Rheological Study of Polypropylene Copolymer/Polyolefinic Elastomer Blends

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ABSTRACT: Blends of polypropylene copolymer (PP-cp) and a polyolefinic elastomer (POE) were prepared by a melt-blending process at 210°C and 60 rpm using a counterrotating twin-screw extruder. The POE content was varied up to 25%. The shear viscosity over a wide range of shear rate was measured. All blend compositions showed well-defined zero shear viscosity and shear thinning behavior. The melt viscosity values were between those of the principal components in all cases. Rheology of blends shows different behavior up to concentrations of POE corresponding to the tough–brittle transition. The linear viscoelastic properties (G', G'', η^*, η', η'') were used to check the miscibility of the two components in the melt state. All blend compositions showed a good degree of miscibility over the range of POE concentrations studied. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 665–671, 2002; DOI 10.1002/app.10376

Key words: polypropylene copolymer; polyolefinic elastomer; blends; rheology; miscibility

INTRODUCTION

The impact properties of any thermoplastic material can be improved either by chemical modification or by blending with an elastomeric impact modifier.[1] Polypropylene is one of the most widely used commodity polymers. A copolymer of propylene containing small amounts of ethylene (PP-cp) has better impact properties than those of polypropylene. Impact properties of PP-cp can be further improved by blending it with a thermoplastic elastomer. Impact modification of PP has been studied by blending it with ethylene propylene rubber (EPR) or ethylene–propylene–diene monomer rubber (EPDM).[2–8] Various aspects of impact modification of PP as well as other thermoplastics were previously reviewed by Martuscelli.[9]

The addition of a rubber phase brings about changes not only in mechanical properties but also in rheological properties. The rheological data of a blend are important for optimizing the processing conditions.[10–12] The rheological properties also influence the blend morphology. In our previous investigation, the effect of Engage, a polyolefinic elastomer (POE), on the mechanical properties was reported and it was observed that for a given grade of PP-cp containing about 10–11% rubber, the transition to brittle behavior was observed when total rubber content was about 20–25%, corresponding to a POE concentration of about 10%.[13] The morphological data suggested that distribution of rubber phase was fine and uniform up to 10% POE. At higher concentration a co-continuous phase was observed.

For most polymers ductile–brittle transition takes place at some specific rubber concentration. The miscibility of two polymers and chain entanglement among them seem to influence the viscous behavior of the blends.[14–19] However, there are no rheological data for compositions showing tough–brittle transition.
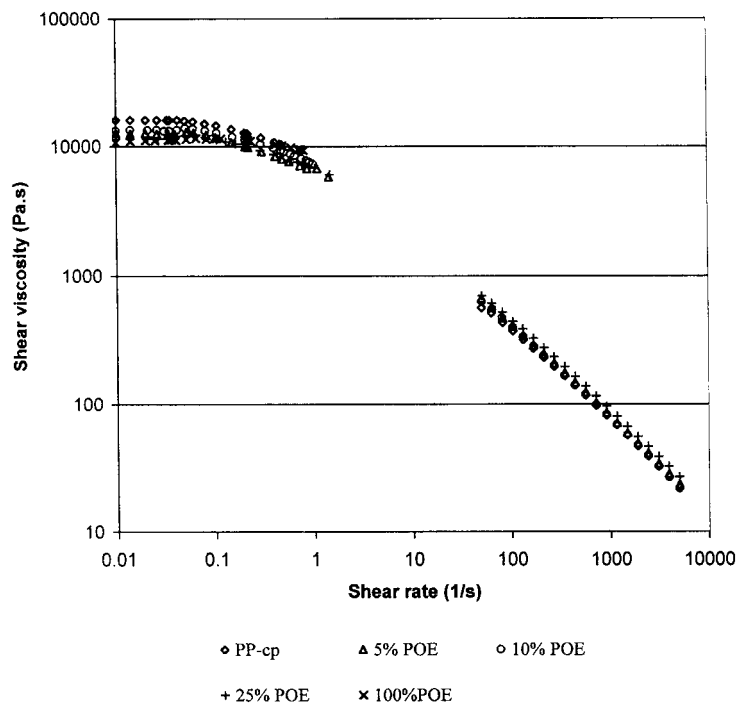
Figure 1   Flow behavior of PP-cp/POE blends at 210°C.

In this present study a relation between melt viscosity, elasticity, and miscibility of the blends with blend composition was investigated.

EXPERIMENTAL

Materials

Commercial grades of PP-cp, CO15EG (Reliance Industries Ltd., India), and Engage [polyolefinic elastomer (POE) EG8150 (Dupont–Dow Elastomers)] were used. The melt flow index (MFI) of these two polymers at 230°C and 2.16 kg load was 1.61 and 1.0 g/10 min, respectively.

Blending

The POE concentration in various blends was varied up to 25 wt %. The required amounts of the two polymers were dry-blended initially and then compounded by using a Haake Rheomix TW100, a counterrotating twin-screw extruder. The temperature profile was as follows: zone I, 120°C; zone II, 150°C; zone III, 190°C; and zone IV, 210°C. The screw speed was maintained at 60 rpm.

Testing

The shear viscosity of the blend over lower shear rate ($0.01–10 \text{ s}^{-1}$) was measured at 210°C using a Haake RT10 apparatus. A parallel-plate geometry (diameter, 35 mm) was used for the study. Shear viscosity over a higher shear rate range up to 5000 s^{-1} was measured at 210°C using a twin-bore capillary rheometer (Rosand Precision Instruments, UK) fitted with two dies, $L/D = 16$ and $L/D = 0$. The pressure drop for a given volumetric flow rate or shear rate was measured simultaneously for both dies. Using these two values of pressure drop, Bagley correction can be applied, as shown below:

$$P_0 = P_S - \frac{P_L - P_S}{L_L - L_S} L_S \qquad (1)$$

where P_0 is the correction to be applied to the pressure measurement across the long die, P_L is the pressure drop (Pa) across the long die ($L/D = 16$), P_S is the pressure drop (Pa) across the short die ($L/D = 0$), L_L is the length of the long die (16 mm in the present work), and L_S is the length of the short die (0.26 mm in the present work).

These capillary rheological data were subjected to Bagley and Rabinoswitch corrections with the help of software provided by the manufacturer. The linear viscoelastic properties as a function of angular velocity (ω) were determined at 210°C over a frequency range of 0.1–40 Hz.

Table I   List of η_0, K, and n of PP–CP/POE Blends at 210°C

% POE	Predicted η_0 (Pa/s)	Experimental η_0 (Pa/s)	K (Pa/s^n)	n (dimensionless)
0	—	16,140	9102	0.78
5	15,851	12,800	6599	0.74
10	15,553	13,670	7773	0.77
25	14,691	11,760	6988	0.78
100	—	11,000	9190	0.85

RESULTS AND DISCUSSION

Steady Shear Flow Behavior

Figure 1 shows the variation of shear viscosity with shear rate for PP-cp/POE blends at 210°C. PP-cp appears to be more viscous than POE and the viscosity of all blend compositions seems to lie between the viscosities of principal components of the blends. All blend compositions exhibited well-defined zero shear viscosity and shear thinning behavior with increasing shear rate. Table I lists the zero shear viscosity (η_0) and power-law pa-

rameters (K and n) for the shear thinning part of viscous behavior, over a shear rate range of $1–5000$ s^{-1}.

The values of zero shear viscosity showed a peculiar behavior. Zero shear viscosity values for all blends are less than that of PP-cp and higher than that of POE. Because zero shear viscosity of POE is less than that of PP-cp, the viscosity of the blend should decrease progressively as the amount of POE increased. However, zero shear viscosity of the blend containing 5% POE was lower than that for the blend containing 10%

Table II   Melt Viscosities of PP–CP/POE Blends at 210°C

| % POE	Shear Rate, γ (1/s)	η (Pa/s) Experimental	η (Pa/s) Theoretical	% Deviation
0	0.01	16,350		
	0.04	15,790		
	0.08	15,000		
	0.2	12,620		
	0.4	11,000		
5	0.01	12,840	16,002	20
	0.04	12,840	15,576	18
	0.08	12,410	14,868	17
	0.2	10,090	12,519	19
	0.4	8,489	11,015	23
10	0.01	13,760	15,693	12
	0.04	13,760	15,321	10
	0.08	13,520	14,676	8
	0.2	11,380	12,457	9
	0.4	9,914	10,982	10
25	0.01	11,580	14,802	22
	0.04	11,580	14,581	21
	0.08	11,580	14,115	18
	0.2	10,090	12,271	18
	0.4	8,636	10,883	21
100	0.01	11,000		
	0.04	11,380		
	0.08	11,580		
	0.2	11,380		
	0.4	10,440		
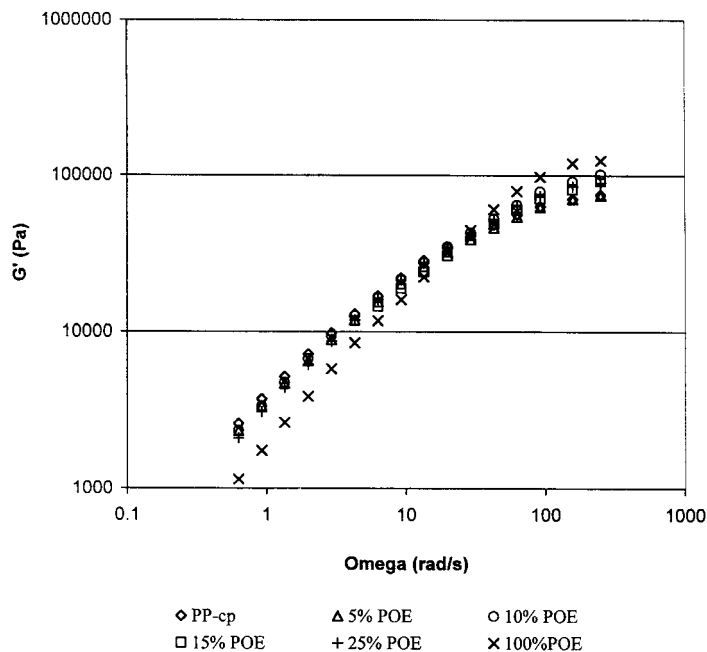
Figure 2   Plot of G' with frequency for PP-cp/POE blends at 210°C.

POE. At a higher concentration (25%) of POE, the zero shear viscosity was lower than that for the other two compositions.

Although values of the consistency index K of PP-cp and POE are almost comparable, the K values of blends were lower than those of PP-cp and POE. The K value for the blend containing 10% POE was higher than that for blends containing 5 or 25% POE. Given that viscosity depends on both K and n, actual viscosities of blends were lower than that of PP-cp. The shear thinning power law index n for all blend compositions was almost comparable to that of PP-cp. The values of
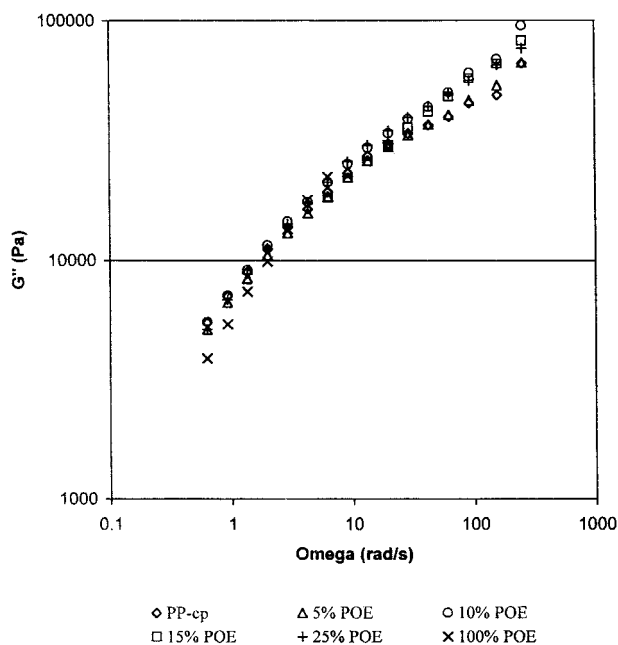

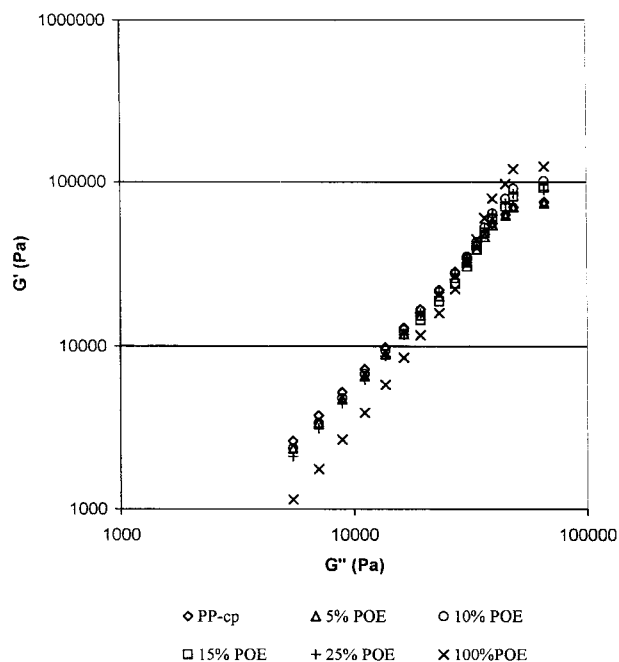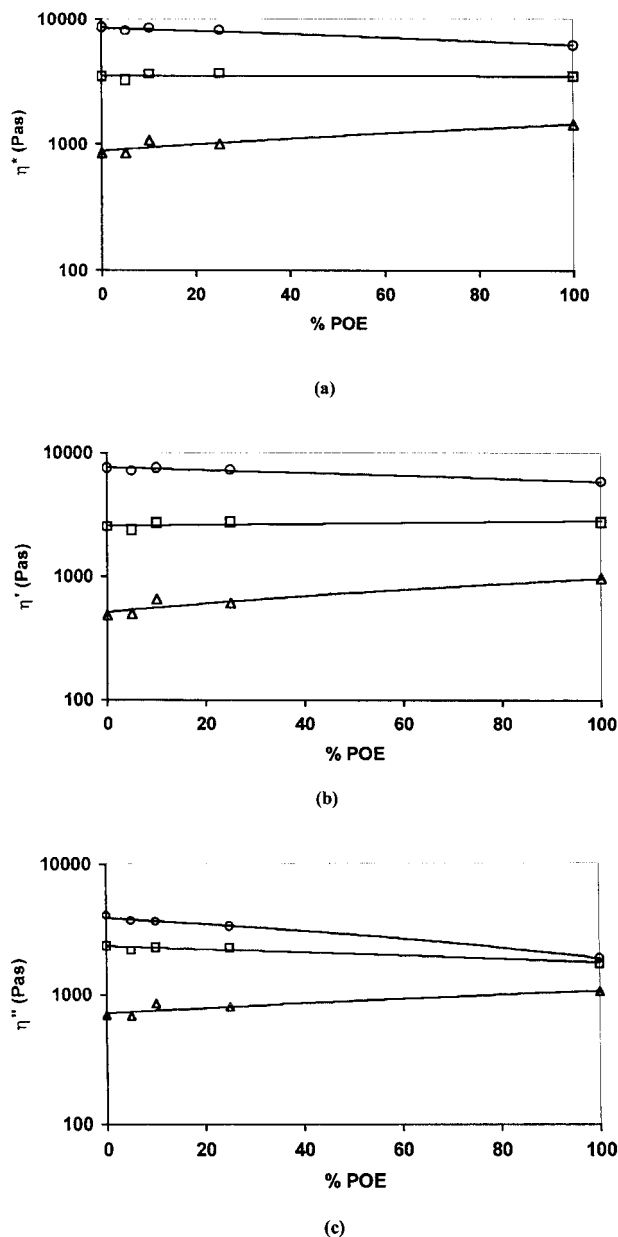**Figure 3**   Plot of G'' with frequency of PP-cp/POE blends at 210°C.

Figure 4   Logarithmic plot of G'' versus G' for PP-cp/POE blends at 210°C.

(a)

(b)

(c)

Figure 5 Plot of (a) η^*, (b) η', and (c) η'' of PP-cp/POE blends at 210°C: —○—, at 0.924 rad/s; —□—, at 9.24 rad/s; —△—, 92.4 rad/s.

n reported in Table I do not show noticeable variation for PP-cp and its blends. The values reported are as per the best fit, computed using linear regression analysis. The POE has a slightly higher power-law index (0.85) compared to that of PP-cp (0.78), indicating that PP-cp was more shear thinning than POE. This also explains the higher viscosity of POE compared to that of PP-cp at higher shear rates. The less shear thinning of POE is obvious, given its highly branched structure. Da Silva et al.[16] reported similar results for PP and polyethylene elastomers.

It is well known that the viscosity of a polymer blend can be described by using the log additivity principle[14,15]

$$\ln \eta_b = \sum w_i \ln \eta_i \qquad (2)$$

where w_i and η_i are the weight fraction and the viscosity of each blend component, respectively, and η_b is the viscosity of the blend.

Table I also compares the prediction of zero shear viscosity based on the log additivity rule. The experimentally observed values were lower than the predicted values. Da Silva et al.[16] reported similar results for the polyolefinic blends. The chain entanglement between PP-cp and POE can be the reason for such higher value. The deviation between predicted and experimental values appears to be the minimum for a POE concentration of 10%. It is known that the tough–brittle transition for PP occurs when the total rubber content is about 20–22%. The present grade of PP-cp contains 10–11% of rubber. Therefore such a transition of PP-cp used in present work would take place when the POE content is around 10%. Results on mechanical properties of this blend of PP-cp with POE were previously reported by Paul and Kale.[13] The maximum improvement of impact properties was observed for POE contents around 10%, corresponding to the transition point. Thus chain entanglement and the viscous behavior seem to be correlated with the tough–brittle transition. If the POE content exceeds the critical limit, the additional amount of POE may not be effective in further chain entanglement and can form just a physical mixture.

Table II lists the predicted melt viscosities of blend compositions at different shear rates calculated from eq. (2) and comparison with experimental results. The predicted values are consistently slightly higher. The difference between predicted values and experimental values was least for the blend containing 10% POE. As argued by Da Silva et al.,[16] the interdiffusion of polymer chains across the phase boundaries can make the polymer blend rheologically a single component. As the POE concentration increased up to a point of maximum interaction, the difference in predicted and experimentally observed viscosity was least. Interestingly, this concentration was also close to the tough–brittle transition. The concentration of POE beyond this limit of such transition seems to result in co-continuous phase morphology[13] and, hence, rheologically different behavior is exhibited.
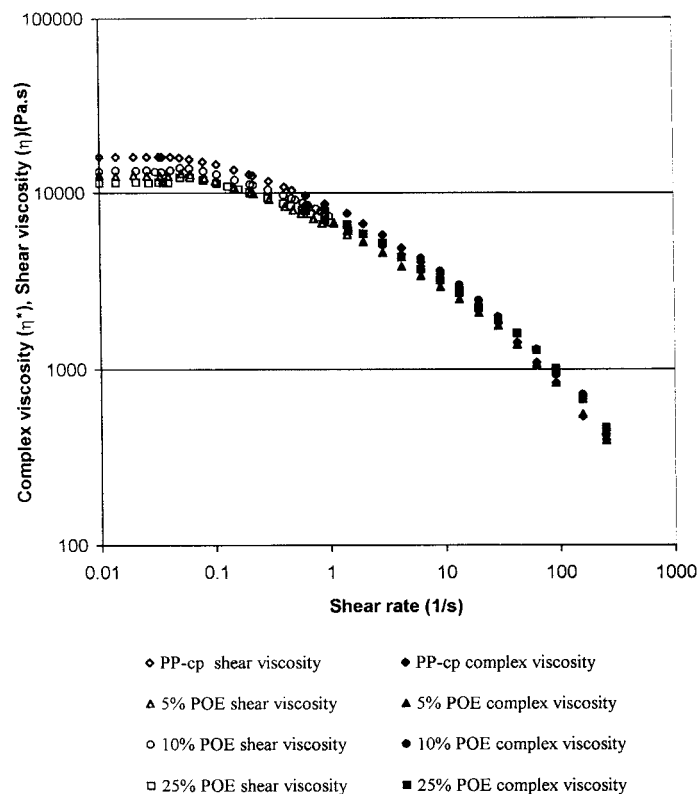
Figure 6 Plot of complex viscosity (η^*) and shear viscosity (η) for PP-cp/POE blends at 210°C.

Dynamic Viscous Behavior

Figures 2 and 3 show the frequency dependency of storage modulus (G') and loss modulus (G'') of the blends. At very low frequencies all blends showed almost the same G' values, but which were higher than that of POE. At higher frequencies, G' values of the blends are between those of the two polymers, PP-cp and POE. POE exhibited the highest G' values at higher frequencies, whereas PP-cp exhibited the lowest. As the POE content increased, the storage modulus increased significantly. It is interesting to see that G' for the blend containing 10% POE is higher than that for the blend containing 25% POE. The increase in G' can be attributed to entanglement of the PP-cp chain segment with POE. It may also indicate positive interaction between the two polymers. Similar observations were reported by Da Silva et al.[16] for the PP and POE blend. At high frequencies, POE presents higher G' values, indicating that the long-chain branches present in POE molecules tend to produce entanglements and, thus, a higher elasticity can be observed. The variation of G'' (loss modulus) also showed similar trends.

As demonstrated by Han and coworkers,[17,18] for polyolefinic blends, certain rheological parameters such as G', G'', η^*, η', and η'' can be used to determine miscibility. The miscibility of polymers can also be judged from the variation of G' and G''. Figure 4 shows the relationship between G' and G''. It is interesting to note that the slopes of these graphs for PP-cp and the blends are almost the same, although that for POE is different. These results suggest that at least up to 25% concentration of POE in PP-cp, a good miscibility between these two polymers can exist. The miscibility between these two polymers has also been demonstrated through morphological data presented by Paul and Kale.[13]

The plot of log complex viscosity (η^*), storage viscosity (η'), and loss viscosity (η'') versus blend compositions for PP-cp/POE blend at 210°C is another classical method to check the miscibility of the blend components (Fig. 5). From the linearity, the PP-cp/POE blend appears to be miscible in a melt state, at least over the range of blend compositions studied. Miscibility of ethylene 1-octene copolymer synthesized by Ziegler–Natta and

metallocene catalysts was also reported by Rana et al.[19] based on similar rheological data and the morphology.

Figure 6 compares the steady-state shear viscosity (η) as a function of shear rate ($\dot{\gamma}$), and the complex viscosity (η^*) as a function of frequency (ω), to check the validity of the Cox–Merz rule; accordingly, $\eta^*(\omega) \cong \eta(\dot{\gamma})$. From Figure 6, it is very clear that the two viscosities match each other at equal values of shear rates or frequencies and, therefore, the Cox–Merz rule applies to the PP-cp/POE blends. Thus, the PP-cp/POE system appears to be a miscible blend, at least up to 25% concentration of POE.

CONCLUSIONS

From the rheological data, it seems that PP-cp/POE blends are characterized by miscibility. The tough–brittle transition appears to be related to rheological behavior. The viscous behavior of blends containing rubber phase up to and beyond such transition is different.

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