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The role of organically modified layered silicate in the breakup and coalescence of droplets in PBT/PE blends

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Abstract

In this study, we investigated the effect of organically modified nanoclay (organoclay) on the morphology of immiscible polymer blends (PBT/PE) with various compositions of PBT ranging from 1 to 90 wt%. When a small amount of organoclay between 1 and 3 phr is added to the blend, the thin clay tactoids of the thickness of the order of 10 nm are located at the interface between PBT and PE phase. As its content is increased, the additional organoclay positions in a specific component depending on its affinity with the component. The addition of a small amount of organoclay results in the effective size reduction for PBT/PE blend. The organoclay located at the interface forms the interfacial phase with a non-homogeneous distribution of clay along the interface and changes the interfacial tension, which result in the coalescence suppression of the droplets. Rigid organoclay with a high aspect ratio allows the blend morphology with long-term thermal stability by suppressing the Brownian motion. This ability of the organoclay to suppress the coalescence of the droplets effectively reduces the droplet size. On the other hand, additional organoclay results in the rheological properties of particular component being increased, which means the change in the viscosity ratio. The change in the viscosity ratio, together with the coalescence suppression effect, affects the determination of the droplet size, depending on the location of the organoclay. Therefore, the organoclay suppresses the coalescence of the droplets at the interface, while simultaneously influencing the breakup of the droplets due to the change of viscosity ratio.

Keywords: Coalescence suppression; Organically modified layered silicate; Polymer blends

1. Introduction

Most polymers are thermodynamically immiscible and their blend produces an immiscible polymer blend with poor interface, due to their unfavorable interaction and high molecular weight. The final properties of the blend are strongly influenced by the interface and the size scale of the minor phase that is determined by the relationship between the processing conditions and morphology development. When a very dilute polymer blend is subjected to mixing, the dispersed phase in the immiscible polymer blends breaks up into smaller domains and evolves to produce the final stable shape due to the deformability of the dispersed domain. As the concentration of the dispersed phase increases, the final size of the dispersed phase is determined by the competition between the coalescence and breakup. It is known that by adding an effective compatibilizer, the morphology can be controlled due to the lowering of the interfacial tension. One of the classical methods to compatibilize two polymers is the physical addition of a block, graft or star polymer consisting of two components. It is known that some block copolymers decrease the droplet size by reducing the interfacial tension. A few research groups have studied the mechanism of the compatibilization effect of block copolymers on the morphology of multiphase blends [1–8]. Their studies show that the significant reduction in size brought about by the addition of the block copolymer originates from the breakup of droplets caused by the coalescence suppression effect. The coalescence suppression effect is induced by the steric repulsion between the block copolymers located at the interface and the Marangoni force caused by the local concentration gradient of the block copolymers. Another method of compatibilizing involves the use of inorganic solid particles. Lipatov [9] reported that the addition of solid particles to an immiscible polymer blend

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stabilizes the morphology due to the compatibilization effect produced by the adsorption of the two polymers on the solid surface. This phenomenon has been made use of to develop polymer nanocomposites [10]. Ray et al. [10] explained that when polymer components are adsorbed on the solid surface, the stabilizing energy gain originates from this adsorption. Especially, in the case of nanoclay or carbon nanotube, the energy gain becomes larger due to their large surface area per unit weight. By using this behavior of inorganic solids, several research groups recently reported the compatibilizing role of clay in various immiscible polymer blends. Simultaneously, they attempted to define the compatibilizing role played by the nanoclay in the polymer blends, in order to understand how the physical properties were improved as compared with unmodified polymer blends [11–15]. Gelfer et al. [11] found that the PS domain size in PS/poly(methyl methacrylate) (PMMA) blend was reduced upon adding organoclays, due to the compatibilizing function of the excessive surfactant present in the organoclays as well as due to the increased viscosity. However, the role of the nanoclay in blends and the mechanism of formation of the blend nanocomposite brought about by the nanoclay has not yet been elucidated. In relation to this, Wang et al. [12] tried to determine how nanoclay compatibilizes the PS/PP system. The PS domain size was greatly decreased upon the addition of organoclay. They attributed this phenomenon to the fact that the two immiscible polymer chains can coexist between the intercalated clay platelets. These two chains play the role of a block copolymer, which acts as a compatibilizer for the PS/PP system. However, if the organoclay has a specific affinity for one component of a multi-component system, there is little opportunity for the organoclay to diffuse into the interface.

To better understand the role of organoclay in the polymer blend, in this study, we focused on determining how organoclay influences the determination of the morphology and why the droplet size is increased or decreased with the addition of organoclay. For this purpose, PBT/PE blend nanocomposites were prepared by the intensive mixing of PBT, PE, and organoclay. The organoclay was purposely chosen to have a rich affinity for one component, specifically the PBT component. The morphology of the PBT/PE blend nanocomposite was systematically investigated as a function of the amount of organoclay and PBT content. TEM observation showed that all the clay platelets are selectively dispersed in the PBT phase. The influence of the organoclay on the morphology of the blend was found to depend on its location.

2. Experimental procedures

2.1. Materials

The 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 used as a matrix has a melt index of 0.9 g/10 min (ASTM D1238, 190 °C/2.16 kg).

Table 1
Complex viscosity (η^*) and viscosity ratio of PBT, PE and PBT with 5 phr clay

Frq. (rad/s)	η^* (Pa)				
	PE (K)	PBT (K)	95/5 (w/w) PBT/clay (K)	Ratio (η_{PBT}/η_{PE})	Ratio ($\eta_{PBT\_5clay}/\eta_{PE}$)
0.1	10.3	0.82	1.39	0.08	0.11
1	7.4	0.8	0.9	0.11	0.12
50	1.3	0.7	0.5	0.54	0.39
100	0.93	0.67	0.47	0.72	0.51

The viscosity of the PBT and PE at 230 °C and its ratio are listed in Table 1. The PBT/PE blend composition was varied from 1 to 90 wt% to compare the effect of the organoclay on the matrix PBT or the dispersed PBT phase. Nanoclay is a layered silicate based on montmorillonite, which is naturally hydrophilic. To increase its compatibility with the polymer, the layered silicate is usually modified by a cation exchange reaction between the silicate cations and an alkylammonium. The nanoclay used in this study was Nanofil 919 (Sud-Chemie Inc.), which is organically modified with long chain hydrocarbon (>C17) based on montmorillonite (organoclay). Since, the cations loosely bonded between the sheets of oxygen and silicon is organically intercalated with stearylbenzyl dimethyl ammonium chloride, the organoclay is specifically compatible with PBT and PA6.

2.2. Blending

The blending of the 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 a rotation speed of 50 rpm. All of the compositions of the blends are listed in Table 2. The blends were then compression molded using a Carver laboratory hot press at 230 °C for 10 min into a mold with a thickness of 1.0 mm and then annealed at room temperature. The organoclay concentration for each PBT/PE blend was

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

Composition (w/w)		Clay (phr[a])	Clay/PBT
PBT	PE		
1	99	5	5/1
5	95	5	5/5
10	90	5	5/10
20	80	5	5/20
80	20	5	5/80
90	10	5	5/90
10	90	1	1/10
10	90	3	3/10
10	90	10	10/10
90	10	1	1/90
90	10	3	3/90
90	10	10	10/90

[a] **x** (phr) = **x**/(100% blend + **x**).

5 phr for each PBT/PE blend and specifically 1, 3, 5 and 10 phr for the 10/90 (w/w) PBT/PE and 90/10 (w/w) PBT/PE blends. The apparent shear rate during mixing should be determined in order to roughly predict the viscosity ratio of the blend, as this is important to predict the size of the dispersed phase by using the theoretical and experimental base. We used a screw speed of 50 rpm throughout this work. At this RPM, the maximum drag flow (neglecting pressure flow) shear rate in the mixer was about 65 s^{-1}.

2.3. Characterization

The blend morphology was examined by scanning electron microscopy (SEM) using a JEOL model JSM-840A apparatus 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 of the sample, the number-average (D_n) and the volume-to-surface area average (D_{vs}) domain diameters were obtained with image analyzing software (Image-Pro®; Media Cybernetics Inc.). The long and short axis diameters of each droplet in the SEM picture were measured and the arithmetic mean of these two values ($D_i=(D_{1i}+D_{2i})/2$) was determined. Then, D_n and D_{vs} were obtained by using the following relation

$$D_n=\sum\frac{D_i}{N},$$

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

where, N is the total number of disperse domains (over 200 drops) observed in the SEM images. The intercalated and exfoliated silicate layers in the polymer were examined by transmission electron microscopy (TEM) using a JEOL model JEM-2000EXII apparatus operated at an accelerating voltage of 200 kV. The TEM specimens were about 40–70 nm thick. They were prepared by cryo-ultramicrotoming the blends encapsulated in epoxy with a diamond knife.

The rheological properties were measured at 230 °C by means of an RMS800 apparatus (Rheometrics Inc.) with a parallel plates fixture (25 mm diameter), which was used to measure the complex viscosity (η^* (Pa s)), storage modulus (G' (Pa)), and loss modulus (G'' (Pa)) as a function of frequency using the dynamic oscillatory mode.

The XRD patterns were recorded on a Simens-500 diffractometer operated at 40 kV and 40 mA, with a beam consisting of Cu Kα radiation ($\lambda=0.154$ nm). Data were obtained from $2\theta=1$–10° at a scanning speed of 1°/min.

3. Results

For the PBT/PE blend, the addition of organically modified nanoclay intercalated with stearylbenzyl di-methyl ammonium chloride led to a different variation of the domain size of the dispersed phase with the composition of the blend. Fig. 1 represents the plot of the averaged domain size (D_n) of the PBT/PE blend and organoclay-filled PBT/PE blend over a wide composition range, where a comparison is made of the domain size taken from several SEM pictures for each composition. Although in the 1/99 (w/w) PBT/PE blend, the PBT domain size is very small (0.37 μm) due to the much lower viscosity ratio, the domain size of the PBT/PE blend increases linearly with increasing PBT content due to the effect of coalescence. With the addition of the organoclay, the domain size converges to an average diameter of about 1.0 μm, regardless of the composition, and the size distribution becomes narrower.

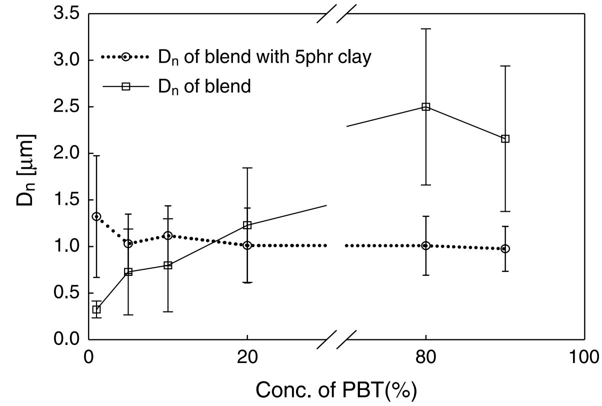

Fig. 1. Average droplet size of PBT/PE blends depending on the composition of PBT.

In the region of the PBT matrix (region B in Fig. 1), a significant reduction in domain size is observed with the addition of a small amount of organoclay. For example, the average domain size of the 80/20 (w/w) PBT/PE blend decreases from 2.5 μm to about 1.0 μm with the addition of the organoclay. Interestingly, with the same amount of organoclay, the domain size increases in the PBT minor region (region A in Fig. 1). Fig. 1 clearly shows that the effect of organoclay on the blend morphology depends on the preference of the organoclay for one of the multiple components, and the amount and composition of this specific component. For example, the morphologies of the 90/10 and 10/90 (w/w) PBT/PE blends are shown in Fig. 2, and these are compared with the SEM pictures of the unmodified and organoclay-filled PBT/PE blends. In the case of the 90/10 (w/w) PBT/PE blend, the size of the PE domain is effectively reduced by the addition of a small amount of organoclay and the distribution of the domain size is narrowed (Fig. 2(a) and (b)). For the 10/90 (w/w) PBT/PE blend, the domain size of the dispersed PBT phase is relatively small compared to that of the 90/10 (w/w) PBT/PE blend, as shown in Fig. 2(c), since the viscosity ratio of the PBT/PE blend is much lower than unity [6,16]. And, the size distribution of the 10/90 (w/w) PBT/PE blend is broadened by the coalescence effect. In both cases, the organoclay seems to suppress the coalescence between the PBT domains and, consequently, the domain size is reduced and uniformly distributed. The other point that should be explained here is that the spherical shape of the domain is slightly deformed, giving rise to an irregular shape, by the addition of a small amount of organoclay. These morphology

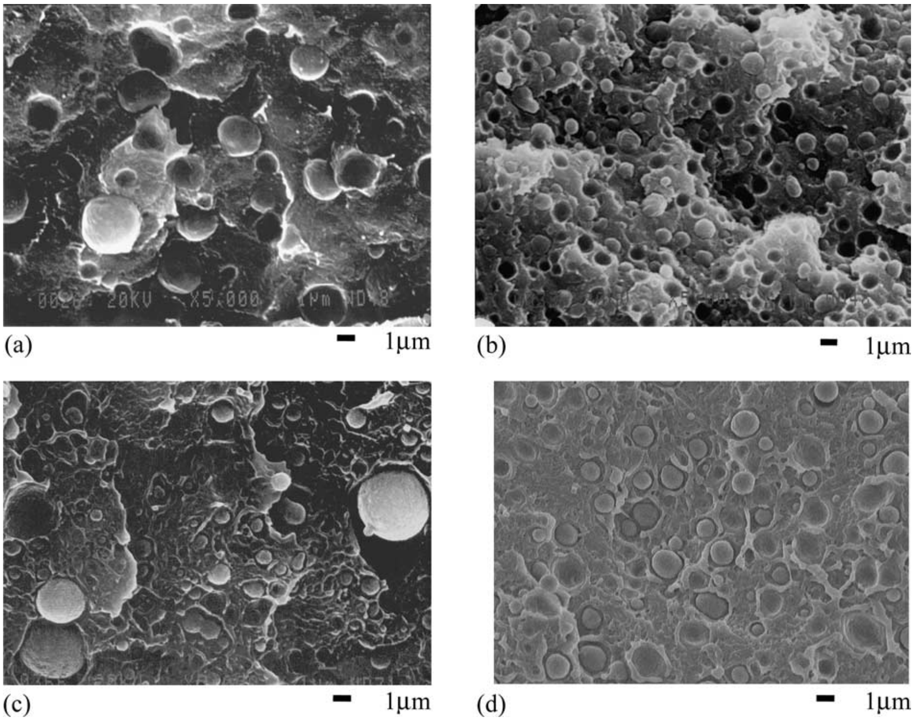

Fig. 2. Comparison of SEM pictures of 90/10 (w/w) PBT/PE (a) and that with 5 phr organoclay (b), 10/90 (w/w) PBT/PE (c) and that with 5 phr organoclay (d).

changes produced by the addition of the organoclay were further studied through rheological, X-ray diffraction and morphological observations.

To investigate the dispersion and preference of the organoclay, the rheological properties of PBT/clay and PE/clay were first compared. Fig. 3 shows a comparison of the storage modulus of PBT/clay and PE/clay and provides an important evidence for the preference of the organoclay for the PBT component more than the PE component. At 230 °C, PBT has much lower rheological properties than PE (Table 1 and Fig. 3). However, when the organoclay of 5 phr is added, the modulus of PBT is significantly increased in the low frequency region but similar to that of the PBT matrix in the high frequency region, as seen in Fig. 3. Although the organically intercalated surfactant on the layered silicate is chemically compatible with the PBT molecules, the high mechanical energy disrupts the silicate layer stacks into the thin clay tactoids of order of some tens of nanometers of thickness during mixing and it results in a good dispersion [17,18]. The clay tactoids are well dispersed in the PBT phase, as can be seen in Fig. 4(b) and (c). These tactoids improve the modulus of the PBT/clay in the low frequency region. In the case of PE, the organoclay forms aggregates with diameters of 300–400 nm, and these particles are dispersed in the PE matrix (Fig. 4(a)). It can be seen that PE has poor compatibility with organoclay. The large size of the aggregated particles and its poor compatibility reduces the modulus of the PE/clay compared to that of PE.

The X-ray diffraction results also show that the organoclay exhibits a greater preference for the PBT and is exfoliated in the PBT. Fig. 5 shows a comparison of the WAXD profiles of the organoclay itself and the nanocomposites with PBT, PE and 10/90 (w/w) PBT/PE blend. It can be seen in Fig. 5 that the organoclay itself exhibits the first characteristic peak at 2.45°, corresponding to a d-spacing of 3.5 nm. In the case of PBT/clay and PBT/PE/clay, the characteristic peak of the clay almost disappears and the second peak is no longer observed. On the other hand, in the PE/clay, the characteristic peak of the clay is shifted to a larger angle. Based on these measurements, it can be concluded that the rheological properties of PBT/clay increase by the good dispersion of thin clay tactoids in PBT.

In addition, the TEM observations make it clear where the organoclay is located in the blend and how well it is dispersed. Fig. 6 shows the TEM pictures of the 10/90 (w/w) PBT/PE

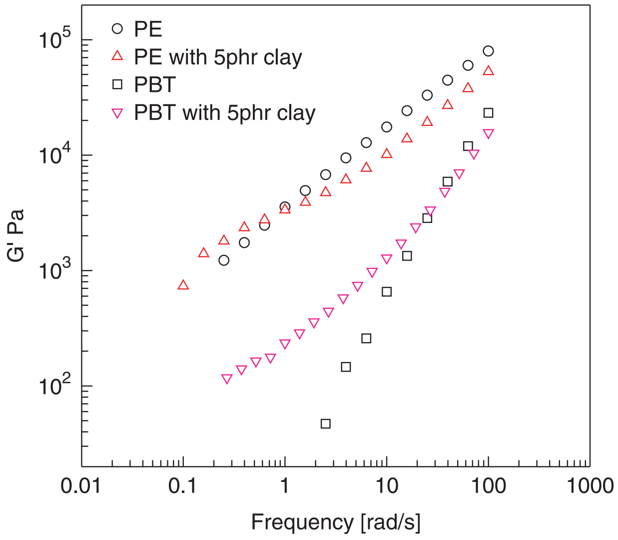

Fig. 3. Storage modulus of PBT, PBT mixed with 5 phr organoclay, PE, and PE mixed with 5 phr organoclay at 230 °C.

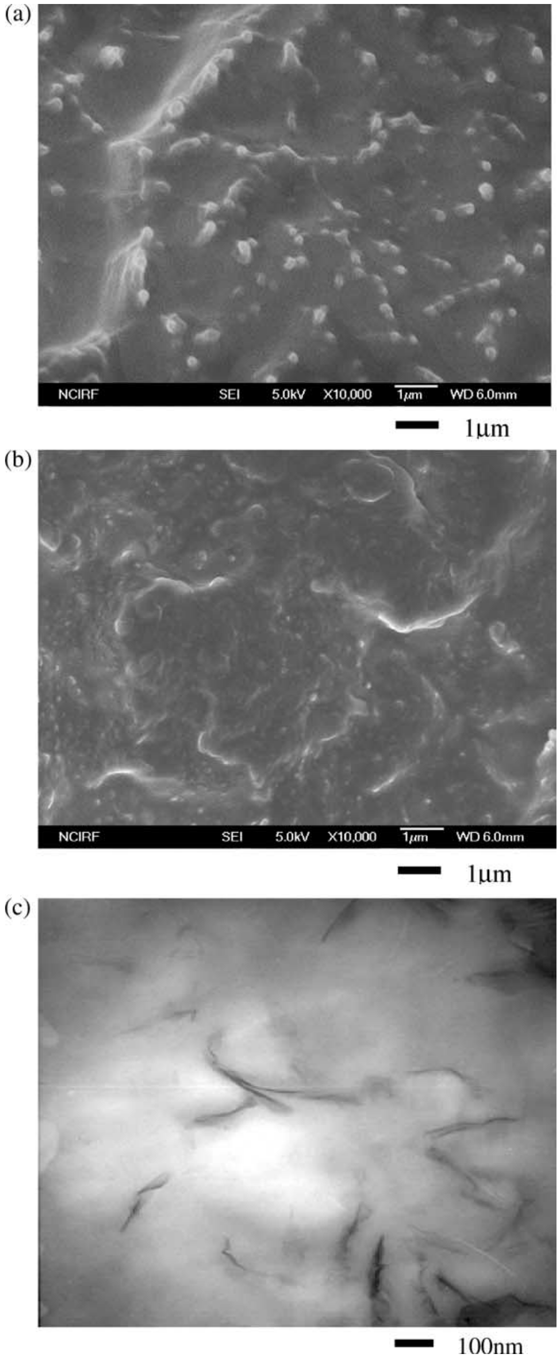

Fig. 4. SEM pictures of the PE mixed with 5 phr organoclay (a), PBT mixed with 5 phr organoclay (b) and TEM picture for PBT mixed with 5 phr organoclay (c).

and 80/20 (w/w) PBT/PE blends mixed with 5 phr of organoclay. The measured droplet size is in good agreement with that obtained from the SEM observation (Fig. 1). The TEM pictures of the PBT/PE blend nanocomposite exhibit consistent results over all compositions and indicate that the clay is located in the PBT phase or interface, and not in the PE phase. For 80/20 (w/w) PBT/PE blend, most clay tactoids are located in the PBT matrix and interface, and it shows a good dispersion of thin clay tactoids with a thickness of about 10–20 nm. Some of the organoclay tactoids in the PBT phase migrate into the thermodynamically stable interface having lower chemical potential by thermal and mechanical force, and try to envelope the PE domain, as can be seen in Fig. 6(b). Even in the case of 10/90 (w/w) PBT/PE blend (Fig. 6(a)), the clay tactoids are dispersed inside the PBT domain though the content of PBT is not enough to incorporate all the clays of 5 phr. The organoclay tactoids are located at the interface as well. This means that the PBT domain containing the dispersed organoclay has enhanced rheological and mechanical properties. As a result, the viscosity ratio of the blend nanocomposite would be expected to be significantly different from that of the PBT/PE blend (as will be mentioned again in the Section 4).

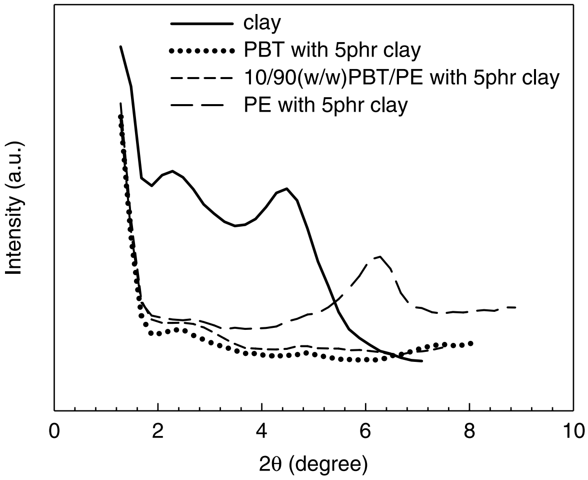

Fig. 5. WAXD results of PBT mixed with 5 phr organoclay, PE mixed with 5 phr organoclay, and 10/90 (w/w) PBT/PE blend mixed 5 phr organoclay.

These rheological and morphological investigations show that the organoclay used in this study has a strong affinity toward the PBT component and is selectively located in the PBT phase. This selective localization of the organoclay in the PBT phase plays a particular role in improving the rheological properties of the PBT phase. Therefore, it should be pointed out that the domain size is altered by the change in deformability originating from the variation of the viscosity ratio as well as the weak interfacial modification.

To further investigate why the domain size is reduced, we compared the rheological properties and morphology depending on the amount of clay. At first, the amount of organoclay was varied from 1 to 10 phr for the 10/90 (w/w) PBT/PE and 90/10 (w/w) PBT/PE blends. In the case of the 10/90 (w/w) PBT/PE blend (Fig. 7(a)), as the quantity of clay increases, the rheological properties and morphology are changed. The PBT domain size (D_n) remains at about 0.8 μm upon the addition of 3 phr of organoclay, and then increases depending on the content of organoclay. The storage modulus of the organoclay filled PBT/PE blend in the lower frequency region is consistently increased with increasing amount of organoclay (Fig. 8). This contribution of the interfacial tension to the storage modulus is increased by the increased interfacial area with a little change in the droplet size [19]. As expected, the PBT/clay domain size is increased a little and more PBT droplets are produced as the amount of organoclay is increased.

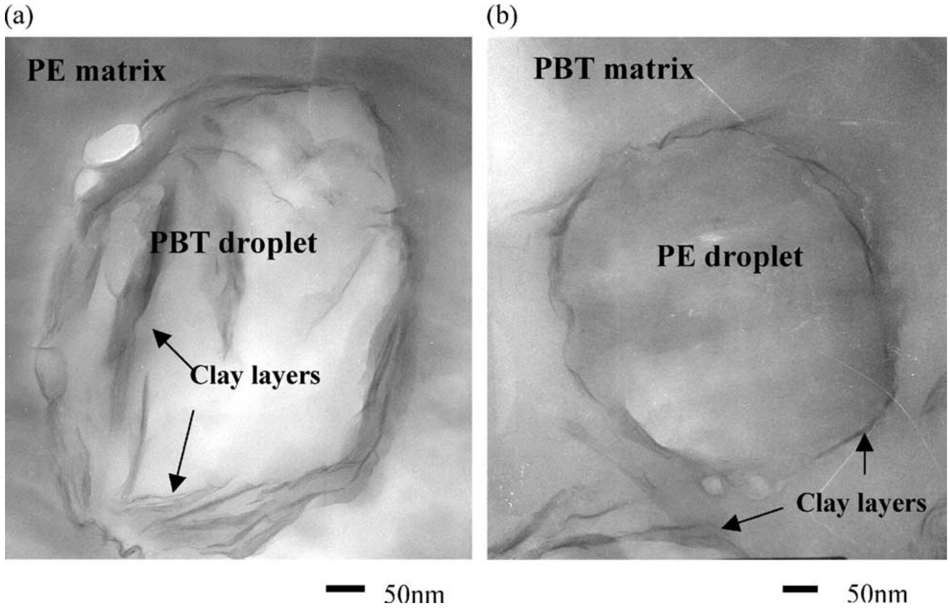

Fig. 6. TEM pictures of 10/90 (w/w) PBT/PE (a) and 80/20 (w/w) PBT/PE (b) with 5 phr organoclay.

Since, all of the organoclay is compactly dispersed only inside the PBT domain, regardless of the amount added, it reduced the deformability of the PBT/clay droplets by improving the modulus of the PBT/clay phase. This reduction in deformability decreases the likelihood of breakup of the PBT/clay domain against the hydrodynamic stress imposed by the PE matrix. Therefore, the domain size increases with increasing amount of organoclay, as can be seen in Fig. 7(a). For the 90/10 (w/w) PBT/PE blend, the rheological properties and morphology are changed only slightly as the amount of clay increases after showing a significant change with the addition of 1 phr organoclay, as can be seen in Fig. 7(b).

TEM observations of the location of the organoclay depending on the amount of organoclay were made in order to gain a further understanding of the effect of organoclay on the morphology. As shown in Fig. 9(a) and (b), when the amount of organoclay is very small, the thin clay tactoids are initially observed at the interface. The addition of only 1 or 3 phr organoclay is enough to modify the interfacial region, since the contact area between the solid surface and polymer melt significantly increases due to the good dispersion of thin clay tactoids and the localization of the organoclay tactoids

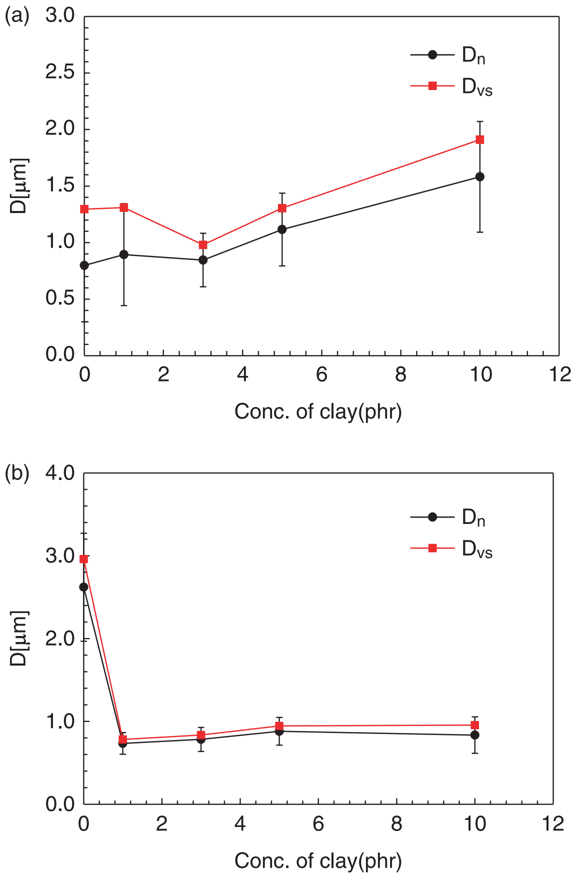

Fig. 7. Variation of the average droplet size of 10/90 (w/w) PBT/PE blends depending on the amount of organoclay (a) and that of 90/10 (w/w) PBT/PE blends (b).

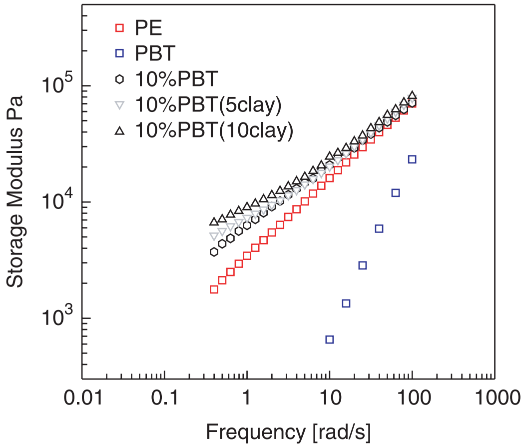

Fig. 8. Storage modulus of 10/90 (w/w) PBT/PE blends depending on the amount of organoclay.

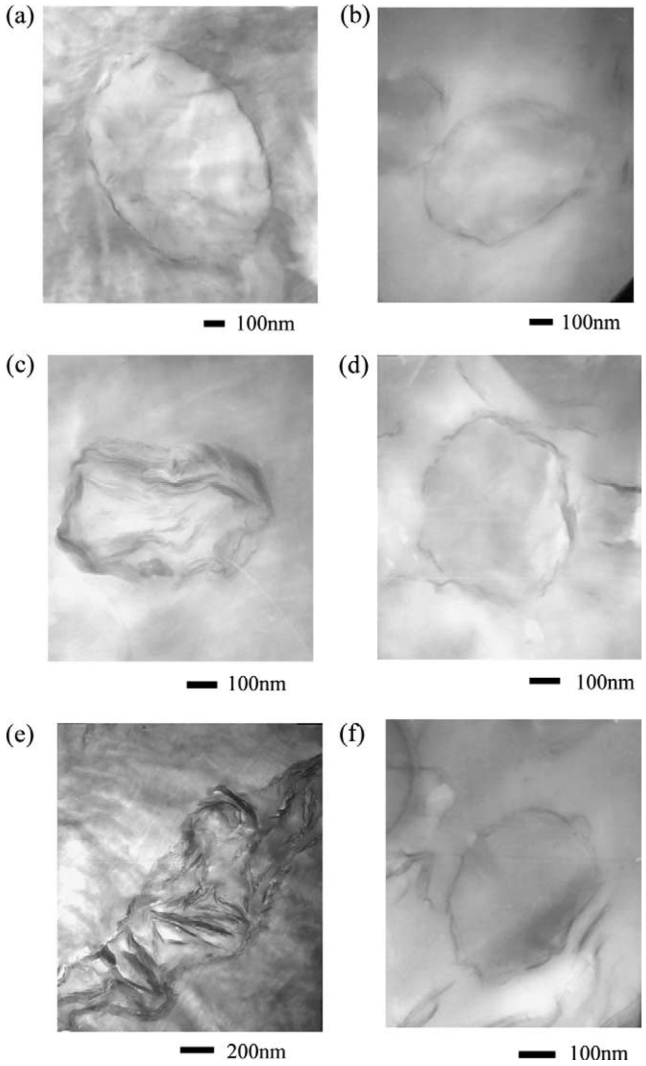

Fig. 9. TEM pictures of 10/90 (w/w) PBT/PE blends (a, c and e) and 90/10 (w/w) PBT/PE blends (b, d and f) with the addition of 1, 5, and 10 phr organoclay.

at the interface. In this region, the non-homogeneous distribution of the organoclay gives rise to an interfacial tension gradient and results in a gradient driven flow along the interface caused by the Marangoni force [1–3,19,20]. In addition, the steric repulsion between the organoclay at the interface effectively suppresses the coalescence caused by the geometrically induced van der Waals force and the collisions caused by the hydrodynamic force. Furthermore, since the rigid organoclay with its high aspect ratio has lower mobility, thermally induced Brownian motion between the droplets can be prevented. For this reason, when the PBT/PE blend nanocomposite is annealed for 8 h at 230 °C, the morphology including the droplet size is not changed. Therefore, it can be said that the addition of a small amount of organoclay prevents coalescence and stabilizes the morphology. When its content is increased, the organoclay is located at the interface as well as being densely located inside the PBT phase, as can be seen in Fig. 9(c)–(f). Since, the organoclay filled PBT domain has further improved rheological properties, the domain size should depend on whether the organoclay goes into the droplet or the matrix. As mentioned above, in the case of the PBT/clay droplet, the domain size tends to increase with increasing addition of organoclay, because the likelihood of breakup of the droplets against hydrodynamic force is decreased by the consequent reduction in the deformability of the droplets. Nevertheless, the suppression of coalescence results in a narrowing of the size distribution (Fig. 7(a)). On the other hand, if the organoclay is dispersed in the PBT matrix, the organoclay becomes more dispersed in the matrix as its content increases (Fig. 9(d) and (f)). By further addition of organoclay, the hydrodynamic stress induced by the PBT/clay, which causes the PE droplets to be deformed or broken-up, is slightly increased. This means that if the organoclay has a preference for the matrix, the reduction in size mainly originates from the suppression of coalescence, rather than from the effective breakup of the droplets.

Based on the rheological and morphological observations, the addition of organoclay to the immiscible blend influences the competitive balance between the coalescence and breakup of the droplets and causes the droplet size to change depending on the location of the organoclay. In relation to this, two possible effects of the organoclay can be explained by considering the increase or decrease of the droplet size: the modification of the interfacial tension and the improvement of the rheological properties.

Though the organoclay tactoids are very rigid and have lower mobility compared to the block copolymer in terms of their ability to act as a compatibilizer, the organoclay located at the interface is heterogeneously distributed along the interface due to the strong hydrodynamic force. This makes it possible for the droplet size to be reduced by the coalescence suppression effect induced by the Marangoni force and steric interaction. Depending on the affinity of the organoclay for one component within the multi-component system, the rheological properties of more compatible component are improved as the amount of organoclay is increased. As a result, the viscosity ratio is changed and this modifies the deformability of the droplets, which in turn influences the breakup of the droplets.

4. Discussion

When immiscible polymer blends are subjected to mixing, the final size of the dispersed phase is determined by the competition between the coalescence and breakup of the dispersed domain. When the very dilute droplets are dispersed in the matrix, their breakup is mainly influenced by the deformability of the domain upon the hydrodynamic stress, which determines the droplet size. Under shear flow, Taylor [8] extended Einstein's work for suspensions containing dilute small drops of another liquid. The size of the largest droplet that can exist in a fluid at any flow rate can be determined by making certain assumptions, including the inviscid interface and the maintenance of its spherical shape, etc. The tangential stress imposed on the surface of the droplet is discontinuous at the interface and is balanced by the interfacial tension that is given by Eq. (1) [8,20]

$$\Gamma(1/R_1 + 1/R_2) = \delta P_\mathrm{i} - \delta P_\mathrm{o} \tag{1}$$

where Γ is the interfacial tension, R_1 and R_2 are the small and large radii of the droplet and P_i and P_o are the inner and outer pressures of the droplet. If the hydrodynamic stress is larger than the interfacial tension, that is,

$$\Gamma(1/R_1 + 1/R_2) < \dot{\gamma}\eta_\mathrm{m}F(\eta), \quad F(\eta) = \frac{((19/4)\eta_\mathrm{d} + 4\eta_\mathrm{m})}{(\eta_\mathrm{d} + \eta_\mathrm{m})} \tag{2}$$

The deformation and breakup of the droplet can be obtained [8]. $F(\eta)$ is nearly unity and is weakly dependent on the viscosities of the dispersed phase (η_d) and matrix (η_m). The breakup of the droplet should occur when the hydrodynamic stress that deforms the droplet overwhelms the interfacial force that resists deformation. For a viscoelastic blend system, Wu [4] experimentally extended Eq. (2) and predicted the maximum droplet size (R) under shear flow

$$R = \frac{2\Gamma}{\dot{\gamma}\eta_\mathrm{m}F(\eta)} \approx \frac{2\Gamma}{\dot{\gamma}\eta_\mathrm{m}}\lambda^{\pm\alpha} \tag{3}$$

where λ is the viscosity ratio ($\eta_\mathrm{d}/\eta_\mathrm{m}$) and the experimental parameter, α, has a value of nearly 0.87, which is positive if the viscosity ratio is larger than one. The viscoelasticity makes the contribution of the viscosity ratio more influential in the determination of the droplet size than it would be in the case of a Newtonian blend. If the blend consists of Newtonian fluids, the effect of the viscosity ratio on the variation of the droplet size is not significant compared to that of the interfacial tension ($R \sim 1/F(\eta)$). The contribution of the interfacial tension to the determination of the droplet size is proportionally increased. For viscoelastic blends, the contribution of the viscosity ratio is comparatively important ($R \sim \lambda^{\pm\alpha}$) though the experimental parameter, α, which is less than one for viscoelastic system (0.87 for PA/EP-Rubber [4]). For example, if estimated with α of 0.87, the droplet size increases by about 180% if the viscosity ratio is doubled at a fixed interfacial tension. On the other hand, when the interfacial tension is multiplied or divided by two at a fixed viscosity ratio, the droplet size is doubled or halved, respectively. This means that though the interfacial tension has a greater influence on the droplet size, the viscosity ratio is also important in the case of a viscoelastic system. For example, in the 10/90 (w/w) PBT/PE blend, the organoclay at the interface clearly has a size reduction effect (Fig. 7(a)). As the amount of organoclay is further increased, the ratio of organoclay and PBT in the PBT droplet is significantly increased from 1/10 to 10/10 due to the selective localization of the organoclay (Table 2). Therefore, the domain size increases since the deformability of the droplets is abruptly reduced due to the significantly increased viscosity ratio. On the other hand, in the 90/10 (w/w) PBT/PE blend, the ratio of organoclay and PBT is slightly increased from 1/90 to 10/90. Therefore, the viscosity ratio is decreased and the viscous stress imposed on the PE droplet by the PBT/clay matrix is increased.

The droplet size of PBT can be estimated by Eq. (3) (in region A of Fig. 1). Since, Eq. (3) quantitatively gives a hint as to the maximum size of the droplet under shear flow, excluding the coalescence effect, this is useful to predict the droplet size in a very dilute composition. For example, for the 1/99 (w/w) PBT/PE blend containing 5 phr organoclay, the PBT droplet size can be predicted quite accurately. Eq. (3) needs the value of interfacial tension to estimate the droplet size. The interfacial tension of the PBT/PE blend can be estimated for the 1/99 (w/w) PBT/PE blend using the Palierne model [21]

$$\begin{aligned} G^* &= G^*_\mathrm{m}\frac{1 + 3\sum\phi_i H_i}{1 - 2\sum\phi_i H_i} \\ H_i &= \frac{(4\Gamma/R_i)(2G^*_\mathrm{m} + 5G^*_\mathrm{d}) + (G^*_\mathrm{d} - G^*_\mathrm{m})(16G^*_\mathrm{m} + 19G^*_\mathrm{d})}{(40\Gamma/R_i)(G^*_\mathrm{m} + G^*_\mathrm{d}) + (2G^*_\mathrm{d} + 3G^*_\mathrm{m})(16G^*_\mathrm{m} + 19G^*_\mathrm{d})} \\ &\sum\phi_i H_i(R_i) = \phi H(\bar{R}_\mathrm{v}) \end{aligned} \tag{4}$$

where G^*, G^*_d, and G^*_m are the complex moduli of the blend, the dispersed phase and matrix, respectively. ϕ is the volume fraction and R_v is the volume average radius of the droplet. This model extended Taylor's criterion for the deformability of the viscoelastic droplet in a viscoelastic matrix under conditions of small deformation. This predicts the interfacial tension of dilute polymer blends very well. The value of the interfacial tension was obtained as 2.38 (cN/m). When the values of the viscosity ratio, interfacial tension, and stress are applied to Eq. (3), the largest droplet size can be calculated as 0.35 μm. This coincides well with the experimental average diameter of 0.37 μm.

If organoclay with a high aspect ratio is added to a very small PBT droplet, the strong preference of organoclay for the PBT phase physically makes the size of the droplet much larger, regardless of its decreased deformability. Then, the droplet size is basically dependent upon the geometry of the organoclay and the ratio of PBT and organoclay. In particular, in the case of 1/99 (w/w) PBT/PE blend, PBT droplet size is most remarkably increased by up to three times with the addition of 5 phr organoclay (Fig. 1). This increase is still observed for 5/95 (w/w) and 10/90 (w/w) PBT/PE because the PBT droplet size is still small with 5 phr organoclay. This shows that if the droplet size is too small for the effect of the organoclay to be observed, the effect of the organoclay on the morphology may be misunderstood and difficult to be defined. On the other hand, if the rheological property of PBT is higher than or similar to that of PE, the droplet size of PBT may be possibly larger than that we observed here. In this case it can be expect that the droplet size may be reduced by the addition of organoclay, which needs to be checked in the further study. Therefore, the organoclay affects the determination of the droplet size, since it influences both the interfacial tension and the viscosity ratio, which are important factors in the determination of the droplet size during mixing, although their effects are somewhat different.

5. Conclusion

When two immiscible polymers, PBT and PE, are mixed, specifically when PBT phase is matrix, a size reduction is obtained by the addition of organoclay having a specific preference for one of the blend components, and the resulting blend shows a stable morphology with a homogeneous domain size. The effect of the organoclay on the reduction in the droplet size is governed by the location of the organoclay, which is determined by the difference in the affinity of the organoclay with each component and the clay content.

When a very small amount of organoclay is added to the blend, the clays are located at the interface and the organoclay tactoids are disrupted into thin tactoids of a thickness of some tens of nanometers. The presence of organoclay at the interface hydrodynamically stabilizes the blend morphology by suppressing the coalescence of the droplets and also makes the morphology thermally stable. As its loading is increased, the organoclay mostly locates in the specific component, which shows more affinity. The organoclay filled component shows an improvement in its rheological properties. Although some of the added organoclay platelets can be attributed to the change in the interfacial tension, this selective localization of the organoclay results in a variation in the blend viscosity ratio as well. If the amount of organoclay inside the dispersed droplet is increased, the deformability of the droplet filled with organoclay is significantly reduced. Therefore, although a reduction in size is obtained by the suppression of coalescence, the less likelihood of breakup of the droplet somewhat hinders the effect of the organoclay on the size reduction. On the other hand, if the organoclay is situated in the matrix, the size reduction effect is enhanced as the amount of organoclay is increased. This study shows that the organoclay tactoids tend to be located at the interface and simultaneously form the blend nanocomposite. Moreover, it is known that the organoclay significantly influences the morphology and rheology of the immiscible polymer blend, in a manner, which is dependent upon its location.

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