

Analysis of brittle–ductile transition of polypropylene/ethylene-octene copolymer blends by scanning electron microscopy and small angle laser light scattering

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Abstract Blends of polypropylene (PP)/ethylene-octene copolymer (EOC) were studied. The influences of blend composition and mixing time on phase morphology development of the blends were investigated by scanning electron microscopy (SEM) and on-line small-angle light scattering (SALS) in detail. The toughness of the PP/EOC blends was investigated over wide ranges of EOC content and determined from the impact fracture energy of the side-edge notched samples. The concept of interparticle distance (ID) and the surface-to-surface interparticle distance (τ) were introduced into this study to probe the size effect on the brittle–ductile transition (BDT) of PP/EOC blends. The results showed that ID based on the SEM photograph and the surface-to-surface interparticle distance (τ) getting from SALS have similar effects on charactering the toughness of the PP/EOC blends. But the surface-to-surface interparticle distance (τ) is more prone to character the BDT of PP/EOC blends than the ID value. On-line SALS can be applied to the research of BDT of PP/EOC blends.

Introduction

Polypropylene (PP) is one of the most versatile commodity polymers because of its excellent properties. It has good chemical and moisture resistance, ductility, stiffness and low density. But its application is limited by its low-impact resistance. In order to improve the low-impact intensity,

different thermoplastic elastomers are added to PP, the brittle–ductile transition (BDT) of PP/elastomers blends is investigated over wide ranges of elastomers content [1–5]. Wu proposed the interparticle distance (ID) model in 1985 [6], it has been extensively used to study the BDT of particle toughened polymers. Experimental results show that the critical interparticle distance (ID_c) depends on the matrix polymers [7, 8]. But the ID model bases on the SEM photograph, which just apply to off-line investigation.

The Small-Angle Light Scattering (SALS) system is one of the most widely used techniques for obtaining structural information, which was applied to study the phase structure and morphology of polymer blends by many researchers [9–14]. It is possible to characterize both microscopic and mesoscopic morphological variables in a single measurement, because SALS provides a statistical evaluation of the shapes and sizes of scattering entities (particles or other morphological structure), and examines the morphologies which are not perfectly defined. Small-angle light scattering has also been used to measure droplet size in flowing two-phase systems [11]. In principle, the shape of the particles can also be derived from the SALS patterns. Unfortunately, two-phase blends under flow are polydisperse and the influences of polydispersity and shape on the SALS patterns are not easily separable, leading to a level of ambiguity in the results and limiting their general acceptance.

Recently, Dow Elastomers Company produces a thermoplastic elastomer, EOC, which is a copolymer of ethylene and octene using Metallocene technology. When EOC is added to PP, it provides enhanced impact properties for automotive exteriors and interiors and other applications requiring superior low-temperature performance. Da Silva [15] compared this blends with EPDM modified polypropylenes and declared that a better process ability

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was noted when EOC was used as an impact modifier. Due to the excellent performance, the blends of PP and EOC have attracted much attention.

Most of the existing investigations on PP/EOC blends have mainly focused on mechanical properties and rheological properties at low-EOC content. For instance, Da silva and his co-workers investigated comprehensively the rheological properties of PP/EOC blends [15–17]. Paul and Kale studied the rheological properties and mechanical properties of PP-cp/EOC blends [18, 19]. Yang [20] studied the BDT of PP/EOC blends in both impact and high-speed tensile tests. McNally [21] investigated the influences of composition on rheology, mechanical properties and phase morphology in PP/EOC of 1–30 wt.% EOC. Kontopoulou and his partners [22] compared the effect of composition on rheology, morphology, thermal and mechanical properties of PP/EOC and PP/ethylene-butene copolymer.

However, no detailed examination has been done on the BDT of PP/EOC blends as a function of blend composition, mixing time until recently. The main objective of this article was to analyze quantitatively the influences of blend composition and mixing time on the BDT of the PP/EOC blends using on-line SALS and traditional method.

Theory

To obtain further information on the phase structure and morphology of polymer blends, the light-scattering theory is introduced in this section. The light scattering signal from on-line SALS, which are analyzed with program compiled by ourselves, and gain I - θ curve (In Fig. 1), where I is luminous intensity (actually gray scale) and θ is scattering angle.

For the case of elastic scattering, the scattering light is described by [23]:

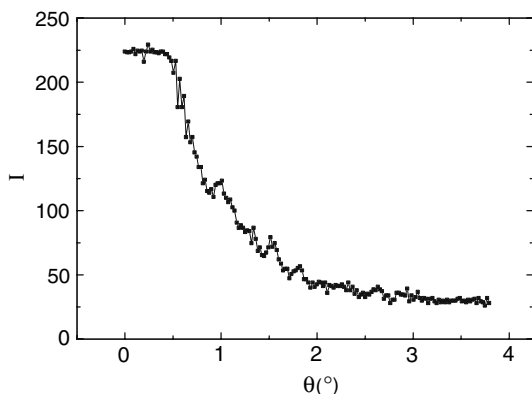


Fig. 1 I - θ curve

$$I_s = 4\pi K V_s \overline{\eta^2} \int_0^\infty \gamma(r) \frac{\sin(hr)}{hr} r^2 dr \quad (1)$$

where K is a proportionality constant and $h = (4\pi/\lambda) \cdot \sin(\theta/2)$. $\overline{\eta^2}$ is the mean square fluctuation and η is the fluctuation in scattering power of the system, which for SALS is equal to the deviation in polarization from its mean value at position r . $\gamma(r)$ is a correlation function corresponding to fluctuation of medium. General for polymer, $\gamma(r)$ may be represented by an empirical equation such as

$$\gamma(r) = \exp(-r/a_c) \quad (2)$$

where the parameter a_c is known as correlation distance and can be used to describe the size of the heterogeneity.

If Eq. (2) is substituted into Eq. (1) one can obtain

$$I(h) = K'' \overline{\eta^2} a_c^3 (1 + h^2 a_c^2)^{-2} \quad (3)$$

Upon rearrangement, this gives

$$\frac{1}{[I(h)]^{1/2}} = \frac{1}{(K'' \overline{\eta^2} a_c^3)^{1/2}} (1 + h^2 a_c^2) \quad (4)$$

Consequently, a plot of $I(h)^{-1/2}$ against h^2 should lead to a straight line having a ratio of slope to intercept of a_c^2 . But a plot of $I(h)^{-1/2}$ against h^2 can lead to two straight lines (see Fig. 2). As for SALS where is small, the corresponding a_{c1} is due to scattering from large particles. As for SALS, when tends to ∞ , the corresponding a_{c2} is due to scattering from small particles. Crugnola and Deanin [24] suggested the dimensions of the a_{c1} and a_{c2} parameters, measured by the light scattering, have the physical significance shown in Fig. 3.

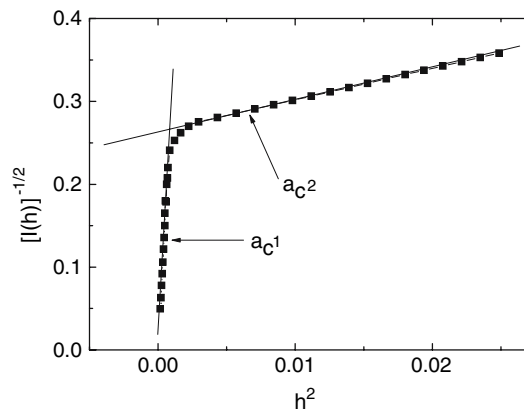


Fig. 2 Sketch map of a_c on curves of $I(h)^{-1/2}$ versus h^2

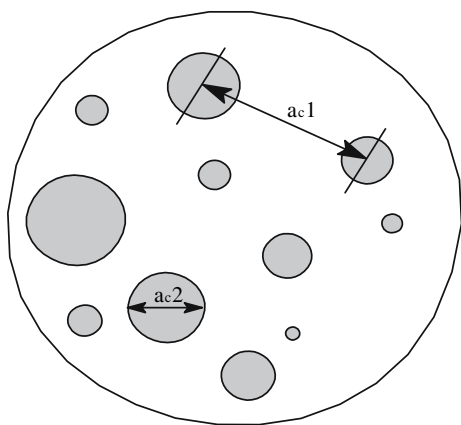


Fig. 3 Physical signification of a_{c1} and a_{c2}

Experimental

Materials

Polypropylene (PP1300) supplied by Yanshan Petrochemical Company, China, and EOC (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 the polymers used are given in Table 1.

Blend preparation

PP and EOC were blended in a rubber mixer (Model: XSM-1/20-80). The morphology of the PP/EOC blends was studied as a function of blend ratio, mixing time. Blends with different compositions [PP/EOC = 70/30, 75/25, 80/20, 85/15, 90/10, 95/5 by weight] were prepared at a rotor speed of 40 rpm for 10 min at 180 °C. In order to study the effect of mixing time on phase morphology evolution, the blend experiments were performed at constant rotor speed of 80 rpm at 180 °C. The mixing time was varied from 1, 1.5, 2, 3, 4, 5, 7, 11 min.

On-line SALS system

The scheme of the on-line SALS system connected to melting mixer is showed in Fig. 4. The detail of on-line SALS system with apparatus and the principle are

Table 1 Characteristics of the polymers used in this work

Polymer	Density (kg/m ³)	MFI (g/10 min) ^a
PP	0.90	1.1
EOC	0.868	0.5

^a For PP, MFI was measured under 2.16 kg at 230 °C. For EOC, MFI was measured under 2.16 kg at 190 °C

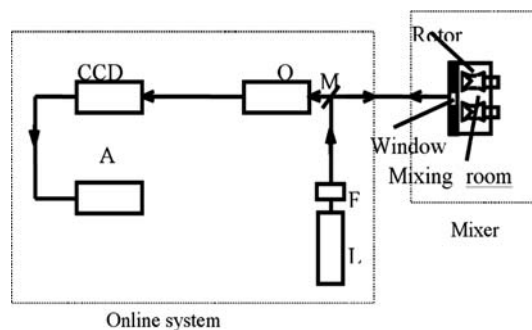


Fig. 4 The Scheme of on-line SALS system

presented [13]. The system is connected to mixer with a window made by quartz glass in case that the laser can throw on the specimen in the mixing room. The scattering information from the mixing specimen is tracked by on-line apparatus and gripped by computer. The data analysis is completed with program compiled by ourselves.

Morphological characterization

The samples were fractured under liquid nitrogen for at least 10 min to make sure that the fracture is sufficiently brittle and one of the phases was preferentially extracted. Since it is difficult to extract the PP phase without having an effect on the EOC phase by using the solvent, all samples were etched in heptane at 60 °C to extract the EOC phase. In order to retain phase morphology, the etching time for different compositions is decided by repeated experiments. All samples were dried for 72 h and coated with gold prior to SEM examination, an XL30ESE scanning electron microscopy operating at 25 kV was used to observe the specimens, several microscopy photographs were taken for each sample.

The photographs were quantitatively analyzed using the IMAGE PRO software. The drop diameter was calculated after analysis of the SEM microscopy photographs. About 200–500 particles were considered to calculate the results. The diameter of a particle was defined by its average length of diameter that was measured at 2-degree intervals passing through the droplet’s centroid. The number average diameter (D_n) and the volume average diameter (D_v) are defined by:

$$D_n = \frac{\sum_i n_i D_i}{\sum_i n_i} \tag{5}$$

$$D_v = \frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3} \tag{6}$$

where D_i is the diameter of each droplet and n_i is the number of droplet with a diameter D_i .

Impact tests

Notched Izod impact tests were performed using a XJ-40A Izod impact tester (made in Wuzhong, China) following ASTM D256, and the sample size was $3.2 \times 12.7 \times 63.5 \text{ mm}^3$. The depth of the notch is 2.7 mm and the width of the notch tip is 0.25 mm. All the tests were performed at $20 \pm 0.5 \text{ }^\circ\text{C}$. All results were the average of at least six measurements.

In order to study the effect of ID and the surface-to-surface interparticle distance (τ) on BDT, it is necessary to determine the ID and τ values of PP/EOC blends. ID and τ are defined by:

$$ID = D_v \left[\left(\frac{k\pi}{6V_r} \right)^{1/3} - 1 \right] \quad (7)$$

$$\tau = a_c1 - a_c2 \quad (8)$$

where V_r is the rubber volume fraction, $k = 1$ for cubic packing, d is the rubber particle diameter. a_c1 and a_c2 are represented as the dimension of matrix phase and dispersed phase, respectively.

Results and discussion

The effect of blend composition on the phase morphology of PP/EOC blends

The morphology of PP/EOC blends with different compositions prepared at the rotor speed of 40 rpm for 10 min at $180 \text{ }^\circ\text{C}$, is depicted in Fig. 5. The light area of the SEM photomicrographs represents the PP phase and black for the EOC phase. The number average diameter (D_n) and the volume average diameter (D_v) of the dispersed phase droplets as a function of the PP concentration are given in Fig. 6. The D_n and D_v are defined by Eq. (1) and Eq. (2), respec-

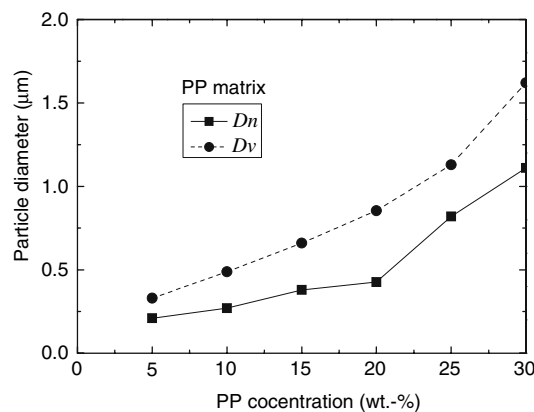


Fig. 6 The D_n and D_v of the dispersed phase as a function of the PP concentration

tively. The effects of EOC concentration on the droplet size distribution in PP/EOC blends are given in Fig. 7.

It can be seen from Figs. 5 to 7 that the dispersed phase domain size increases as the concentration of dispersed phase rises and the size distribution of the dispersed phase domain broadens simultaneously. This can be attributed to

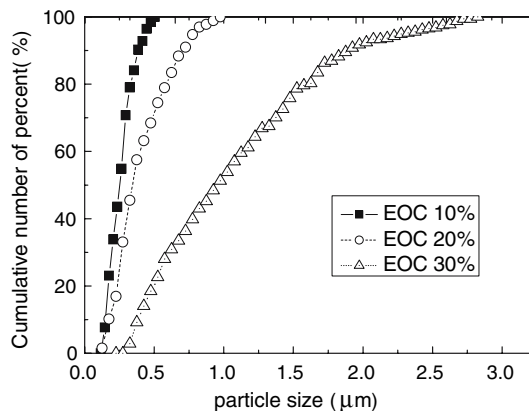
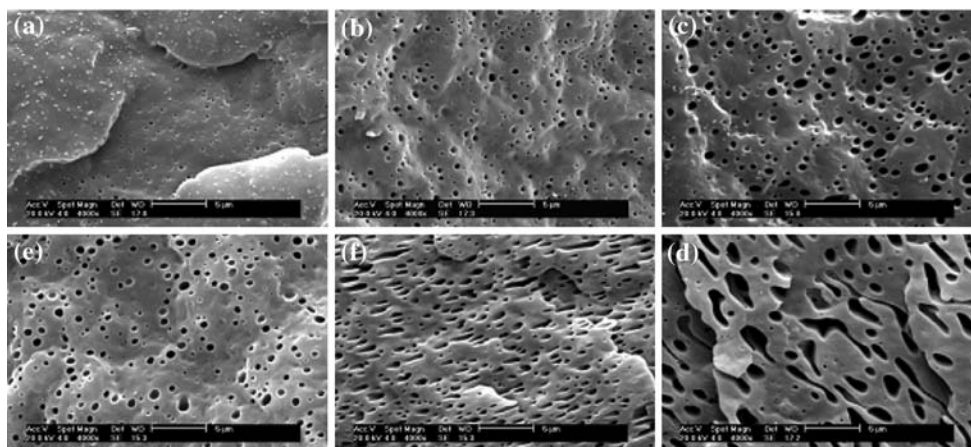


Fig. 7 The effect of EOC concentration on the droplet size distribution in PP/EOC blends

Fig. 5 SEM photomicrographs showing the effect of blend composition on the morphology development of PP/EOC blends (a) PP/EOC = 95/5, (b) PP/EOC = 90/10, (c) PP/EOC = 85/15, (d) PP/EOC = 80/20, (e) PP/EOC = 75/25, (f) PP/EOC = 70/30



the increase of dispersed phase coalescence with dispersed phase concentration. Breakup and coalescence occurred simultaneously during the mixing at the higher concentrations, which led to a much broader distribution of particle size. Very small particles may result from breakup in the high shear regions, while increased coalescence due to more drop interactions will result in very large particles.

The effect of ID and τ on the impact strength of PP/EOC blends

On the basis of SEM micrographs and Eqs. (6), (7), the ID and the impact strength for PP/EOC blends are shown in Fig. 8. The surface-to-surface interparticle distance (τ) on the basis of on-line SALS system is shown in Fig. 9.

It can be seen from Figs. 6 to 8 that when the EOC content increases from 5% to 20%, the domain size of dispersed phase and notched impact strength of the blends increase as the concentration of dispersed phase rises, but the ID decreases with the increase of the concentration of dispersed phase. While the EOC content increases from 20% to 30%, it is obvious that the extent of notched impact strength's increase and ID's value decrease show much less than from 5% to 20%. It reveals that the impact strength of the blends suddenly increases up to a critical value; thereafter it increases slowly with an increasing EOC content. So the critical value of the blends is called as the critical BDT point, which are represented as the critical content (EOC 20 wt.%) and the critical interparticle distance ($ID_c \approx 0.32 \mu\text{m}$). These results indicate that an increasing EOC content, namely, decreasing ID can induce a BDT in the PP/EOC blends. Moreover, the results reveal that these parameters depend on each other at the critical BDT point.

Figure 9 shows the effect of EOC content on impact strength and τ of PP/EOC. The results indicate that the transition from brittle to tough behavior in PP/EOC blends can be achieved by increasing EOC content and decreasing τ .

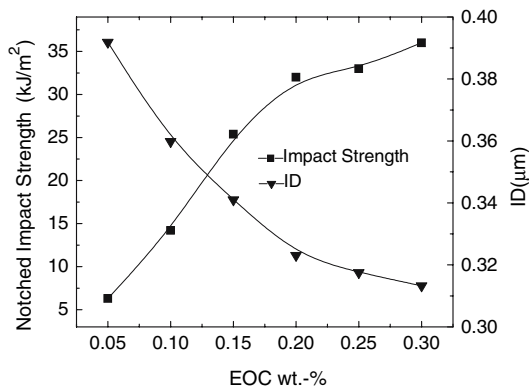


Fig. 8 Effect of EOC content on impact toughness and ID of PP/EOC

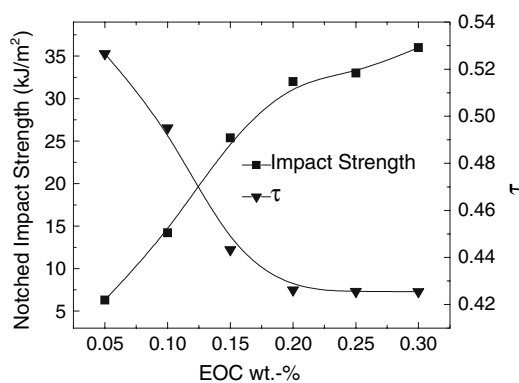


Fig. 9 Effect of EOC content on impact strength and τ of PP/EOC

The surface-to-surface interparticle distance (τ) has a more obvious effect at EOC 20 wt%, there is critical surface-to-surface interparticle distance ($\tau_c = 0.44$) in the blends. It is more prone to character the BDT of PP/EOC blends than the ID value.

The effect of mixing time on the phase morphology development

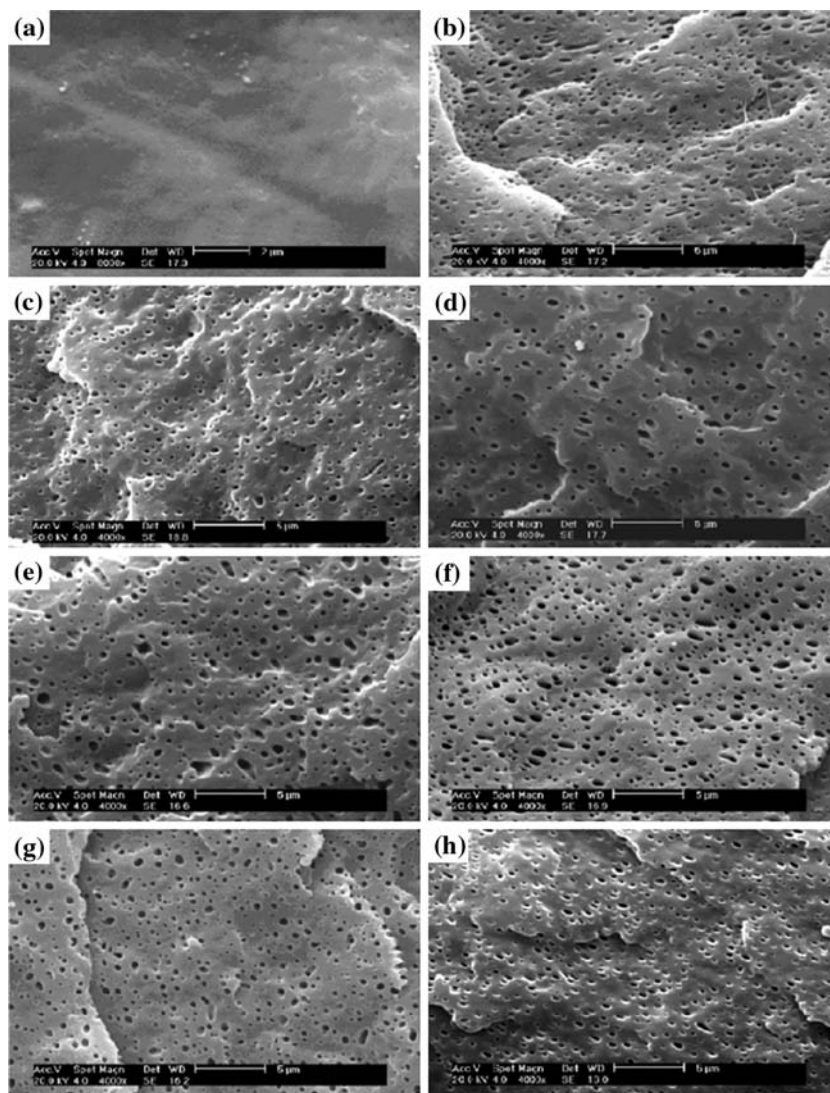
The phase morphology development photomicrographs of PP/EOC (80/20) blends mixed at different mixing time are shown in Fig. 10. PP/EOC (80/20) blends were chosen to study the effect of mixing time on phase morphology development of PP/EOC blends, since the BDT of the blends occurs in PP/EOC (80/20) and the phase morphology shows well-defined droplet-matrix morphology in this blend composition. In Fig. 10(a, b), it can be observed that after 1.5 min of mixing time, PP/EOC (80/20) blends had already formed a well-established droplet/matrix morphology in which the PP component formed the matrix phase and the EOC component became the droplets dispersed in the matrix phase. From Fig. 10(c) to (h), the similar phase morphology persisted in the blends when the mixing time was extended to 11 min.

The number average diameter (D_n) and the volume average diameter (D_v) of the EOC domain as a function of the mixing time in PP/EOC (80/20) blends are presented in Fig. 11. The most significant domain break-up phenomenon occurs within the first 1–2 min of mixing, when melting and softening occur. The phase dimensions do not change significantly with further increase of mixing time. The invariant morphology is dependent on the dynamic equilibrium between droplet breakup and coalescence.

The effect of mixing time on impact strength of PP/EOC blends

It can be seen from Fig. 12 that when the mixing time is prolonged from 1.5 min to 6 min, the notched impact

Fig. 10 SEM micrographs showing the morphology evolution of PP/EOC (80/20) blends as a function of mixing time: (a) 1 min, (b) 1.5 min, (c) 2 min, (d) 3 min, (e) 4 min, (f) 5 min, (g) 7 min, (h) 11 min



strength of the blends increases as mixing time prolongs, but the ID decreases with the prolonging of mixing time. While the mixing time increased from 6 min to 11 min, the

notched impact strength of the blends and the ID do not change significantly. It is obvious that the extent of notched impact strength's increase and ID's decrease show much

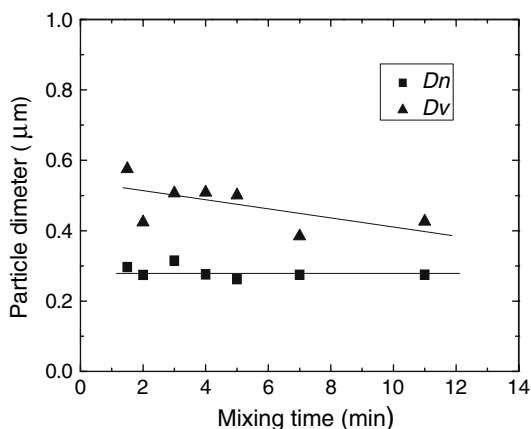


Fig. 11 The D_n and D_v of the dispersed phase as a function of the mixing time in PP/EOC (80/20) blends

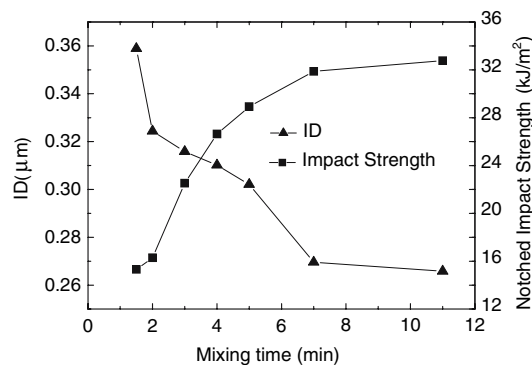


Fig. 12 Effect of mixing time on impact toughness and ID of PP/EOC

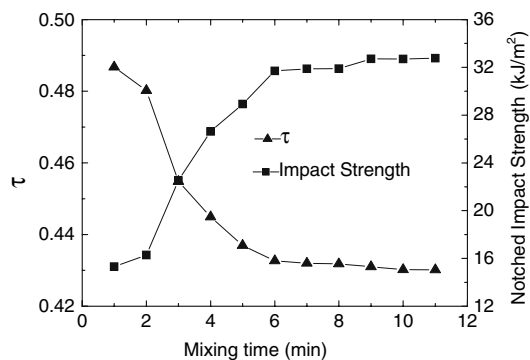


Fig. 13 Effect of mixing time on impact strength and τ of PP/EOC

less than from 1.5 min to 6 min. It reveals that the impact strength of the blends suddenly increases up to a critical value; thereafter it increases slowly with an increasing mixing time. So the critical mixing time of the blends is about to 6 min.

Figure 13 shows the effect of mixing time on impact strength and τ of PP/EOC in detail. It can be more obvious that the increase of the notched impact strength and the decrease of τ occurred in the mixing time from 1 min to 6 min. It can be found that the notched impact strength and the surface-to-surface interparticle distance (τ) have well corresponding relative.

Consequently, when we describe the BDT of the PP/EOC blends, the surface-to-surface interparticle distance (τ) have a better reflection than the ID. Moreover, some experimental results show that the ID_c depends on the matrix polymers [6–8], but the blend composition and the mixing time can be important effects on the BDT of blends in the PP/EOC blends.

Conclusion

The concept of ID and the surface-to-surface interparticle distance (τ) were introduced into this study to probe the size effect on the BDT of PP/EOC blends. The results showed that ID and the surface-to-surface interparticle distance (τ) have a similar effect on charactering the toughness of the PP/EOC blends. SALS can be applied to

the research of BDT of PP/EOC blends. When the BDT of the PP/EOC blends was described, the surface-to-surface interparticle distance (τ) has a better reflection than the ID. The blend composition and the mixing time can be important effects on the BDT of blends in the PP/EOC blends.

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