

Interfacial tension reduction in PBT/PE/clay nanocomposite

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Abstract We investigated the effect of organically modified nanoclay (organoclay) on immiscible polymer blends [polybutylene terephthalate (PBT)/polyethylene (PE)] with a special focus on the role of clay as a compatibilizer. When organoclay (Nanofil 919; Sud-Chemie, Inc.) is added to the blend, the clay first locates at the interface and then selectively locates in the PBT phase due to its affinity with PBT. This results in effective size reduction and narrowed size distribution of the dispersed phase. However, with a small amount of organoclay, it is observed that the clay locates at the interface regardless of its affinity for a specific component to minimize the chemical potential. The interfacial tension change of the blend with the addition of organoclay was quantitatively predicted from extensional force measurement. When the blend is subjected to an extension, the interfacial tension functions as a resistance against drop deformation. When we added organoclay to the blend, the extensional force was significantly reduced, which means that the contribution of the interfacial tension to the total force is reduced. For a 10/90 PBT/PE blend, the interfacial tension was reduced from 5.76 to 0.14 cN m⁻¹ when 1 wt% of organoclay was added. This interfacial

tension reduction arises from the localization of the organoclay at the interface and its nonhomogeneous distribution along the interface, suppressing the coalescence between the droplets, which is a role of a compatibilizer. Conclusively, the immiscible polymer blends can be compatibilized with organoclay. The organoclay changes the blend morphology by interfacial tension reduction due to the localization of the organoclay at the interface and by the viscosity ratio change due to the selective localization by its affinity to a specific component in the blend.

Keywords Morphology · Compatibilization · Coalescence suppression · Interfacial tension · Polymer blend

Introduction

Most polymer blends are thermodynamically immiscible, and they form an interface, due to the unfavorable interaction between the components and high molecular weight. The final properties of blends are strongly influenced by the interface and the size of the minor phase that is determined by the relation between processing conditions and morphology development. When a polymer blend of dilute composition is subjected to mixing, the dispersed phase breaks up into smaller domains due to the deformability of the dispersed phase and evolves to form a final morphology. As the concentration of the dispersed phase increases, the final size of the dispersed phase is determined by the competition between coalescence and breakup. By adding an effective compatibilizer, the morphology can be controlled by lowering the interfacial tension (Lacroix et al. 1996, 1997; Lyu et al. 2002a,b; Sundararaj and Macosko 1995; Wu 1987).

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One of the classical methods to compatibilize two polymers is the physical addition of a block, graft, or star polymer consisting of two components. Block copolymers consisting of two components decrease the droplet size by reducing the interfacial tension. The reduction in domain size by the addition of the block copolymer originates from the breakup of droplets caused by the coalescence suppression effect (Lyu et al. 2002a,b; Sundararaj and Macosko 1995; Puyvelde et al. 2001). This is induced by the steric repulsion between the block copolymers located at the interface and the Marangoni force caused by the concentration gradient of the block copolymer along the interface. Meanwhile, the inorganic solid particles sometimes provide the compatibilizing effect in polymer blend systems. Some research groups have reported the role of organoclay in several immiscible polymer blends as a compatibilizer or as a barrier (Gelfer et al. 2003; Li and Shimizu 2004; Lipatov 2002; Khatua et al. 2004; Voulgaris and Petridis 2002; Ray and Bousmina 2005a,b; Wang et al. 2003; Hong et al. 2006). Ray and Bousmina (2005a,b) defined the role of organoclay for the PP/PS blend and tried to explain the mechanism of compatibilization effect thermodynamically. They described that the adsorption energy of polymer chain to clay at the interface induces the compatibilization of an immiscible blend. However, most of these studies were based on morphology observation, and the explanation of the mechanism of the effect of clay was often inconsistent depending on the blend system investigated [Gelfer et al. 2003 (PS/PMMA); Khatua et al. 2004 (PA6/EPDM); Wang et al. 2003; Ray et al. 2004 (PS/PP)]. The role of solid particles in blends and the formation mechanism of the blend nanocomposite have not yet been clearly elucidated.

Interfacial tension induces unique rheological behavior such as stress overshoot under step shear or additional relaxation time that is often larger than the relaxation time of the homopolymer (Gramespacher and Meissner 1992; Lacroix et al. 1997; Handge and Potschke 2004). In this study, we investigate the change of interfacial tension of blends with and without organoclay by comparing the rheological properties under oscillatory shear and uniaxial extension. For this purpose, polybutylene terephthalate (PBT)/polyethylene (PE) blend composites were prepared

by intensive mixing of PBT, PE, and organoclay. The organoclay was selectively chosen to have more affinity for the PBT component. The morphologies of the PBT/PE blend composites were systematically observed with special focus on the location of organoclay either at the interface or in the PBT phase. Because the compatibilization effect is closely related to the role of organoclay at the interface and results in interfacial tension reduction, we compare the morphology and interfacial tension for the blend systems with and without organoclay.

Experimental

Materials

High-density polyethylene (PE, $M_w=151$ K) used in this study was supplied by Honam Petrochemical Corp. PBT ($M_n=30$ K, $M_w=53$ K) was purchased from Sigma-Aldrich Co. The PE has a melt index of 0.9 g 10 min $^{-1}$ (ASTM D1238, 190 °C 2.16 kg $^{-1}$). The complex viscosity of the PBT and PE at 230 °C and its ratio are listed in Table 1. The nanoclay used in this study is commercially available (Nanofil 919; Sud-Chemie, Inc.). It is organically modified with stearylbenzyl dimethyl ammonium chloride based on montmorillonite, which has affinity with PBT. The PBT/PE blend compositions were varied from 1 to 90 wt% to compare the effect of organoclay on the matrix PBT or on the dispersed PBT phase (Table 2).

Blending

The blending of PBT, PE, and organoclay was performed in an intensive mixer (Rheocord 90, Haake) having a volume capacity of 120 ml. Blends of each composition were prepared under the same mixing conditions. Each blend was dry-mixed before being loaded into the mixer and then mixed for 15 min at a temperature of 225 °C and at a rotation speed of 50 rpm. Blend compositions are listed in Table 2. The blends were compression-molded using a Carver laboratory hot press at 230 °C for 7 min into a mold with a

Table 1 Complex viscosity and its viscosity ratio of PE, PBT, and PBT/clays

Frq (rad/s)	η^* (Pa)				Viscosity ratio		
	PE (K)	PBT (K)	95/5 PBT/clay (K)	90/10 PBT/clay (K)	$\eta_{\text{PBT}}/\eta_{\text{PE}}$	$\eta_{95/5\text{PBT}/\text{clay}}/\eta_{\text{PE}}$	$\eta_{90/10\text{PBT}/\text{clay}}/\eta_{\text{PE}}$
	0.1	10.3	0.82	1.39	69.6	0.08	0.11
1	7.4	0.8	0.9	10.8	0.11	0.12	1.46
50	1.3	0.7	0.5	0.88	0.54	0.39	0.68
100	0.93	0.67	0.47	0.72	0.72	0.51	0.77

Table 2 Composition of PBT/PE blends and the weight ratio of clay/PBT

Blend	Composition (wt%)			Clay/PBT
	PBT	PE	Clay	
1/99 PBT/PE	1	99	0	
5/95 PBT/PE	5	95	0	–
10/90 PBT/PE	10	90	0	–
20/80 PBT/PE	20	80	0	–
80/20 PBT/PE	80	20	0	–
90/10 PBT/PE	90	10	0	–
1/99/5 PBT/PE/clay	0.9	94.3	4.8	5/1
5/95/5 PBT/PE/clay	4.8	90.4	4.8	5/5
10/90/5 PBT/PE/clay	9.5	85.7	4.8	5/10
20/80/5 PBT/PE/clay	19.0	76.2	4.8	5/20
80/20/5 PBT/PE/clay	76.2	19.0	4.8	5/80
90/10/5 PBT/PE/clay	85.7	9.5	4.8	5/90
10/90/1 PBT/PE/clay	9.9	89.1	1	1/10
10/90/3 PBT/PE/clay	9.7	87.4	2.9	3/10
10/90/10 PBT/PE/clay	9.0	82.0	9.0	10/10
90/10/1 PBT/PE/clay	89.1	9.9	1	1/90
90/10/3 PBT/PE/clay	87.4	9.7	2.9	3/90
90/10/10 PBT/PE/clay	82.0	9.0	9.0	10/90

thickness of 1.0 mm and were then annealed at room temperature. In one set of blends, the organoclay concentration was 4.8 wt% for various PBT/PE blends. In another set of blends, organoclay content was varied from 1 to 9 wt% for two different blends, 10/90 PBT/PE and 90/10 PBT/PE blends.

Characterization

To check for any possible reaction or miscibility between PE and PBT, differential scanning calorimetry (DSC) was performed for all blends with 10 mg of each sample under nitrogen flow after the following procedure: first heating run at 10 °C min⁻¹ up to 250 °C and maintaining this temperature for 10 min, cooling to 50 °C at 10 °C min⁻¹, and then second heating run at 10 °C min⁻¹ up to 250 °C min⁻¹ to eliminate thermal history during the blend preparation. There was no shift of the melting temperature during first and second heating. Figure 1 shows the DSC thermograms of the first run of PE and PBT with organoclay and the melting temperatures (T_m) of 20/80 PBT/PE, 20/80/5 PBT/PE/clay, 80/20 PBT/PE, and 80/20/5 PBT/PE/clay blends in the inset. We compared the first run of DSC thermodiagram to show any possibility of reaction between the components. The first run is more informative to indicate the possibility of structural change during processing. In the first run, we did not get the cold crystallization peak of PBT. Most blends did not show any displacement of the T_m peak compared with the T_m of PE and PBT or the formation of a new peak between PE and PBT

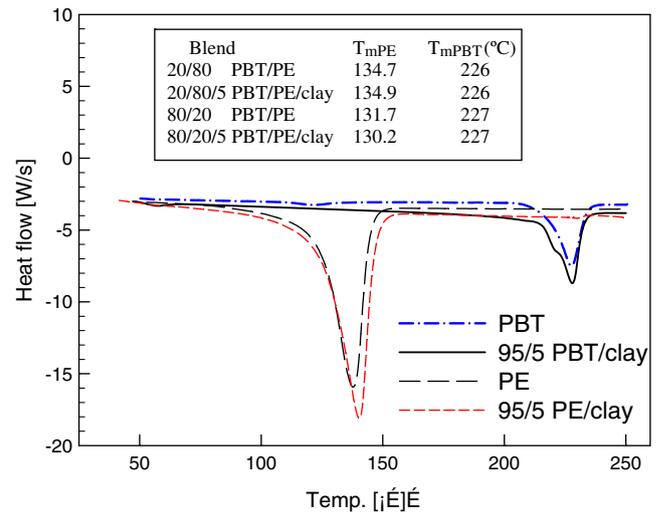


Fig. 1 DSC thermogram of PE, PBT, 95/5 PE/clay, and 95/5 PBT/clay. The melting temperature of 80/20 and 20/80 PBT/PE blends are listed in inset table

when blends were prepared as evidenced in Fig. 1. This implies there is little interaction between PE and PBT. For 80/20 PBT/PE blend, however, the melting temperature of PE was shifted from 134 to 131 °C, which means that the crystal structure of PE was changed due to the existence of PBT chains.

The blend morphology was examined by scanning electron microscopy (SEM; JSM-840A, JEOL, Inc.) operating at an accelerating voltage of 20 K. The samples were fractured in liquid nitrogen and then sputtered with palladium to avoid charging on the fractured surface. To quantitatively analyze the morphology of the fractured surface, the number average (D_n) and the volume-to-surface-area average (D_{vs}) diameter of the dispersed phase were obtained with an image analyzing software (Image-Pro; Media Cybernetics, Inc.). The diameters of long and short axis of each droplet in the SEM picture were measured, and the arithmetic mean of these two values ($D_i = \frac{D_{li} + D_{si}}{2}$) was determined. Then, D_n and D_{vs} were obtained by using the following relation:

$$D_n = \sum D_i / N,$$

$$D_{vs} = \sum D_i^3 / \sum D_i^2$$

where N is the total number of disperse domains (more than 200 drops) observed in the SEM image. The clay dispersion was examined by transmission electron microscopy (TEM; JEM-2000EXII, JEOL, Inc.) operated at an accelerating voltage of 200 kV. The TEM specimens were approximately 40-nm thick and were prepared by cryoultramicrotoming the blends encapsulated in epoxy with a diamond knife.

The rheological properties of samples were measured at 230 and 240 °C by means of RMS800 (TA Instruments) using parallel plates of 25-mm diameter. Complex viscosity

$[\eta^*(\text{Pa})]$, storage modulus $[G'(\text{Pa})]$, and loss modulus $[G''(\text{Pa})]$ as a function of frequency were measured using the dynamic oscillatory mode. A Meissner-type extensional rheometer (RME, TA Instruments) was used to measure the extensional force in uniaxial extension (Schweizer 2000). A small strain rate of 0.05 s^{-1} was chosen to observe the influence of interfacial tension on the extensional force. All measurements were conducted under nitrogen environment to reduce the possibilities of degradation at high temperatures of 230 and 240 °C.

Results

Morphology

For the PBT/PE blends, the addition of organoclay led to a reduction in domain size. Figure 2a shows the average domain sizes (D_{vs}) of the PBT/PE blends and the organo-

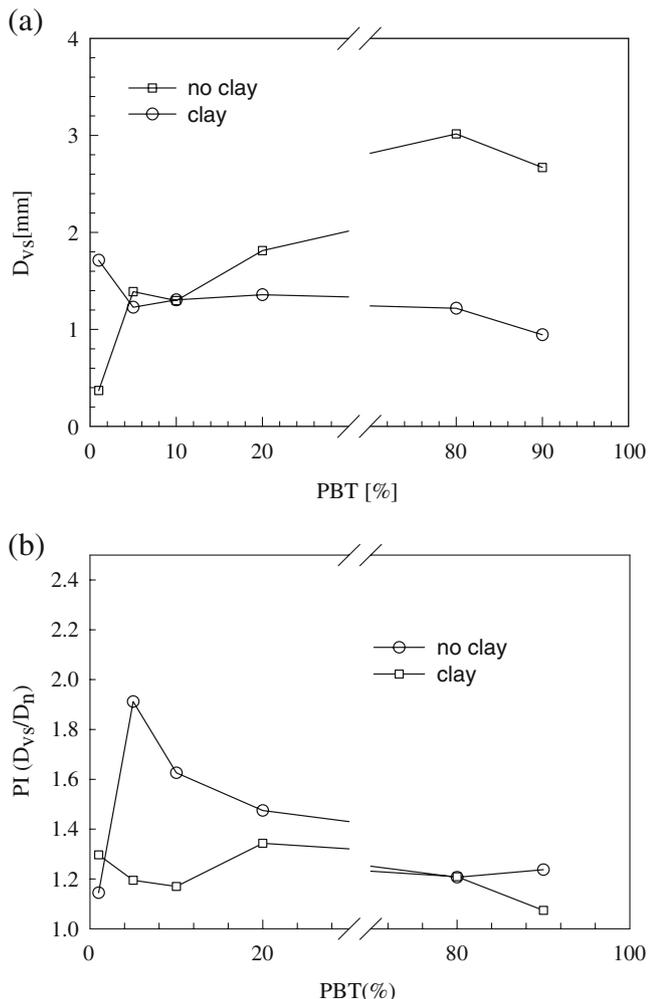


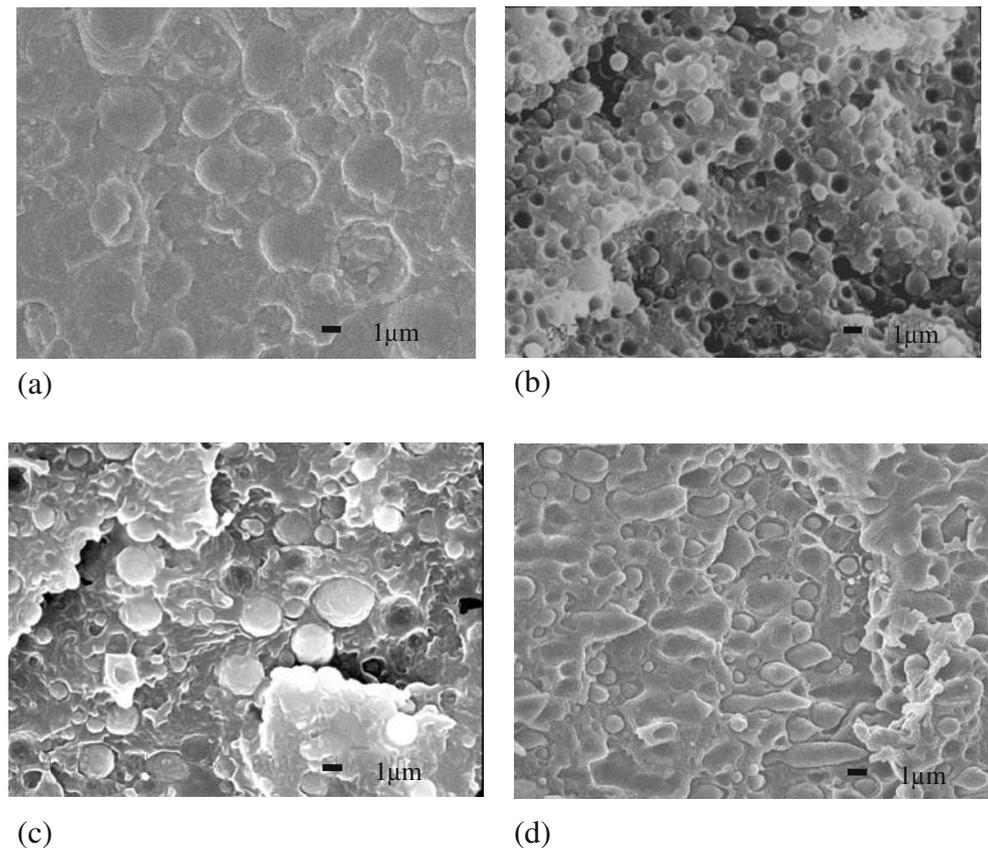
Fig. 2 Average droplet size (D_{vs}) of PBT/PE blends depending on PBT composition (a) and PI (D_{vs}/D_n) (b)

clay-filled PBT/PE blends over a wide composition range. The domain size of the blends increases with PBT content. This is due to the large difference in viscosity ratio. The viscosity ratio is much lower than unity for the blend with PE matrix (Table 1), whereas the viscosity ratio is higher than unity for the blend with PBT matrix. With the addition of organoclay, the domain size converges to an average diameter of 1.0 μm , regardless of the composition. In the blend with PBT matrix, a significant reduction in domain size can be observed with the addition of 4.7 wt% organoclay. Figure 3 compares the SEM pictures of the unmodified 80/20 and 20/80 PBT/PE blends and organoclay-filled 80/20/5 and 20/80/5 PBT/PE blends. The average domain size of the 80/20 PBT/PE blend decreases from 2.5 to approximately 1.0 μm with the addition of organoclay, and the domain is homogeneously distributed (Fig. 3a,b). In the 1/99 PBT/PE blend, it is difficult to expect the size reduction by the addition of organoclay because the PBT domain size is very small (0.37 μm). The polydispersity index of the droplet ($PI=D_{vs}/D_n$) is provided in Fig. 2b to compare the drop size distribution as a function of PBT concentration. The dispersed PE phase has a narrower distribution than that of the dispersed PBT phase, and the PI index is reduced with the addition of organoclay over the entire composition range, which means that the size distribution of the droplets is effectively narrowed with clay.

The TEM observations show where the organoclay is located and how well it is dispersed in the blends. Figure 4 shows the TEM pictures of 10/90/1 PBT/PE/clay, 10/90/5 PBT/PE/clay, 90/10/1 PBT/PE/clay, and 90/10/5 PBT/PE/clay. The TEM pictures exhibit consistent results over all compositions and indicate that all the clay is located in the PBT phase or at the interface, not in the PE phase. When a small quantity of organoclay of 1 wt% is added to 10/90 PBT/PE and 90/10 PBT/PE blends, the organoclay is located at the interface with a nonhomogeneous distribution along the interface (Fig. 4a,c). Although the organoclay used in this study has compatibility with PBT, it locates at the interface (being thermodynamically stable with minimum chemical potential) and appears to envelop the PBT or PE domain. As the clay content increases, additional clay goes inside the PBT phase due to its compatibility with PBT (as can be seen in Fig. 4b,d).

According to morphological observations, the location of organoclay depends on the amount of organoclay and its affinity to the component. With a small amount of organoclay, all of the organoclay is located at the interface. In this region, the nonhomogeneous distribution of the organoclay gives rise to an interfacial tension gradient and results in a tension-gradient-driven flow along the interface caused by the Marangoni force (Lyu et al. 2002a,b; Sundararaj and Macosko 1995; Larson 1999; Edwards et al. 1991). In addition, the steric repulsion between the organoclay at the

Fig. 3 Comparison of SEM pictures of 80/20 PBT/PE (a), 80/20/5 PBT/PE/clay (b), 20/80 PBT/PE (c), and 20/80/5 PBT/PE/clay (d)



interface effectively suppresses coalescence caused by thermal Brownian motion and the collisions caused by hydrodynamic force. When its content increases, a portion of the organoclay locates at the interface, and the rest goes inside the PBT phase.

As the viscosity of clay-filled PBT is higher than the untreated PBT, the addition of clay will change the viscosity ratio of the blend (as shown in Table 1), which is an important parameter in determining the droplet size. The viscosity ratio of PBT and PE significantly increases to 6.76 when 10 wt% clay is added to PBT, whereas it is 0.08 for the unfilled PBT and PE. In the PBT minor region, the deformability of PBT domain changes according to the addition of clay, and the size of PBT domain is determined by the competition of the coalescence suppression effect due to the organoclay at the interface and the viscosity ratio change due to the selective localization of organoclay into the PBT domain. Therefore, it should be pointed out that the change of blend morphology by the addition of organoclay depends on the content and the location of organoclay. In addition, the organoclay located at the interface can morphologically induce the compatibilizer effect on the immiscible polymer blends. To make it clear whether the organoclay located at the interface brings about

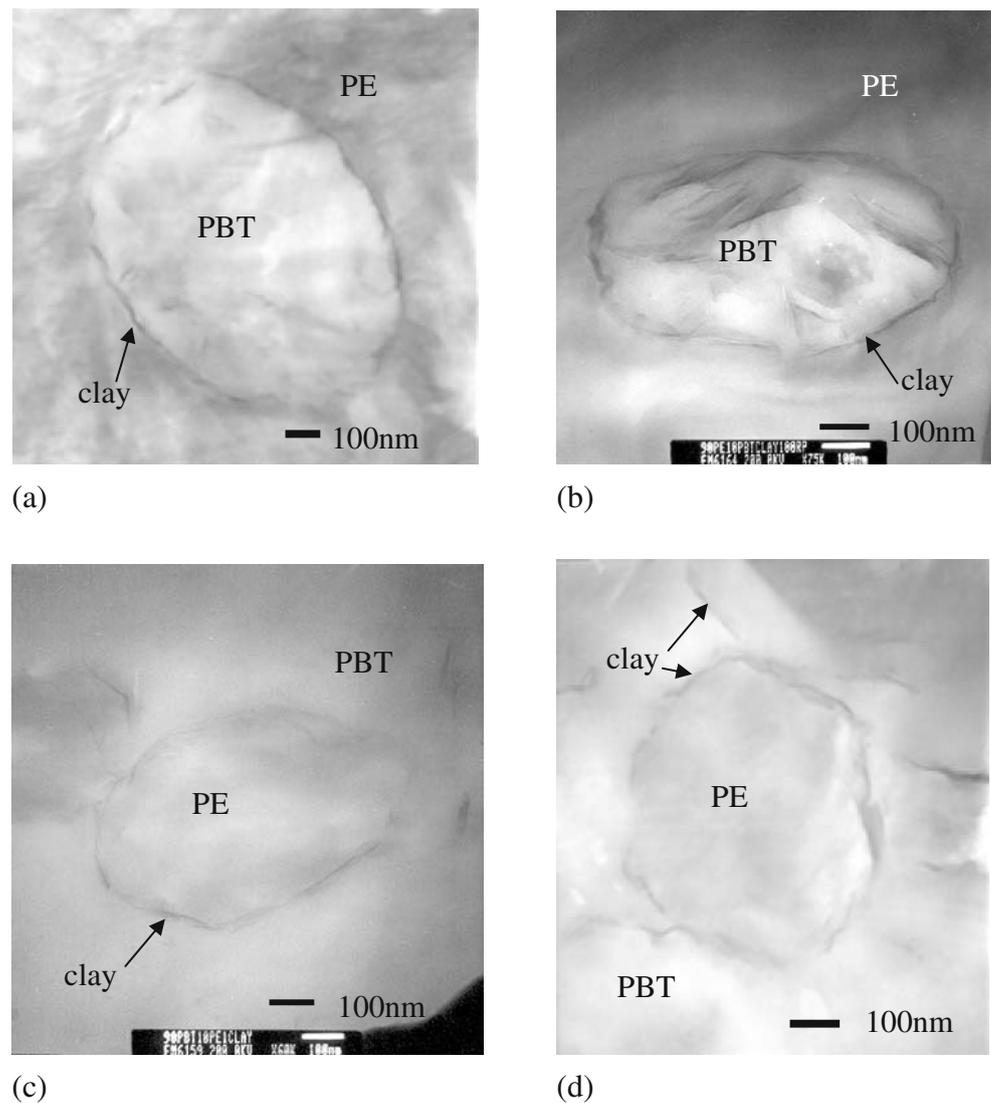
the change of interfacial tension and induces a role as a compatibilizer, the rheological measurements were carried out under oscillatory shear and extensional flow.

Rheology

From the morphological observations, we believe that as PBT content increases, the organoclay first locates at the interface and then fills inside the specific component that is more compatible with clay. This behavior may change the droplet size by its significant influence on the interfacial tension and on the viscosity ratio. The change of interfacial tension arising from clay addition is to be probed through rheological measurements under oscillatory shear and extensional flow.

Under oscillatory shear flow or cessation of shear, the effect of interfacial tension is reflected in the modulus. For example, recovery of the blend exceeds the recovery of each component, which means that the interfacial tension increases the elasticity of the sample (Gramespacher and Meissner 1995, 1997). Vinckier et al. (1999a,b) reported that a single drop in viscous flow plays an important role in stress relaxation after shear deformation. Under oscillatory shear flow, the modulus (G^*) of a blend is determined by

Fig. 4 TEM pictures of 10/90/1 PBT/PE/clay (a), 10/90/5 PBT/PE/clay (b), 90/10/1 PBT/PE/clay (c), and 90/10/5 PBT/PE/clay (d)



the contribution of each component and the interfacial tension:

$$G_{\text{blend}}^* = G_{\text{components}}^* + G_{\text{interface}}^* \quad (1)$$

Palierne (1990) suggested a model such that the modulus of a blend can be determined from that of each component (Eq. 2):

$$G_{\text{blend}}^* = G_m^* \frac{1 + 3 \sum \phi_i H_i}{1 - 2 \sum \phi_i H_i} \text{ and} \quad (2)$$

$$H_i = \frac{\frac{4\Gamma}{R_i} (2G_m^* + 5G_d^*) + (G_d^* - G_m^*) (16G_m^* + 19G_d^*)}{\frac{40\Gamma}{R_i} (G_m^* + G_d^*) + (2G_d^* + 3G_m^*) (16G_m^* + 19G_d^*)}$$

$$\sum \phi_i H_i (R_i) = \phi H(\bar{R}_v)$$

where G_{blend}^* , G_d^* , and G_m^* are the complex moduli of the blend, dispersed phase and matrix, respectively. ϕ is the volume fraction, and \bar{R}_v is the volume average radius of

the droplet. This equation extended Taylor's criterion for the deformability of the viscoelastic droplet in a viscoelastic matrix under small deformation. This enables us to predict the interfacial tension of dilute immiscible blends from the rheological measurements. Using Eq. 2, the interfacial tension of 10/90 PBT/PE blend can be predicted as 2.31 cN m^{-1} . According to this model, if the modulus of a blend is changed due to the addition of organoclay with the same matrix and dispersed phase, qualitatively, it is from the change of the ratio of interfacial tension and radius of droplets.

As the storage modulus is a very sensitive indicator of elasticity, the comparison of storage modulus manifests the change of interfacial tension. Figure 5 shows the comparison of the storage moduli of PBT/PE blends depending on the composition. In PE matrix region, the storage modulus at lower frequency increases with PBT content because the interfacial area increases. With the addition of organoclay, PE, PBT, and PBT/PE blend show somewhat different behavior. Figure 6 compares the storage modulus of PE

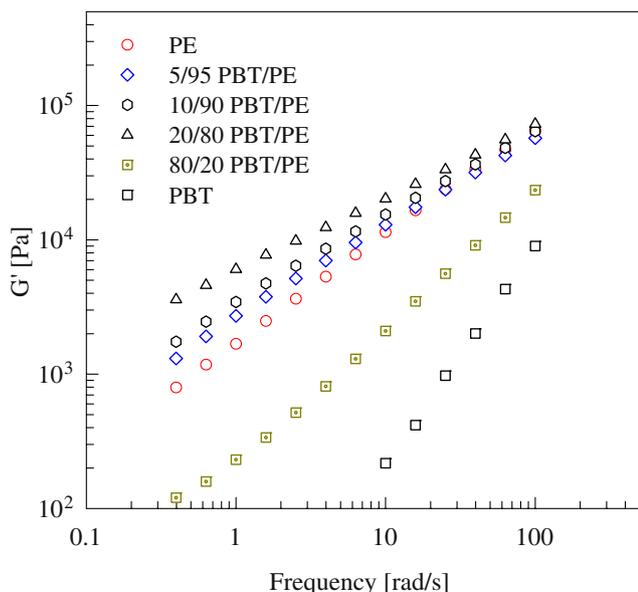


Fig. 5 Storage moduli (G') of PBT/PE blends with diverse compositions at 240 °C

and PBT with organoclay. At 230 °C, PBT has much lower storage modulus than PE. However, when 5 wt% organoclay is added, the modulus of PBT significantly increases at low frequency due to the good dispersion of organoclay tactoids in the PBT phase. In the case of PE, the rheological properties rather decrease due to the poor dispersion of the clay. For the 10/90 PBT/PE blend, as can be seen in Fig. 7, the storage modulus slightly decreases over the observation frequency range investigated with the addition of clay, although it is slightly increased at lower frequency region by the filling effect of the clay. In the 10/90 PBT/PE blend with organoclay, the modulus of the dispersed phase (PBT/clay domain) is expected to increase by the selective

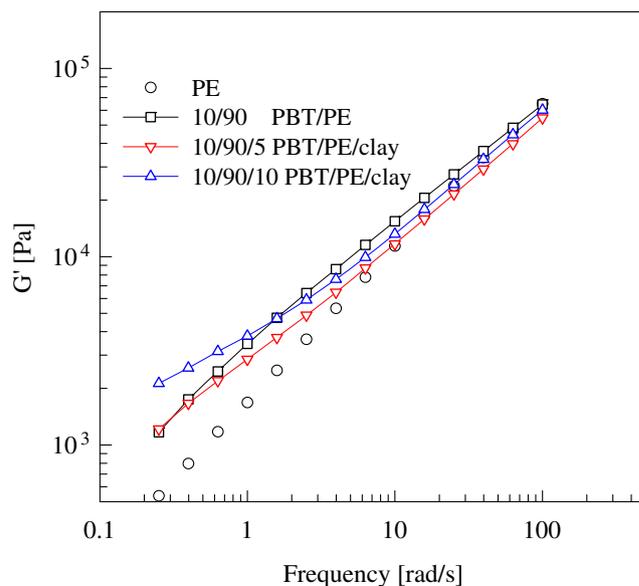


Fig. 7 Storage moduli (G') of 10/90 PBT/PE blends with different clay compositions at 240 °C

localization of clay into PBT domain. If there is no change in the interfacial tension with the addition of organoclay, the contribution of the interfacial tension to the storage modulus should always increase due to the increased interfacial area with a slight change in the droplet size (Larson 1999). Different from expectation, the storage modulus of the blend with organoclay is somewhat decreased, which means that the interfacial tension is changed by the addition of organoclay. The change of interfacial tension with the addition of organoclay is also observed when the blend is subject to the extensional deformation. Figure 8 presents the measured extensional force of the blend as a function of Hencky strain (ϵ) for several compositions. In the PE matrix region, the

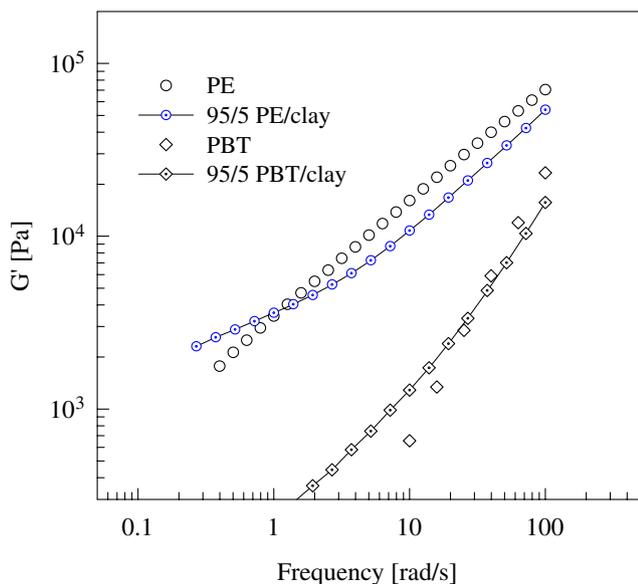


Fig. 6 Storage moduli (G') of PBT, PE, 95/5 PBT/clay, and 95/5 PE/clay at 230 °C

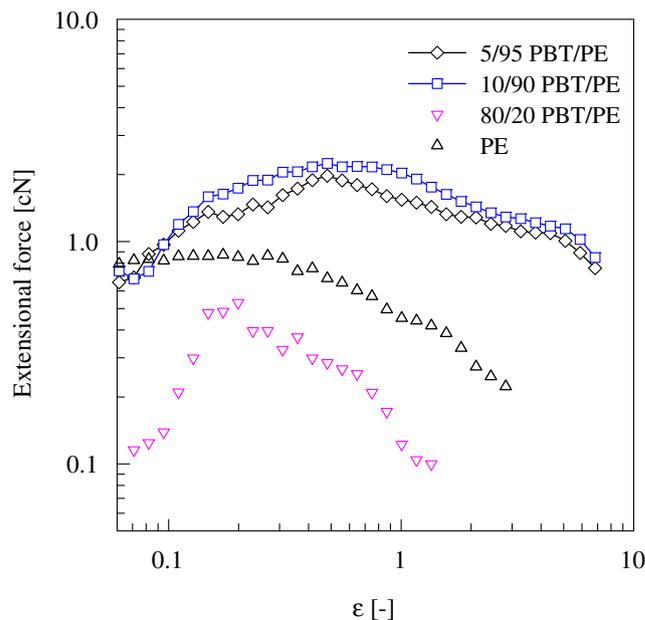


Fig. 8 Extensional force of PBT/PE blends at 240 °C

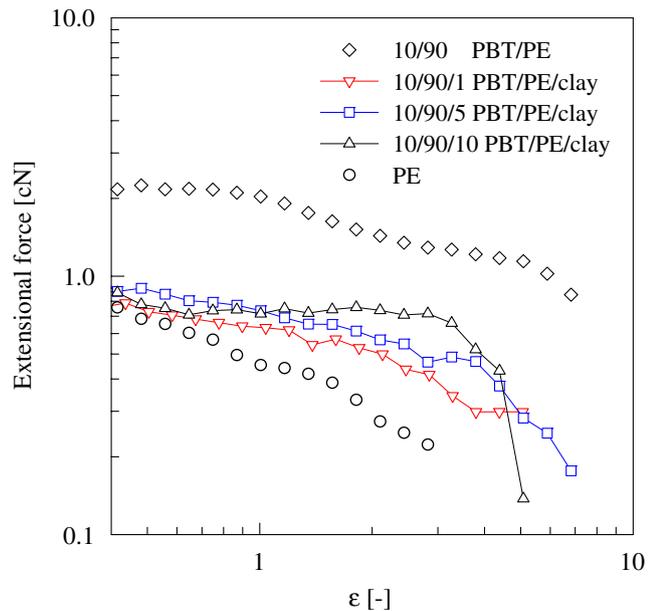


Fig. 9 Extensional force of 10/90 PBT/PE blends with different clay content at 240 °C

extensional force of the blend increases with PBT content, which is consistent with the results under oscillatory shear. PE shows the extensional force of approximately 0.8 cN at small Hencky strain, and PBT shows much lower value than PE. Although the extensional forces of PBT and PE are lower than unity (in centinewtons), the extensional force of the blend becomes higher than that of PE or unity (in centinewtons) due to the interfacial tension. Under small extensional deformation, the droplet rarely deforms because the interfacial tension functions as a strong resistance against the droplet deformation (Handge and Potschke 2004). The extensional force of the blend increases with the volume fraction of PBT droplets. When PBT content is high and it forms a matrix, it is difficult to observe the contribution of interfacial tension from the extensional force measurement due to experimental difficulty; the viscosity of PBT is too low to maintain deformation of the blend during the slow extensional flow, and the small measured force is outside of reliable range.

The effect of clay addition on the extensional force is compared with 10/90 PBT/PE blend. The extensional force of 10/90 PBT/PE blend decreases even with only 1 wt% of clay addition, although it is still higher than that of PE, as can be seen in Fig. 9. This reduction in the extensional force means that the interfacial tension has decreased. Therefore, the organoclay significantly influences the determination of droplet size because it simultaneously changes both interfacial tension and viscosity ratio, which are two important factors in determining the droplet size during mixing. In the next section, we will try to separate the effect of interfacial tension change from the extensional force of the blend.

Discussion

When the droplets of one polymer are dispersed in a matrix of another, their breakup in flow is mainly influenced by the deformability of the droplets under hydrodynamic stress, which determine the droplet size. Under shear flow, Taylor (1932) described suspensions containing dilute small drops. The size of the largest droplet at shear rate ($\dot{\gamma}$) can be determined as follows with some assumptions, including inviscid interface and maintenance of spherical shape (Taylor 1932; Edwards et al. 1991):

$$2 \frac{\dot{\gamma} \eta_m}{F_o} = \Gamma (1/D_1 + 1/D_2), \quad (3)$$

$$F_o = \frac{16\lambda + 16}{19\lambda + 16},$$

where Γ is the interfacial tension, D_1 and D_2 are two characteristic diameters (equivalent to two times the radius of curvature) of the droplet, and η_m is the viscosity of the matrix. If the hydrodynamic stress is larger than the interfacial tension ($4 \frac{\dot{\gamma} \eta_m}{F_o} > \Gamma (1/R_1 + 1/R_2)$), then the breakup of a droplet can be realized. On the other hand, if the hydrodynamic stress is much lower than the interfacial tension, the droplet just deforms without breakup. Under extensional deformation, the contribution of interfacial tension is more significant in droplet deformation. With this concept, the effect of organoclay on the interfacial tension change is to be separated from the measured extensional force of blend (F_{blend}). Levitt et al. (1997) studied the extensional behavior of a multilayer polymer system under uniaxial extension and suggested a direct method to measure the interfacial tension in the two-phase blend system. They considered the measured force composed of the volumetric contribution of each constituent (PE and PBT in this case) and of the interfacial tension as follows:

$$F_{\text{blend}} = \phi_{\text{PBT}} F_{\text{PBT}} + \phi_{\text{PE}} F_{\text{PE}} + F_{\text{interface}}, \quad (4a)$$

where F_{PBT} , F_{PE} , and $F_{\text{interface}}$ are the force of each component (PE, PBT, and interface, respectively), and ϕ_{PE} and ϕ_{PBT} are the volume fractions of the PE and PBT, respectively. The interfacial force in Eq. 4a can be estimated from the definition of Wu (1982). The interfacial tension is defined as the required work (J) to create new interfacial area (A) ($\Gamma = dJ/dA$, $J = F_{\text{interface}} L$, where L is an interfacial length). If the prediction is restricted to the early stage of extension or small deformation, we can assume the interfacial force of a single spherical droplet as follows:

$$F_{\text{interface}} = \Gamma \times \text{interfacial area} / \text{interfacial length}$$

$$= \Gamma \times D_{\text{avg}}, \quad (4b)$$

where D_{avg} is the volume-averaged diameter of domain.

The total amount of the interface in the cross section is calculated from the total number of droplets in the cross section. Then, from Eqs. 4a and 4b, the measured force of the blend becomes as follows:

$$F_{\text{blend}} \approx \phi_{\text{PBT}}F_{\text{PBT}} + \phi_{\text{PE}}F_{\text{PE}} + \Gamma \times D_{\text{avg}} \times N_{\text{droplet}}, \quad (4c)$$

where N_{droplet} is the initial number of droplets in the cross section of the rectangular parallelepiped ($V=55 \times 1.4 \times 7$ mm for RME), or $N_{\text{droplet}} = \phi_{\text{PBT}}A/(\pi R_{\text{avg}}^2)$. At a very early stage of deformation, the number of droplets in the cross section of the blend is not different from the initial number (N_{droplet}) because the droplet just slightly deforms without breakup. Then, N_{droplet} can be used to predict the interfacial tension from Eq. 4c. In addition, the capillary number Ca at a rate of 0.05 s^{-1} is approximately 0.028 ($\eta_{\text{cPE}} \times \text{rate} \times D/\Gamma \approx 1 \times 10^4 \text{ Pas} \times 0.05 \text{ s}^{-1} \times 1.3 \text{ }\mu\text{m}/2.31 \text{ cNm}^{-1} \approx 0.028$). At low capillary number ($Ca < 1$), the interfacial tension becomes a significant resistance against drop deformation, and its contribution increases with the volume fraction of the droplets. In other words, the contribution of the interfacial tension is large enough to be discriminated from the measured extensional force, and it can be expected that the droplet maintains its shape for a while during extension. Using Eq. 4c, the interfacial tension can be predicted from the measured extensional force (F_{blend} , F_{PBT} , and F_{PE}). The extensional forces of PE (F_{PE}), PBT (F_{PBT}), and blend (F_{blend}) were averaged at small Hencky strain between 0.1 and 0.5 (Table 3). In the case of PBT, $F_{90\text{PBT/PE}}$ was used instead of F_{PBT} because it was impossible to measure the extensional force of pure PBT at this condition due to low viscosity.

To confirm the reliability of the model calculation, we first compare the predicted extensional force with 5/95 and 10/90 PBT/PE blends. The interfacial tension (Γ) predicted from Eq. 2 for 10/90 PBT/PE blend was 2.31 cN m^{-1} . This interfacial tension and the extensional forces of PE (F_{PE}) and PBT (F_{PBT}) listed in Table 3 were applied to Eq. 4c to predict $F_{10/90 \text{ PBT/PE}}$ and $F_{5/95 \text{ PBT/PE}}$. The predicted $F_{10/90 \text{ PBT/PE}}$ and $F_{5/95 \text{ PBT/PE}}$ were then compared with the measured $F_{10/90 \text{ PBT/PE}}$ and $F_{5/95 \text{ PBT/PE}}$ (Fig. 10). The

Table 3 Extensional force of the blends at 240 °C and their interfacial tension

Materials	Extensional force [cN/m]	Interfacial tension (Γ) from Eq. 4c (cN/m)
PE	0.8	
PBT	0.1	
10/90 PBT/PE	1.90	5.76 (2.31 from Eq. 2)
10/90/1 PBT/PE/clay	0.77	0.14
10/90/5 PBT/PE/clay	0.89	0.26
10/90/10 PBT/PE/clay	0.79	0.16

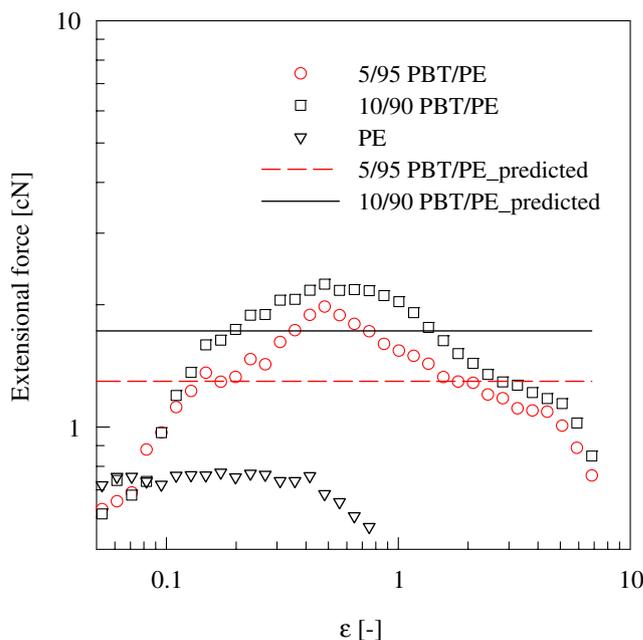


Fig. 10 Extensional force of 5/95 PBT/PE and 10/90 PBT/PE blends, and the predicted values from Eq. 4c

prediction from Eq. 4c matches well at least in the order of magnitude with the measured extensional forces for 5/95 and 10/90 PBT/PE blends. This means that Eq. 4c is available to predict the interfacial tension from the extensional force measurement at small extension.

When the interfacial tension is predicted from Eq. 4c with the measured $F_{10/90 \text{ PBT/PE}}$, it becomes 5.76 cN m^{-1} , which is twice as large as the value of 2.31 cN m^{-1} predicted from Eq. 2. In the same way, for 10/90 PBT/PE blend with organoclay, the interfacial tension change can be predicted from the measured extensional force of the blend using Eq. 4c (Table 3). When the organoclay was added, the interfacial tension was reduced significantly from 5.76 to 0.14 cN m^{-1} even with the addition of only 1 wt% of organoclay. The clay locates at the interface, as can be seen in Fig. 4, and reduces the interfacial tension, which means the organoclay at the interface suppresses coalescence and makes the breakup of droplets easier, thereby resulting in the size reduction (Lyu et al. 2002a,b; Sundararaj and Macosko 1995). Therefore, it can be concluded that the organoclay at the interface suppresses the coalescence and functions as a compatibilizer.

Conclusion

A study of the effect of organoclay on the morphology of polymer blends reveals that the addition of organoclay gives rise to hydrodynamic and thermal stabilization in the blend morphology by coalescence suppression. The organo-

clay located at the interface significantly influences changes in the morphology such as droplet size and size distribution. These morphological changes are caused by the compatibilization effect of organoclay involved in the interfacial tension reduction. From the comparison of the storage modulus and uniaxial extensional force of the blends, the interfacial tension reduction was verified. In addition, the interfacial tension reduction was predicted from the extensional force measurement. At a small strain rate, which is slow enough to reflect the effect of interfacial tension, the extensional force of the blend was reduced with the addition of organoclay. This reduction is attributed to the change in the interfacial tension. For a 10/90 PBT/PE blend, the interfacial tension was reduced from 5.76 to 0.14 cN m⁻¹ when 1 wt% of organoclay was added. From these morphological and rheological investigations, it was found that when a small amount of organoclay is added, the clay first locates at the interface with nonhomogeneous distribution along the interface and then fills inside the specific component. Similar to typical compatibilizer, the organoclay at the interface reduces the interfacial tension, which suppresses coalescence between droplets.

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