Effect of blend composition on the rheology property of polypropylene/poly (ethylene-1-octene) blends

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Abstract In the present study, the dynamic viscoelastic properties for binary blends consisting of polypropylene (PP) and poly (ethylene-1-octene) (POE) were investigated using a Stresstech Rheometer in molten states at 210 °C. The results show that the blends with different content of POE present diversified rheological behaviors. Meanwhile, the blends with 10 wt% and 20 wt% POE show especial rheological behaviors. The dynamic complex viscosity of the blends with 10 wt% and 20 wt% POE are higher than that of others. The storage modulus and loss modulus of the blends with 10–40 wt% POE are different from other blends, and the blends with 10 wt% POE present the largest relaxation time. This behavior is probably related to the miscibility and long chain branch of POE in the PP/POE blends.

Introduction

Polypropylene (PP) is a semi-crystalline polymer with many mechanical and thermal properties, but its toughness, and in particular its notched toughness, is insufficient for PP to be used as an engineering plastic. In the past two decades, much attention has been paid to blends of polypropylene and polyolefin elastomer [1–6], such as ethylene-propylene copolymer (EPR) and ethylene propylene diene monomer (EPDM).

Recent developments in Metallocene catalysts for olefin polymerization have allowed the control of molecular weight distribution, proportion, and distribution of comonomer incorporation. Dow Elastomers Company produces a thermoplastic elastomer, poly (ethylene-1-octene) (POE), which is a copolymer of ethylene and octene, using metallocene technology. When POE is added to PP, it provides enhanced impact properties for automotive exteriors and interiors and other applications requiring superior low temperature performance. Due to this excellent performance, the blends of PP and POE have attracted much attention [7–15].

Most of the existing investigation on PP/POE blends has mainly focused on mechanical properties and rheological properties of low POE content. For instance, Paul S and Kale DD [7, 8] studied the rheological properties and mechanical properties of PP-cp/POE blends. Yang JH [9] studied the brittle-ductile transition of PP/POE blends in both impact and high speed tensile tests. McNally T [10] investigated the influence of composition on rheology, mechanical properties, and phase morphology in PP/POE of 1–30 wt% POE. Kontopoulou M [11] and his partners compared the effect of composition on rheology, morphology, thermal and mechanical properties of PP/POE and PP/ethylene-butene copolymer. Besides, Carriere CJ and Silvis HC [12] measured the interfacial tension between PP and POE using the imbedded fiber retraction technology and researched the effect of POE type on the interfacial tension of PP/POE blends. Da silva ALN and his co-workers [13–15] investigated the mechanical and rheological properties of PP/POE blends of low POE content. They found that the storage modulus of PP/POE blends with 5 wt% and 20 wt% POE were higher than that of the virgin polymers.

However, no detailed examination has been done on the rheological properties of PP/POE blends as a function of blend composition until recently. The main objective of

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this article was to analyze quantitatively the influence of blend composition on the rheological properties of the PP/POE blends and give some especial phenomenon in our study.

Experimental

Materials

Polypropylene (PP1300) supplied by Yanshan Petrochemical Company, China, and POE (Engage 8150, a metallocene catalyzed copolymer of ethylene and 1-octene with 25 wt% of comonomer) provided by Dow Elastomers Company were used in this study. Characteristics of these polymers are given in Table 1.

Blends preparation

PP and POE were mixed in a rubber mixer (Model: XSM-1/20-80). Blends with different compositions [PP/POE = 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, by weight] were prepared at a rotor speed of 64 rpm for 10 min at 210 °C. Disks of 25-mm radius and 2-mm thickness were prepared by clipping the sample of PP, POE, and PP/POE blends.

Rheological measurement

The viscosity and modulus of PP, POE, and PP/POE blends were measured using a Stress Tech Fluid Rheometer (Model: Stress Tech, Relogical Instrument AB, Sweden), a parallel plate configuration was used with a gap of 2 mm and plate radius of 25 mm. Strain sweeps were performed to ensure that all measurements were within the linear viscoelasticity regime, the maximum strain was fixed less than 4%. The linear viscoelastic properties were measured over a frequency of 0.01–100 Hz at 210 °C. The linear viscoelastic properties, namely the complex viscosity $\eta*$ (defined as $\eta* = \eta'–i\eta''$, where η' is the dynamic viscosity or the real part of the viscosity and $i\eta''$ is the imaginary part of the viscosity), the storage modulus G', and the loss modulus G'' were measured.

Results and discussion

Dynamic complex viscosity analysis

The dependence of the logarithm of the complex viscosity value ($\eta*$) on the logarithm of investigated frequencies for PP, POE, and PP/POE blends at 210 °C is shown in Fig. 1. Different rheological behaviors of the blends at low and high frequency range were observed in Fig. 1. All samples at low frequency range present higher complex viscosity values than that at high frequency range. Moreover, as shown in the whole range of explored frequency, PP, POE, and the blends exhibit a drastic decrease in the viscosity value with an increase of frequency, that is, the rheological behavior of the blends system is of pseudoplastic liquid.
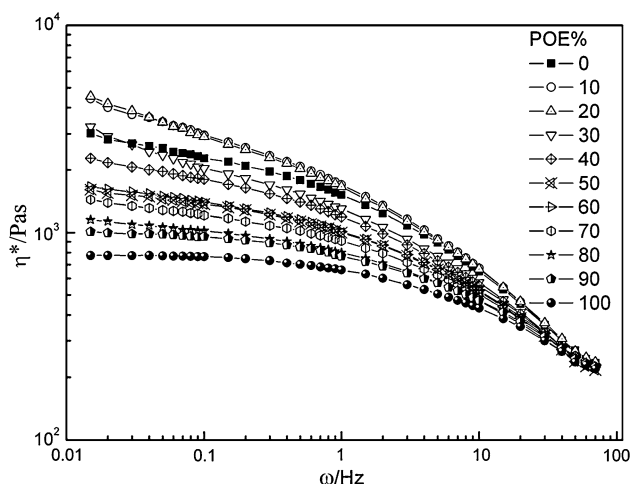
The higher the frequency, the higher is the shear rate. Graessley and co-works [16, 17] derived the viscosity at high shear rates as

$$\eta = (\text{const})M^{0.1}|\dot{\gamma}|^{-3/4} \tag{1}$$

Equation 1 indicates that, at high shear rates, the viscosity is a very weak function of molecular weight and is proportional to $|\dot{\gamma}|^{-3/4}$. According to the entanglement theory, the decrease in viscosity is attributed to a decrease in the entanglement deformation of the entanglement network. Graessley and co-works [16–19] have indeed shown that experiment data fit the theoretical prediction. It is of interest to point that Eq. 1 is in accord with the Bueche-Harding semi-empirical Eq. 2

$$\frac{\eta}{\eta_0} = \frac{1}{1 + 0.006(\lambda_1\dot{\gamma})^{3/4}} \tag{2}$$

In the Graessley theory, the decrease in viscosity with shear rate is viewed as a consequence of the net decrease in entanglement density induced by flow.

Table 1 Characteristics of the polymer sample

Materials	i-PP1300	POE8150
Manufacturer	Yanshan petrochemical (China)	Dow chemical (USA)
mol%1-octene	–	25
Density (kg/m³)	0.900	0.864

Fig. 1 The effect of scanning frequency on the complex viscosity of PP, POE, and PP/POE blends at 210 °C

It should also be noted that for the POE, the non-Newtonian flow only starts at higher frequency; that is, which exhibit a wider range of Newtonian behavior in the experimental conditions analyzed in this work. It is because the flow of blends melting is the result of the chain segments' creep deformation. In the case of PP, the chain conformation mainly takes a compact 3_1 helix conformation. The entanglement of the chain segments is low. When melting, it has better fluidity. And POE has the higher entanglement density than PP due to its long chain branch.

The blends with 10 wt% and 20 wt% POE present a different rheological behavior in relation to the others. It was observed that the blends present a higher viscosity than virgin PP at explored frequency. However, previous studies show a certain degree of miscibility between the components of PP/POE blends at lower POE content [10, 14]. It is generally thought that particle size of dispersed phase is small when blends exhibit miscible behavior. So the distance of molecular chains of matrix (free volume) is big enough to allow infiltration of the dispersed phase. Then the interaction and entanglement between the two polymers are improved to some extent, increasing the melts viscosity.

When the POE content is higher than 30 wt%, the blends show immiscibility and the interaction between PP and POE is small. Therefore, the viscosity of PP/POE blends decreased with POE content. From another point of view, as the proportion of POE increased (more than 20 wt%), POE increased strongly the average end-to-end distance between PP coils, reducing the occurrence of interactions between PP molecules, and the viscosity of the blends decreased. It is also shown that the viscosity gap of the blends decreased as the frequency increased. In the high frequency range, the chain segments align in the shear direction and then viscosity gap of the blends decreased as the frequency increased.

Dynamic modulus analysis

All viscoelastic materials behave more or less solid-like (elastic) and liquid-like (viscous) depending on the rate at which they are deformed. This behavior is related to the fact that strained macromolecules tend to pull back to their original conformation. The dynamic storage modulus, G', is related to the elastic behavior of the energy stored. The dynamic loss modulus, G'', represents the amount of energy dissipated [7, 15]. From the dependence of G' and G'' on molecules in the bulk, some important information about the flow behavior of melts can be found.

The dependence of the storage modulus (G') on the scanning frequency of PP, POE, and PP/POE blends is shown in Fig. 2. It indicates that storage modulus (G') of all samples increase as the frequency increased, so the
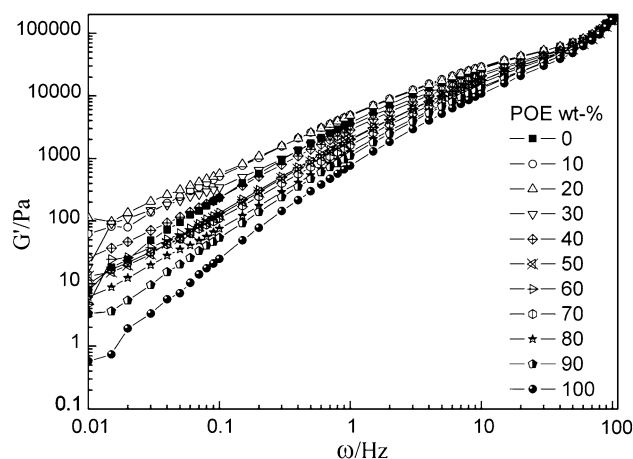
Fig. 2 The effect of scanning frequency on the storage modulus of PP, POE, and PP/POE blends at 210 °C

blends shows higher melt elasticity at high frequency. It also shows that the G' values of blends with POE content 10 wt%, 20 wt%, 30 wt%, 40 wt% are higher than that of virgin PP and other compositions at low frequency. This is because both phases possess elasticity, and therefore they can store in themselves a part of the elastic energy. However, it is reasonable to expect that the dispersed phase would dissipate less of the energy while in the parallel plate, than the continuous phase that wets the parallel plate. Hence the dispersed phase would store more recoverable elastic energy than the continuous phase. Therefore the total recoverable elastic energy would be greater in the two-phase system containing elastomer particles [20]. Moreover, the PP/POE blends presented similar G' value at high frequency.

The dependence of the loss modulus (G'') on the scanning frequency for PP, POE, PP/POE blends is given in Fig. 3. It is shown that the blends with 10 wt%, 20 wt%,
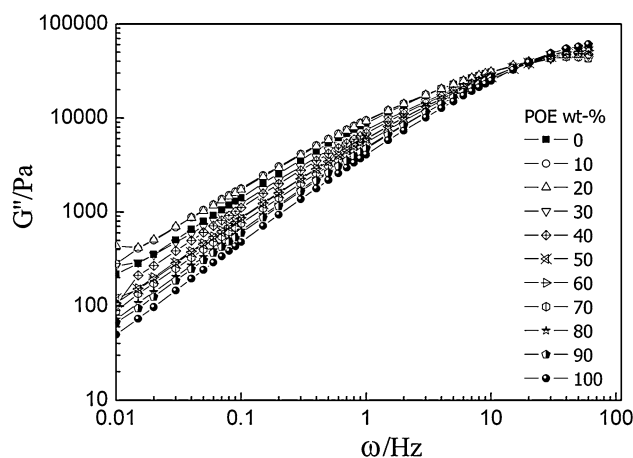
Fig. 3 The effect of scanning frequency on the less modulus of PP, POE, and PP/POE blends at 210 °C

and even 30 % POE have higher G″ values than that of other blends at low frequency. Because the dynamic loss modulus G″ represents the viscous behavior (i.e., the amount of energy dissipated), the addition of POE 10 wt% and 20 wt% to the virgin PP produced a material with the highest energy dissipation. From the view of miscibility of blends, the interaction between blends increased to some extent at lower POE content. The amount of energy dissipated of blends melting with alternating load increase result in the increased loss modulus.

Relaxation time analysis

It is known that the inverse of ω_x can be correlated to the characteristic relaxation time [21, 22]. The relaxation time can be defined from the dynamic modular G′ and G″.

$$\tau_x = 1/\omega_x \qquad (3)$$

where ω_x is the crossover frequency at which G′ and G″ are equivalent. All our samples showed this crossing point in the range of the investigated frequencies, allowing us to determine the τ_x values. According to Doi-Edwards's theory [23], the characteristic relaxation time of polymer chains is directly proportional to the monomeric friction coefficient and somewhat related to the molecular weight.

Figure 4 shows the effect of POE content on the relaxation time τ_x of PP, POE, and PP/POE blends at 210 °C. It could also be observed that the addition of 10 wt% POE caused an increase in the relaxation time of the PP/POE blends. The blend with 10 wt% POE has the largest relaxation time. The relaxation time of the virgin PP is smaller than that of blends with 10 wt% and 20 wt% POE. The relaxation time of the blends decrease with POE content and virgin POE has the smallest relaxation time. This is mainly due to the fact that both storage modulus and loss modulus increase at different rates. These phenomena showed that the blends with 10 wt% and 20 wt% POE had different elasticity and molecular entanglement compared to PP and POE. Moreover, this conclusion agreed well with the results of Fig. 1. The longer relaxation time the blends had, the harder the molecular chains move [15]. Thus, the viscosity and modulus values of blends with POE content 10 wt%, 20 wt% are higher than that of PP, POE, and other blends.

Conclusion

Rheological studies were performed on the blends of PP and POE. The viscoelastic properties of PP, POE, and PP/POE blends were investigated using a Stresstech Rheometer. The complex viscosity η^*, the storage modulus G′, and the loss modulus G″ were all dependent on the sweep frequency. Different rheological behavior was observed with different content of POE in PP. The blends with 10 wt% and 20 wt% POE showed especial rheological behavior. The dynamic complex viscosity and loss modulus of the blends with 10 wt% and 20 wt% POE were higher than that of others due to the miscibility of the blends. At low frequency the G′ values of blends were higher than that of others when PP was matrix. The blend with 10 wt% POE presented the largest relaxation time. This behavior was probably related to entanglement of the long chain branch of POE presented in blends.

Fig. 4 The effect of POE content on the relaxation time τ_x of PP, POE, and PP/POE blends at 210 °C

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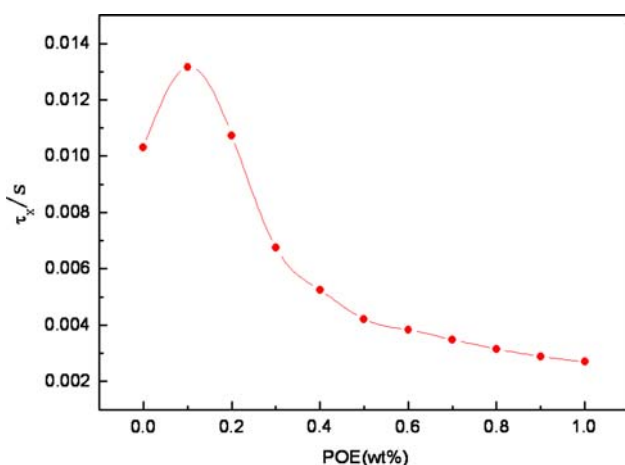
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