

A Novel Modification on Melt Intercalation via Exothermal MMT

Xin Wang, Jingjing Lin, Xuyun Wang, Zhaobo Wang

Qingdao University of Science and Technology, 266042, China

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ABSTRACT: This article presented a novel modification on the melt intercalation. Montmorillonite (MMT) with exothermal enthalpy effect was prepared by the compounding of MMT with AIBN in solution. An exfoliated polystyrene (PS)/MMT nanocomposites could be obtained by the introduction of exothermal MMT via melt mixing, and the com-

parison with the counterpart indicated the exfoliation of MMT was accelerated by the *in situ* exothermal enthalpy and nitrogen released during melt intercalation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2230–2236, 2004

Key words: melt mixing; nanocomposites; clay; polystyrene

INTRODUCTION

Polymer/clay nanocomposites have been the focus of intensive scientific research because of their excellent properties and potential industrial applications.^{1,2} Smectite clays, especially montmorillonite (MMT) in most cases, were used in the preparation of this kind of composites for their high aspect ratio and high surface area. Montmorillonite has a typical layered structure that can be entirely exfoliated, so it was developed by melt intercalation and *in situ* polymerization to take advantage of this character.

According to various synthesized monomers, there are mainly two kinds of *in situ* polymerizations. The first is to intercalate functional monomer into interlayer gallery and synthesize them. Nylon-6-³ and epoxy-⁴based nanocomposites were successfully prepared this way. The second type of *in situ* polymerization involved intercalation of initiators of catalyst system and the following polymerization of vinyl monomers. Poly(methyl methacrylate) (PMMA) and polystyrene (PS) nanocomposites were synthesized via this method.^{5,6} For polyolefins, where Ziegler-Natta catalyst is involved, the relevant method was named polymerization-filling. Although developed from supported catalyst technique, it was also a kind of *in situ* polymerization.⁷

Melt intercalation is another approach for the preparation of polymer-based nanocomposites, and it is more attractive to industry because of its simplicity. The process of melt intercalation is just the mixing of clay with a molten polymer. It was found that the rate

of polymer intercalation is almost the same as the rate of diffusion of the molecular chains in clay agglomerates.^{8,9} No additional time is required, so melt intercalation exhibits no great difference with a traditional melt mixing. However, the simple mixing of polymer melts with inorganic clays is not a reliable way for intercalation, not even for separation of clay agglomerates. Most of the successful mixing intercalation systems reported in literature showed their limit to the MMT content in the composites. MMT could be exfoliated in the simple mixing when the content of MMT was no more than 5.0 wt %.

As to the microstructure of exfoliated polymer/clay nanocomposites, it is featured by the strong polymer-clay interaction and the inner ordered structure. For example, Han et al.¹⁰ investigated poly(ethylene oxide)-Lopnite solutions with flow birefringence and small-angle neutron scattering, and the experimental results revealed a dynamic polymer-clay network resulting from the equilibrium of absorption and desorption of molecular chain on the clay layers. Interesting enough, 6 wt % was found to be the threshold value of Lopnite loading, beyond which the exfoliated structure could not be maintained. Xu and Xu¹¹ reported a percolation network through strong interaction between exfoliated layers in the PP/MMT composites, which led to a solidlike rheological behavior of the melt. Further study showed this special rheological behavior could be reduced by the clay surface coupling, indicating the breakdown of the percolation network while the exfoliated layer structure still remained. Above all, the standard interpretation of the microstructure of exfoliated clay layers was not reached. Therefore, it remains an important question in both theory and industry, where did the failure of melt intercalation on the manufacture of high MMT

Correspondence to: X. Wang (wangxihh@qingdaonews.com).

content exfoliated nanocomposites come from, the low efficiency of melt intercalation or the threshold value of the percolation from exfoliated structure to agglomerate one?

From the viewpoint of thermodynamics, enthalpy was much more important than entropy in the driving of exfoliation of MMT in melt intercalation. To modify melt intercalation, many methods were tried to improve the interaction or miscibility between inorganic fillers and polymer matrix.^{12,13} Among the methods, maleic anhydride modification of polypropylene was a successful example.¹⁴ The effect of maleic anhydride modification in the improvement on mixing intercalation was easy to understand; a great decrease in enthalpy, namely the increase in interfacial interaction, was induced by the modification.

In summary, although the intercalation process of MMT is still poorly understood, the enthalpy showed itself an import factor, whether the enthalpy was released from the synthesis of monomer or from the strong interfacial interaction in melt-mixing. In this article, a novel way was presented to improve mixing intercalation. MMT with exothermal enthalpy was prepared via solution compounding, and its local *in situ* enthalpy in the melt intercalation with PS was proved by experimental results to help the formation of exfoliated structure. Exfoliated structured PS/MMT composites with 7 wt % MMT loading were manufactured via melt intercalation and the relevant mechanism was analyzed.

EXPERIMENTAL

In the experiments, the first step involved was the preparation of the exothermal MMT. Sodium montmorillonite (Na-MMT), with the cation exchange capacity of 100 meq/100 g, was provided by Huaxia Montmorillonite Factory (Weifang, Shandong Province, China). MMT was organized by interlayer ion exchanging reaction in the solution of cetyl trimethyl ammonium bromide (CTAB; Jining Chemical Institute, Jining, China) at 80°C, featured by the increase of the interlayer distance of MMT from 1.52 to 2.00 nm. The following step was to introduce organized MMT into the toluene solution of azobisisobutyronitrile (AIBN; Shanghai Chemical Reagent Factory, Shanghai, China) at a weight ratio of MMT to AIBN of 1/0.15. The semi-pellucid colloidlike mixture was dried in open atmosphere, and the remainder was smashed. The final product was named exothermal MMT.

The melt intercalation was carried out in a Brabender mixer (PLE-331 type, Germany) at 170°C. The matrix polymer, PS, with a weight-averaged molecular weight of 200,000, was provided by Lanzhou Petrochemical Corp. (China). After the introduction of PS and MMT into the cavity of the mixer, the mixing would last for 10 min with a rotating speed 40 rpm.

The melt of the hybrids was molded into sheets for further characterization.

PS/MMT composites were also prepared with bulk polymerization and emulsion polymerization as counterparts to investigate the influence of the preparation conditions, especially the shear stress, on the microstructure formed. Both the polymerizations were carried out in the presence of CTAB-treated organic MMT. AIBN was used as the initiator of bulk polymerization at 80°C. Sodium oleate and sodium hydrocarbonate were used as emulsifier, and potassium persulfate was used as initiator of emulsion polymerization at 85°C.

The interlayer distance of MMT was determined by X-ray diffraction (XRD) with a Rigaku-D/max-Rb diffractometer equipped with an intrinsic germanium detector system by using CuK α radiation. The wavelength of the X-ray was 0.154 nm and the angle scanning was carried out at the rate of 6°/min.

The thermal behaviors of the samples were recorded on a Netzsch thermal analysis DSC 204 cell. The rate of temperature scanning was 10°C/min from room temperature to 200°C.

RESULTS AND DISCUSSION

Formation of exfoliated structure of PS/MMT composites

The formation of exfoliated structure was a twofold process, both the intercalation or the exfoliation of MMT layers and the segmentation and the dispersion of MMT agglomerates in polymer matrix were involved. In our experiments, three kinds of PS/MMT composites were manufactured with bulk polymerization, emulsion polymerization, and melt intercalation, respectively, and their microstructures were investigated with the complementary techniques of XRD and TEM. In curves b and c of Figure 1, the lack of low-angle diffraction peak in the XRD pattern indicated that MMT had been thoroughly exfoliated in the process of emulsion polymerization and melt intercalation. The counterpart prepared via bulk polymerization exhibited a diffraction peak at low angle zone, which indicated the enhancement of the interlayer distance from 1.98 nm of the organic MMT to 3.50 nm.

As shown in Figure 2, TEM provided a direct observation on the dispersion of MMT layers in the polymer matrix. As for the composites via melt intercalation, MMT dispersed in the form of tiny units with a length of about 200 nm and a width of about 10 nm. Obviously it performed an approximate parallel layer structure induced by the shear stress. The composite via emulsion polymerization possessed similar exfoliated layer structure, and MMT dispersed in the form of units with the length \sim 200 μ m and width \sim 20 nm. The dispersed units were a bit larger than those in the

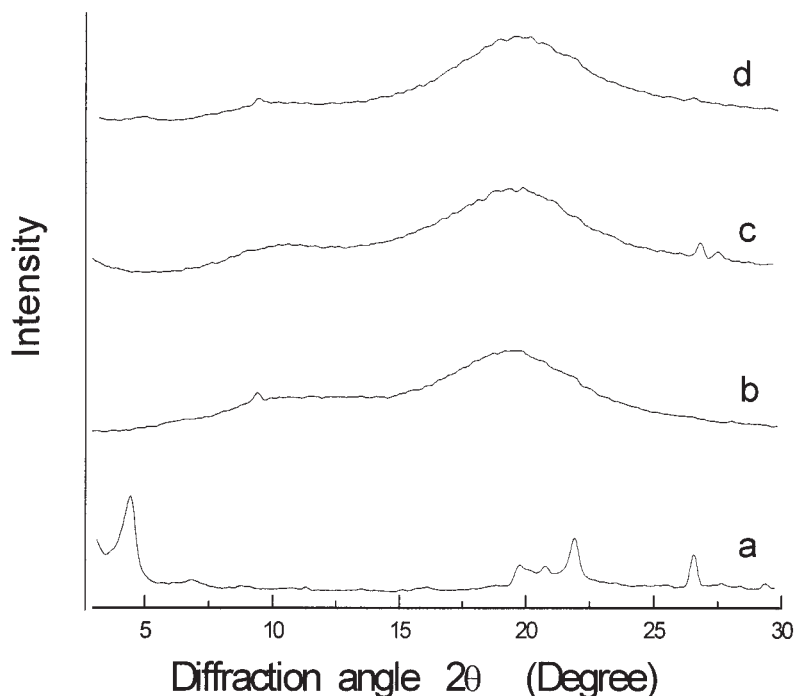


Figure 1 XRD patterns of (a) CTAB-treated MMT; and PS/MMT composites with 3 wt % MMT loading prepared via different methods: (b) melt mixing; (c) emulsion polymerization; (d) bulk polymerization.

composite via melt intercalation; however, the biggest dissimilarity was the irregular arrangement of the layers. Both the XRD and the TEM revealed the exfoliated layer structure of the composites via melt intercalation and emulsion polymerization, and the diversity of the exfoliated structure was clear. The presence of shear stress in melt intercalation induced the featured orient layer structure and smaller dispersed units.

Bulk polymerization provided the composite a very distinct layer structure. Large MMT agglomerates could be found in the TEM image. Combined with the XRD results, it was concluded that the MMT in the

composite via bulk polymerization had not been thorough exfoliated, which resulted from the high viscosity of the polymers in bulk polymerization. Moreover, due to the lack of shear stress, the agglomerate of MMT could not be segmented into tiny units. So, MMT was poorly dispersed in the process of bulk polymerization.

Characterization of exothermal MMT

Exothermal MMT was prepared in our experiment and introduced into the melt intercalation with PS.

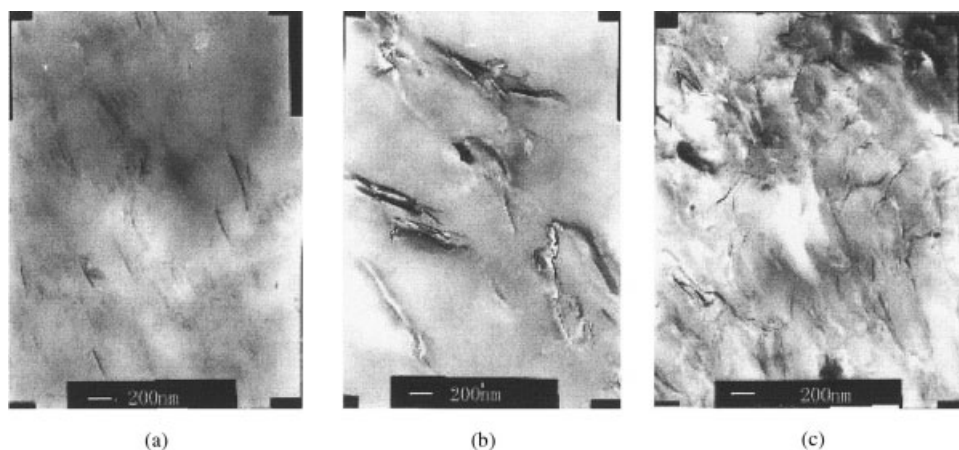


Figure 2 TEM photographs of PS/MMT composites with 3 wt % MMT via (a) mixing intercalation; (b) bulk polymerization; (c) emulsion polymerization.

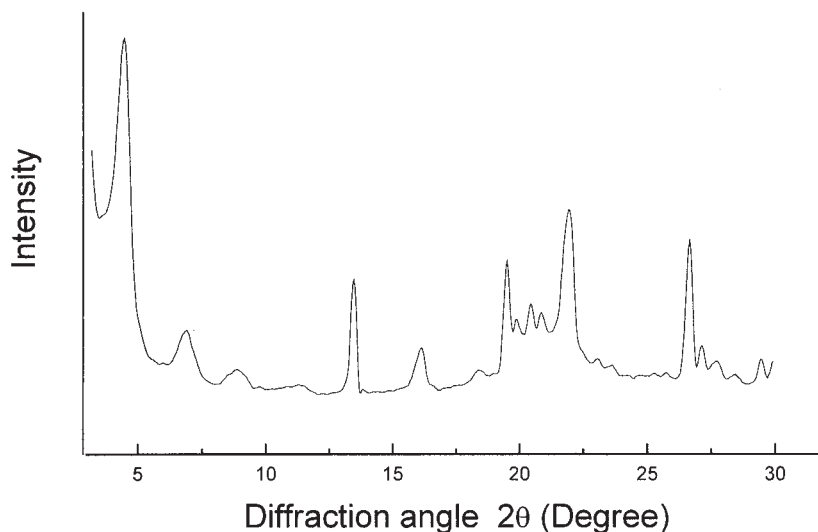


Figure 3 XRD patterns of exothermal MMT.

The characterization indicated it was not the simple mixture of MMT and AIBN. During the preparation, the evaporation of toluene was accompanied by crystallization of AIBN in the presence of MMT. As Figure 3 showed, the interlayer distance of exothermal MMT was almost the same as the original organic MMT, so there was little AIBN embedding into the interlayer gallery of MMT.

The thermal decomposition behavior of exothermal MMT was shown in Figure 4; it performed a mild decomposition from 100 to 140°C, with the exothermal enthalpy of -193.3 J/g MMT, namely, -1288.7 J/g AIBN. The counterpart, pure AIBN, performed both the exothermal decompositions from ~ 105 to 140°C

and the endothermic process during a narrow temperature zone peaked at 103.4°C. The endothermic process before exothermal decomposition was obviously the melting of AIBN crystal. The lack of endothermic process of exothermal MMT indicated the crystal of AIBN in the exothermal MMT was different from the original.

In Figure 3, the big dispersion peak in the low-angle zone of the XRD pattern was the contribution of the interlayer structure of MMT and the sharp ones were that of the crystal structure of AIBN. The crystal structure of AIBN in exothermal MMT could be detected in XRD, whereas no enthalpy effect of crystal melting was detected in DSC. Analysis in detail showed the

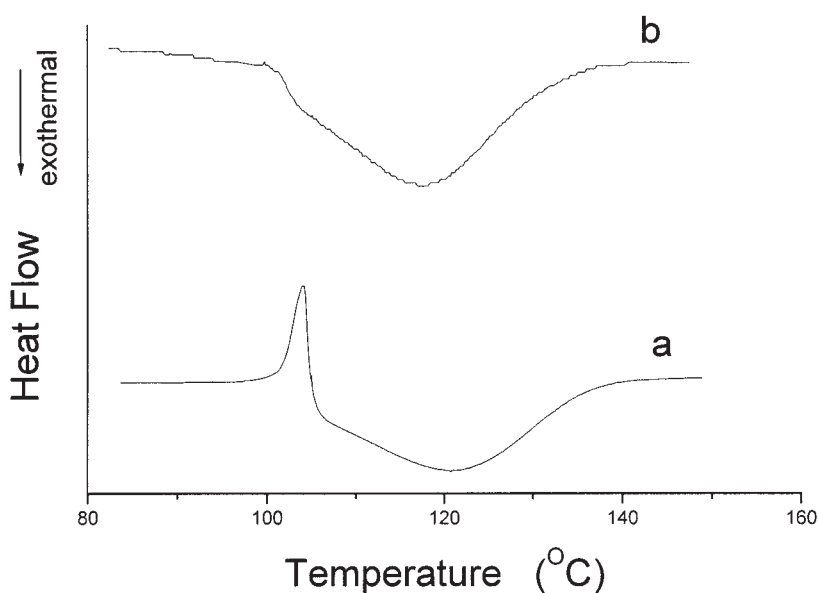


Figure 4 DSC curves of (a) AIBN; (b) exothermal MMT.

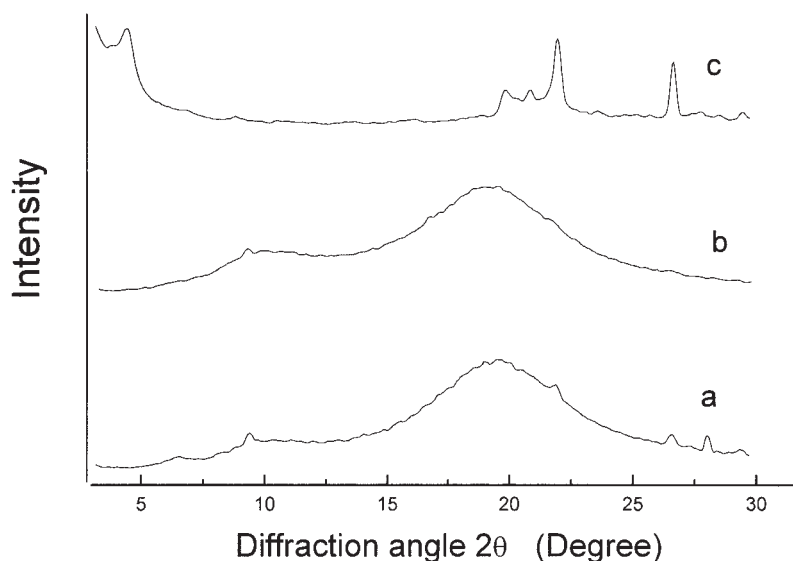


Figure 5 XRD patterns of composite with 7 wt % clay loading (a) organic MMT; (b) exothermal MMT; and (c) exothermal MMT after the decomposition at atmosphere.

enthalpy of MMT attributive to AIBN was -1288.7 J/g, and the exothermal enthalpy of AIBN was -1241.0 J/g, so little difference could be neglected as the deviation in experiments. Therefore, it could be concluded that the decomposition enthalpy of AIBN was changed little by the compounding with MMT, but the crystals of AIBN showed itself closely correlative to compounding, after which the enthalpy of melting of crystals was too little to be detected.

Although it was supposed that the interfacial energy of little crystals could compensate the energy dissipated in crystal melting, consequently, the melting performed no apparent enthalpy, a simple calculation negated the hypothesis. A spherical crystal with a radius of $10 \mu\text{m}$ possesses the interfacial energy of 0.015 J/g, providing the relative density of AIBN is 1 and the surface tension is 5.0×10^{-2} N/m. This was a rather approximate calculation, but the interfacial energy found was different in magnitude from the endothermic enthalpy in Figure 2, 128.5 J/g.

Above all, the enthalpy behavior of exothermal MMT was still ill interpreted and the coexistence state of AIBN and MMT was almost in a covered case. However, it was certain that AIBN dispersed in microunits together with MMT and would provide an *in situ* exothermal enthalpy.

Melt intercalation with exothermal MMT

As mentioned above, the melt mixing of organic MMT and PS exhibited not only good compounding effect but also induced the exfoliation of MMT when MMT content was 3.0 wt %. The lack of diffraction peak in the low-angle zone in curve b of Figure 1 indicated that the MMT was thoroughly exfoliated during melt

intercalation. In the literature, the similar successes in the preparation of nanocomposites with low MMT content via melt intercalation was already reported. With the increase of MMT content to 7% in weight, the MMT had been intercalated in the composites prepared via melt intercalation, and the interlayer distance increased from the original 2.00 to 3.89 nm as shown in curve a of Figure 5; however, the MMT had not been exfoliated during the melt mixing. Therefore, the experimental results above revealed clearly the limitation of melt intercalation.

To be compared, the introduction of 7% exothermal MMT in weight via melt mixing could manufacture an exfoliated nanocomposite successfully. As curve b of Figure 5 showed, no diffraction peak was found in the low-angle zone. There was a great difference between this curve and its counterpart, curve a in Figure 5, and so the improvement on mixing intercalation by *in situ* enthalpy effect was influenced.

Because of the midst miscibility between MMT and PS, their melt intercalation was indeed a dispersive mixing. The formation of exfoliated structure was a twofold process, both the intercalation or exfoliation of MMT layers and the segmentation and the dispersion of MMT agglomerates in polymer matrix were involved. The segmentation of MMT was a mesoscopic process influenced mainly by the parameters such as shear stress and viscosity, whereas the intercalation of MMT was a microscopic process with the dominant dependence on molecular diffusion. During the melt mixing, the *in situ* enthalpy released by AIBN in MMT helped the formation of local hot points where the polymer would behave at a lower viscosity and higher mobile ability of molecular chains. Then, the acceleration of molecular diffusion and the follow-

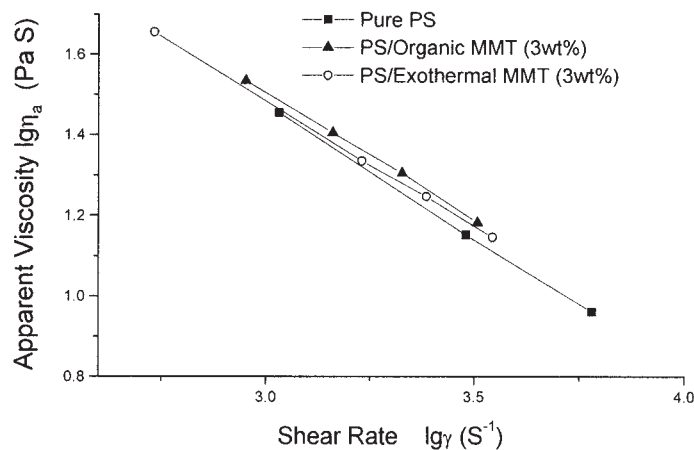


Figure 6 Rheological behaviors of PS/MMT composites and PS.

ing exfoliation of MMT accelerated by the exothermal enthalpy was reasonable. Curve c of Figure 5 indicated that no notable change in interlayer distance could be found after the exothermal MMT had undergone the decomposition of AIBN at atmosphere with an external heating provided. Therefore, the increase in induced molecular mobility, rather than the enthalpy itself, played an important role in the exfoliation of MMT.

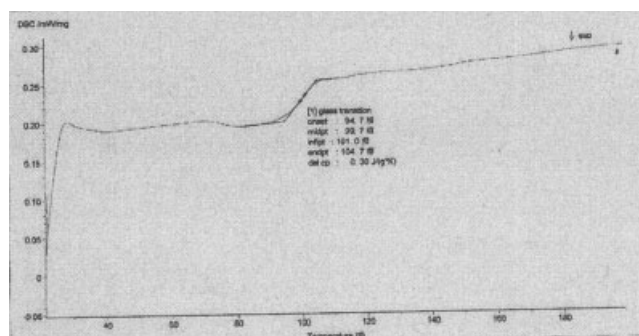
As is well known, nitrogen will be given up during the decomposition of AIBN, and its dissolution in the polymer melt will result in the increase of the free volume and consequently of the molecular mobility. In Figure 6, we presented the flow curves of two kinds PS/MMT composites. The introduction of CTAB-treated organic MMT led to a distinguished increase in the melt viscosity, whereas exothermal MMT brought only a slight rise in the viscosity. These two composites possessed the same MMT content and exfoliated layer microstructure, so the comparison indicated the presence of nitrogen inside of the polymer melt and the change of the inner free volume.

Another proof came from the measurement of the glass transition temperature (T_g). Although several feature temperatures were provided by the analyst software in the DSC curves, as shown in Figure 7, the 0.5–1.0°C difference in T_g was large enough to reveal the difference in molecular mobility.

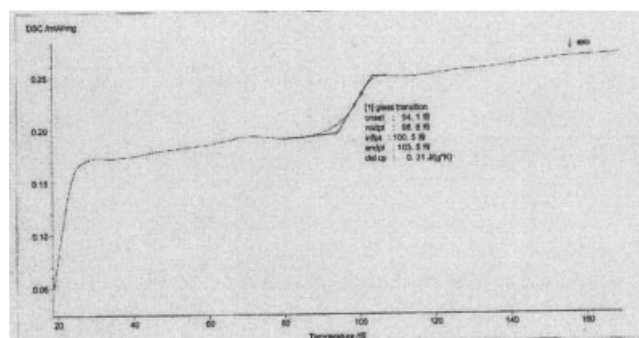
In summary, two factors were involved in the acceleration of the exfoliation of MMT during the process of melt intercalation of exothermal MMT: the local hot point coming resulting from the *in situ* enthalpy effect and the increase in free volume resulting from nitrogen released. Both factors could enhance the molecular mobility; then, the diffusion of polymer into interlayer gallery of MMT would arise.

The formation of exfoliated nanocomposites was a twofold process, and our results indicated clearly the inefficiency of simple melt mixing in the polymer dif-

fusion into interlayer gallery. The success of the preparation of exfoliated PS/MMT nanocomposite with high MMT loading by the use of exothermal MMT opened a new field for the development of melt intercalation. Although some threshold values had been reported,¹⁰ the maximum of MMT loading in exfoliated



a)



b)

Figure 7 DSC curves of PS/MMT composites to indicate a 0.5–1.0°C difference in T_g between composites with (a) organic MMT; (b) exothermal MMT.

nanocomposite had not been reached because of the diversity of microstructure of the exfoliated MMT layers.

However, there were still some unsolved problems in the application of exothermal MMT. In the above model interpreting the special exfoliation behavior of MMT, the miscibility should be good enough to ensure the increase of the molecular mobility induced by the release of the *in situ* enthalpy or the nitrogen. Therefore, the application of exothermal MMT was still limited by the miscibility between MMT and polymer material. The direction application of exothermal MMT on the nonpolar polymer, the copolymer of ethylene and octene (POE), had encountered great failure in our experiment. Therefore, the enhancement of the application of exothermal MMT was still in need of further investigation.

CONCLUSION

1. The exothermal MMT was prepared by the compounding of MMT with AIBN in solution and the combination of DSC and XRD revealed that the AIBN dispersed in the microunit together with MMT and would provide MMT the *in situ* exothermal enthalpy during its decomposition.

2. An exfoliated nanocomposite of PS/MMT with MMT content of 7 wt % was manufactured by the melt intercalation of exothermal MMT and PS, whereas the

counterpart exhibited a intercalated layer structure. Further analysis indicated the exfoliation of MMT could be accelerated by the *in situ* exothermal enthalpy and the increase in free volume induced by the nitrogen released during melt intercalation.

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