

# Exfoliation of Organically Modified Montmorillonite Driven by Molecular Diffusion in Maleated Polypropylene

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**ABSTRACT:** This work is focused on the factors influencing the intercalation of maleated polypropylene (PPMA) into organically modified montmorillonite (OMMT). Two kinds of PPMA were used to explore the optimal candidate for effective intercalation into OMMT. The grafting degree of maleic anhydride and the viscosity of PPMA have effects on the diffusion of polymer molecules. Moreover, the loading level of surfactant was varied to optimize the modification of montmorillonite because the appropriate loading

level can provide a balance between interlayer distance and steric hindrance. The kind of surfactant changes the interaction between OMMT and PPMA, and accordingly the intercalation of PPMA is different, resulting in the discrepancy of the intercalation of PPMA. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 678–684, 2009

**Key words:** diffusion; intercalation; maleated polypropylene; montmorillonite; nanocomposites

## INTRODUCTION

For most applications, maximum benefits are achieved when organically modified montmorillonites (OMMT) are homogeneously exfoliated in polymer matrices.<sup>1–3</sup> Generally, the exfoliation of OMMT via melt-mixing under shear field takes place when the attractions between sheets of OMMT, such as van der Waals force and electrostatic interaction, are broken via molecular diffusion or shear process, which is determined by the chemical structure and the viscosity of polymer matrix. Stronger interaction between polymer and OMMT and higher melt viscosity of polymer matrix will promote exfoliation of OMMT via shear process.<sup>4–7</sup>

However, there are few reports on formation of exfoliated polymer/OMMT nanocomposites via molecular diffusion process,<sup>8,9</sup> which are the cases of thermodynamic driving. Balazs<sup>10,11</sup> proposed the structure of polymer facilitating the penetration into the gallery of OMMT. The polymer must contain a fragment highly attracted to OMMT sheets and a longer fragment not attracted to the sheets, which attempt to gain entropy by pushing the sheets apart.

In this case, the exfoliated structure can be created via the diffusion of polymer.

In recent years, many polar polymers have been used as the compatibilizers for apolar polymer/OMMT composites,<sup>1–3,12–18</sup> and maleated polypropylene (PPMA) is a representative polymer. Therefore the exfoliation process of OMMT in PPMA is crucial. In this report, we demonstrated that maleated polypropylene (PPMA) with lower molecular weight could diffuse into the interlayer of OMMT to exfoliate OMMT during annealing. Although there are many reports about compatibilization of PPMA for apolar polymer/OMMT composites,<sup>1–3,12–18</sup> realizing exfoliation of OMMT in PPMA only via molecular diffusion is not reported. In fact, the intercalation of polymer chain into interlayer of OMMT depends on both chemical structure of polymer chains and spacial environments of OMMT. The structure of PPMA accords with the model proposed by Balazs; thus PPMA probably creates stable exfoliated composites via molecular diffusion. However, the appropriate MA content is a crucial factor influencing the diffusion of PPMA chains. More MA content will increase the miscibility between PPMA and OMMT, benefiting the intercalation of PPMA. However, the superabundant MA group will hinder the further diffusion of PPMA.<sup>19,20</sup> In addition, the discrepancy of viscosity also results in different ability of molecular diffusion.<sup>21</sup> Moreover, the intercalation of PPMA strongly depends on the concentration of surfactants in the interlayers. Previous work suggested that the higher concentration of surfactant

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TABLE I  
Loading and Adsorption Levels of OMMTs

	18C-20	18C-40	18C-100	18C-250	CTAB-100
Loading level (normalized to CEC)	0.2	0.4	1	2.5	1
Adsorption level (normalized to CEC)	0.15	0.34	0.65	1.74	0.68

achieved larger interlayer distance, whereas it increased the steric hindrance, not benefiting the intercalation of PPMA.<sup>22,23</sup> In addition, the interaction between PPMA and OMMT can be adjusted by varying the structure of surfactant. Szazdi et al.<sup>24</sup> found that PPMA can interact with the surfactant containing active hydrogen atoms in the interlayers. Therefore the structure of surfactant probably influences the intercalation of PPMA.

## EXPERIMENTAL

### Materials

Na<sup>+</sup>-montmorillonite (MMT) (from Kunimine, Japan) had a cation exchange capacity (CEC) of 119 mequiv/100 g. Octadecylamine was from Wako Pure Chemical Industries (Japan) and cetyltrimethylammonium bromide (CTAB) was from Shanghai Huishi Chemical (China). Two maleated polypropylenes (PPMA) with 4.6 wt % and 2.3 wt % maleic anhydride, respectively, were purchased from Sanyo Corp. (Japan) and signed with PPMA1010 and PPMA1001, respectively. Succinic anhydride (SA) was from Zhongyuan Chemical (China). PPMA were dried in a vacuum oven at 80°C for 12 h before using.

### Sample preparation

Montmorillonite modified by octadecylammonium chloride [18C-X, X represents the loading of octadecylammonium chloride (18C) normalized to CEC of MMT] was synthesized as described in our previous papers,<sup>22,23</sup> and four loading levels were used in this work. Montmorillonite modified by CTAB was prepared under the same conditions. The absorption levels of OMMTs were estimated by thermogravimetric analysis, and the results are shown in Table I.

The previous researchers have found that the chemical structure and viscosity of polymers influenced the intercalation of polymer chains<sup>10,21</sup>; thus, two kinds of PPMA, i.e., PPMA1010 and PPMA1001, were used to investigate the intercalation of PPMA. PPMA was milled to powder and mixed with the OMMTs in a stirring vessel at room temperature, and the mixtures were pressed to a disk and annealed in a quartz tube at 180°C under N<sub>2</sub>.

### Characterization

Wide-angle X-ray diffraction (WAXD) was carried out with a Rigaku model Dmax 2500 with a Cu K $\alpha$  radiation. The morphologies of the composites were observed by transmission electron microscope TEM (JEM, JEOL1011) on microtome sections of the composites. Ultrathin sections were cryogenically cut at a temperature of -80°C using a Leica Ultracut. Rheological measurements were performed on a PHYSICA MCR 300 at 180°C under a nitrogen atmosphere. Parallel plates of 25 mm diameter were used and the sample disk was 1 mm thick and 25 mm diameter. The complex viscosity was measured as a function of angular frequency (ranging from 0.1 to 100 rad/s). Fourier transform infrared spectroscopy (FTIR) was performed on BRUKER Vertex 70 at a resolution of 2 cm<sup>-1</sup>. All the samples were dried in a vacuum oven at 80°C for 12 h before characterization.

## RESULTS AND DISCUSSION

### Effect of molecular structure and viscosity of PPMA

The results of PPMA1010/18C-100 = 2/1 and PPMA1001/18C-100 = 2/1 mixtures annealed for 15 min show that the (001) diffraction peak of 18C-100 had shifted to a lower angle (Fig. 1), suggesting that both PPMA1010 and PPMA1001 intercalate into

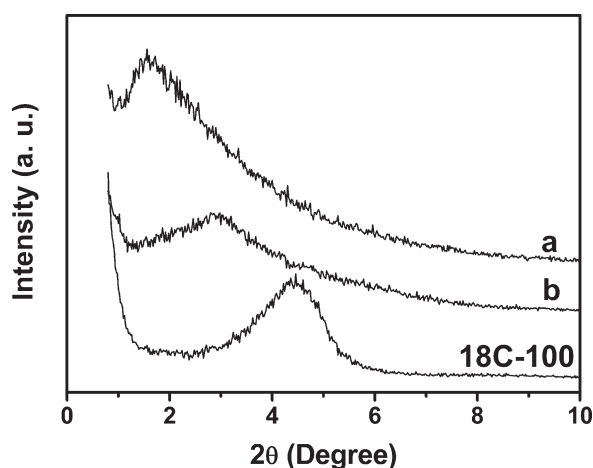


Figure 1 WAXD profiles of (a) PPMA1010/18C-100 = 2/1; and (b) PPMA1001/18C-100 = 2/1.

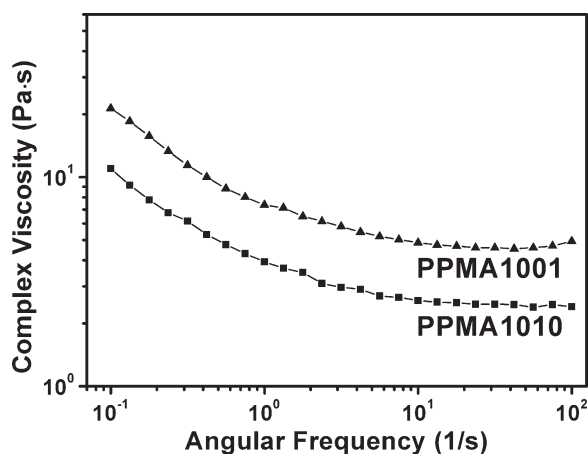


Figure 2 The viscosities of two kinds of PPMA.

the interlayer of 18C-100. However, the larger interlayer distance is achieved in the PPMA1010/18C-100 system, which is attributed to the smaller molecular weight and higher maleic anhydride (MA) content of PPMA1010. Owing to the smaller molecular weight, the viscosity of PPMA1010 is lower than that of PPMA1001 (Fig. 2), benefiting the intercalation of polymer chains.<sup>21</sup> Furthermore, the higher MA content strengthens the interaction between polymer chains and the OMMT, promoting the capability of intercalation. Therefore, PPMA1010 can intercalate into the galleries of OMMT better than PPMA1001.

The mixtures of PPMA1010/18C-100 with different weight ratios were annealed under the same conditions. The WAXD results suggest that the interlayer distance of 18C-100 increases with the content of PPMA1010 (Fig. 3). When the weight ratio of PPMA1010 to 18C-100 is 9 : 1, the (001) diffraction peak of OMMT disappears, denoting the formation

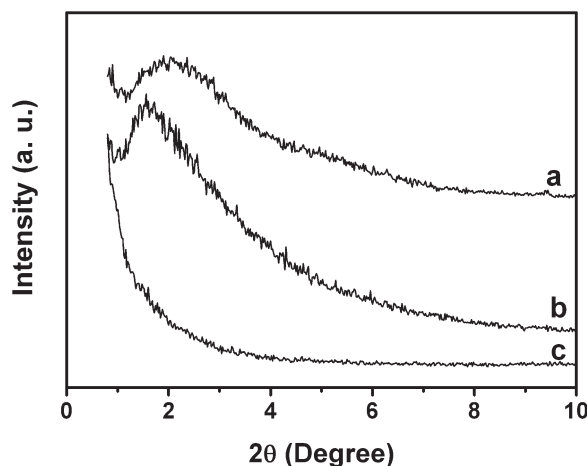


Figure 3 WAXD profiles of (a) PPMA1010/18C-100 = 1/1; (b) PPMA1010/18C-100 = 2/1; and (c) PPMA1010/18C-100 = 9/1.

of exfoliated structure. It suggests that the exfoliation of the OMMT can be achieved via the molecular diffusion of PPMA. The molecules of PPMA1010 can continually diffuse into galleries of 18C-100, and interlayer distance expands gradually with the increase of PPMA1010 content; consequently, the exfoliated structure is formed. Moreover, PPMA1010 is an optimal candidate for creating exfoliated nanocomposites via molecular diffusion.

#### The effect of loading level and structure of surfactant

The loading level and structure of surfactant in OMMT are also crucial to the intercalation of PPMA. Our previous research has suggested that the dispersion of OMMT becomes unfavorable in PPMA matrix as the increase of surfactant loading.<sup>23</sup> Generally the modification of MMT by the surfactant decreases the level of attraction between adjacent platelets due to the increase of the interlayer distance. However, the higher content of surfactant not only increases the steric hindrance but also weakens the interaction between OMMT and PPMA. Therefore the appropriate loading of surfactant is crucial to molecular diffusion of PPMA into the gallery of OMMT to realize the exfoliation of OMMT. Table I shows adsorption level of the surfactant in the OMMTs with different loading of surfactant. The WAXD profiles of these OMMTs are compared in Figure 4. As the surfactant loading increases, the (001) diffraction peak shifts to a lower angle, and the intensity of the diffraction peak strengthens. It suggests that the interlayer distance expands gradually and the alignment of MMT platelets is more regular.

The physical mixtures of PPMA1010 powder with four kinds of OMMT (powder) in the weight ratio of 9/1 by weight were annealed at 180°C for different

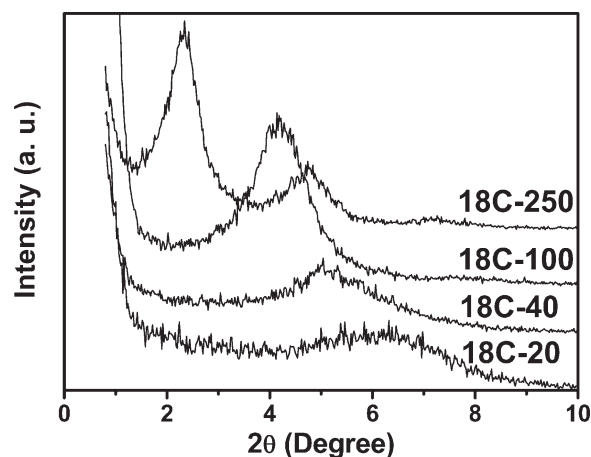
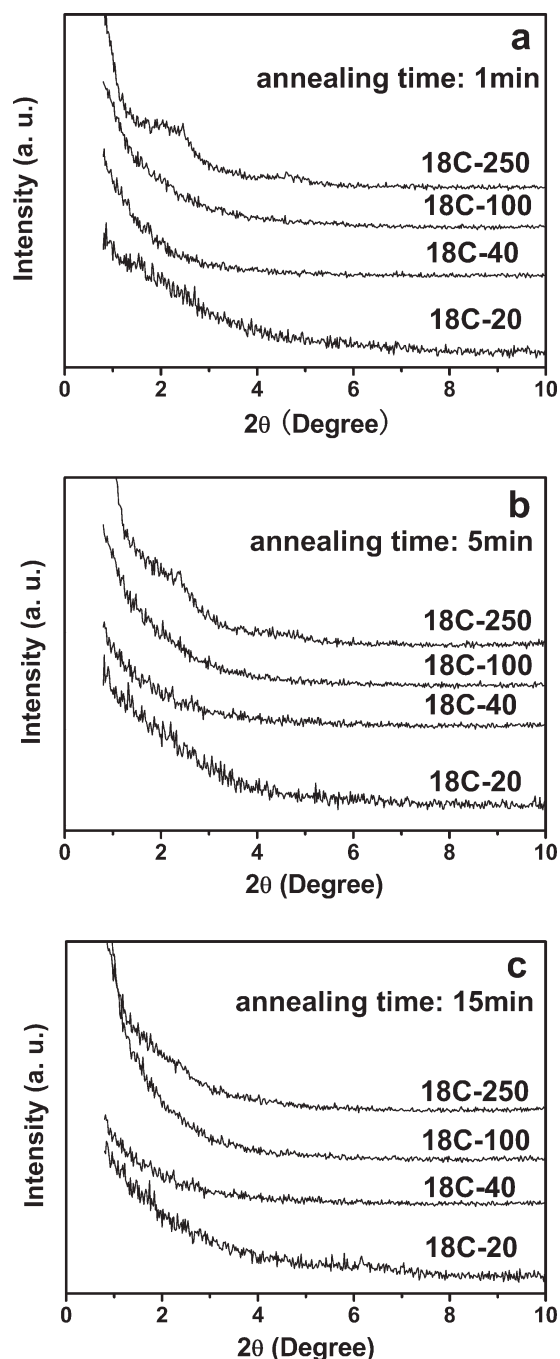


Figure 4 WAXD profiles of various OMMTs as a function of surfactant loading level.

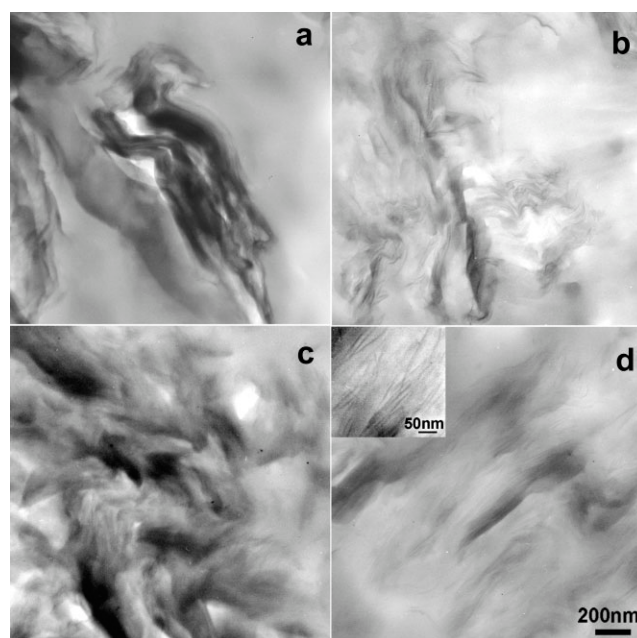


**Figure 5** WAXD profiles of PPMA1010/OMMTs = 9/1 annealing for different time.

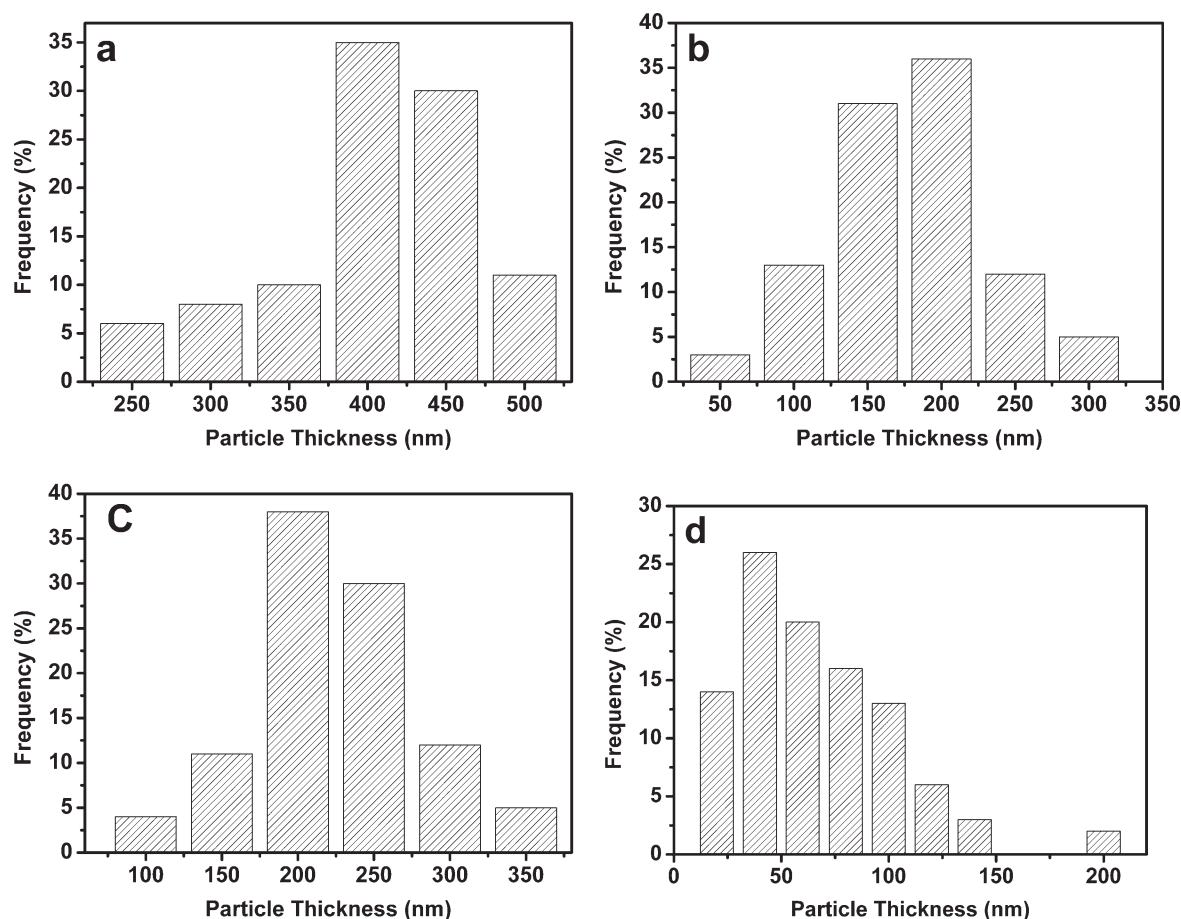
times under  $N_2$ , respectively. Figure 5 shows WAXD profiles of these mixtures annealed for different time. When annealed for 1 min, the (001) diffraction peaks of 18C-100 and 18C-40 disappear, indicating that a large amount of PPMA molecules can quickly diffuse into the galleries of OMMTs and make the interlayer distance expand greatly. However, the consecutive diffraction peaks still exist in 18C-250 and 18C-20 systems. With the increase of annealing time, the intensities of the (001) diffraction peaks for

18C-250 and 18C-20 weaken continuously. The results suggest that 18C-100 and 18C-40 provide more appropriate environments for the intercalation of PPMA1010 than 18C-250 and 18C-20. More surfactant in the interlayer of 18C-250 hinders the intercalation of PPMA1010, and the rate of molecular diffusion is obviously lower than other systems; accordingly, the exfoliation of 18C-250 needs longer time. In 18C-20 system, the interlayer distance is smaller and the attraction between adjacent platelets is stronger, which are unfavorable to the molecular diffusion of PPMA into the galleries. In contrast, in both 18C-100 and 18C-40 systems, PPMA1010 chains can quickly intercalate into the galleries and achieve larger interlayer distance. It suggests that the interlayer distances of 18C-100 and 18C-40 are adequate for the intercalation of PPMA1010, and at the same time the steric hindrances are not large due to the medium loading level of surfactant. Therefore 18C-100 and 18C-40 provide a good balance between interlayer distance and steric hindrance, and consequently PPMA1010 chains can quickly intercalate into the galleries and achieve larger interlayer distance.

TEM observation is used to evaluate the difference in the microstructures of PPMA1010/18C-100 and PPMA1010/18C-40 mixtures (Fig. 6). When annealed for 1 min, the agglomerate of OMMTs still exists in both systems though the diffraction peaks of OMMTs has disappeared in WAXD profiles.



**Figure 6** TEM images of PPMA1010/OMMT annealing for different time (a) PPMA1010/18C-40 for 1 min; (b) PPMA1010/18C-40 for 15 min; (c) PPMA1010/18C-100 for 1 min; and (d) PPMA1010/18C-100 for 15 min.



**Figure 7** Distribution histograms of particle thickness (a) PPMA1010/18C-40 for 1 min; (b) PPMA1010/18C-40 for 15 min; (c) PPMA1010/18C-100 for 1 min; and (d) PPMA1010/18C-100 for 15 min.

However, the aggregating level of 18C-40 is apparently larger than that of 18C-100, which should be ascribed to the smaller interlayer distance of 18C-40. When annealed for 15 min, the dispersion levels of the OMMTs are improved obviously, and the dispersion level of 18C-100 is better than that of 18C-40. In high-resolution imaging [Inset in Fig. 6(d)], many sheets of 18C-100 have been exfoliated in the matrix. The statistical results in Figure 7 provide more detailed information and suggest the results of TEM images. The results further confirm that OMMT can be exfoliated in PPMA matrix only via molecular diffusion, and the loading level of 18C-100 is more suitable for the intercalation of PPMA1010 comparing with that of 18C-40. However, the TEM images suggest that the homogeneous dispersion of platelets within a short time requires appropriate shear force.

Szazdi et al.<sup>24</sup> have found that PPMA could react chemically with the surfactant containing active hydrogen groups, whereas the surfactant not containing active hydrogen atoms cannot react with PPMA. To compare the effect of the chemical reaction between the surfactant and PPMA on the inter-

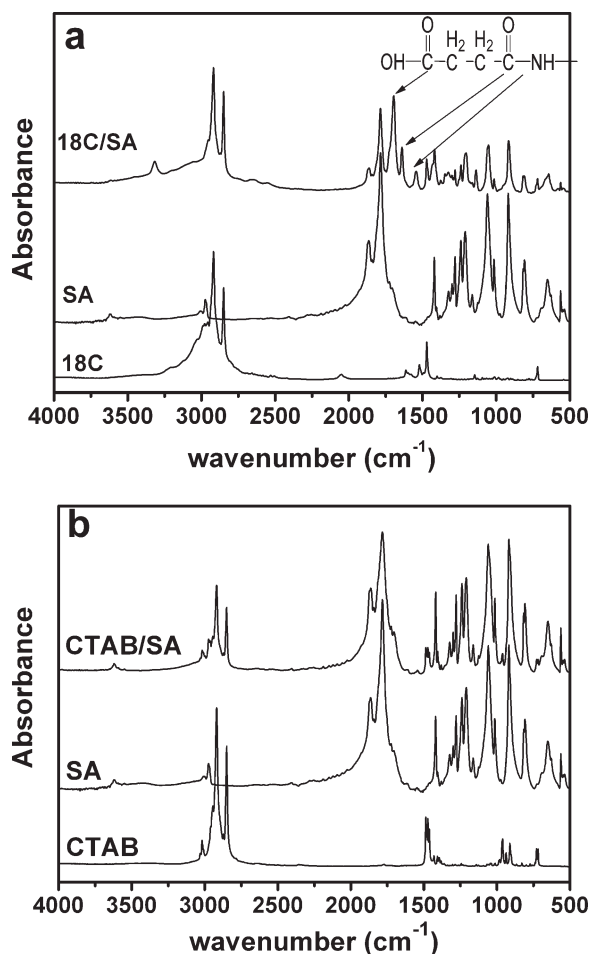
calation of PPMA1010 chain, cetyltrimethylammonium bromide (CTAB) is also chosen to modify MMT (Table I). Succinic anhydride (SA) as a model of the grafted MA is employed to combine with 18C and CTAB to estimate the reaction between the surfactant intercalated into MMT and PPMA. After the mixture of 18C (or CTAB) and SA is annealed at 180°C, FTIR spectra of the mixture of 18C/SA [Fig. 8(a)] show that some new peaks appear ranging from 1697 to 1547  $\text{cm}^{-1}$  and at 3320  $\text{cm}^{-1}$ , denoting the formation of carboxylic acid and amide group. Thus anhydride group of SA reacts with amine group of 18C. However, there is no new peak in the FTIR spectra of the mixture of CTAB/SA [Fig. 8(b)], indicating CTAB did not react with SA.

In Figure 9, the original interlayer distances and surfactant contents of 18C-100 and CTAB-100 are similar, but the expanding levels of interlayer distance are different when the OMMTs are mixed with PPMA1010. Owing to the reaction between 18C-100 and PPMA1010, the PPMA1010 chains can intercalate into the galleries of 18C-100 easily; thus more PPMA1010 chains enter the gallery and larger

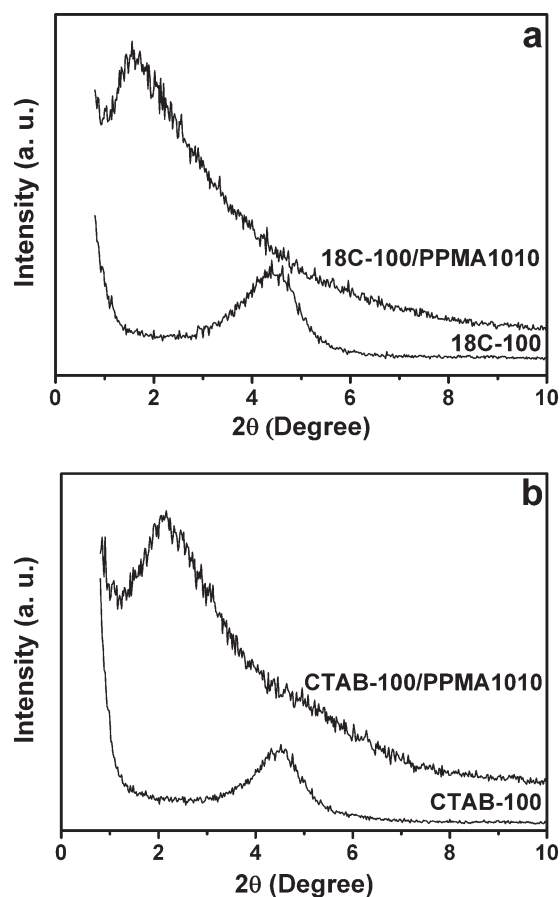
interlayer distance is achieved in PPMA1010/18C-100 system. Therefore, the reaction between the surfactant and PPMA is favorable to the intercalation of PPMA.

### CONCLUSION

This work discerns the effects influencing the intercalation of PPMA and benefits the optimization of fabricating nanocomposites. The intercalation of PPMA into OMMT is influenced by the structure and viscosity of PPMA and the loading level and structure of surfactant. More MA content and lower viscosity are beneficial to the intercalation of PPMA. The loading level of surfactant is also a crucial factor for the intercalation of PPMA. A medium level of surfactant can provide a good balance between interlayer distance and steric hindrance, facilitating the intercalation of PPMA chains. The chemical reaction between surfactant and PPMA improves the interaction between OMMT and PPMA and accordingly promote the ability of intercalation of PPMA. The goal of our work is to shed more light on the factors



**Figure 8** FTIR spectra for the mixture of SA and surfactants in a weight ratio of 1 : 1 annealing at 180°C.



**Figure 9** WAXD profiles of the mixture of PPMA1010 and OMMTs in a weight ratio of 2 : 1 annealing for 15 min.

influencing the intercalation of PPMA, which benefits the optimization of the structure of PPMA and the modification of MMT. However, it is complicated how exfoliation of OMMTs in a polymer matrix is realized, considering the above-mentioned factors. To prepare high-performance polymer nanocomposites, more work will be needed in the optimization of fabricating nanocomposites.

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