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Polymer Communication

Clay locked phase morphology in the PPS/PA66/clay blends during compounding in an internal mixer

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Abstract

In this communication, we will demonstrate, by using poly(*p*-phenylene sulfide) (PPS)/polyamide66 (PA66) blends as an example, the clay can not only affect the phase morphology in immiscible polymer blends, but also frozen in the phase inversion. By adjusting the processing method, an inversed phase, where the minor component PA66 forms the continue phase and the major component PPS forms the dispersed phase, is observed for the first time. This is explained as due to the locking effects of clay layers on the phase development. The result is interesting and also very important, which provides a new way to control the phase morphology and phase inversion in immiscible polymer blends by using clay.

Keywords: Clay; Locking effects; Morphology

1. Introduction

During the last decades, making polymer/clay nanocomposites has been an important path to tailor properties of polymeric materials because of their excellent properties and potential industrial applications [1–4]. The key is to control the dispersion of clay in polymer matrix [5,6]. In the recent years, there has been a growing interest in the polymer/polymer/clay ternary composites [7–14]. According to the interaction of clay with the two polymers, three basic structures exist: clay is dispersed in one phase, dispersed in both polymers and located at the interface. Due to its high aspect ratio and high surface area, clay has been found to affect dramatically the phase morphology of polymer blends. Some research groups showed that clay could play a role as a compatibilizer for immiscible polymer blends [7–11]. Wang et al. [8] reported a decreased domain size in PS/PP blend by the addition of clay and attributed it to the fact that two immiscible polymer chains may exist together between the intercalated clay platelets acting as block (or graft) copolymers. Ray and Bousmina described the compatibilization efficiency of organically modified montmorillonite (OMMT) in immiscible polycarbonate (PC)/poly(-methyl methacrylate) (PMMA) blends [9] and Kamal et al. observed not only a reduced dispersed phase but also a change from spherical to laminar shape in high-density polyethylene/N6 blends by adding 5 wt% clay into the blends [10]. Khatua and Lee, et al. found that for the 80:20 (w/w) N6/ERP blend, the dispersed domain size (*D*) of EPR phase in the N6 matrix decreased significantly even if a small amount of the clay was added. And the exfoliated clay plates effectively prevent the coalescence of the dispersed domains [11].

Feng and Gong, et al. found that in poly(propylene) (PP) and polyamide 6/clay nanocomposites (NPA6) system, at low clay content (3, 5 wt%), NPA6 exhibited continuous lamellar structure in PP matrix, as pristine PA6 did in PP/PA6 blend, but at a higher clay content (10 wt%) only ellipsoids or elongated ellipsoids were observed [12]. Li and Shimizu reported a significantly decreased domain size in the poly(phenylene oxide) (PPO)/polyamide 6 (PA6) blend by adding 2% clay, but a co-continuous morphology by adding 5% clay. They own it to the change of the viscosity ratio at higher clay content [13]. A similar co-continuous morphology was found in polyamide 6 (PA6)/acrylonitrile–cutadiene–styrene (ABS) nanocomposites too [14].

Generally, there are three major factors that govern the morphology of immiscible polymer binary blends. They are: (1) the rheological and interfacial properties of the constituent components (such as, shear viscosity and fluid elasticity, interfacial tension); (2) blend composition; and (3) processing variables (such as temperature, shear rate). In the past, a lot of work has been done on how these three factors determine blend morphology [15]. It is well established that the blend

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morphology can be grouped roughly into: (1) co-continuous morphology and (2) dispersed morphology. Usually, the minor component forms the dispersed phase and the major component forms the continuous phase. However, it is not clear whether the co-continuous morphology is stable, giving rise to equilibrium morphology, or an intermediate step that eventually leads to dispersed morphology [16]. For immiscible polymer/polymer/clay ternary blends, the development of phase morphology may be more complicated. The competition exists between the intercalation of clay into one or two polymers and coalescence of the dispersed phase. So depending on the sequence of intercalation and coalescence, the phase morphology will be totally different. In this communication, we will demonstrate, by using poly(*p*-phenylene sulfide) (PPS)/polyamide66 (PA66) blends as an example, the clay can not only affect the phase morphology immiscible polymer blends, but also frozen in the phase inversion. By adjusting the processing method, an inversed phase, where the minor component PA66 forms the continue phase and the major component PPS forms the dispersed phase, is observed for the first time. This is explained as due to the locking effect of clay layers on the phase development.

2. Experimental part

Poly(*p*-phenylene sulfide) (PPS) in a powder form (M_w = 48,000 melting temperature = 285 °C) was purchased from Sichuan Deyang Science Tech. Shareholding Company. Polyamide66 (PA66) (M_w = 20,000 melting temperature = 250 °C) came from Shenma Company. Organically modified clay with a cation/charge capacity value of 100 mequiv/100 g was prepared in our lab. The dioctadecyl dimethylammouium bromide (2C-18) an alkylammonium salt was used for cation exchange. Melt blending of PPS/PA66/clay system with fixed composition (60:40:1) was conducted using an internal mixer, which had two counter-rotating cam-type blades. In our experiment, the samples were dry mixed in a bag for about 5 min before being put into the mixing chamber, which had been heated to a preset temperature. In all experiments, about 70% of the total available volume was filled with material and the rate was 50 rpm. Two processing methods were adopted in the experiments. By the method the sample was mixed first at 260 °C, and then gradually the temperature was increased to 300 °C linearly in 5 min. By method 2 the sample was mixed directly at 300 °C. In the method 1, PA66 melts first and PPS melts later. In the method 2, two polymers melt at the same time. All the compounds used are listed in Table 1. Mixing time was counted from the time of sample loading into the mixing chamber, where about 30 s were required to load the sample. At 1, 5, 10 and 15 min a small amount of sample was taken out and immediately pressed between two cold iron boards to freeze phase morphology. Hereafter, we named each sample as a letter with a number, which means different compounds at different mixing time. For overseeing the morphology of blends, the samples were fractured in liquid nitrogen and two etched methods, namely chemical etching and physical etching, were used to make contrast among PPS, PA66 and clay. For PPS/PA66 binary blends, the chemical etching was performed by the immersion of the fractured specimens in formic acid (10 min, room temperature), which dissolved the PA66 phase selectively. For PPS/PA66/clay ternary system the physical etching was carried out, in which the fractured surface of the specimen was subjected to argon ion bombardment at 500 eV. The beam was focused perpendicularly to the surface of the specimens. Depending on the different resistance of the components to the ion beam etch (clay > PPS > PA66), the phase morphology and the location of the clay in the blend can be studied by this method. XRD analysis was performed by a Rigaku Denki RAD-B with Cu $K_?$ ($\lambda = 0.154$ nm) radiation at room temperature. The basal spacing of the clay was estimated from the (001) peak in the XRD pattern.

Table 1
The companions and processing method of each sample

	PPS (wt%)	PA66 (wt%)	Clay (phr)	Processing method
A	60	40	0	1
B	60	40	1	1
C	60	40	1	2

3. Results and discussion

Fig. 1 shows the SEM images of the blends with or without clay, which were prepared by two different methods at a rotor speed of 50 rpm for 1, 5, 10 and 15 min, where the dark areas represent the PA66 phase and the light areas represent the PPS phase. Since, T_m of PA66 is 250 °C and T_m of PPS is 285 °C, at methods 1 the PA66 melts first, forming the matrix phase in which PPS pellets are suspended until the temperature reaches to 285 °C (about 4 min). Upon melting temperature at 285 °C, the PPS starts to melt and then two possibilities exist: PPS remains as the discrete phase and dispersed in the PA66 matrix or transforms into the continuous phase, in this case a phase inversion will take place.

From the Fig. 1(a), it can be found that the PPS is first suspended in the PA66 matrix till 5 min (A1, A5), but at 10 min, the PPS droplets are deformed and contacted each other to form a continuous phase (A10). In the same time, PA66 is kept as the continuous phase, thus a co-continuous morphology is observed. But this structure is not stable, the PA66 phase is quickly broken down into small droplets, and the PPS become the continuous matrix (A15). This phenomenon can be understood as due to dominate volume fraction of PPS in the blends (60:40 wt% PPS/PA66). If the viscosity difference between these two components is not big enough, the major component PPS will eventually form the continuous phase and the minor component PA66 forms the dispersed phase.

Nevertheless, after 1 phr of clay is introduced in to the blend, the development of phase morphology will change dramatically. Fig. 1(b) shows the morphology development in different time. The same morphology is seen within 5 min compared with the one without clay (B1, B5). However, very

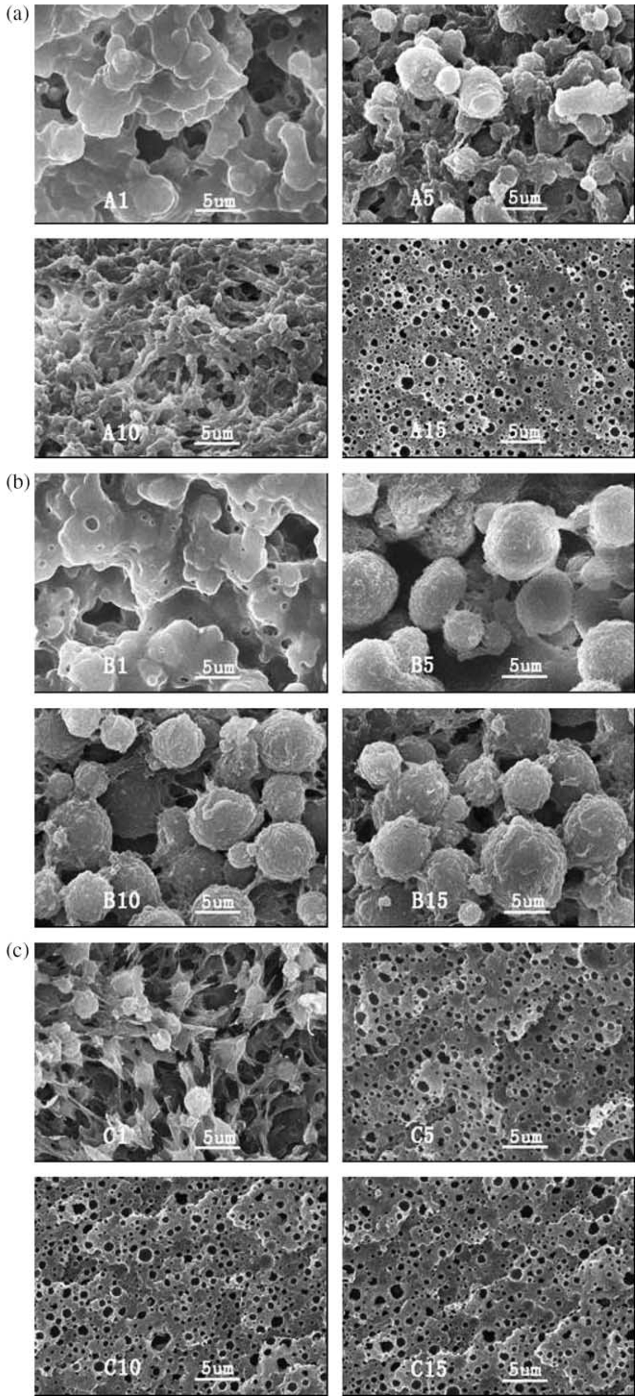

Fig. 1. SEM images show the development of phase morphology of PPS/PA66 blends (60:40 wt%) without and with clay during compounding at different mixing time (a) without clay and processed by method 1 (b) with 1 phr clay and processed by method 1 (c) with 1 phr clay and processed by method 2.

interestingly, when the mixing time increases to 10 min, the PPS droplets still keep separated even at this time PPS is in molten state, they do not touch together (B10) (this is very much different from A10). This structure stands for even at 15 min (B15) and seems quite stable, after 25 mining time, the same phase morphology is still observed (not shown here). It is surprising that only 1 phr clay can lock the major component and prevent it becoming the continuous phase. To make sure, the same experiment was repeated several times, the same result was always observed. To explain this, one may first think about the change of viscosity ratio induced by adding clay. From the classical theory (Eq. (1)), the viscosity ratio decrease will make the phase inversion occurs earlier [17].

$$\frac{\eta_1}{\eta_2} = \frac{\phi_1}{\phi_2} \tag{1}$$

Where ϕ_x is the volume fraction of x at phase inversion, and η_x is the viscosity of phase. The melt viscosity of PPS (solid line) and PA66 (dash line) at 300 °C as a function of shear rate is shown in Fig. 2. Since, clay is selectively dispersed in PA66 (see below), its content in this phase will be double. Thus PA66 with 2 and 10 wt% clay, which corresponds to roughly 1 and 5 wt% clay, respectively, in the components, was chosen for the experiment. From the data, the viscosity of PPS decreases with increasing of clay content, while the viscosity of PA66 increases slightly by adding clay. So the viscosity ratio of PA66: PPS will increase by adding clay, indicating that the minor phase PA66 will easier to form the dispersed phase and PPS to form the continuous phase for PPS/PA66/clay ternary system compared with the PPS/PA66 binary blends at the same composition. This is in contrary with the experimental observation. Thus there must have other reason for the observed morphology. For this reason the experiment was carried out by method 2, that is: all the components were mixed directly at 300 °C at the same time. Fig. 1(c) is the result of morphology development. Interestingly, only by changing initial processing temperature, the locking effect of clay does not work anymore. One observes even at 1min, the PPS droplets start to contact each others (C1). Only at 5 min, the PPS forms the continuous phase (C5). And this structure keeps stable within the mixing time investigated (C15). In this case, the development of phase morphology more or less looks like the binary blends, and clay has not much effect on the phase morphology, except that a slight increased PA66 particles are seen. Now the most important thing is to examine the location

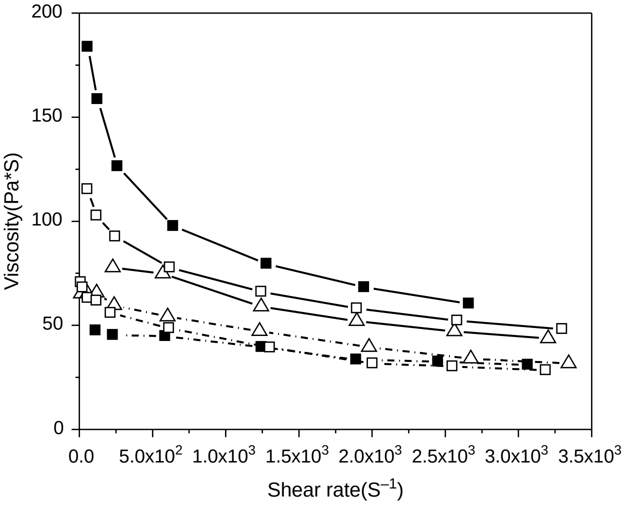

Fig. 2. The melt viscosity of PPS (solid line) and PA66 (dash line) at 300 °C as a function of shear rate. Solid square: without clay; hollow square: with 2 wt% clay: hollow triangle: with 10 wt% clay.

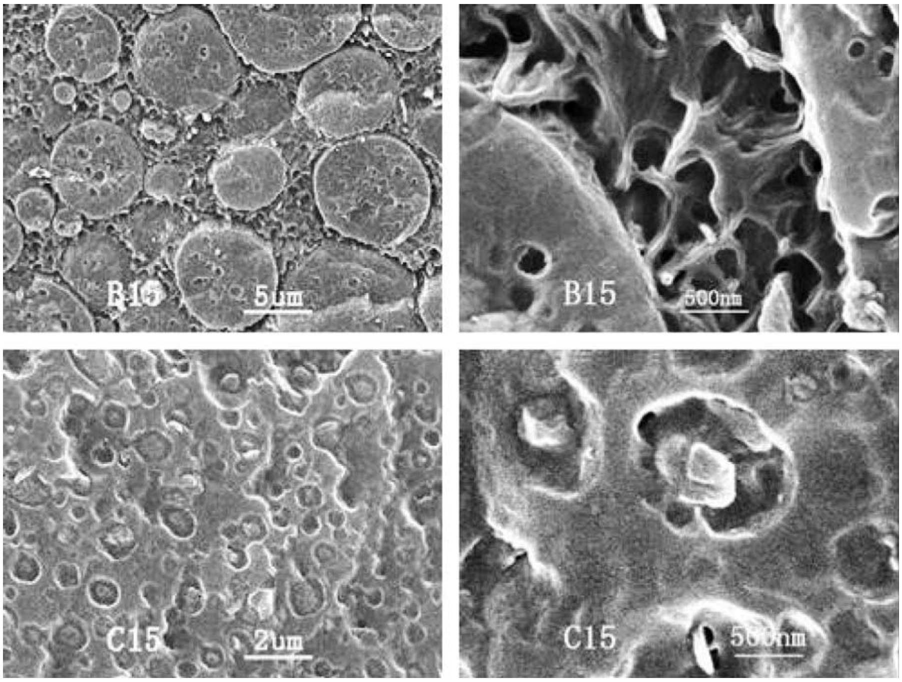

Fig. 3. SEM images show the location of the clay. The samples were etched by ion beam.

of clay in these two methods. The physical etching using ion beam was conducted and the result is shown Fig. 3. For the sample obtained by method 1 (Fig. 3(a)), at the low magnification, one observes the same dispersed PPS droplets as shown in Fig. 1 (b15). At the high magnification, the clay can be clearly seen, which is located in PA66 matrix exclusively. This can be understood as due to the stronger interaction between the PA66 and clay than that between PPS and clay. In fact the exfoliated structure has been reported in PA66/clay nanocomposites [18,19], but only limited intercalation was seen in PPS/clay composites [20].

To further prove this, WAXD experiment was carried out and this is shown in Fig. 4. The pure organic clay and mixed samples in different stages were chosen to explore the structure development of clay before and after the formation of continuous PPS phase. The (001) diffraction of pure organic clay is at $2\theta = 2.5°$, which corresponded to *d*-spacing of 3.5 nm. For the composites prepared via method 1, the PPS phase presumably melted at 5 min. At that time, no peak is found, suggesting that the parallel stacking of the nano-filler is totally disrupted already (Fig. 4(a)) Oppositely, for the composites prepared via method 2, at 1 min, the co-continuous phase formed and the distance of the clay layer is 3.65 nm (Fig. 4(b)). It means that the exfoliation does not happen yet at this time. When the time goes to 5 min, the peak at $2\theta = 2.5°$ disappears and little peak still is left at $2\theta = 6.5°$. This indicates that most of the clay is exfoliated but small amount of clay is still stacked together. This phenomenon can be understood as due to the decomposition of the organic modifier, which had been discussed thoroughly in the literatures [20,21]. This result indeed suggests that the exfoliation occurs before PPS melts in the composites prepared via method 1 and after PPS melts in the composites prepared via method 2.

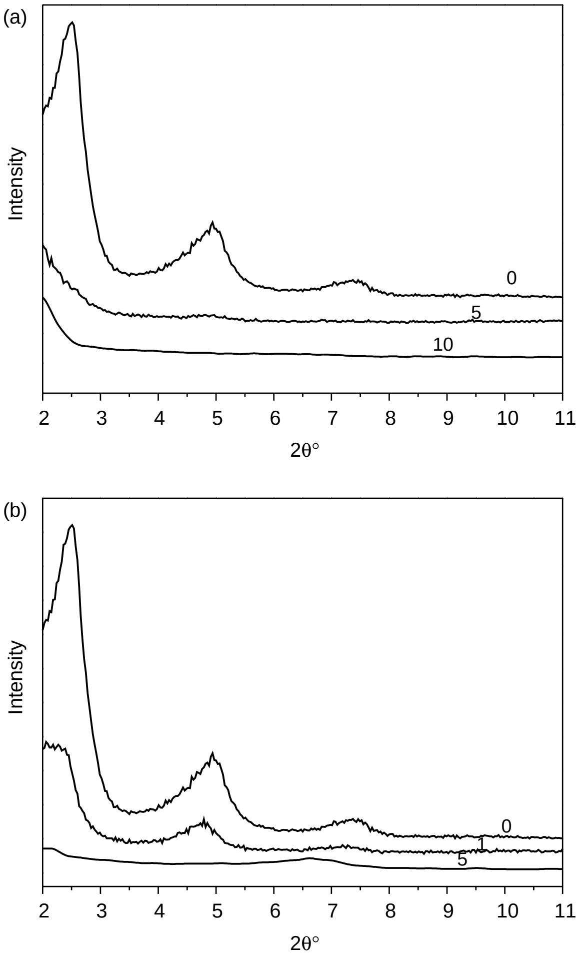

Fig. 4. WAXD patterns (a) for composites prepared via method 1 and (b) for composites prepared via method 2. The number is melt processing times and the clay content is 1 phr for all nano-composite.

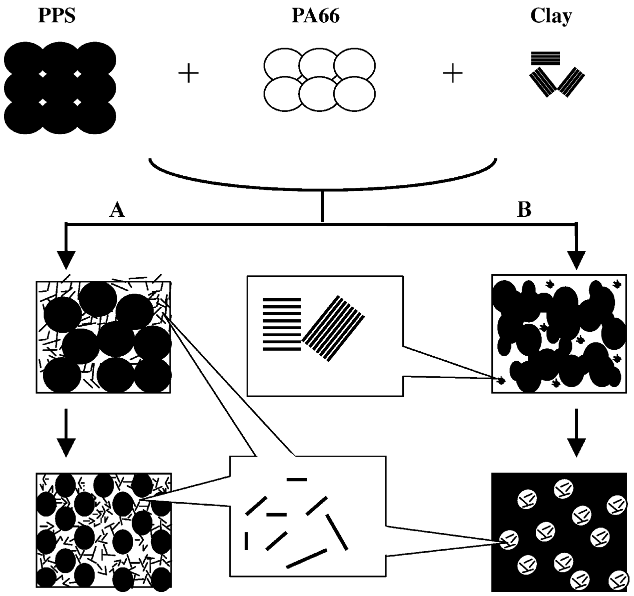

Fig. 5. Sketch of a possible formation mechanism of two different morphologies (A) in method 1, clay is exfoliated simultaneous with the formation of PA66 continuous phase. The early inversed phase can be locked (B) in method 2, the intercalation/exfoliation of clay into the molten PA66 is behind the formation of continuous PPS phase. The intercalation/exfoliation occurs after PA66 phase is broken into the droplets. The early formed phase morphology could not be locked.

Even more a network of the exfoliated clay layers is most likely formed in PA66 matrix since the clay layers are seen to stack each other. The formation of clay layers' network has been reported in many polymer/clay systems [22–26]. Since the clay is seen to locate in PA66 phase, its content in this phase will be more than 2 phr, which increase the possibility for the formation of clay network in PA66 phase. For the sample obtained by method 2, the clay is also seen to locate mainly in PA66 phase. Since PA66 in this case forms the dispersed phase, the formation of clay network is not possible by method 2.

So the development of phase morphology by the method 1 and the method 2 can be understood as following. In the method 1, within the mixing temperature of 260–300 °C, a simultaneous process of PA66 melting and the intercalation /exfoliation of clay into the molten PA66 is expected to occur. That is the formation of PA66 continuous phase and clay network take place earlier than the melting of PPS. Once the exfoliated clay layers exist in the continuous PA66 phase, the coalescence of the dispersed PPS will be blocked or locked even after the melting of PPS. So one observes in this case that minor component PPA6 form the continuous phase and major component forms the dispersed phase. It should be noted that it is not necessary for clay layers to form the network to block the phase morphology, even though the formation of a clay network may lock the phase morphology permanently. The existence of exfoliated clay layers will also slow down the coalescence of the dispersed phase.

On the other hand, in the method 2, the two polymers melt almost at the same time. Though PA66 also forms continuous phase first (Fig. 2 C1), but it is quickly destroyed with the melting of PPS. That is: the intercalation/exfoliation of clay into the molten PA66 are behind the formation of continuous PPS phase. The intercalation/exfoliation occur after PA66 phase is broken into the droplets. In this case, clay cannot 'lock' the early formed phase morphology any more. The sketch representations of phase formation by both methods are illustrated in Fig. 5.

Now it is interesting to check if the observed locking effect is indeed a general trend or just a single point (composition). For this reason the same experiment on the composites with changed composition has been carried out, particularly for the composites with less PA66 content. We found that at the early stage, the phase developments followed the same way. The PA66 melt first melt and form the matrix, and then a co-continued morphology is formed. But when the PA66 content is 30 wt%, even after 25 min, the co-continued morphology is maintained, as shown in Fig. 6(a). When the PA66 content is decreased to 20 wt%, the PA66 phase is broken down quickly, and forms island-sea morphologies shown in Fig. 6(b). The result indicates that whether the locking action of clay takes effect not only depending on the clay but also on composition. Only when the PA66 content is between a certain range, the unique phenomena will occur due to the interplay among three factors: phase separation, wetting and anisotropic inter-particle interactions. The finding that some novel morphologies only appear in a given content range, such as 50:50 [13] or 40:60 [14] (wt%) provides additional evidences for our observation. The reasons behind this phenomenon, however, need further investigation.

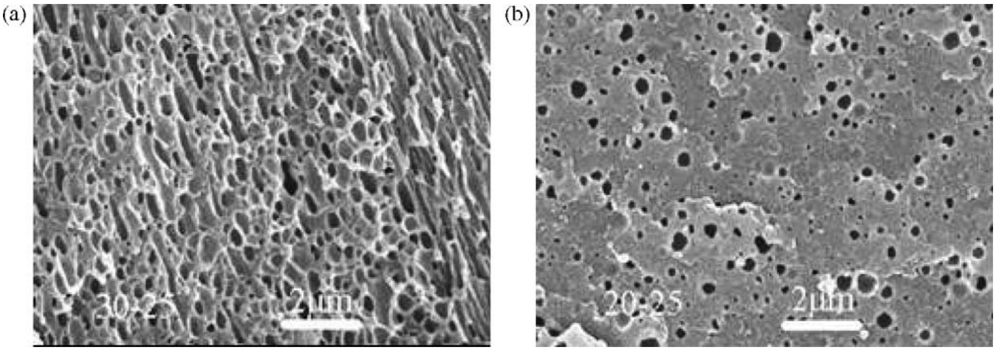

Fig. 6. SEM images show the phase morphology of PPS/PA66 blends after mixed 25 min under method 1 (a) PPS/PA66 blends (70:30 wt%) with 1 phr clay (b) PPS/PA66 blends (80:20 wt%) with 1 phr clay.

4. Conclusion

Depending on the sequence of intercalation and coalescence, the phase morphology of PPS/PA66/clay ternary system will be totally different. Just by adding small amount of clay and using method 1, the phase inversion of blends can be completely locked. An inversed phase, where the minor component PA66 forms the continue phase and the major component PPS forms the dispersed phase, is observed for the first time. The result is interesting and also very important, which provides a new way to control the phase morphology and phase inversion in immiscible polymer blends by using clay.

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