

Effect of Steady Shear on the Microstructural Evolution of Melt-Intercalated Polymer/Clay Nanocomposites

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ABSTRACT: A sheet sample composed of poly(butylene terephthalate) and clay prepared by solid-state compression was melt-annealed in a rheometer under steady shear flow to investigate the whole hybridization process. The results of the offline morphology and thermogravimetric analysis as well as Fourier transform infrared characterization show that shear flow can reduce the dynamic process of hybridization, facilitating the formation of an intercalated nanoscale structure. With an increase in the shear intensity, the detachment level of clay increases more remarkably than the swollen degree. However, an increase in the shear intensity

does not induce an exfoliated structure but can decrease the average thickness of the clay tactoids, leading to a remarkable enhancement in the thermal stability due to the increase in the effective filling volume of the clay. Furthermore, those intercalated nanocomposites annealed at a high shear rate still present a distinct hierarchical structure, which suggests that steady shear is not as good as dynamic or complex shear for promoting hybridization effectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1740–1748, 2007

Key words: clay; nanocomposites; polyesters; shear

INTRODUCTION

The polymer melt intercalation of layered silicates (clay) is a viable approach to the synthesis of a variety of polymer/layered silicate nanocomposites (PLSNs). Since the possibility of direct melt intercalation was first demonstrated by Giannelis and coworkers,^{1,2} the melt-intercalation method has become mainstream in the preparation of intercalated polymer nanocomposites because of its environmentally benign character, versatility, and compatibility with current polymer processing techniques.^{3–5} As a result, the morphology evolution of clay and its kinetics, that is, how polymer chains crawl into the interlayer space of clay forming either intercalated or exfoliated nanocomposites, have attracted much attention.

Hitherto, many excellent works have been reported on this important question. Vaia and coworkers^{6,7} first studied the static kinetics of polymer melt intercalation in polystyrene/organoclay. They

found that silicate particles are effectively agglomerates of smaller, primary particles consisting of 10–20 layers in a coplanar orientation (usually called tactoids), and polystyrene melt intercalation in an organoclay is controlled by mass transport into the primary particles of the silicate and is not specifically limited by the diffusion of the polymer chains within the silicate gallery. The activation energy of hybrid formation is similar to that of polystyrene self-diffusion in the bulk melt. Further studies of the morphology evolution of clay in PLSNs under dynamic shear environments were conducted by Krishnamoorti et al.⁸ and Galgali et al.⁹ through a rheological method. However, limited by the experimental method, they did not actually explore the intercalation process in the rheometer because the intercalation in their experimental samples produced by an extruder had almost completed before the rheological characterization. Li et al.¹⁰ prepared a multilayered sample and succeeded in investigating the whole intercalation progress and kinetics of polypropylene/clay hybrids in a dynamic shear flow by a rheometer.

The effect of complex shear flow on a clay dispersion in a polymer matrix has also been well investigated. Fu and coworkers^{11,12} studied the effect of dynamic shear on the dispersion of clay in a polymer matrix via dynamic packing injection molding. They found that only an intercalated structure of clay could be obtained without shear flow, whereas

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an exfoliated morphology in the core region of the annealed samples could be achieved after the dynamic annealing process. Paul et al.¹³ recently demonstrated the importance of processing conditions, such as the residence time and intensity of shear, on the delamination level of silicate stacks in polyamide-6/clay nanocomposites prepared through conventional melt intercalation in a corotation two-screw extruder.

On the basis of those reports, it can be concluded that shear processing, as performed by an ultrasonicator, parallel-plate rheometer, or conventional compounding equipment, can facilitate the detachment of clay from agglomerates to primary particles and increase the uniformity of the layers or tactoid distribution in the polymer matrix. However, all this work mainly focuses on the intercalation kinetics and morphology evolution of clay in PLSNs during a quiescent annealing process without shear flow or under dynamic annealing conditions such as small-amplitude oscillatory shear by a rheometer and complex shear by an extruder, whereas no report has been found in the literature on the effect of steady shear flow on the morphology evolution and kinetics of PLSNs until now.

In our previous work,^{14–16} we studied the rheological behavior of intercalated poly(butylene terephthalate) (PBT)/clay nanocomposites and found a further local hierarchical structure development of the clay tactoids during the dynamic annealing process. The formation of the liquid-crystalline-like phase structure in a PLSN might be the major driving force for the percolation of tactoids. However, the kinetic process of network formation strongly depends on both the chemical environment and the shear flow. Then, to investigate the kinetics of PBT melt intercalation under dynamic shear flow, we prepared a multilayered sample and studied the whole intercalation process, using a rheological approach.¹⁷

In this work, we studied the intercalation kinetics and morphology evolution of PBT/clay hybrids under steady shear flow in a rheometer. To investigate the whole intercalation process, a sheet sample prepared by the solid-state mold compression of a mixture of PBT powder and clay was annealed in the rheometer. However, the waferlike sheet sample changed into a bread-ring-like one after being annealed in steady shear flow because of its structure, which was looser than that prepared by melt compression (see Fig. 1). Accordingly, those rheological data obtained could not be used to establish the quantitative kinetic relationship with the development of the relative volume fraction of intercalated tactoids. However, those results from offline morphology characterization may still afford some useful information about the effect of steady shear on the formation of PLSNs.

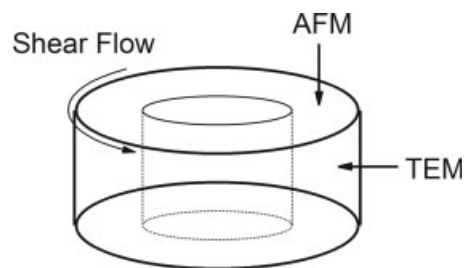


Figure 1 Schematic depiction of the annealed samples and observation direction of the morphology characterization.

EXPERIMENTAL

Materials and sample preparation

The PBT (1097A; number-average molecular weight = 23,200, melting point = 223°C) used in this study was a commercial product of Nantong XinChen Synthetic Material Co., Ltd. (Nantong, Jiangsu Province, People's Republic of China). The organoclay (trade name DK4), with a particle size of less than 50 μm , was supplied by Zhejiang FengHong Clay Co., Ltd. (Huzhou, Zhejiang Province, People's Republic of China), and it was modified with hydrotallow 2-hydroxyethyl ammonium. Its 5 wt % loss temperature was about 280°C.

The PBT pellet was first comminuted into powder with a pulverizer and mixed well with the clay subsequently. Then, the blends were solid-state-compressed into films with a thickness of about 2 mm at 200°C, which was lower than the melting point of PBT, 223°C, to avoid intercalation. The clay loadings were 4 wt %.

Annealing process under steady shear flow

The annealing process of the samples was performed in a rheometer (Gemini 200, Bohlin Co., Malvern, Worcestershire, UK) equipped with a parallel-plate geometry with 25-mm-diameter plates. The sample was annealed at 230°C under a predetermined shear rate in a nitrogen environment. The shear rate was 1, 2, 5, 10, or 20 s^{-1} . The annealed samples presented a hollow bread-ring-like shape because the steady shear flow changed its loose structure into a compact one. At the various annealing stages, the molten sample was cooled rapidly to the solid state from 230 to 190°C within less than 1 min and then placed in liquid nitrogen to keep the morphology frozen for further offline morphology characterization (see Fig. 1). A blank sample annealed without shear flow was also characterized for comparison.

Morphology characterization

The swollen degree of the clay in the samples was determined by X-ray diffractometry (XRD). The

experiments were performed with a Rigaku Dmax-rC diffractometer (Tokyo, Japan) with a copper target and a rotating-anode generator operated at 40 kV and 100 mA. The scanning rate was $2^\circ/\text{min}$ from 2 to 10° .

The transmission electron microscopy (TEM) micrographs of 80–100-nm-thick, ultramicrotomed sections were taken with a Tecnai 12 transmission electron microscope (Philips Co., Eindhoven, The Netherlands) with a 120-kV accelerating voltage.

The atomic force microscopy (AFM) micrographs were carried out in air with a Nanoscope III multi-mode microscope from Digital Instruments (Veeco Instruments Inc., New York) operating in the tapping mode. The image ($512 \text{ pixels} \times 512 \text{ pixels}$) was obtained at selected magnifications.

Fourier transform infrared (FTIR) spectroscopy

With a FTIR spectrometer (Equinox 55 FTIR, Bruker Co., Karlsruhe, Germany), *in situ* FTIR spectra were obtained at room temperatures in a reflection mode. The spectral resolution was maintained at 1 cm^{-1} .

Thermogravimetric analysis (TGA)

All TGA was performed on a PE Instruments TGA-7 (Boston, MA). Samples of 10–12 mg were heated from room temperature to 800°C at a rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. All TGA results are the averages of a minimum of three determinations; the temperatures were reproducible to $\pm 1^\circ\text{C}$, whereas the error bars on the fraction of nonvolatile material was $\pm 3\%$.

RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of those samples annealed for various times. In the original sample, the d_{001} peak of the organoclay can be observed at $2\theta = 4.9^\circ$, and the interlayer distance is about 1.8 nm. Figure 2(a) shows that during the quiescent annealing process without shear flow, the d_{001} peak shifts to lower angles gradually, indicating that the clay gallery is swollen by PBT chains to some extent. With 120 min of annealing, the interlayer spacing of clay increases to about 2.1 nm, only slightly larger than that of the initial state. However, to the sample annealed under the steady shear at a shear rate of 20 s^{-1} , as can be seen in Figure 2(b), the d_{001} peak shifts to lower angles remarkably, suggesting that the clay tactoids are well intercalated by PBT chains.

To further confirm the morphology of the clay, a TEM study was carried out on those samples annealed for 120 min. Figure 3(a) shows the TEM image of the sample quiescently annealed without shear flow. Clearly, the swollen degree of stacks and/or tactoids of the clay is very small. The sample is still a microcomposite. However, for the sample

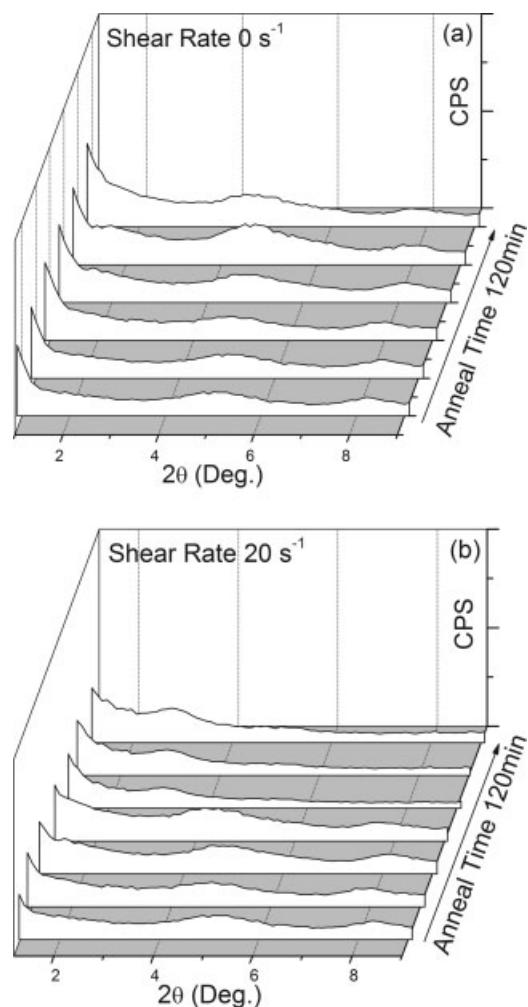


Figure 2 XRD traces of samples quiescently annealed (a) without shear flow and (b) at a shear rate of 20 s^{-1} for various times. CPS is the relative diffraction intensity, which is often used as measurement of y-axis in XRD patterns.

annealed under steady shear at a shear rate of 20 s^{-1} , the tactoids composed of several tens to hundred of silicate layers show a typical intercalated structure, as can be seen in Figure 3(b).

The results for the clay dispersion from XRD and TEM were further confirmed by FTIR measurements. Figure 4 presents the FTIR spectra of neat PBT and those annealed samples. The absorption band for PBT appears at about 1720 cm^{-1} , representing the free carbonyl stretching vibration peak.^{18,19} The carbonyl peak is one of the most widely used peaks in the analysis of FTIR spectra because it not only exists in numerous organic compounds but also shows an important shift due to an electron density change resulting from the environmental elements. To the sample annealed without shear flow, the carbonyl peak is still at 1720 cm^{-1} , indicating that few interactions take place between the PBT chains and clay. The results from XRD and TEM indicate that although it is partially soaked or swollen by PBT

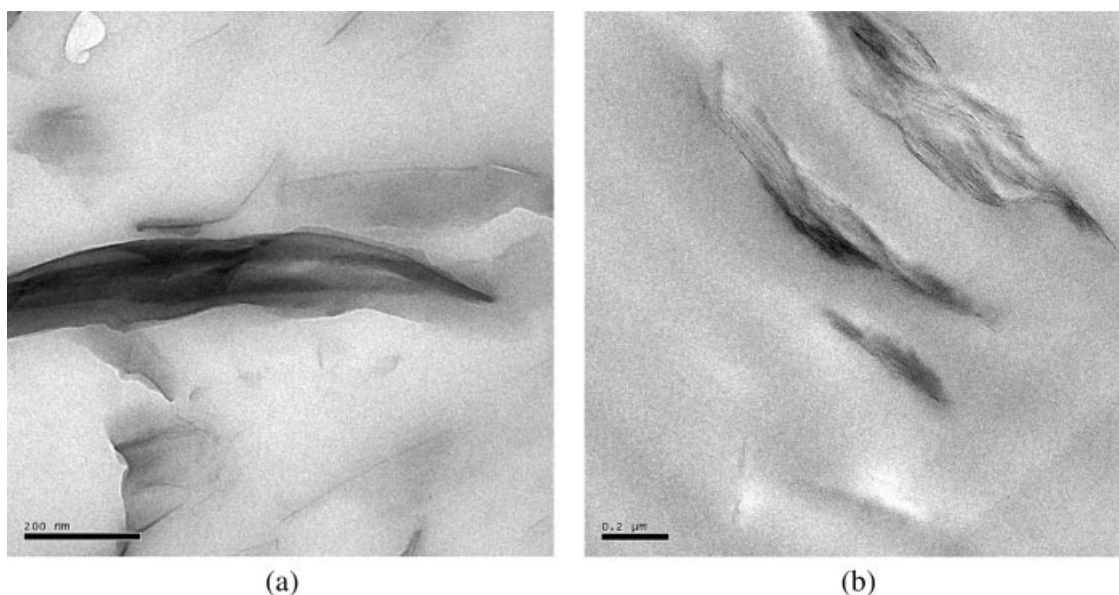


Figure 3 TEM images of samples quiescently annealed (a) without shear flow and (b) at a shear rate of 20 s^{-1} for 120 min.

chains, the clay presents a dispersion state mainly in stacks or compact tactoids. Therefore, the interactions between the PBT matrix and clay are very weak. However, the sample annealed under steady shear at a shear rate of 20 s^{-1} shows two stretching peaks (see the amplificatory image of the part in the ellipse), one peak at about 1725 cm^{-1} attributable to the free carbonyl stretching peak and another peak at about 1716 cm^{-1} attributable to the stretching vibration of those carbonyl groups subjected to strong interactions (see the arrow). Apparently, shear flow can promote the detachment of clay agglomerates and the intercalation of PBT chains, producing more intercalated tactoids in a smaller thickness. Both the confinement effect on PBT chains by the clay gallery and the increasing phase interface

enhance the interactions between the PBT chain and tactoid surfaces. As a result, the stretching vibration peak of the C—O bond in PBT at 1265 cm^{-1} also shows a shoulder at 1250 cm^{-1} (see the arrow).

All these results indicate that PBT chains can diffuse into clay particles spontaneously during a quiescent annealing process because of their chemical affinity. However, the whole intercalation may be a very long dynamic process. In other words, the intercalation cannot complete within a predetermined experimental time, 120 min, under quiescent annealing conditions without shear. However, in the steady-shear-flow environment, the whole hybridization process of the samples decreases remarkably. That is, simple steady shear flow can also promote hybridization like that of dynamic or complex shear

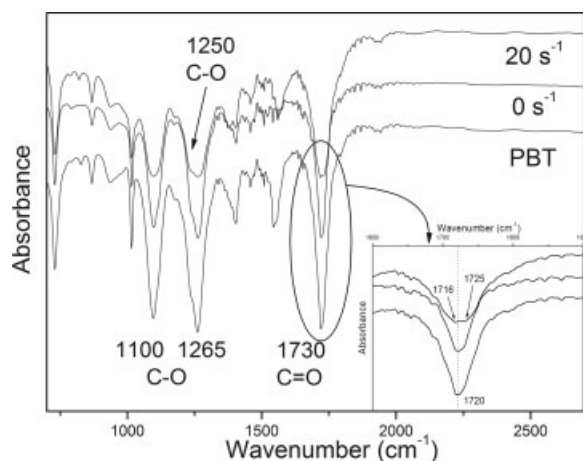


Figure 4 FTIR spectra for neat PBT, a sample annealed without shear flow, and a sample annealed at a shear rate of 20 s^{-1} for 120 min.

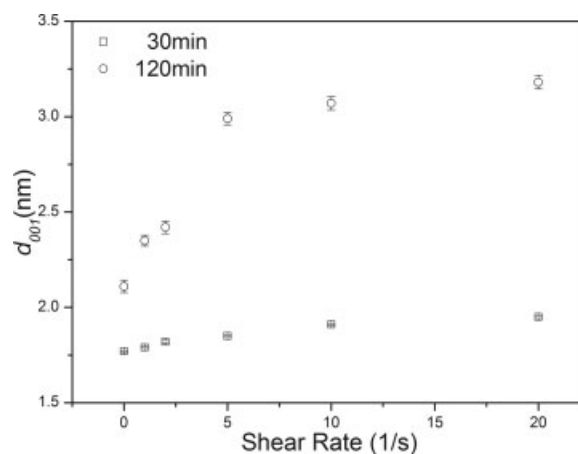


Figure 5 Interlayer spacing of clay as a function of the shear rate for samples annealed for 30 and 120 min.

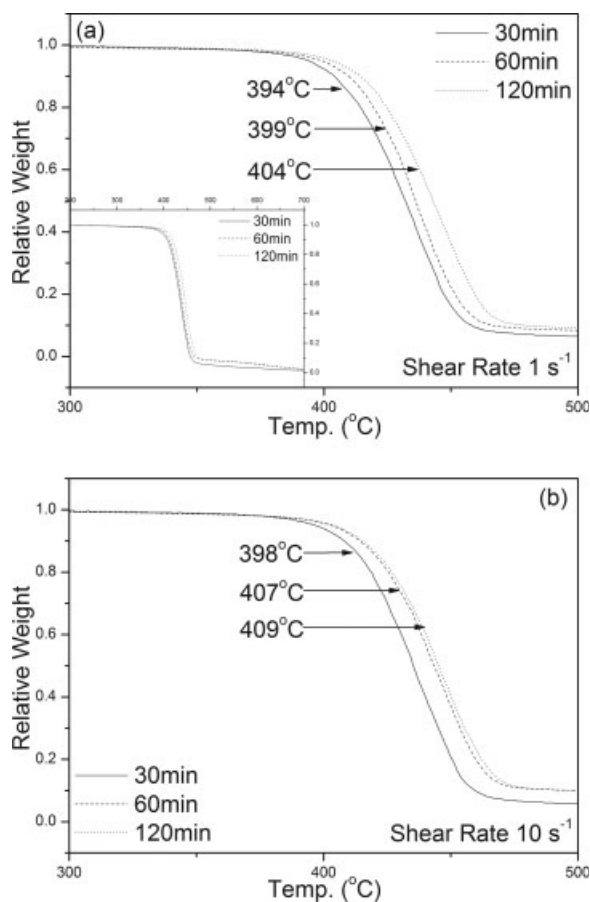


Figure 6 TGA curves for samples annealed at shear rates of (a) 1 and (b) 10 s⁻¹ for various times. The temperature is the 5 wt % loss temperature.

flow by a mixing machine. Well then, the one interesting question is whether the shear intensity influences the hybridization process or not.

Figure 5 presents the interlayer spacing of clay as a function of the shear rate for the samples annealed for 30 and 120 min. Obviously, with 30 min of annealing, the d_{001} -spacing of the sample annealed at 20 s⁻¹ only increases slightly compared with that of the sample annealed without shear. Vaia and co-workers^{6,7} concluded that the hybrid formation is limited by mass transport into the primary particles of the host silicate and not specifically by the diffusion of the polymer chains within the silicate galleries. Accordingly, in the initial stage of hybridization, the detachment of clay particles but not intercalation may be the dominant process. However, with the prolonging of the annealing time, those annealed samples at the low shear rate (1–2 s⁻¹) present d_{001} -spacings close to that of the sample annealed without shear, whereas those samples annealed at a high shear rate (≥ 5 s⁻¹) show a distinct increase in the d_{001} -spacing. The results suggest that steady shear with a low shear intensity may not promote the whole hybridization effectively, whereas

enough shear intensity can facilitate both the detachment of clay particles and the intercalation of polymer chains (discussed later in Figs. 8–10). As a result, the intercalation level shows a dependence on the shear intensity to some extent. However, it is notable that as the shear rate achieves a critical value, 5 s⁻¹ or more, the d_{001} -spacings of clay in the annealed samples are close to one another, suggesting that an increase in the shear intensity may make nearly no contribution to the further intercalation of more polymer chains into clay galleries; only the intercalated nanoscale structure can form in the samples annealed under the steady shear (discussed later in Fig. 11).

It is well known that PLSNs show remarkable thermal stability due to an ablative reassembling of the silicate layers that may occur on the surface of nanocomposites, creating a physical protective barrier on the surface of the material; on the other hand, volatilization might also be delayed by the labyrinth effect of the silicate layers dispersed in the nanocomposites.^{20,21} Figure 6 shows TGA curves for the samples annealed at shear rates of 1 and 10 s⁻¹. The 5 wt % loss temperature is also given in Figure 6.

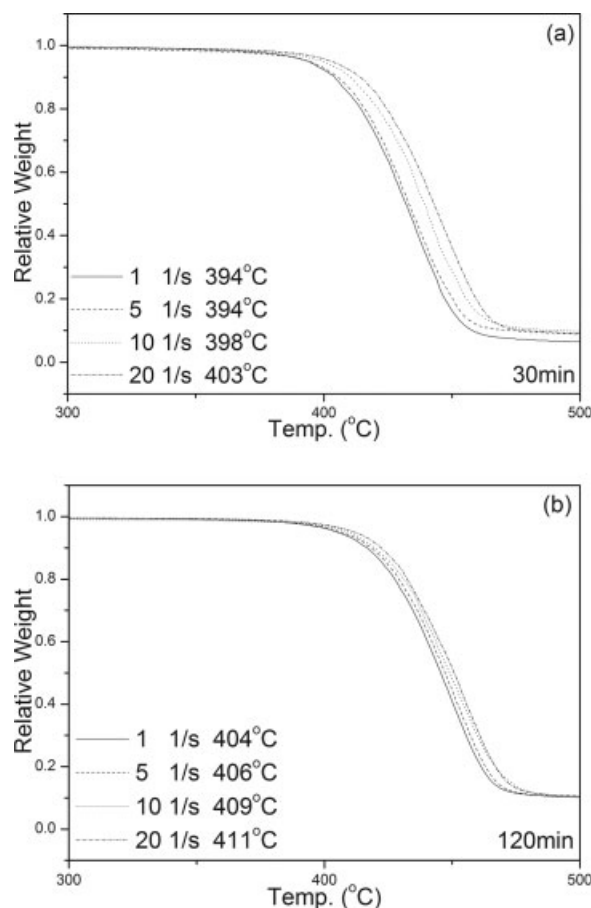


Figure 7 TGA curves for samples annealed at various shear rates for (a) 30 and (b) 120 min. The temperature is the 5 wt % loss temperature.

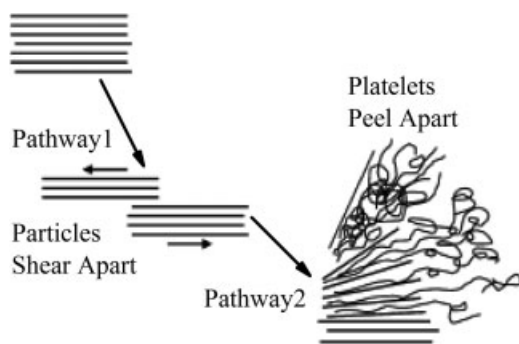


Figure 8 Proposed mechanism for how the clay particles disperse into polymers in the melt-annealing process under shear flow.

Clearly, all samples shown an improvement in the thermal stability with the prolonging of the annealing time, indicating an enhancement of the detachment level or effective filling volume of the clay. However, almost equal char residues can be observed on those samples as the temperature reaches 700°C and above, and this is due to their identical clay loadings [see the inset graph in Fig. 6(a)]. For those samples annealed at a shear rate of 1 s^{-1} , when they are annealed from 60 to 120 min, the thermal stability of the samples still increases remarkably, as can be seen in Figure 6(a). However, the thermal stability of those samples annealed at a shear rate of 10 s^{-1} increases only slightly in the

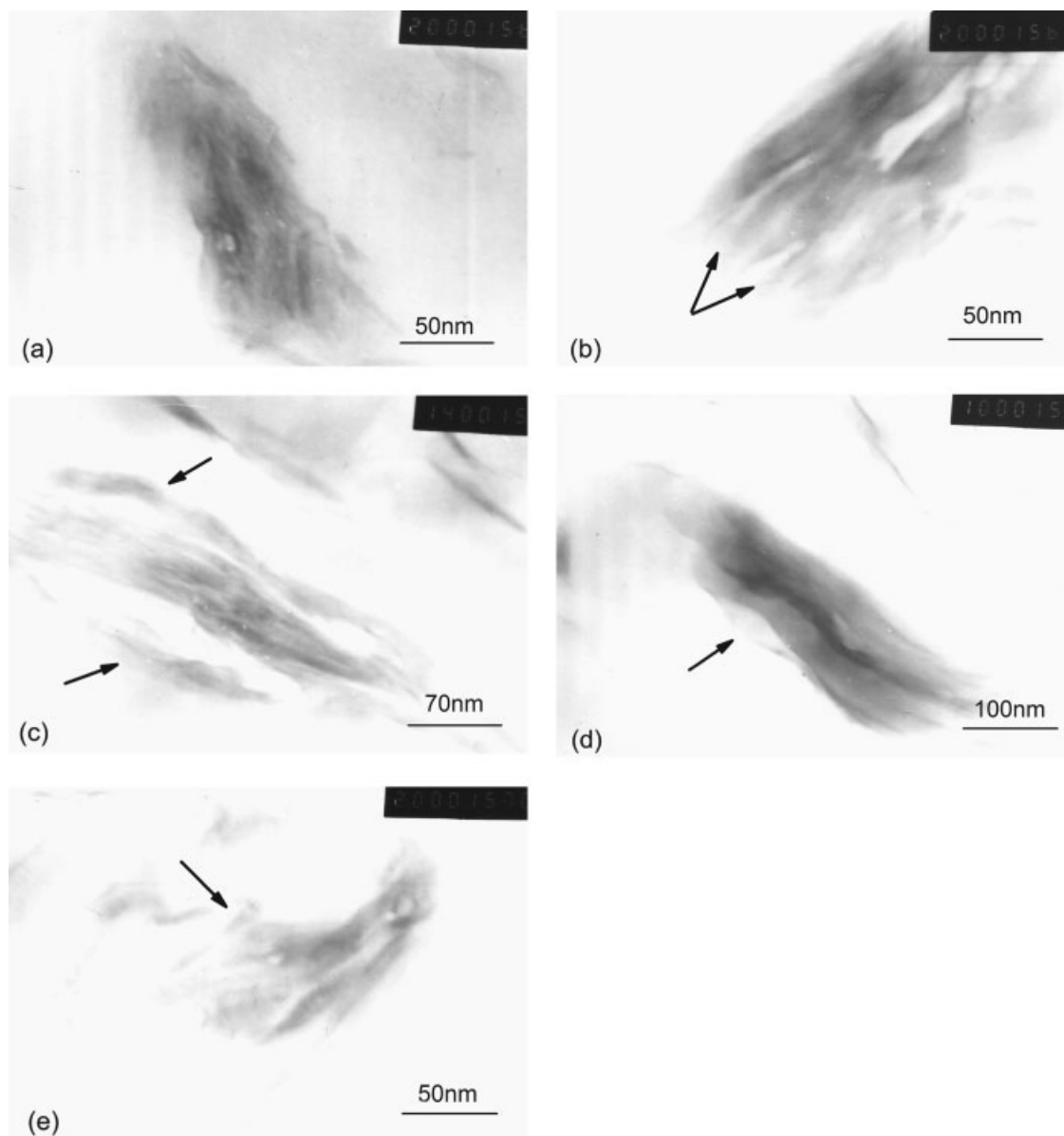


Figure 9 TEM images of sample annealed under a steady shear flow at magnifications of (a) 200,000×, (b) 200,000×, (c) 140,000×, (d) 100,000×, and (e) 200,000×.

same situation, as can be seen in Figure 6(b). Moreover, the 5 wt % loss temperature of the sample annealed at 10 s^{-1} is larger than that of the sample annealed at 1 s^{-1} for an identical time. This suggests again that the dominant step in hybridization, mass transport into the primary particles, is accelerated by steady shear flow with enough intensity. The detachment of clay particles occurs and is almost completed in the earlier stage of hybridization as a result.

That dependence of the detachment level on the shear intensity is clearly shown in Figure 7, which gives the TGA curves for the samples annealed at various shear rates for identical times. Figure 7(a,b) shows that with an increase in the shear intensity, the thermal stability of the annealed sample is enhanced. Apparently, shear flow can promote the clay particles detaching into small tactoids during the annealing process. The number of tactoids increases with increasing shear intensity, leading to the enhancement of the effective filling volume of clay and/or the interactions or confinement effect between the PBT chains and clay surface.

Therefore, the steady shear has a large influence on the formation of nanoscale structures in PLSNs. However, compared with the intercalation level, the detachment level shows a stronger shear intensity dependence. What is the mechanism of that dependence? Paul et al.¹³ concluded that there are two possible clay delamination pathways in the melt process, as can be seen in Figure 8. In pathway 1, the stacks of platelets can decrease in height by platelets sliding apart from one another, which requires shear intensity. In pathway 2, polymer chains can diffuse into the clay galleries, and this does not require a high shear intensity but involves physical or chemical affinity between the matrix and clay surface. They studied the effect of processing conditions on the exfoliation extent of clay and found that both pathways are involved in the formation of PLSNs.

In our study, some special morphologies of clay in those samples annealed under steady shear flow were captured by TEM measurements. Figure 9(a,b) shows the compact and swollen tactoids, respectively. The small tactoids are sheared apart from the big ones [see the arrows in Fig. 9(c)]. However, as more polymer chains diffuse further between clay platelets, the platelets, especially those near the defect [see the arrow in Fig. 9(d)] or edge of the clay galleries [see the arrow in Fig. 9(e)], appear to be curled and to peel apart. Therefore, it suggests that both mechanisms take place during the annealing process under steady shear flow.

Figure 10 shows the final morphology of annealed samples at shear rates of 5, 10, and 20 s^{-1} . Obviously, the average thickness of clay tactoids in the sample annealed at 20 s^{-1} is far smaller than that of

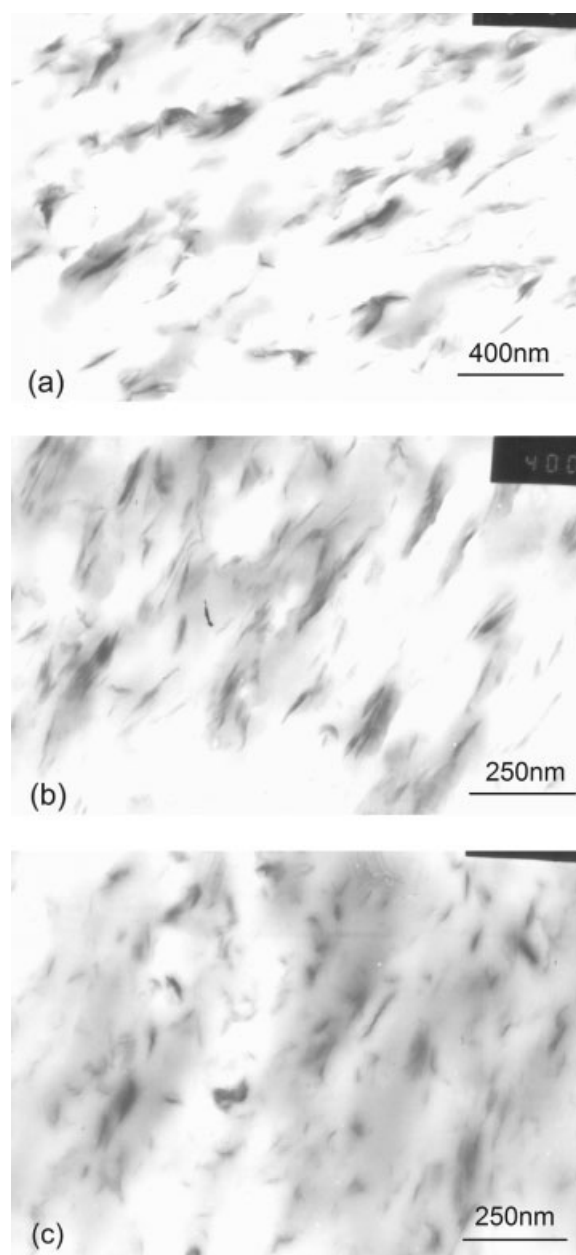


Figure 10 TEM images of samples quiescently annealed at shear rates of (a) 5, (b) 10, and (c) 20 s^{-1} for 120 min.

the sample annealed at 5 s^{-1} [see Fig. 10(a,c)], despite their close swollen degrees [Fig. 5(b)]. This indicates that shear flow can facilitate the delamination of clay particles and the diffusion of polymer chains. However, at a low shear rate, steady shear is not strong enough to make more small tactoids detached, and the platelets and fragments peeling apart may be the dominant mechanism. As a result, the clay presents an inhomogeneous dispersion, whereas with increasing shear intensity, the detachment level of clay increases, resulting in a better dispersion. Therefore, the thermal stability of an annealed sample increases because of the increase in

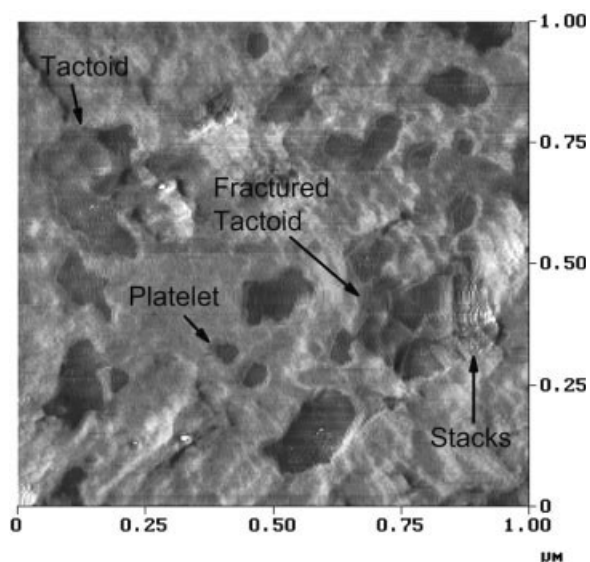


Figure 11 AFM image ($1 \mu \times 1 \mu\text{m}$; tapping mode) of a sample annealed at a shear rate of 20 s^{-1} for 120 min.

the filling volume fraction of small tactoids, as discussed in Figures 6 and 7.

However, the AFM image shows that the clay also presents a hierarchical structure in the sample annealed at 20 s^{-1} , as can be seen in Figure 11. Clay particles appear dark, whereas the polymer appears bright. A number of topological features are observable from this image. Yalcin and Cakmak²² concluded that a clay platelet has a preferred hexagonal structure or any other morphological habit with hexagonal angles, but because of fracture or embedment by the matrix, it is difficult to visualize the regular edges completely. Obviously, the tactoids (fractured or not) and platelets as well as fragments coexist in the annealed sample, forming a hierarchical structure (see the arrows in Fig. 11). This indicates that those swollen tactoids and platelets are rather fragile and are easily broken (fractured) during the annealing process under steady shear flow with enough intensity.

Nevertheless, compared with those of the PBT/clay nanocomposites annealed under dynamic shear flow or prepared under periodic complex shear deformation by a rheometer in our previous work,^{14,17} both the intercalation and detachment level of the clay in the sample annealed under steady shear flow are somewhat poor. Fu et al.¹¹ studied the effect of dynamic shear on the dispersion of PLSNs. They concluded that in the shear environment, the polymer chains are oriented by the direction of the shear flow and that the clay particles are sheared apart first. Then, with the diffusion of oriented polymer chains into clay galleries, the intercalated structure forms. Finally, polymer chain relaxation can induce an exfoliated morphology during the dynamic

annealing process. Therefore, for the sample annealed under steady shear flow, there are two possible reasons for the worse dispersion of clay than that of annealed samples under complex or dynamic shear flow. First, the steady shear is relatively weak and monotone in contrast to periodic complex shear by an extruder or mixing machine and may not shear apart the clay tactoids very effectively; second, those oriented polymer chains confined by clay tactoids lack relaxation like that in a dynamic annealing process, and this may prevent the further expansion of tactoids. As a result, only the intercalated nanocomposite can form in the annealing process under steady shear flow.

CONCLUSIONS

In this work, to investigate the whole hybridization process of PLSNs under steady shear flow, a sheet sample composed of PBT and an organoclay was prepared by solid compression. The effect of steady shear on the formation of PLSNs was studied by off-line measurements such as XRD, TEM, AFM, FTIR, and TGA. The results were as follows.

The spontaneous diffusion of PBT chains entering clay particles is a very long dynamic process but can be reduced by steady shear flow. With an increase in the shear intensity, the detachment level of clay increases more remarkably than the swollen degree. The shear-apart and peel-apart mechanisms may act together on the clay particles, facilitating the formation of a nanoscale structure.

However, only an intercalated nanocomposite can form in the annealing process under steady shear flow. An increase in the shear intensity will not induce an exfoliated structure, which may be attributed to a lack of relaxation of those oriented polymer chains confined by tactoids. Additionally, a distinct hierarchical structure of clay can still be visualized even in a sample annealed at a high shear rate, suggesting that the promotion effect on hybridization by steady shear is lower than that by dynamic or complex shear.

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