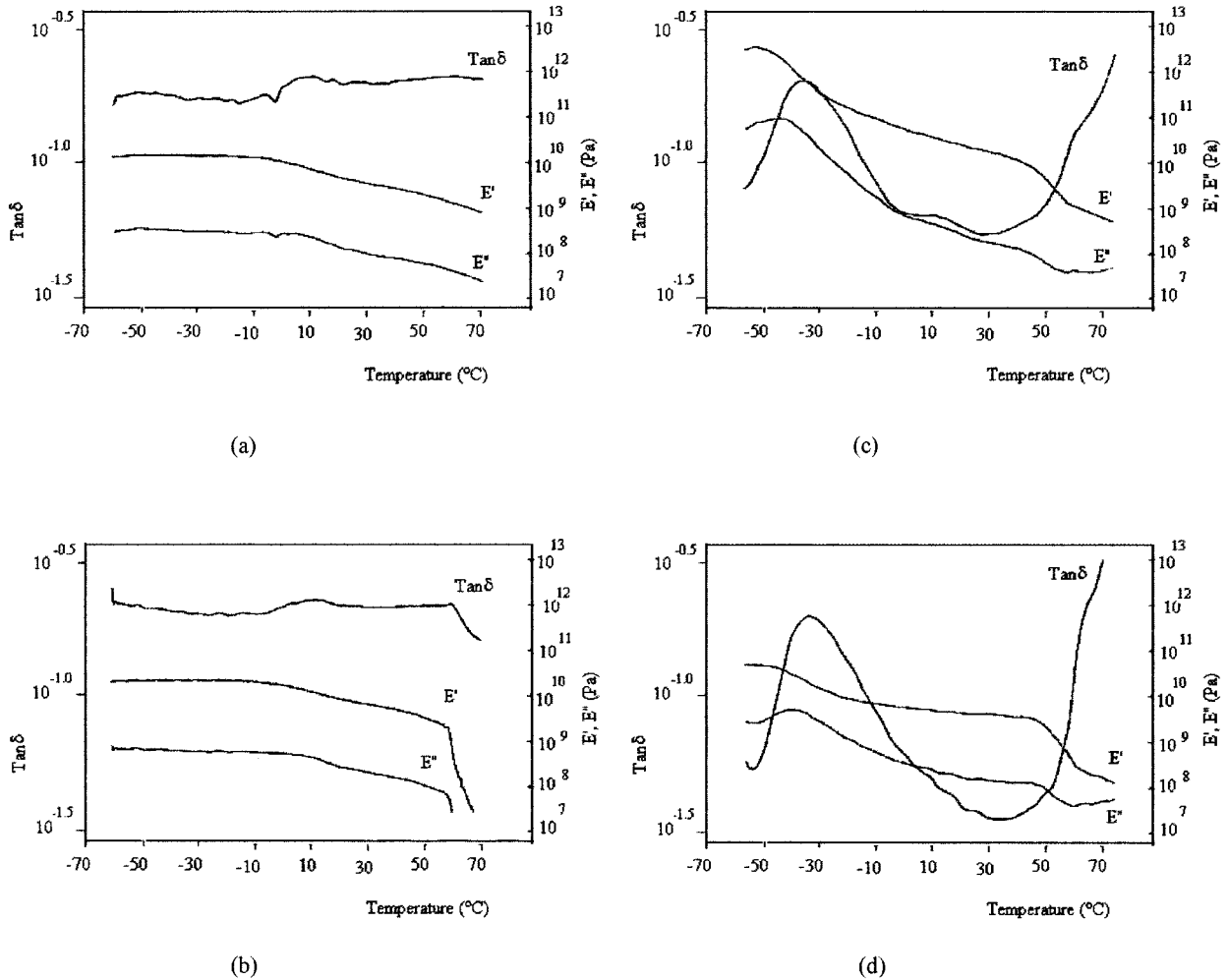
(a)

(c)

(b)

(d)

Figure 4 Dynamic mechanical properties of (a) A; (b) B; (c) C; (d) D.

around 10°C and between 40 and 50°C. These dispersions are assigned as β and α, respectively. Numerous studies on the dynamic mechanical dispersions of i-PP have been reported.[12–14] According to their results, the α-relaxationcan be ascribed to intracrystalline chain motion; the β-relaxation corresponds to T_g in the amorphous regions. PEE presents a more accentuated dispersion peak between -50 and -40°C. This dispersion is attributed to micro-Brownian motion of amorphous chains, i.e., glass–rubber transition emperature (T_g). Figure 4 shows the dynamic mechanical properties of PEE/PP blends. It can be seen that samples with high PEE contents present two peaks of tan δ at temperatures between -50 and -40°C and at around 10°C, which are assigned to β_1 and β_2, respectively. The higher relaxation peak β_2 is attributed to the T_g of the amorphous region of the i-PP, and the lower

relaxation peak β_1 is identified as the T_g of the PEE. For samples with low PEE contents (sample A) only the β_2 peak is observed. This suggests that PEE molecules can be incorporated in the amorphous region of i-PP, indicating a certain degree of miscibility between the components of these blends. These results are in accordance with the results of the rheological analysis.

CONCLUSION

In the present study, we investigate the compatibility for the binary blends of i-PP with ethylene-1-octene copolymer by their rheological and thermal properties. It was found by these properties that blends with high PEE contents are immiscible with i-PP component, and blends with low

PEE contents present a certain degree of miscibility.

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