Shear-Induced Migration of Nanoclay During Morphology Evolution of PBT/PS Blend

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ABSTRACT: In this study, we investigated clay migration and its localization in multiphase blend nanocomposite systems during the evolution of blend morphology to elucidate how a hydrodynamic stress and chemical affinity between the polymer and clay induce them. To observe the morphology evolution, a multilayered blend, alternatively superposed poly(butylenes terephthalate) (PBT) and polystyrene (PS)/clay films or PBT/clay and PS films, was subjected to homogeneous shear flow, 1 s^{-1}. Furthermore, the morphology was observed at different shear rates 1 s^{-1}. When the PBT/(PS/clay) multilayered blend is subjected to flow, the clay dispersed in the PS layer first migrates to the interface depending on the amount of applied strain. The clay at the interface causes the average drop size of blend morphology to become smaller and the blend morphology becomes more stable because of the coalescence suppression effect. As more shear is applied, the clay at the interface moves further into more compatible phase, PBT, although the viscosity of PBT is higher than PS. On the contrary, the clay in the PBT layer does not migrate to the PS phase at any shear rate, which means that its chemical affinity is strong enough to prevent shear-induced migration. The clay increases the viscosity of the PBT phase and results in a different morphology with a droplet, cocontinuous structure. As a result, when the clay is induced to migrate by hydrodynamic stress, it migrates into thermodynamically more stable positions at the interface or in the chemically more compatible phase, depending on the applied strain. Once it is located at a thermodynamically more stable position, it is difficult to push it out only by hydrodynamic stress. The location of clay is significantly affected by the morphology during evolution, which means that the blend morphology can control the droplet form and cocontinuous structure by control of the clay migration kinetics. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 565–575, 2008

Key words: clay migration; interface; morphology evolution; blend nanocomposite

INTRODUCTION

For the last decade, inorganic solid particles have been widely used to improve polymer performance. Nanoclay has attracted great attention from industry as well as from academia because of its larger surface area per unit weight. Such an improvement in physical properties with the addition of nanoclay platelets depends significantly on polymer–clay intercalation and its dispersion. Several polymer nanocomposites have been successfully developed by diverse methods such as solution intercalation, polymer melt intercalation, and so on.[1] These methods improve dispersion of nanoclays in the matrix using chemical or mechanical forces, as the properties of a nanocomposite are strongly dependent upon the degree of dispersion. Recently, blending of a second component has been suggested as a new

method to improve the dispersion of nanoclays in polymer melts.[2] The tendency of nanoclays to be localized at the interface of the multiphase system improves their homogeneous dispersion. The surface energy at the interface between the two phases improves clay dispersion.[3] On the other hand, this blending method has been suggested as a way to compatibilize immiscible polymer blends such as PP/polystyrene (PS), EVA/PP, and PE/poly(butylenes terephthalate) (PBT). Organically modified nanoclays (organoclay) frequently exhibit a synergic effect on the blend morphology beyond the reinforcing effect in a blend.[2–8] Previously Hong et al. investigated the compatibilization effect of organoclay on the blend morphology (PBT/PE).[9,10] When the organoclay is added to the polymer blend, it is localized at the interface and favorably dispersed in one specific component depending on chemical affinity. The organoclay localized at the interface results in effective size reduction of the dispersed phase and narrowed size distribution.[11–15] Furthermore, if the organoclay has a different chemical affinity with each phase, it selectively locates in a specific phase and results in a significant change in viscosity ratio of the blend by its reinforcing effect, which is rarely

TABLE I
Viscosity of PBT, PS, Composite with Nanoclay (PBT/clay and PS/clay) and Its Viscosity Ratio

Frequency (rad/s)	η (Pa s)				Viscosity ratio		
	PS	PBT	95/5 PBT/clay	85/15 PS/clay	η_{PS}/η_{PBT}	$\eta_{85PS/15clay}/\eta_{PBT}$	$\eta_{PS}/\eta_{PBT/clay}$
0.1	0.66K	0.65K	3.0K	0.92K	1.03	1.43	0.22
1	0.60K	0.65K	1.4K	0.65K	0.93	1.00	0.44
50	0.29K	0.58K	0.55K	0.28K	0.51	0.47	0.54
100	0.23K	0.55K	0.48K	0.22K	0.43	0.40	0.48

observed in the case of polymer blend mixed with a typical compatibilizer. Hence, the compatibilization or reinforcing effect of organoclay on a polymer blend can be determined depending on its degree of dispersion and its localization. For multiphase systems, the organoclay at the interface may suppress coalescence by steric repulsion between droplets that are surrounded by clay layers, when the droplets are approaching each other by thermal motion or hydrodynamic stress.[9–15] The coalescence suppression between the droplets effectively reduces the droplet size, and makes the dispersion more homogeneous. As a result, it is important to fully understand the effect of organoclay on the multiphase system to obtain good dispersion and compatibilizing effect. Though there has been considerable work on polymer blend nanocomposite, we know little about the kinetics of clay migration, or how clay tactoids migrate into the interface or cross the interface to the other phase.

In this study, we have tried to investigate the clay migration between phases during morphology evolution under well-defined flow conditions to further understand the kinetics of clay migration. It is assumed that the migration of clay tactoids between phases is induced by thermal Brownian motion, hydrodynamic force, and chemical affinity. For this purpose, two different polymers (PS, PBT) having different chemical affinities with organoclay and an organoclay that has a preference for PBT have been selected. A multilayered film was prepared and its morphology evolution was systematically investigated under controlled shear flow.

EXPERIMENTAL

Materials

The polystyrene (PS 2680, M_w: 230 K) used in this study is a commercial product manufactured by Cheil Industries (Gyeonggi-Do, Korea). PBT (M_n: 30 K; M_w: 53 K) was purchased from Sigma-Aldrich (St. Louis, MO). The PS has a melt index of 17.6 g/10 min (ASTM D 1238, 200°C/2.16 kg). The viscosity of PBT and PS at 240°C and its ratio are listed in Table I. Nanoclay used in this study (Nanofil 919; Sud-Chemie, Moosburg, Germany) was organically modi-

fied with stearylbenzyl dimethyl ammonium chloride (>C17) based on montmorillonite, and is known to be compatible with PBT and PA6. PS and PBT were premixed with nanoclay to fabricate PS/clay or PBT/clay nanocomposite through a twin screw extruder at a rotor speed of 100 rpm. The temperature profile of the extruder from solid conveying to die was set at 160-190-220-200°C and 210-230-240-225°C for PS and PBT, respectively. The PS/clay, PS, PBT/clay, and PBT were then compressed into a thin film with a thickness of 0.2 mm using a Carver laboratory hot press. PS was compressed at 180°C and PBT at 240°C. Three PBT and two PS/clay films were alternatively superposed and compressed to form a multilayered disc with a thickness of 1 mm at 180°C for 3 min as schematically drawn in Figure 1. A multilayered disc from three PBT/clay and two PS films was also prepared in the same way.

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}) diameters were calculated with image analyzing software (Image-Pro®; Media Cybernetics, Bethesda, MD). The long and short axis diameters of each droplet in the SEM picture were measured, and arithmetic mean of these two values $\left(D_i = \frac{D_{1i}+D_{2i}}{2}\right)$ was determined.
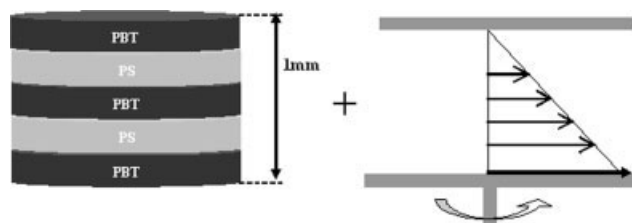

Figure 1 Schematic description of the experiment: side view of the multilayered PBT/PS blend and the shear field.
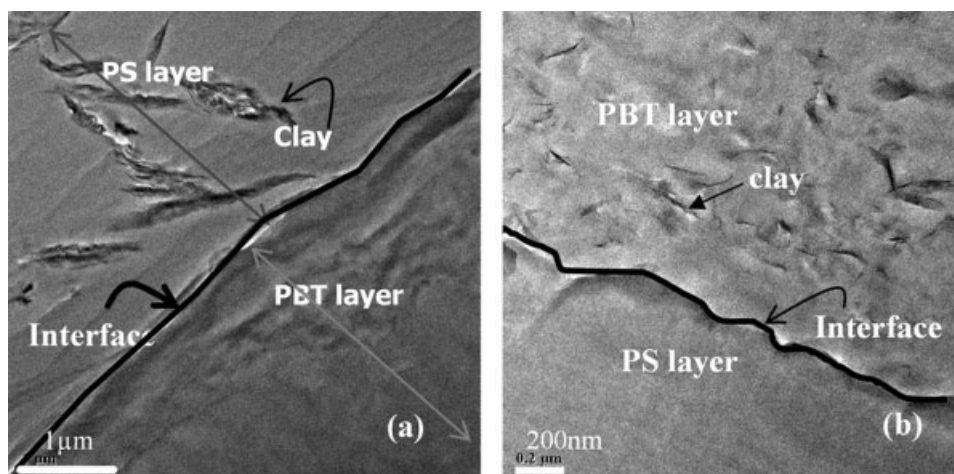
Figure 2 TEM pictures of (a) PBT/(PS/clay) and (b) (PBT/clay)/PS after 3600 s at 240°C (no flow).

Then, D_n and D_{vs} were obtained by using the following relation:

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

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

where, N is the total number of dispersed domains (over 200 drops). To observe morphology at lower magnification, confocal scanning laser microscope (LEXT OLS3000) was also used. 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 cryoultramicrotoming the blends encapsulated in epoxy with a diamond knife. The rheological properties were measured at 240°C using a RMS800 (Rheometrics, Twin Lakes, WI) with a parallel plate fixture (25 mm diameter). Complex viscosity [η (Pa s)], storage modulus [G' (Pa)], and loss modulus [G'' (Pa)] were measured as a function of frequency in the dynamic oscillatory mode.

RESULTS AND DISCUSSION

In the previous article, we reported the coalescence suppression effect of nanoclay in some immiscible polymer blends.[9,10] When two immiscible polymers, PBT and PE, are mixed with nanoclay, the average drop size is reduced and its distribution becomes more homogeneous. The nanoclay at the interface stabilizes the blend morphology by suppressing the coalescence between drops and reduces the interfacial tension. The effect of nanoclay is determined by its location and its degree of dispersion. Hence, to control the blend morphology or to achieve high performance of the nanocomposite, it is necessary to understand how clay migrates during morphology evolution, where it localizes, and which driving force(s) induces its dispersion. This work focuses on clay migration and its localization between the phases under shear flow. For this purpose, sandwich-type multilayer films have been fabricated such that the nanoclay is dispersed only in one phase, and are subjected to isothermal, uniform shear flow. A PS and PBT multilayered film is schematically illustrated in Figure 1, and the clays are dispersed only in one component, respectively. If PBT and PS/clay are superposed to form a multilayered film, it is named PBT/(PS/clay) [(PBT/clay)/PS is for PBT/clay and PS multilayered film]. The behavior of clay in this sandwiched film will be examined with regard to morphology evolution from the early stage under a well-defined flow field.

Thermal diffusion of clay

The PS/PBT blend was retained at 240°C for 3600 s in a dynamic time sweep mode (1 rad/s). For 3600 s, the rheological properties of each component were maintained constant without any change by thermal degradation (not shown here). Figure 2 shows the resulting cross-sectional area of PS/PBT after processing. In each case, (PS/clay)/PBT and PS/(PBT/clay) does not show any obvious clay migration across the interface. In the case of (PS/clay)/PBT, the clay tactoids have a length scale of a few microns and its thickness is of the order of a hundred nanometers. In PS/(PBT/clay), the size of the clay is much smaller than that in (PS/clay)/PBT, several hundred nanometers in length and a few nanometers in thickness. When the clay is in PBT phase, the degree of thermal migration can be estimated by
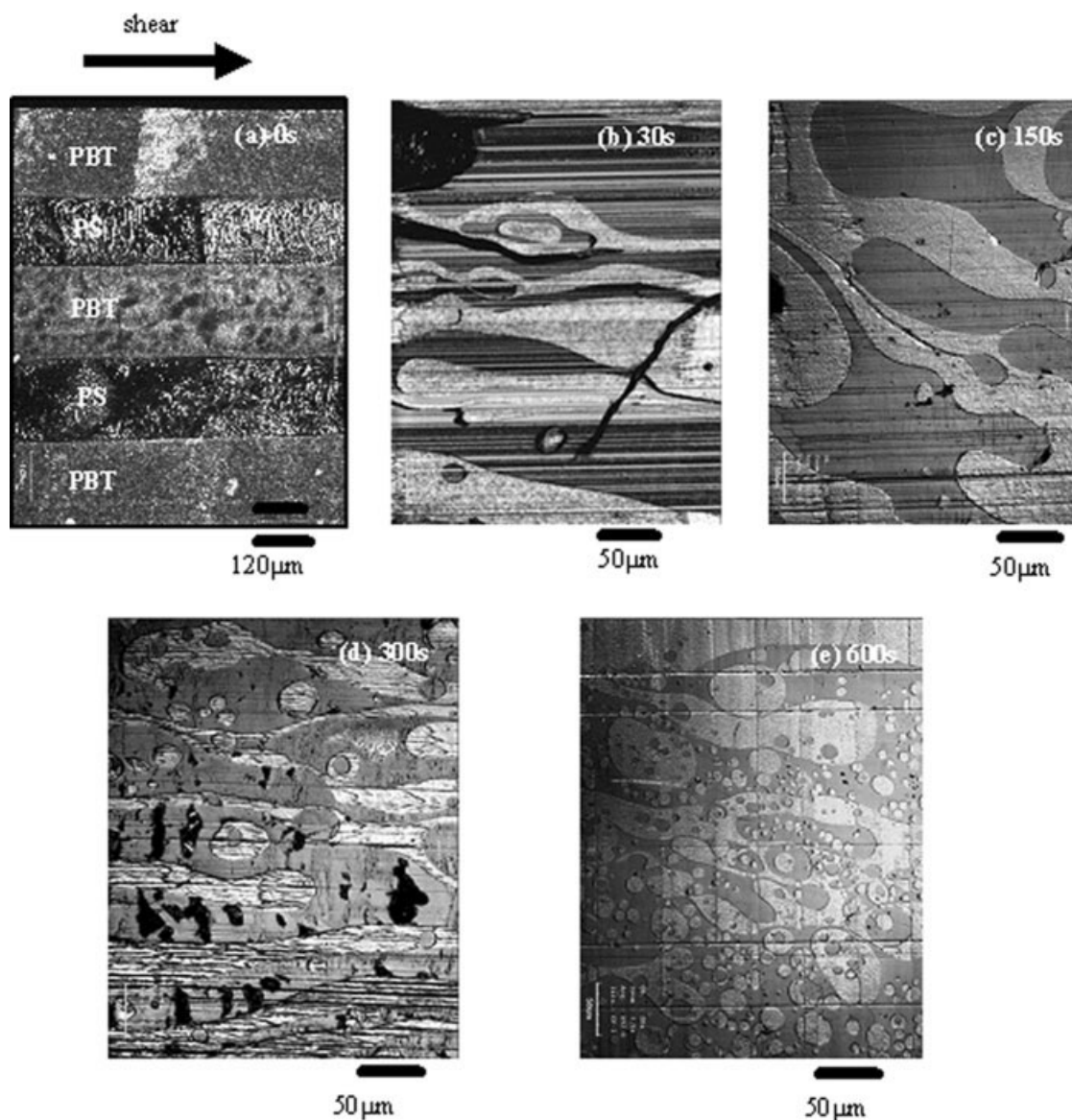
Figure 3 Morphology evolution of PBT/PS multilayered film at 1 s^{-1}: (a) 0 s, (b) 30 s, (c) 150 s, (d) 300 s, and (e) 600 s.

a rough calculation of thermal diffusivity (D_o), with the assumption of spherical clay particles of 0.3 μm in diameter (d)[16];

$$D_o = \frac{k_B T}{6\pi\eta_s d} \approx 2.0 \times 10^{-6}(\mu m^2/s)$$

where k_B is the Boltzmann constant, temperature T = 513 K, and medium viscosity η_s = 650 Pa s (see Table I). From this simple calculation, it can be presumed that the clay hardly migrates without any other driving force. For the clay in the PS phase, D_o is even smaller due to the much larger size of the clay particle, though the viscosity of PS is lower than PBT at this temperature. Therefore, it is clear that another driving force is necessary to disturb the equilibrium distribution of interparticle spacing and

to induce clay migration across the interface between the phases; furthermore, the force to induce clay motion must be supplied externally.

Deformation of multilayer films under shear flow

PBT/PS multilayer

The PS/PBT (without clay) was subjected to shear flow at 1 s^{-1} and 240°C. Figure 3 shows the morphology evolution of PS/PBT multilayered film, specially focusing on the early stage of evolution at 30, 150, 300, and 600 s. The initial thickness of each film is 200 μm. The viscosity of PS is lower than that of PBT and its ratio is a little lower than unity as shown in Table I. At the early stage of shear, the flow does not destroy or change the interface
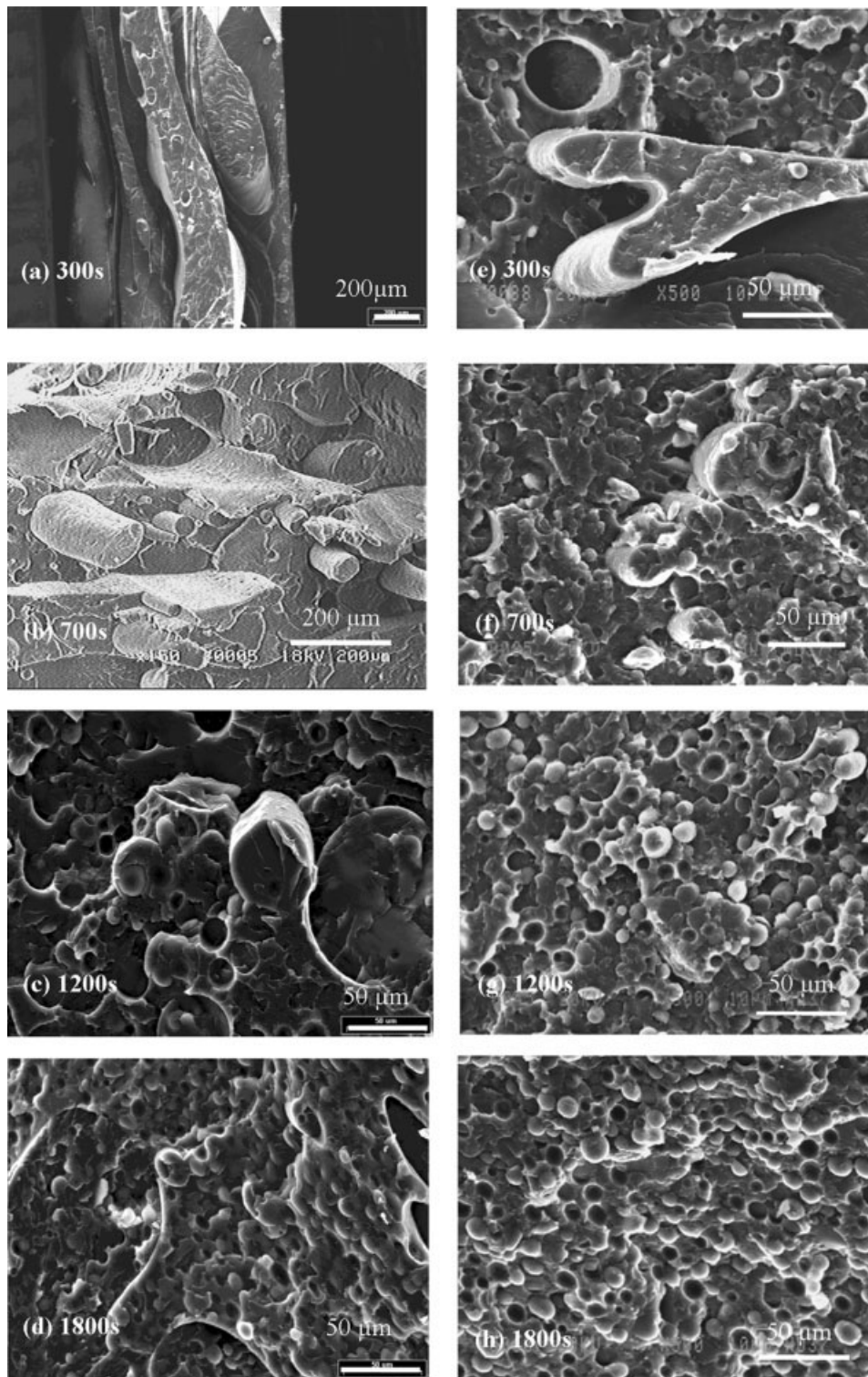
Figure 4 Morphology evolution of (a–d) PBT/PS and (e–h) PBT/(PS/clay) at 1 s^{-1} at various evolution times: (a, e) 300 s, (b, f) 700 s, (c, g) 1200 s, and (d, h) 1800 s.

between the phases because PBT and PS are thermo-dynamically immiscible, and the deformation is not large enough to cause significant mixing between the layers. However, at the interface there is a discontinuity in stress between the layers ($\tau_{PBT\ layer}$ − $\tau_{PS\ layer}$), and it is balanced by the interfacial stress

(Γ/R). Hence, this interfacial tension results in deformation along the y-direction to minimize the curvature at the interface.

When the multilayered film is beginning to deform under flow, each layer deforms affinely with the global shear deformation. Each polymer layer is
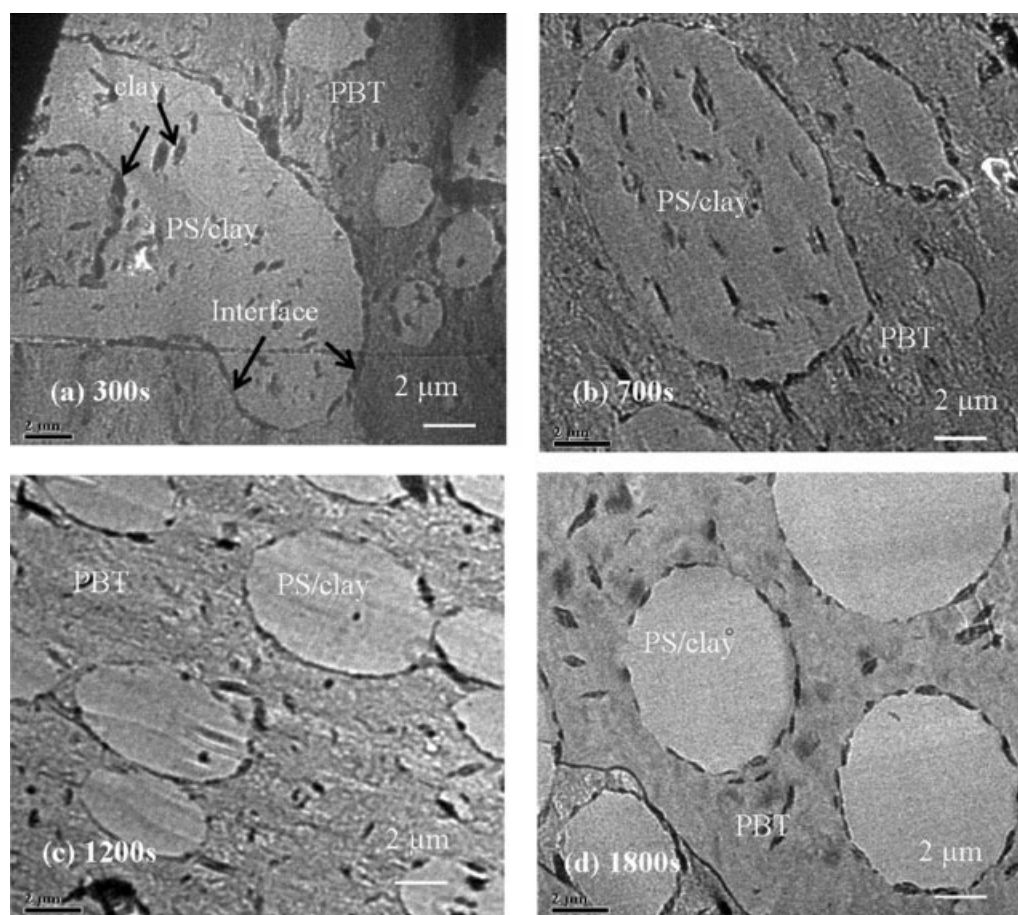
Figure 5   TEM pictures of PBT/(PS/clay) at 1 s^{-1} at various evolution times: (a) 300 s, (b) 700 s, (c) 1200 s, and (d) 1800 s.

deformed by viscous drag transferred through another polymer layer of different viscosity and interfacial tension. The interface between the films becomes undulated by gradient-direction deformation induced by interfacial tension as the flow continues. The film structure is essentially retained until the evolution time of 30 s. After 150–300 s, the film structure macroscopically recedes, and the PS or PBT layer forms a phase of irregular shape. After 300 s, the fibril structure is competitively generated [Figs. 3(d) and 4(b)]. This means that the interfacial area begins to increase dramatically because a phase of macro length scale splits into a fibril structure of micron size. After 1200 s, the fibril structure evolves into a droplet structure. Fibrils are actively broken up into many droplets of micrometer scale under the influence of interfacial tension and hydrodynamic stress. When the multilayered PS/PBT blend is subjected to shear flow for 1800 s, it shows stable droplet morphology. PBT/PS shows a typical morphology evolution of polymer blends; at shear rate 1 s^{-1}, the film evolves into fibril structure after 600 s and evolves further into droplet structure at 1800 s, sequentially.

PBT/(PS/clay) multilayer

When the clay is added to the PS phase, the viscosity ratio (λ) increases slightly from 0.93 to 1.0 at shear rate 1 s^{-1}, which means that the average droplet size can increase and the breakup of the dispersed phase by Rayleigh instability can frequently occur during morphology evolution.[17] When the morphology evolution of PBT/(PS/clay) is compared to that of PS/PBT, the film structure of PBT/(PS/clay) evolves more quickly to a droplet structure. Figure 4 compares the morphology evolution of PBT/PS [Fig. 4(a–d)] and PBT/(PS/clay) [Fig. 4(e–h)] under the shear flow of 1 s^{-1} and 240°C. In the case of PBT/(PS/clay), it shows a dramatic reduction in domain size when it is subjected to the flow for 700 s. The film structure quickly evolves into droplet structure as seen in Figure 4(e,f), though few fibrils are still observed in Figure 4(f). After the evolution for 1200 s, the dispersed phase forms a droplet structure with the diameter range of 10–20 μm. This discrepancy in morphology evolution comes from the addition of clays in the PS phase. As expected from previous work,[9,10] the clay localized at the interface reduces the interfacial tension, making breakup eas-
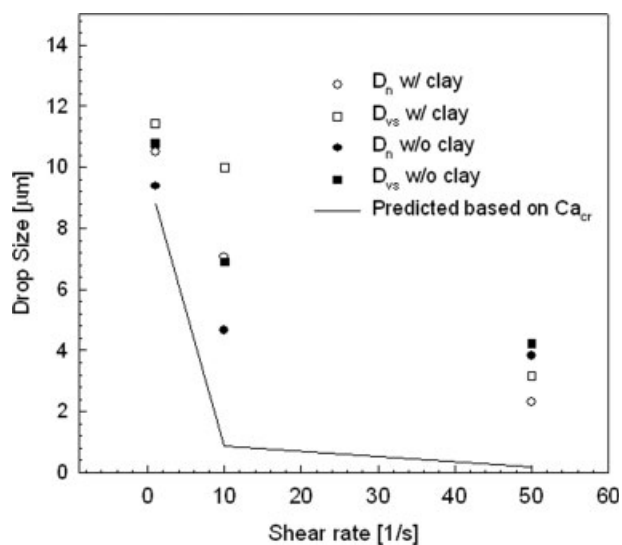
Figure 6 Number-average and volume-to-area averaged drop size of PBT/PS and PBT/(PS/clay) as a function of shear rate (evolution time is 1800 s for 1 s^{-1} and 700 s for 10 and 50 s^{-1}).

ier. In addition, the clay tactoids in PS phase migrate into the PBT phase as more strain is applied. TEM photographs clearly show (Fig. 5) that the clay in the PS phase migrates into the interface—such migration cannot be caused simply by thermal motion during the observation time (Fig. 2). At the early stage of evolution (300 s), most clay tactoids are located inside the PS phase [see Fig. 5(a)]. When evolved up to 700 s, though some clay tactoids still remain inside of PS domain, many of them are observed at the interface as well [see Fig. 5(b)]. This implies that the hydrodynamic stress induces the nanoclay in the viscous medium to migrate into the interface which is thermodynamically stable with the minimum chemical potential in the multiphase system. At 1200 s, most clay tactoids in PS phase are migrated into the interface by shear. As shear is applied more and more, the clay tactoids at the interface migrate further into the PBT phase due to their chemical affinity with PBT. In Figure 5(c,d), the clay tactoids which were initially in the PS phase have now migrated into the interface and present only in the PBT phase.

When PBT/(PS/clay) evolves into a droplet structure under the shear flow of 1 s^{-1}, the nanoclay significantly affects the morphology evolution because the clay shear-migrates to the interface or even to the other phase. In the early stages of morphology evolution, clay tactoids in the PS phase migrate into the interface. As further shear is applied (critical strain of 700 at shear rate 1 s^{-1}), they cross the interface. Clay tactoids at the interface reduce the interfacial tension. Above the critical strain, the clays in PS phase crossover into the PBT phase though the viscosity of PBT is higher than PS. The affinity of clay

toward PBT is strong enough to drive the clay out of the interface that is thermodynamically metastable.

When enough shear is applied to disturb the static state of clay distribution, the time scale (t_D) to diffuse a distance equal to its size (a) can be estimated as follows:[16]

$$t_D = \frac{6\pi\eta_s a^3}{k_B T},$$

where k_B is the Boltzmann constant, T is 513 K, and η_s is the viscosity of the matrix (PS), 660 Pa s at 0.1 rad/s. For example, for a clay tactoid of 100-nm radius to diffuse as much as its radius in a viscous medium of 660 Pa s, it takes about 1800 s. Furthermore, it will take a much longer time, $\sim$3.8 h if the radius of clay particle is doubled as much as 200 nm. This means that, if the magnitude of shear exceeds a critical value, the clay particle can migrate and its time scale depends on its size. Hence, the motion of clay tactoids can be accelerated by flow as long as enough hydrodynamic stress is applied. When the shear rate ($\dot{\gamma}$) increases from 1 to 50 s^{-1}, the Peclet number (Pe) increases significantly from 90 to 2000, which means that a large amount of force is supplied from the hydrodynamic shear flow to accelerate particle migration;[16]

$$Pe = \frac{\eta_s \dot{\gamma} a^3}{k_B T} \propto \dot{\gamma} t_D.$$

To observe the effect of flow on migration, flow of a different shear rate was applied and the corresponding morphology evolution was observed. The droplet size and the location of clay are significantly dependent upon the applied shear rate. Figure 6 compares the change of droplet size with shear rate. As the shear rate increases, the average droplet size (D) is reduced as predicted by Taylor ($D = \Gamma/\eta_s\dot{\gamma}$, where Γ is the interfacial tension). According to Taylor's prediction,[18] provided that it is dilute enough to exclude coalescence, the diameter is simply calculated as 8.8, 0.88, and 0.18 μm for shear rate 1, 10, and 50 s^{-1}, respectively (the interfacial tension of PBT/PS is 5.7 mN/m, which was measured by the breaking thread method[19] and cross checked with the Palierne model[20]). But in this case, the average diameter is much larger than expected due not only to the viscoelasticity of each phase, but also to the coalescence and breakup of PS drops (the blend composition in this study is as high as 30 wt %).

With clay addition, the droplet size of the dispersed phase (PS) is a little larger than that of the blend without clay at lower shear rates of 1, 10 s^{-1} but becomes smaller at higher shear rate. When the blend morphology is compared for three different flow rates (1, 10, and 50 s^{-1}), TEM photographs
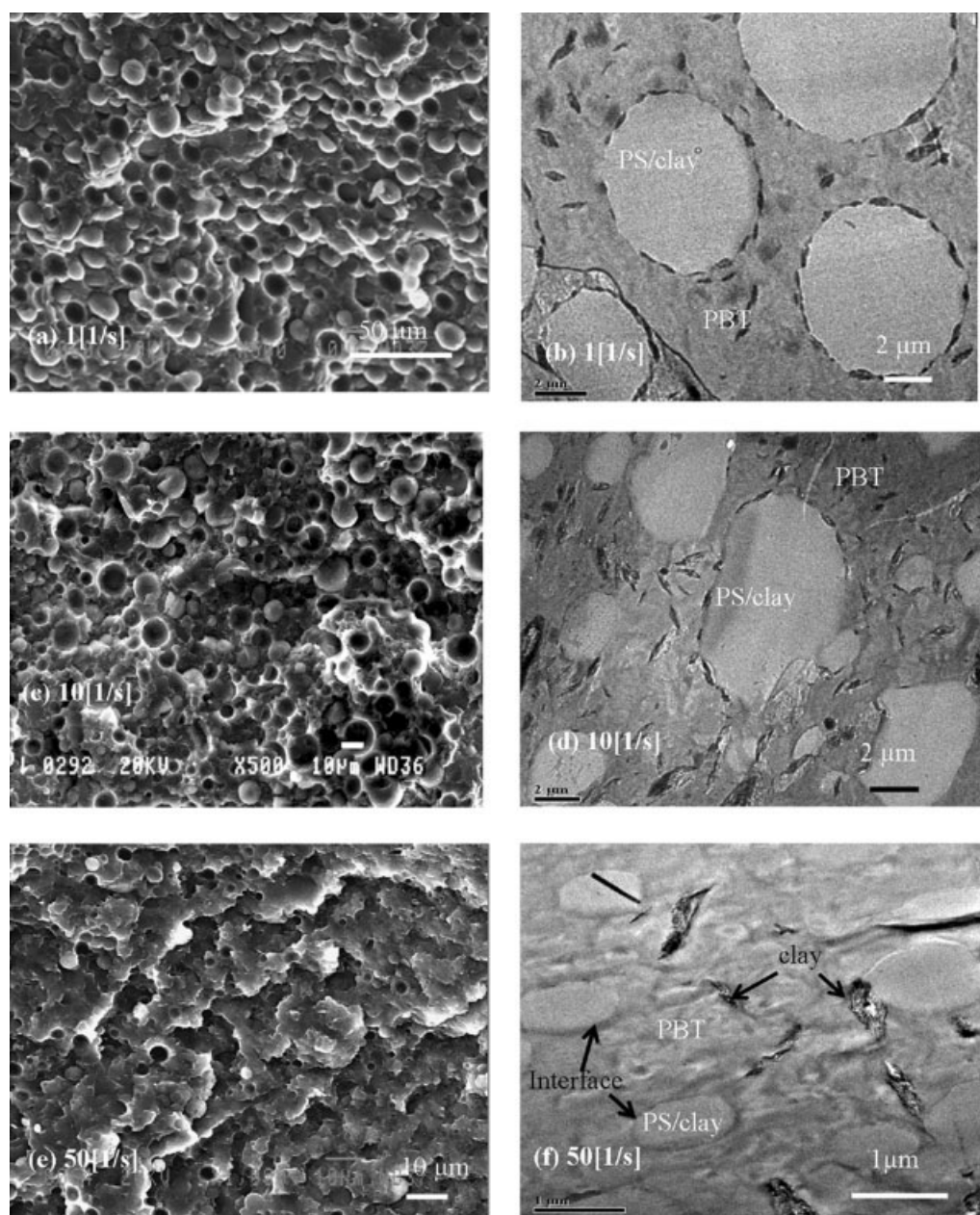
Figure 7 Morphology of PBT/(PS/clay) depending on shear rate: (a, b) 1 s^{-1} for 1800 s, (c, d) 10 s^{-1} for 700 s, (e, f) 50 s^{-1} for 700 s.

always confirm that the clays are located at the interface (Fig. 7) or in the PBT phase, and they do not remain in the PS phase. As a result, the clay plays an important role in determining the droplet size; the interfacial tension is reduced by the localization of clay at the interface and the viscosity of PBT and PS would be changed depending on the kinetics of clay migration. That is, the clay shows an opposite effect on the droplet size.

At lower shear rates, the droplet size of the dispersed phase (PS) is a little larger than the blend without clay due to the filling effect of clay (λ is increased from 0.9 to 1.0 at shear rate of 1 s^{-1}). The

clay remains in the PS phase for most of time during morphology evolution (1800 s). Although clay tactoids are migrated into PBT after 700 s (Fig. 5), the evolution time may not be enough to observe the effect of clay migration on blend morphology. However, at larger shear rates, the clay migrates into the interface or PBT phase at early stage of morphology evolution and the average domain size is reduced by the harmonic effect from the reduced interfacial tension and the filling of clay into PBT. At shear rate 10 s^{-1}, the rheological properties of blend in the middle of morphology evolution were measured to understand the degree of the evolution and the time
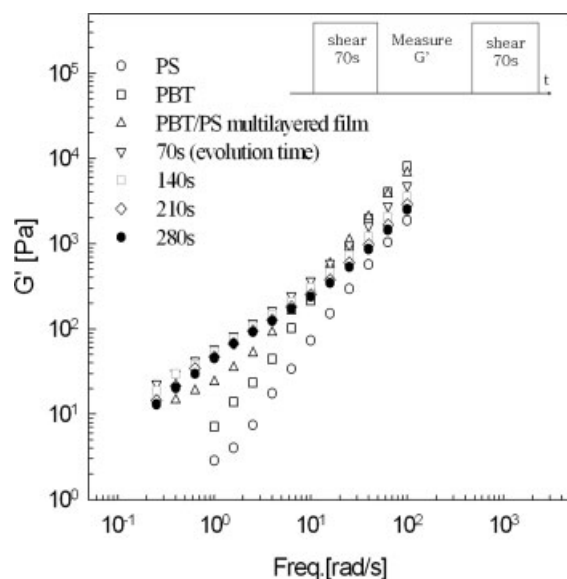
Figure 8 Storage modulus of PBT/(PS/clay) at 10 s^{-1} depending on evolution time.

needed to reach stable morphology. Steady shear of 10 s^{-1} was applied to the blend for 70 s and the modulus of blend was measured for about 100 s. Shear is applied again as illustrated in the inlet schematics of Figure 8. The modulus in the lower frequency region increases with evolution time as can be seen in Figure 8 because the increase of interfacial area is increased as the morphology evolves from a film into a droplet structure. In addition, the morphology has already reached a stable droplet morphology before 210 s (strain < 2100). From the morphology evolution point of view, the stable droplet structure is obtained at around strain = 1200 (after 1200 s at shear rate of 1 s^{-1}, Fig. 4), which means that both rheological and morphological observations represent the overall state of morphology evolution very well. From the observations on morphology evolution as well as the clay migration in PBT/(PS/clay) blend under shear flow, it becomes evident that the clay can shear-migrate into the interface at an early stage of morphology evolution and it significantly affects the overall morphology evolution. As a result, the droplet size is affected by the degree of migration because the clay can change not only the viscosity ratio but the interfacial tension according to its localization.

(PBT/clay)/PS multilayer

Compared to the clay tactoids in the PS/clay phase, they are well dispersed in PBT phase with a thickness < 70 nm because the surfactant on the clay surface has a strong preference for PBT. When (PBT/clay)/PS is subjected to flow with the same condi-

tion as before, the morphology evolves differently as can be seen in Figure 9. This different morphology evolution is strongly related to two factors. First, there is a significant increase in viscosity of the PBT/clay phase by the good dispersion of clay tactoids and the viscosity ratio (λ) is large ($\lambda = \eta_{PBT/clay}/\eta_{PS} \approx 2.0 > 1$). It is well known that the breakup of droplets under shear flow is highly dependent on the viscosity ratio because the critical capillary number (Ca_{cr}) changes with viscosity ratio. When λ is between 1 and 2, the droplet is prolonged by shear flow and broken up at the middle of the prolonged domain depending on the hydrodynamic stress. As λ becomes larger, the breakup of the droplet is unexpected because Ca_{cr} rapidly increases. In this case, the morphology evolution occurs only with difficulty under the shear flow. In this case, the blend composition of PS and PBT/clay layers ($\phi_{PS}/\phi_{PBT/clay} \approx 0.55$) is close to the phase inversion region ($\phi_{PS}/\phi_{PBT/clay} = \eta_{PS}/\eta_{PBT/clay} \approx 0.44$–0.54, see Table I), and the morphology tends to form a cocontinuous structure.[16] Second, the interfacial tension is not reduced effectively due to a few migrated clay tactoids at the interface. The clay migration that was easily observed in PBT/(PS/clay) blend is rarely observed in (PBT/clay)/PS blend even under high shear of 50 s^{-1}. Figure 9 compares the morphology of (PBT/clay)/PS evolved for 700 s under different shear rates, 1, 10, and 50 s^{-1}, respectively. At a shear rate of 1 s^{-1} [Fig. 9(a,b)], the PBT/clay layer is deformed but the dispersed phase is still in the tens of micrometers scale, which is very different from the previous case, PBT/(PS/clay) [Figs. 4(f) and 5(b)]. As mentioned earlier, the large droplet and fibril structure can be frequently observed during the formation of the cocontinuous phase. When the shear rate increases from 1 to 10 s^{-1}, the morphology may evolve into a droplet structure. However, even then, fibrils larger than 20 μm in diameter are occasionally observed. At the shear rate 50 s^{-1}, (PBT/clay)/PS actually shows a cocontinuous structure as expected because the viscosity ratio at 50 s^{-1} satisfies the condition for phase inversion ($\phi_{PS}/\phi_{PBT/clay} = \eta_{PS}/\eta_{PBT/clay}$).

When we tried to observe the location of nanoclays in PBT/clay phase with high magnification (not shown here), most clays remained inside the PBT/clay phase and only a few clay tactoids are localized at the interface. Also the clay tactoids, whether they are at the interface or in PBT phase, never migrate into the PS phase even at higher shear rate, which means that the critical factor to induce clay migration in this blend system is not the flow but the chemical affinity between the phase and clays. If there is no affinity between the components (PBT and clay in this case), the clay particle in PBT may migrate more easily into the PS phase com-
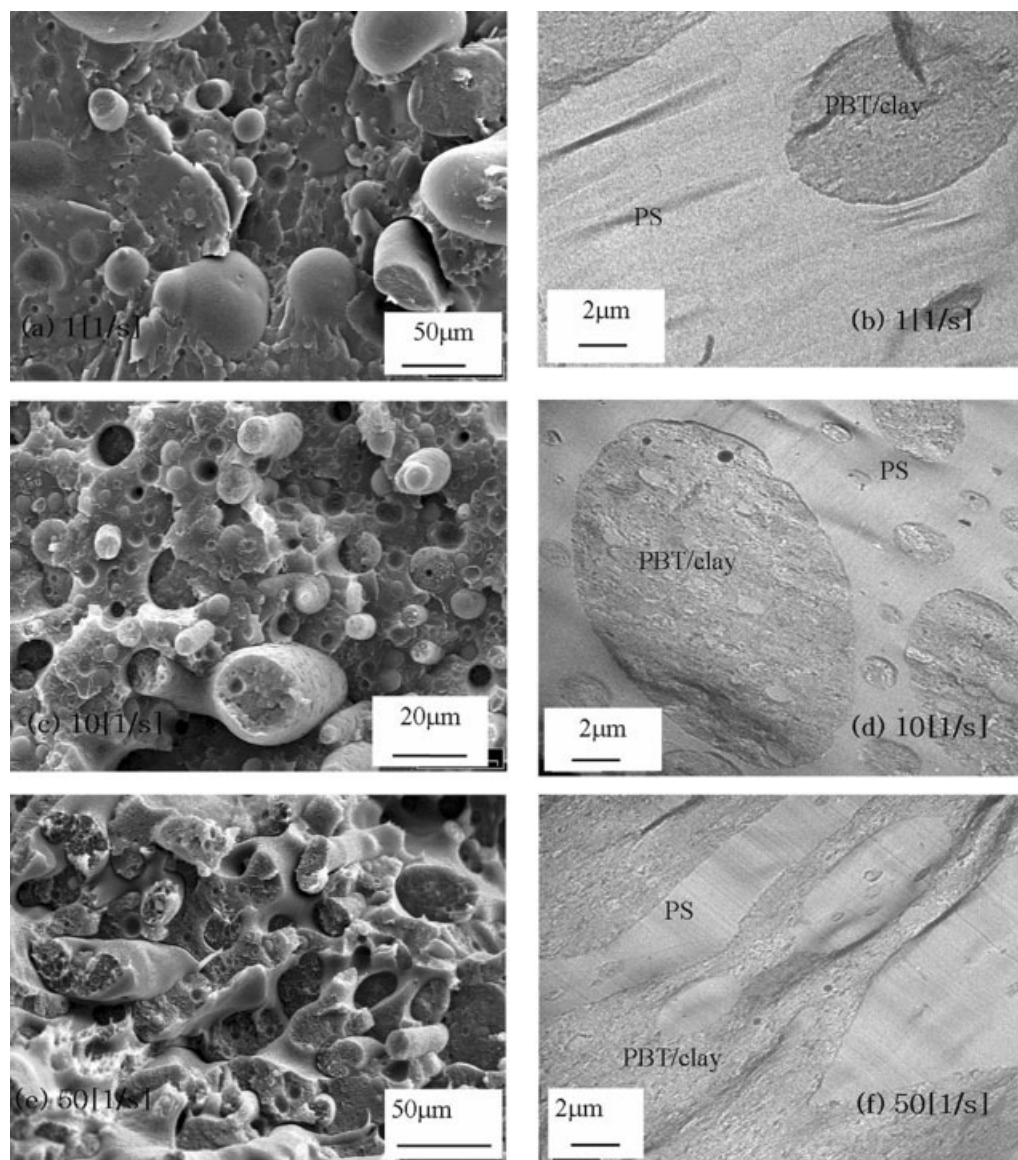
Figure 9 Morphology of (PBT/clay)/PS after 700 s at different shear rates: (a, b) 1 s^{-1}, (c, d) 10 s^{-1}, (e, f) 50 s^{-1}.

pared to the migration from PS to PBT phase ($Pe_{clay\ in\ PBT} > Pe_{clay\ in\ PS}$) because the viscosity of PBT is higher than that of PS. However, the migration into the PS phase was not observed at all, which means that, under our experimental conditions, the chemical affinity between PBT and clay is strong enough to prevent clay migration into the other layer by hydrodynamic stress.

CONCLUSIONS

This study shows how hydrodynamic stress and chemical affinity between the polymer and clay control the localization of nanoclays and morphology evolution in multiphase blend nanocomposite sys-

tems. The role of clay in an immiscible polymer blend, whether reinforcing or compatibilizing, is determined by the location of the clay and the degree of dispersion. Within the time scale of our investigation, there was little thermal migration of clay tactoids in polymer melts because they are too large to diffuse (diffusion constant is too small) and the matrix viscosity is high. When the PBT/PS multi-layered blend is subjected to flow, the clay tactoids dispersed in the PS layer first migrate to the interface depending on the amount of applied strain. The clay tactoids at the interface render the blend morphology more stable compared to the blend without clay because of the coalescence suppression effect of clay at the interface. As more shear is applied, the clay tactoids at the interface move further into the

more compatible phase, PBT, although its viscosity is higher than PS. On the contrary, the clay tactoids in PBT layer do not migrate to the PS phase at any shear rate, which means that their chemical affinity is strong enough to prevent shear-induced migration. When the clay tactoids are induced to migrate by hydrodynamic stress, they migrate into thermodynamically more stable positions, at the interface or in the chemically more compatible phase, depending on the applied strain. Once they are located at thermodynamically more stable position, it is hard to push them out by hydrodynamic stress alone.

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