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Morphology evolutions of organically modified montmorillonite/polyamide 12 nanocomposites

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Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

Organically modified montmorillonites (OMMTs) by octadecylammonium chloride with two adsorption levels were dispersed in polyamide 12 (PA12) matrices with two molecular weights for different melt mixing times in order to investigate morphology evolutions and factors influencing fabrication of PA12 nanocomposites. Different adsorption levels of the modifier in the OMMTs provide different environments for diffusion of polymer chains and different attractions between MMT layers. Wide-angle X-ray diffraction (WAXD), transmission electron microscope (TEM) and gas permeability were used to characterize morphologies of the nanocomposites. Both OMMTs can be exfoliated in the PA12 matrix with higher molecular weight, but only OMMT with lower adsorption level can be exfoliated in the PA12 matrix with lower molecular weight. It was attributed to the differences in the levels of shear stress and molecular diffusion in the nanocomposites. The exfoliation of OMMT platelets results from a combination of molecular diffusion and shear. After intercalation of PA12 into interlayer of OMMT in the initial period of mixing, further dispersion of OMMTs in PA12 matrices is controlled by a slippage process of MMT layers during fabricating PA12 nanocomposites with exfoliated structure.

Keywords: Exfoliation; Montmorillonite; Nanocomposites

1. Introduction

Polymer-layered silicate nanocomposites have attracted many interests because of their superior properties comparing with pure polymers, especially as an exfoliated state in polymer matrices [1–8]. Therefore, one of the ultimate aims in the fabrication of polymer-layered silicate nanocomposites is to obtain an ideal homogeneous exfoliated state. Since Giannelis et al. [9] proved the possibility of polymer melt intercalation into organically modified montmorillonites (OMMTs), the preparations of exfoliated polymer nanocomposites via melt intercalation have been paid attention widely, and the formation mechanism of polymer nanocomposites was also investigated comprehensively [10–12].

Generally, the compatibility between polymers and MMT layers, the shear stress and the molecular diffusion are considered as three important factors influencing the formation of well exfoliated nanocomposites. Balazs et al. provided a design criterion for synthesizing optimal exfoliating agents [13,14]. They found that the optimal polymer for preparation of exfoliated nanocomposites should contain the fragments both that are highly attracted to the surface of MMT and that are not attracted to the sheets of MMT. The experiments of Fornes [15] also proved the theory of Balazs. Homminga et al. [16] thought the extent of exfoliation was determined by the compatibility between polymers and MMT. And some other

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previous works showed that the shear stress was essential for the exfoliation of MMT. It was found that the nanocomposite based on nylon 6 with higher molecular weight prepared by melt mixing had higher degree of exfoliation due to higher melt viscosity [11]. Paul and Cho [17] indicated that OMMT was well exfoliated in nylon 6 matrix compounded with the twin screw extruder which affords stronger shear stress, but the use of a single screw extruder was far less effective. The diffusion of polymer was also thought to play a primary role in preparing exfoliated nanocomposites [18].

In addition, the structure of OMMT also influences the molecular diffusion and shear. In our previous work [19], it was found that the interlayer distances of OMMTs increased with the content of modifiers, meanwhile the steric hindrance would be incremental simultaneously. It is unfavorable for polymer chains to intercalate into the galleries of MMT and maintain contact with the surface of MMT. However, the electrostatic attraction between two adjacent MMT layers will weaken with increasing interlayer distance of OMMTs, which will lead to the reduction of slippage friction coefficient of MMT layers [20], and the layers of MMT can slip easily under the shear stress. Fornes et al. [21] also found that increasing the number of alkyl tails of modifiers could decrease the attraction between adjacent platelets, yet it decreased the affinity between nylon 6 and clay because the interaction between hydrocarbons and polyamides is strongly repulsive. Bousmina [22] thought that the organic modification increased the interlayer distance and decreased the energy of adhesion between layers, which made the exfoliation of platelets easier. Kadar et al. [23] thought that organic modification of MMT decreased the surface free energy of clay and it facilitated the exfoliation of platelets.

The formation process of polymer nanocomposites with exfoliated morphology was proposed. For instance, the exfoliated evolution was attributed to peeling apart of the platelets of MMT by both molecular diffusion and shear stress [10,11]. Also it was reported that polymer chains diffused into the galleries and the relaxation of macromolecular chains induced exfoliated morphology of polymer nanocomposites [12].

However, the exfoliation evolution has not been characterized specifically because the exfoliation of clay tactoids is a complex process. Observing intermediate states during morphology evolution of the nanocomposites will be profitable to clarify exfoliation of MMT layers. More exploration on exfoliation process of layered silicates in polymer matrix is necessary. Owing to the favorable compatibility of polyamide 12 (PA12) with OMMTs, OMMT/PA12 nanocomposite is selected as a model system to investigate morphology evolution of the nanocomposites and the factors affecting the exfoliation process in this work. In recent years, some works on PA12 nanocomposites have been reported [24–26]. But most of these work researched the relation between the morphology and properties, the intermediate state of exfoliation was not investigated. This work focuses on the intermediate state of exfoliation process to investigate the roles of the shear stress and the molecular diffusion in the exfoliation process. Two kinds of PA12 with different molecular weights were used due to the differences of melt viscosity and diffusion ability. Two OMMTs with different contents of the modifier, OMMT-1 and OMMT-2, were also employed to provide different environments for molecular diffusion of polymer chains and the different static attractions between the adjacent MMT layers.

2. Experimental part

2.1. Materials

Na^+-montmorillonites (MMTs) used in this work, from Kunimine Co., is with a cation exchange capacity (CEC) of 119 mequiv/100 g. Octadecylamine from Wako Pure Chemical Industries Co. was used as a precursor of modifier. Two kinds of commercial polyamide 12 (PA12) with different molecular weights were purchased from Elf Atochem, and were marked PA12L for PA12 with lower molecular weight ($M_w = 15,800$) and PA12H for PA12 with higher molecular weight ($M_w = 50,000$), respectively. All the materials were fully dried before using.

2.2. Preparation of the samples

Organically modified montmorillonites (OMMTs) were synthesized by cation exchange reaction as described in our previous papers [19,27]. Octadecylammonium chloride (octadecylamine protonated with equal molar concentrated HCl in deionized water at 80 °C) as a modifier was poured into the hot dispersion of MMT. The mixtures were stirred vigorously for 30 min and washed with deionized water at 80 °C and finally dried. Two loading levels of the modifier with respect to the cation exchange capacity (CEC; mequiv/g) were varied: 100% and 200%, and marked as OMMT-1 and OMMT-2. The factual adsorption levels of the modifier are 65.4% CEC and 145.7% CEC, and organic contents in OMMTs are 15.9 wt% and 28.4 wt%, respectively (estimated by TGA [19]).

The nanocomposites were prepared in a Brabender mixer with a rotating speed of 60 and 100 rpm at 210 °C for 5, 20 and 40 min. Fifty grams of sample were added in the Brabender. PA12s were milled to powder and mixed with OMMTs in a stirring vessel at room temperature, the mixture was pressed into a disk at room temperature and annealed at 210 °C and 230 °C in a quartz tube under N_2. The nanocomposites contain 5 wt% OMMT, and the volume fractions of MMT are 0.016 and 0.013 for OMMT-1/PA12 and OMMT-2/PA12 nanocomposites (the density of PA12 is 1.02 g/cm^3 and that of MMT is 2.8 g/cm^3).

2.3. Characterization

Wide angle X-ray diffraction (WAXD) was carried out with a Rigaku model Dmax 2500 with a CuKα radiation and the interlayer distances (d_{001}) of MMT were estimated from the (001) peaks in the WAXD patterns with Bragg formula. The morphologies of the composites were observed by transmission electron microscope (TEM, JEOL2010) on microtome sections of the nanocomposites. Ultrathin sections were cryogenically cut at −40 °C using a Leica Ultracut. Rheological measurements were performed on a PHYSICA MCR 300 at 210 °C under a nitrogen atmosphere. Parallel plates of 25 mm diameter were used and the sample disk was 1 mm thick and 25 mm in diameter. The complex viscosities were measured as a function of angular frequency (ranging from 0.1 to 100 rad/s, 5% amplitude). Thermogravimetric analyses (TGAs) of the OMMTs were done by a Perkin–Elmer TGA 7 thermal analyzer at 210 °C under N_2, and TGAs of the PA12s were measured at 210 °C in air. The hydrogen transmission rates through neat PA12L and the nanocomposites were measured with a G.T.R. measurement apparatus K-315-N-03 at 30 °C. The thickness of sample is about 30 μm. The static mechanical properties were measured with Instron 1121 tensile testing machine, and the crosshead rate was set at 50 mm/min. For each data point, five samples were tested and the average value was taken. All the samples were fully dried before characterization.

3. Results and discussion

Different melt mixing times were used to analyze the whole exfoliation process of the OMMTs in PA12 matrices at 210 °C. Our preliminary experiments showed that melt mixing for 40 min was enough to observe exfoliation process of the OMMT/PA12 nanocomposites when mixed at 100 rpm. The degradations of the modifier and PA12s in this process were investigated by TGA at 210 °C. Because the OMMTs were embedded in PA12 matrices in mixing process, the TGA scans of the OMMTs were performed under N_2, whereas the TGA scans of PA12s were performed in air. The results show that the modifier degrades gradually with increase in annealing time (Fig. 1a). The extent of degradation of OMMT-2 is larger than that of OMMT-1 due to the different adsorption states of the modifier. In Fig. 1b, two kinds of PA12s degrade slightly with increase of the time, and the extent of degradation of PA12L is larger than that of PA12H. Moreover, in order to investigate the change of melt viscosities of PA12s in the mixing process, the rheological measurements were performed. In Fig. 2, the melt viscosities of PA12s do not change greatly during the mixing process, implying that the shear stress and diffusion ability do not change obviously. The interlayer distances of OMMTs annealed at 210 °C were characterized by WAXD (Fig. 3). With increase of annealing time, the layer distances of OMMTs decrease appreciably due to degradation of the modifier.

The microstructure evolution of OMMTs/PA12 nanocomposites was followed by means of WAXD. WAXD profiles show that the position of (001) diffraction peak of OMMT-1 in the OMMT-1/PA12L nanocomposite mixed for 5 min shifts to lower 2θ angle compared to that of the original OMMT-1 (Fig. 4a), and the position of (001) diffraction peak does not change when the nanocomposite was mixed for 20 min. It suggests that the PA12L chains have intercalated into the galleries of OMMT-1 when mixed for 5 min, and the interlayer distance does not change when mixed for 20 min. When mixed for 40 min, the (001) diffraction peak disappears. This tendency also can be observed in the OMMT-1/PA12H nanocomposite (Fig. 4b).

In Fig. 4c and d, the interlayer distances of OMMT-2 in the nanocomposites mixed for 5 and 20 min are the same as that of the original OMMT-2. However, it has been proved that the interlayer distance of OMMT-2 slightly decreased with increase in annealing time (Fig. 3b). Therefore, a small quantity of PA12 molecules should intercalate into the galleries of OMMT-2. In order to further prove that the intercalation of PA12H occurs in PA12H nanocomposites, the annealed OMMT-2 for 40 min at 210 °C was mixed with two PA12s for 1 and 5 min. When mixed for 5 min, the interlayer distance of the annealed OMMT-2 in the nanocomposites increases again (Fig. 5). It suggests that a small quantity of PA12s intercalate into the galleries of OMMT-2. An exfoliation state of OMMT-2 is attained in the OMMT-2/PA12H nanocomposite mixed for 40 min (Fig. 4d), whereas OMMT-2 cannot be exfoliated in the PA12L matrix (Fig. 4c). The exfoliation of OMMT-2 in the PA12H matrix should be attributed to higher melt viscosity of the PA12H owing to its higher molecular weight, and PA12H matrix can provide stronger shear stress during melt mixing to separate the platelets of OMMT-2 as

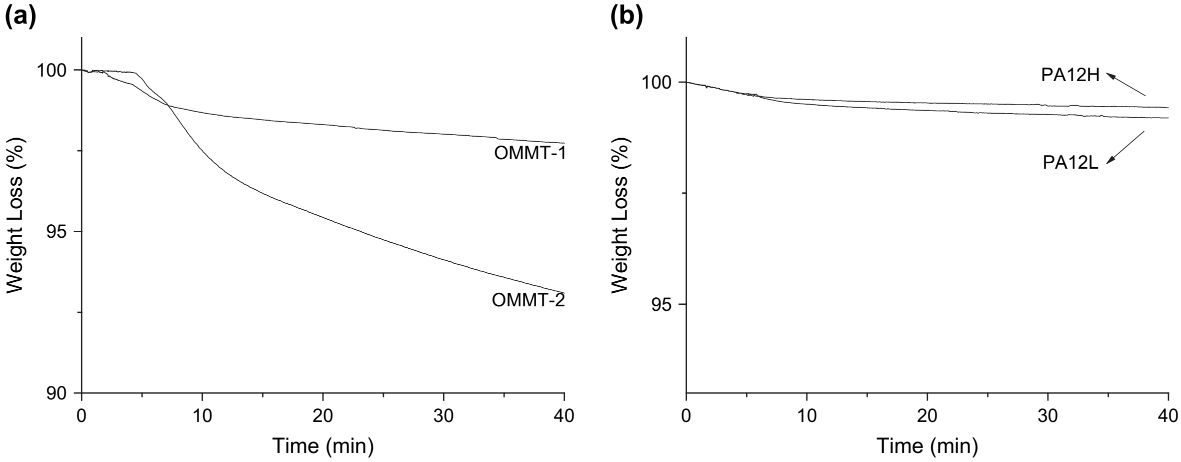

Fig. 1. TGA thermograms of OMMTs and PA12s at 210 °C. (a) OMMTs under N_2; (b) PA12s in air.

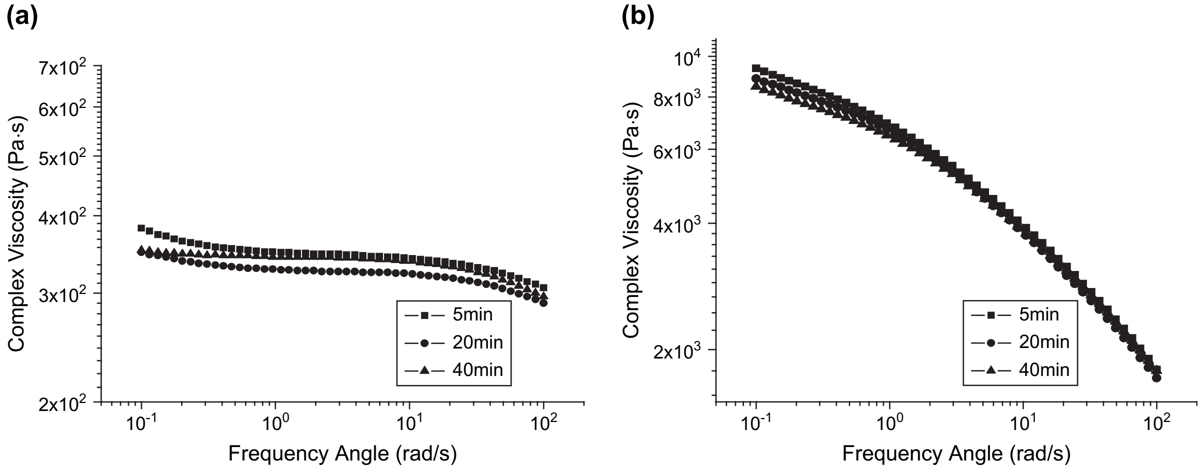

Fig. 2. Complex viscosities of polyamide 12 matrices mixed for different times as a function of frequency angle. (a) PA12L; (b) PA12H.

Ref. [11] reported. In contrast, the PA12L cannot make OMMT-2 exfoliate after a small quantity of polymer molecules intercalate into MMT layers. The results of WAXD show that the interlayer distances of the OMMTs remain unchanged after the amount of PA12 molecules in the gallery reaches a certain degree. However, the exfoliated state can be achieved with increase of mixing time. In the mixing process, the change of interlayer distance is slight, suggesting that a slippage process of OMMT layers along the lateral direction of layers possibly occurs.

If the slippage process of OMMT layers occurs during fabrication of the nanocomposites via melt mixing, the average length of OMMT agglomerates will increase with mixing time. TEM micrographs provide a visible evidence of morphology evolutions of the nanocomposites. For the OMMT-1/PA12L nanocomposites (Fig. 6a–c), though WAXD profiles show the same interlayer distances of OMMT-1 when mixed for 5 and 20 min, the average length of OMMT-1 agglomerates in the latter is much larger than that in the former, and the layers of OMMT-1 are dispersed regularly in both situations. It proves that the slippage of OMMT layers occurs in OMMT-1/PA12L nanocomposites. When mixed for 40 min, the length of OMMT-1 particles decreases and the layers of OMMT-1 are disorderly exfoliated in the matrix. For the OMMT-2/PA12H nanocomposite, the delamination extent of OMMT platelets becomes noticeably greater with increase of mixing time (Fig. 6d–f). Moreover, the ordered degree is enhanced with mixing time. When mixed for 40 min, the platelets of OMMT-2 are orderly exfoliated. Though only a small quantity of polymer molecules intercalate into the galleries of OMMT-2, the PA12H chains still can maintain contact with the external surface of OMMT-2 layers because the quantity of modifier on the external surface is smaller than that on the internal surface [28]. It ensures that the shear stress can act on the layers of OMMT-2 and makes the platelets slip. The final morphology of OMMT/polymer nanocomposites evolves via four stages: intercalation, dual states of intercalation and exfoliation, ordered exfoliation, and disordered exfoliation [29,30]. Because only a few polymer chains intercalate into the MMT interlayers, the platelets of OMMT-2 only are orderly exfoliated, implying that the intercalation of PA12 molecules into OMMTs is helpful to the exfoliation.

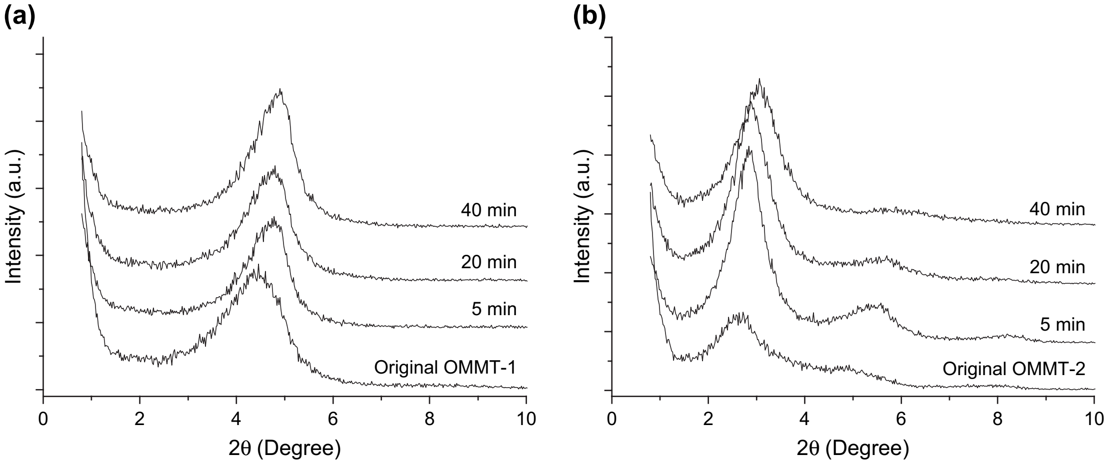

Fig. 3. WAXD profiles of OMMTs annealed for different times at 210 °C under N_2. (a) OMMT-1; (b) OMMT-2.

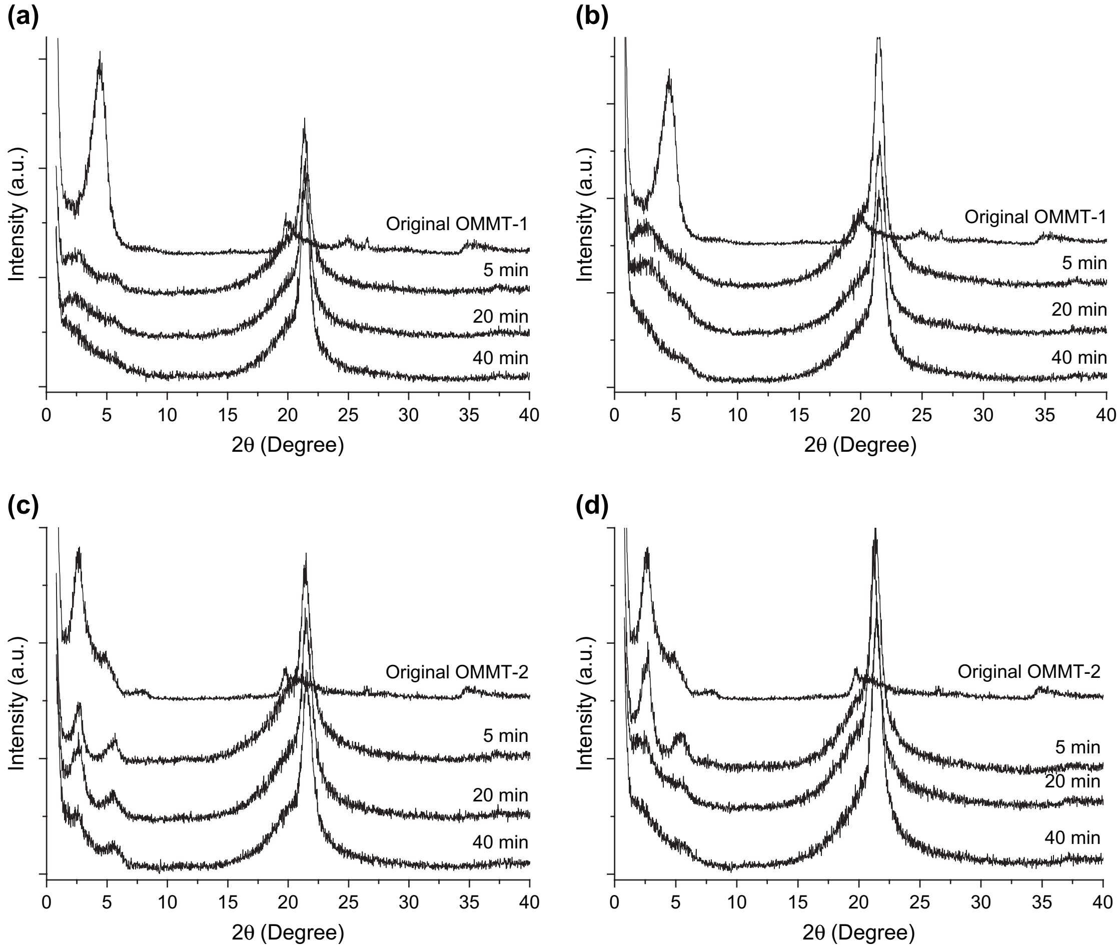

Fig. 4. WAXD curves of polyamide 12 nanocomposites mixed for different times at 100 rpm. (a) OMMT-1/PA12L; (b) OMMT-1/PA12H; (c) OMMT-2/PA12L; (d) OMMT-2/PA12H.

The statistical study based on TEM images was performed over a large number of particles. Fig. 7 compared the distributions of particle length in OMMT-1/PA12L nanocomposites mixed for different times at 100 rpm. The lengths of particles in the images were measured manually with a vernier caliper and transformed to actual sizes based on the scale. The number average length is defined as

$$\bar{l} = \frac{\sum l_i N_i}{N_{\text{total}}} \tag{1}$$

where l_i is the length of a particle, N_i is the number of particles with the length of l_i, N_{total} is the total number of particles. When counting the length distribution, the lengths of particles were approximations, such as 84 nm and 87 nm were thought

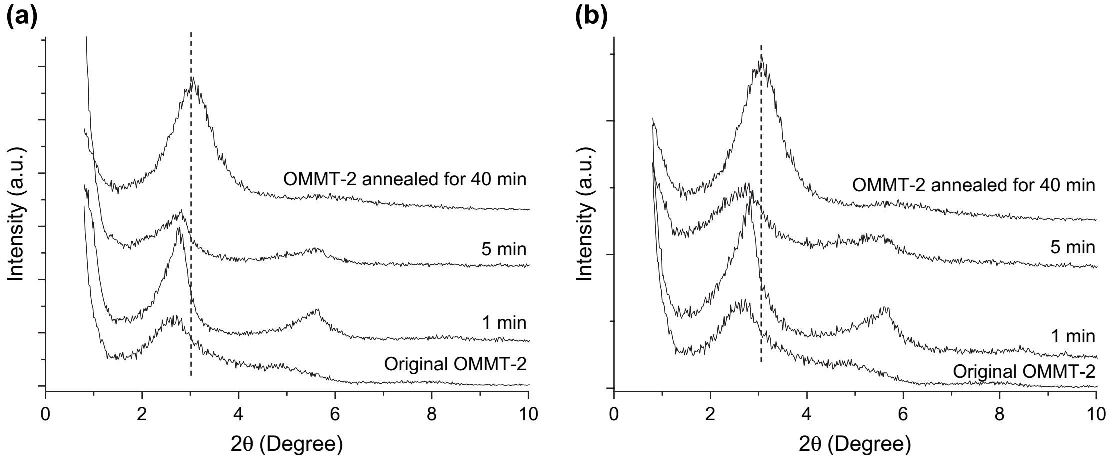

Fig. 5. WAXD profiles of OMMT-2 (annealed for 40 min)/PA12s nanocomposites mixed for 1 and 5 min. (a) PA12L; (b) PA12H.

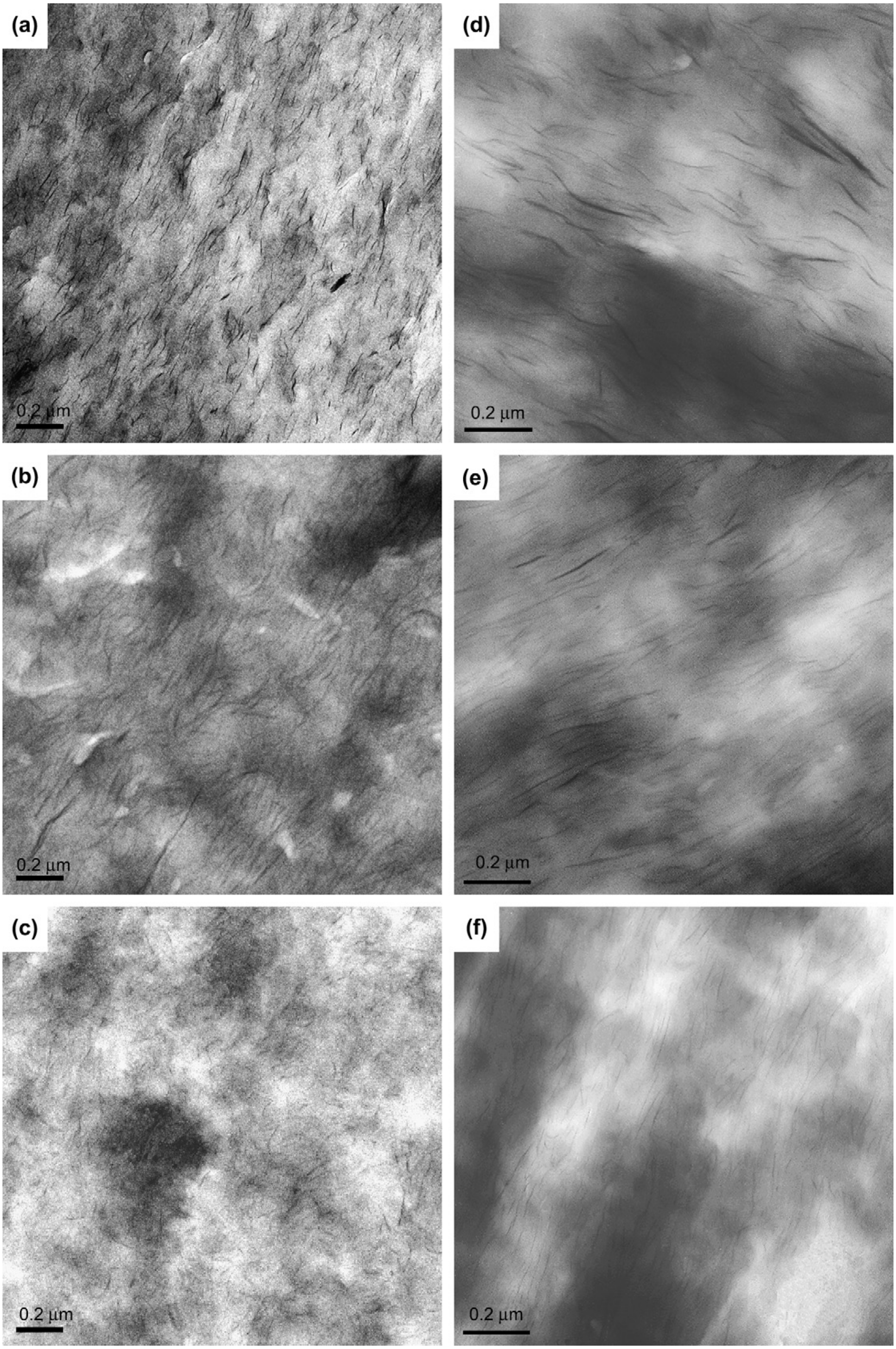

Fig. 6. TEM images: (a–c) OMMT-1/PA12L mixed for 5, 20 and 40 min at 100 rpm; (d–f) OMMT-2/PA12H mixed for 5, 20 and 40 min at 100 rpm.

as 80 nm and 90 nm, and the percentages of these approximations were calculated. The similar approximate method was used in previous paper [31]. However, the statistical average length will be smaller than the true diameter [32]. But the trend in change of distribution of particle length still provides detailed information about the exfoliation process. In the

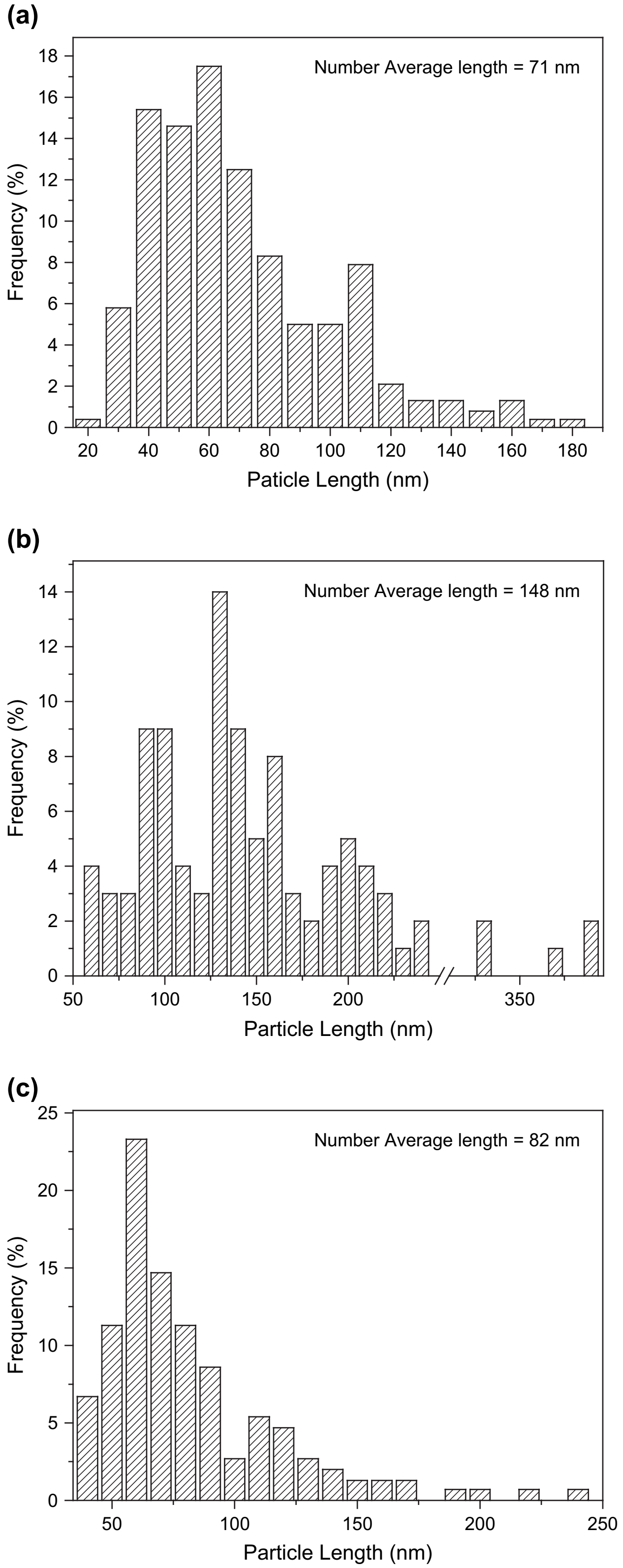

Fig. 7. Distribution histograms of particle length in OMMT-1/PA12L nanocomposites mixed for different times at 100 rpm: (a) 5 min; (b) 20 min; (c) 40 min.

statistical histograms (Fig. 7), the number average length is about 70 nm when mixed for 5 min. And the main length distribution locates in the region between about 30 and 110 nm. When mixed for 20 min, the average length of particles increases twofold compared with that when mixed for 5 min and the main distribution shifts to the region between about 60 and 220 nm. The obvious increase in the average length of particles should be attributed to the lateral slippage under shear field. When mixed for 40 min, the average length decreases to about 80 nm and the main distribution shifts to the region between 40 and 120 nm. It suggests that the platelets keep on slipping and separate. Finally, the platelets are exfoliated in the matrix, and the average length becomes smaller. Therefore, the slippage of the OMMT layers under shear stress occurs during fabricating the exfoliated PA12 nanocomposites.

For further confirming the role of shear stress, the blade's rotational speed was decreased to change the shear stress. OMMT-1 was mixed with two kinds of PA12 with a rotational speed of 60 rpm for 5, 20 and 40 min. The WAXD results in Fig. 8 suggest that OMMT-1 cannot be exfoliated in PA12L matrix at 60 rpm when mixed for 40 min. But OMMT-1 still can be exfoliated in PA12H matrix at 60 rpm. The shear stress provided by PA12 decreases at 60 rpm because the shear stress weakens with decrease of shear rate judging from the torque of Brabender mixer. And PA12L cannot provide enough shear stress to make OMMT-1 exfoliated within 40 min, whereas PA12H still can provide enough shear stress. In TEM images of Fig. 9, many larger particles of OMMT-1 exist in PA12L matrix when mixed for 5 min. When mixed for 20 min, the average length of OMMT-1 increases compared with that mixed for 5 min. When mixed for 40 min, the size of particles decreases obviously, but the layers still disperse orderly in the matrix. However, OMMT-1 can be exfoliated disorderly in PA12L matrix at 100 rpm within 40 min. Therefore, OMMT-1 can better be dispersed when mixed at 100 rpm than at 60 rpm, and shear stress plays a crucial role in the exfoliation process of OMMT. The similar results about PA12 nanocomposites were reported [26], i.e. long mixing times and high blade rotational speeds lead to a good dispersion and a well exfoliated structure.

In order to prove that the molecular diffusion is slow after the amount of PA12 molecules in the interlayers reaches a certain degree, the powder mixture of PA12L and OMMT-1 was annealed for different times at 210 °C. The (001) diffraction peak of OMMT-1 in the annealed OMMT-1/PA12L mixture shifts to lower value (Fig. 10a), which suggests that a part of the PA12L chains has diffused into the interlayers of OMMT-1. The interlayer distances of OMMT-1 in the mixtures annealed for different times are almost uniform, and there are still many agglomerates of OMMT-1 in the mixture annealed for 2 h (Fig. 11a). It shows that the PA12L chains can diffuse rapidly into the galleries of OMMT-1 when annealed at 210 °C, but the PA12L molecules cannot continue intercalating into the interlayer of OMMT-1 with annealing time. It was found that the diffusion coefficient of polymer was unaffected by the addition of 5 vol% clay in a PS matrix and was reduced by a factor of 3 with the addition of the same volume fraction of clay in a PMMA matrix [33,34]. It was attributed to the stronger interaction between the PMMA chains

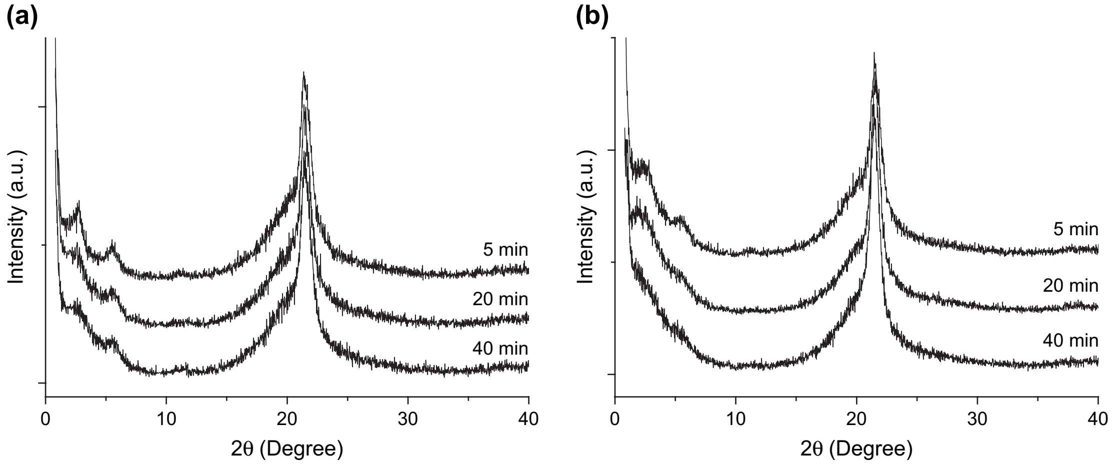

Fig. 8. WAXD curves of PA12 nanocomposites mixed for different times at 60 rpm. (a) OMMT-1/PA12L; (b) OMMT-1/PA12H.

and the clay. Some reports showed that polyamides (such as nylon 6) had stronger interaction with the platelets of OMMTs due to the presence of amide groups in the polyamides [35,36]. Similarly, PA12 also has stronger interaction with the platelets of OMMTs, and PA12 molecules can easily maintain contact with the surface of the OMMT layers, but the diffusion of PA12 chains into the interlayers of OMMTs will be confined due to the strong interaction between PA12 chains and MMT layers. Thus it is difficult for the PA12 chains to keep on intercalating into the interlayers of the OMMTs after the amount of PA12 molecules in the interlayers reaches a certain degree. Zhulina et al. [37] investigated the behavior of telechelic polymers confined between two surfaces within a melt. They found that the bridging chains could prohibit the formation of exfoliated structure. In PA12 nanocomposites, the adjacent layers may be bridged by the PA12 chains, so it is difficult to form the exfoliated structure only by the diffusion of PA12 molecules. The powder mixture of PA12H and OMMT-2 was also annealed for different times at 210 °C. The interlayer distances of the OMMT-2 are the same as that of original OMMT-2, and the diffraction peaks are almost unchanged when annealed for 2 h (Fig. 10b). It further testifies that PA12H chains cannot keep on intercalating into the interlayers of the OMMTs. There are also many large agglomerates of OMMT-2 in the mixture annealed for 2 h (Fig. 11b).

In addition, the annealed temperature of powder mixture of OMMT-1 and PA12L was increased to 230 °C in order to make molecular diffusion easier. When the mixture was annealed for 2 h, the OMMT-1 still existed in intercalated state (Fig. 12). Although the ability of molecular diffusion was promoted by increasing the temperature, the interlayer distance still remains unchanged after the amount of PA12 molecules in the gallery reaches a certain degree.

Paul et al. have proposed the mechanism of organoclays dispersion in polymers during melt processing [10,11]. They thought that shear helped to break large organoclay particles into dispersed stacks of silicate tactoids when clay was melt blended into a polymer. And these silicate tactoids were sheared into smaller stacks. Ultimately, individual plates peeled apart through a combination of shear and diffusion of polymer chains in the interlayers. However, our experimental results obtained from the intermediate states of the morphology evolution in PA12 nanocomposites show some different process (Fig. 13). It is believed that the exfoliation of platelets is achieved through a combination of shear and molecular diffusion, but the opinion about the roles of shear and molecular diffusion is partially different. The chains of the PA12s intercalate into the galleries of the OMMTs in short time and the interlayer distance increases when the large agglomerates of OMMTs are sheared into the smaller tactoids in the initial period of mixing. After that, the interlayer distance is unchanged and further molecular diffusion becomes weak as observed from the WAXD data (Fig. 4). It suggests that the platelets are not peeled apart because the peeling process of platelets will result in the gradual increase of interlayer distance. Moreover, the PA12 can glue the two surfaces together as it moves through the interlayer and thereby the chains of the PA12s cannot push the sheets apart [37]. PA12 molecules can quickly diffuse into the interlayers of OMMT due to the favorable interaction between the polymer and OMMT. At the same time, the interaction also blocks the further diffusion of chains into the interlayers [33,34], which does not allow the interlayer distance to change obviously within the observed time. In Bousmina's experiments [22] for Cloisite 30B/ethylene-octene-*g*-maleic anhydride/poly(ethylene-*co*-octene) system, however, the interlayer distance increased and the intensity of the (001) diffraction peak reduced with the increase of shear time. This shows that the exfoliation of Cloisite 30B results from combination of molecular diffusion and shear during the period of fabrication. The differences between Bousmina's results and our results in this work should be attributed to the differences of chemical structure and viscosity of polymers. In our experiments in OMMT/PA12 system, the change in length of silicate tactoids obtained from statistic results of TEM images suggests that the platelets of OMMTs slip gradually along the shear direction under continuous stronger shear stress. Although the interlayer distances of OMMTs remain unchanged in the middle of mixing, the aspect ratios of the

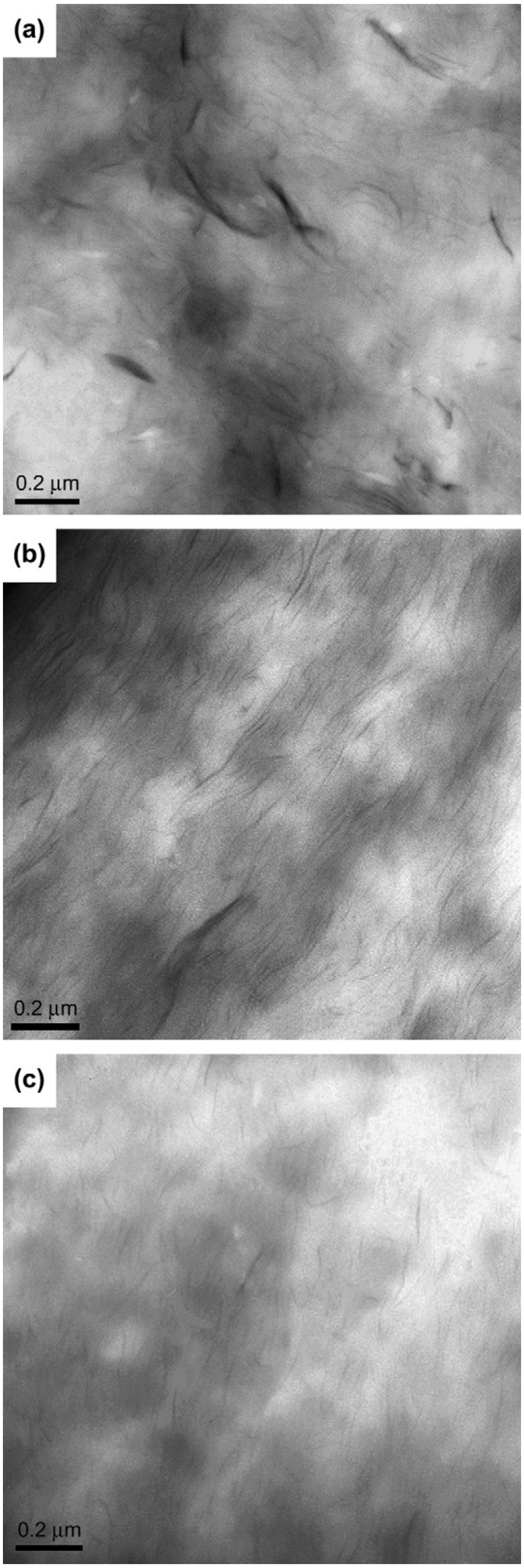

Fig. 9. TEM images of OMMT-1/PA12L nanocomposites mixed for different times at 60 rpm: (a) 5 min; (b) 20 min; (c) 40 min.

particles augment. Finally the platelets of OMMTs are separated and exfoliated in PA12 matrices instead of peeling apart the platelets. Shear dominates the slippage of platelets and finally results in the exfoliation. However, the molecular diffusion of PA12 chains into the OMMTs in the initial period of mixing results in the decrease of attraction between OMMT layers and the increase of contacting sites between platelets and PA12s, which makes the slippage of OMMT platelets easier under shear field.

Further evidences for the morphology change of the OMMT/PA12 nanocomposites were obtained from gas permeability. Both Gusev [38] and Osman [39] proved that the gas permeation was a function of the aspect ratio, volume fraction, and orientation of filler. Here the hydrogen gas permeability of the neat PA12L and the PA12L/OMMT-1 nanocomposites mixed for different times were measured. In Table 1, the addition of OMMT-1 decreases the permeability of hydrogen gas greatly, and the transmission rate of hydrogen gas reduces gradually with increase of mixing time. It suggests that the dispersion of OMMT-1 becomes better with increase of mixing time. This tendency is consistent with the results of WAXD and TEM. Moreover, the average aspect ratios can be deduced from a simple two dimensional model developed by Nielson by predicting the barrier performance of polymer composites containing layered fillers, as can be written by the following Eq. (1) [40,41]:

$$\frac{P_c}{P_m} = \frac{(1-\phi)}{1+\frac{\alpha\phi}{2}} \tag{2}$$

where P_c and P_m represent the gas permeabilities of the composite and the polymer matrix, respectively, α and ϕ represent the aspect ratio and the volume fraction of platelets. In this model the fillers should align in polymer matrix. As mentioned above, the platelets of OMMT-1 align in the nanocomposites mixed for 5 and 20 min as seen from TEM images (Fig. 6a and b). According to Nielson's model, the average aspect ratios of OMMT-1 particles in these nanocomposites are 21.9 and 54.0, respectively, which accord with the results obtained from TEM observations, i.e., the aspect ratio of OMMT-1 in the nanocomposite mixed for 20 min is much larger than that for 5 min. Therefore, the results of gas permeation are helpful to prove the morphology evolutions of the nanocomposites under shear field.

The measurements for mechanical properties prove that the structures of nanocomposites have the effect on properties. The tensile moduli of two kinds of neat PA12s (the neat polymers were also processed for 5, 20 and 40 min at the same condition as the nanocomposites in Brabender) and the exfoliated nanocomposites were measured (Table 2). Owing to the degradation of PA12s, the moduli of neat PA12s decrease with increase of mixing time. The modulus of OMMT-1/PA12H decreases slightly with increase of mixing time, and the modulus of OMMT-2/PA12H increases first and then decreases because the degradation degree of polymers increases with the increase of mixing time (Fig. 1b). In order to investigate the relation between modulus and exfoliated degree of OMMTs, the relative increment ΔE is defined as $\Delta E = E_t^{\text{nanocomposite}} - E_t^{\text{polymer}}$, where $E_t^{\text{nanocomposite}}$ and E_t^{polymer} are the moduli of nanocomposite and polymer, respectively, at

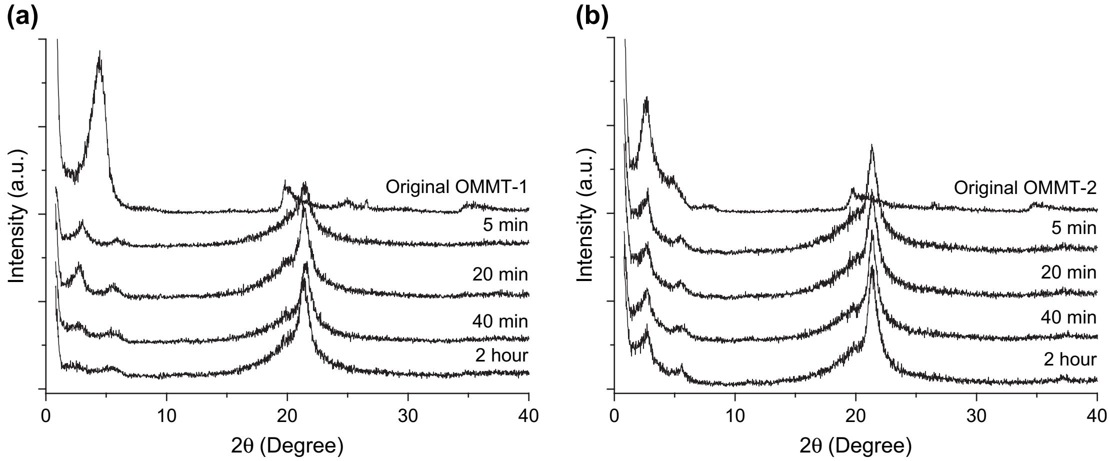

Fig. 10. WAXD curves of (a) OMMT-1/PA12L powder mixture annealed at 210 °C for different times; (b) OMMT-2/PA12H powder mixture annealed for different times.

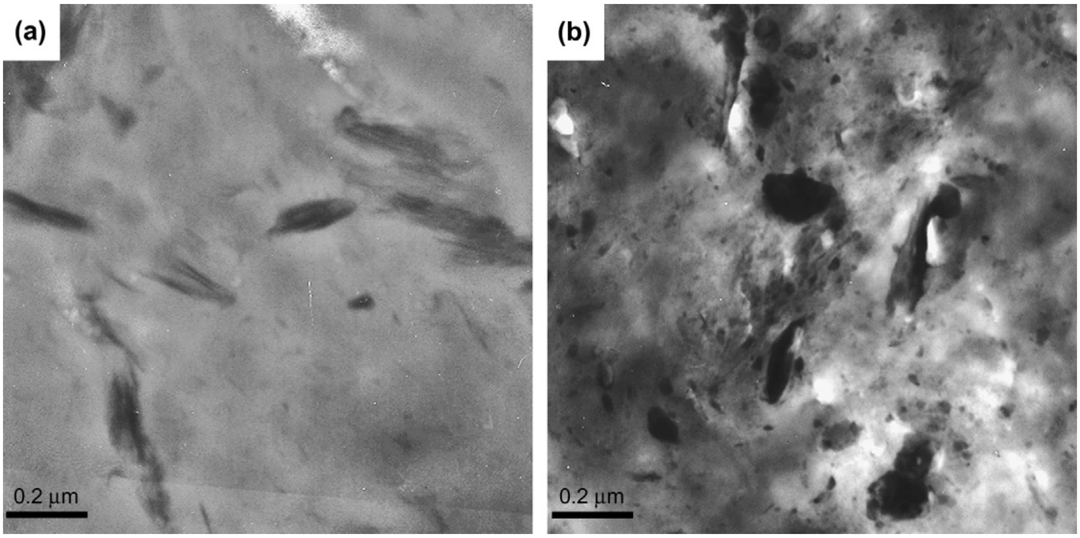

Fig. 11. TEM images of (a) OMMT-1/PA12L powder mixture annealed for 2 h; (b) OMMT-2/PA12H powder mixture annealed for 2 h.

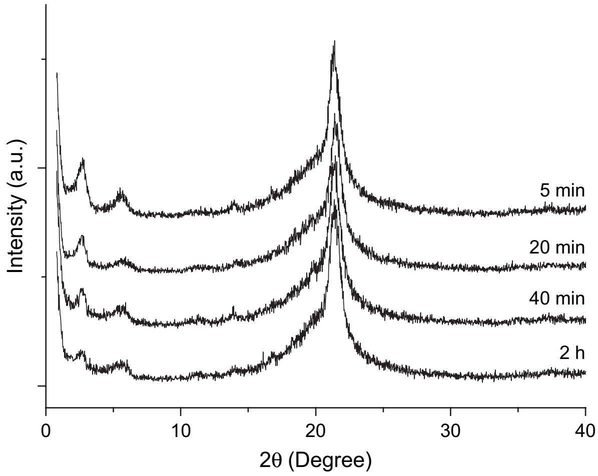

Fig. 12. WAXD curves of OMMT-1/PA12L powder mixture annealed at 230 °C for different times.

mixing time $t = 5$, 20, 40 min. The relative increments of moduli are showed in Table 2. The relative increments of nanocomposites increase with the increase of mixing time. It is attributed to the increase of exfoliated degree of OMMT with the increase of mixing time. Furthermore, the relative

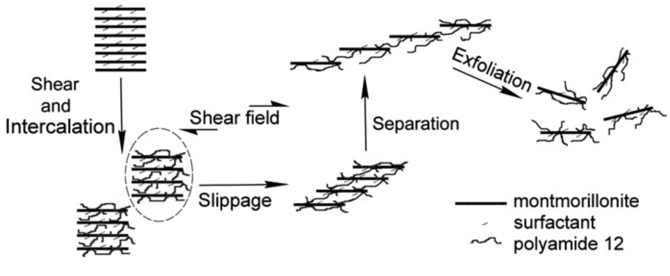

Fig. 13. Scheme of morphology evolution of OMMTs/PA12 nanocomposites under shear field.

Table 1
The hydrogen permeations of neat PA12L and OMMT-1/PA12L nanocomposites mixed for different times

Sample	Neat PA12L	Mixing time (min) of nanocomposites		
		5	20	40
Hydrogen permeation (cm^3(STP)cm/cm^2scmHg)	1.79	1.50	1.23	1.21

Table 2
The tensile modulus of neat PA12s and their nanocomposites for different mixing times

Samples	PA12L	OMMT-1/ PA12L	PA12H	OMMT-1/ PA12H	OMMT-2/ PA12H
$E_{5\ \mathrm{min}}$ (MPa)	849 ± 26	952 ± 30	876 ± 25	1282 ± 39	1079 ± 35
$\Delta E_{5\ \mathrm{min}}$ (MPa)		103		406	203
$E_{20\ \mathrm{min}}$ (MPa)	878 ± 28	1045 ± 38	854 ± 27	1280 ± 44	1182 ± 47
$\Delta E_{20\ \mathrm{min}}$ (MPa)		167		426	328
$E_{40\ \mathrm{min}}$ (MPa)	710 ± 25	1080 ± 44	772 ± 27	1270 ± 52	1106 ± 54
$\Delta E_{40\ \mathrm{min}}$ (MPa)		370		498	334

increment of tensile modulus of the OMMT-1/PA12H nanocomposite is larger than that of the OMMT-1/PA12L nanocomposite. Because OMMT-1 can be exfoliated better in PA12H matrix owing to stronger shear stress provided by PA12H with higher molecular weight. Therefore, the modulus of nanocomposites increases with the improvement of exfoliated degree of OMMTs.

4. Conclusion

The investigation shows that the exfoliation of OMMT platelets results from a combination of shear and molecular diffusion. The molecular diffusion of PA12 chains into the OMMTs mainly occurs in the initial period of mixing. The slippage of OMMT platelets driven by shear takes place in the morphology evolutions of the OMMT/PA12 nanocomposites, which results in the final exfoliation of OMMTs. When the shear stress acting on the OMMT layers is strong enough, the platelets of the OMMTs can be exfoliated even only a small quantity of polymer chains intercalate into their interlayers. The intercalation of PA12 chains into the OMMTs results in the decrease of attraction between OMMT layers and the increase of interaction between platelets and PA12s, which is helpful for the slippage of the OMMT platelets under shear field. Moreover, the favorable interaction between the PA12s and the OMMTs is the guarantee of efficiently transferring the shear stress onto the OMMT layers. Based on the exfoliation process of nanocomposites, achieving exfoliated state of OMMT in polymer matrix via melt mixing requires better interaction between components, weaker cohesion of MMT layers and proper shear stress in the different periods of mixing (for example, mild shearing condition in the initial period of mixing and high shear intensity in the middle and final periods of mixing). It is recommended to use the modifier with appropriate structures or introduce additional components to make the slippage of OMMTs easier in polymer matrices, which has further been confirmed in OMMT/thermoplastic polyurethane system. In addition, the higher adsorption of modifiers can decrease the cohesion of MMT layers, but it will block the intercalation of polymer and destroy thermal stability of the nanocomposites. Therefore, the adsorption level of modifiers in the OMMTs is also an important factor. Controlling the above factors properly is beneficial to fabricate exfoliation nanocomposites quickly, thus the properties of polymers can be improved effectively.

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