Study of the Exfoliation Process of Epoxy–Clay Nanocomposites by Different Curing Agents

Qi Wang, Chunfang Song, Weiwei Lin

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

ABSTRACT: Epoxy–clay nanocomposites were synthesized using two organoclays cured with different chemicals at different temperatures. Interlayer distance of the clay layers and curing process were investigated by X-ray diffraction and infrared spectra. The clay treated with facilitated curing agent, 2,4,6-tris[(dimethylamino)methyl]phenol, can exfoliate at all curing conditions, but for the other clay treated with low-speed curing agent, p,p'-diaminodiphenylmethane, exfoliation of the clay layers does not occur. It was found that the relative curing speed between the interlayer and extralayer was the most important factor determining clay exfoliation. Exfoliated epoxy–clay nanocomposites can be prepared if the curing speed of the interlayer is higher than that of the extralayer, irrespective of the curing agent and temperature used. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 511–517, 2003

Key words: nanocomposites; exfoliation; curing agent; clay; synthesis

INTRODUCTION

Polymer layered silicate nanocomposites have been studied for nearly 50 years,[1] although the concept was first introduced by researchers from Toyota,[2] who discovered the possibility of building a nanocomposite from polyamide 6 and an organophilic clay. These new materials showed dramatic improvement in barrier properties, fire resistance, and mechanical properties. Many different approaches have been investigated to synthesize these nanocomposite materials,[3] such as exfoliate adsorption, melt intercalation, and *in situ* polymerization. Numerous investigators have tried to prepare nanocomposites based on epoxies,[4–6] polystyrene,[7] polyamide,[8] polypropylene,[9] poly(ethylene terephthalate),[10] and polyurethane.[11] However, full separation of the clay layers in the polymer matrix is not easy. A critical problem in the synthesis of nanocomposites is to disperse the inorganic clay in an organic medium on a molecular scale.

Montmorillonites (MMTs) are layered silicates. Epoxy–MMT nanocomposites produced by melt intercalation and *in situ* curing have been the focus of continued attention during these years. The practical problem in the synthesis of these nanocomposites is the exfoliation of clays. Usuki[12] referenced in the patent that exfoliation of clay can be accomplished by using amine curing agents, but a swollen solvent of DMF must be used to make the epoxy resins interca-

late into clay layers. Messersmith and Giannelis[13] used anhydride species curing agents to prepare exfoliated nanocomposites, whereas use of amine curing agents allowed them to prepare only intercalated composites. Pinnavania and colleagues[14,15] used amine curing agents and successfully synthesized a series of clay exfoliated nanocomposites, but they emphasized that whether exfoliation can take place depends on the curing temperature. Only at an appropriate temperature—when the curing speed of interlayer and extralayer is almost the same—can exfoliation take place. Kornmann et al.[17] conducted experiments showing that the structure of epoxy–clay composites depends on the activity of the curing agents. All these studies focused on the influence of curing agents, curing temperature, and other curing conditions on clay exfoliation. Even controversial conclusions were proposed by different authors. The purpose of this study was to explore the key factor determining clay exfoliation by investigation of the curing process of MMT/clay composites with different curing agents and at different temperatures.

EXPERIMENTAL

Materials

The clays used in this study were industrially purified montmorillonites (MMTs) provided by Huate Company (Zhejiang, China). The epoxy resin was the diglycidylether of bisphenol A (EPON 828) provided by Wuxi Chemicals (Jiangsu, China). 2,4,6-Tris[(dimethylamino)methyl]phenol (DMP, **1**), diethyltriamine (DETA, **2**), and p,p'-diaminodiphenylmethane (DDM,

5) were used as received. Two modified amino curing agents, copolymer of DETA with acrylonitrile (Amine 1, **3**) and copolymer of DETA with thiourea (Amine 2, **4**), were prepared according to published procedures.[16]

Preparation of organoclay

The crude clay was purified and dispersed into the solution of NaCl to obtain a homoionic clay.[17] Purified clay (10 g) was then dispersed into 1000 mL of distilled water at 80°C. $[(CH_3)_2NCH_2]_2C_6H_2OHCH_2N^+(CH_3)_2HCl^-$ was prepared by mixing 5.3 g DMP with 1 g HCl solution (10N) in 200 mL distilled water. It was poured into the hot MMT/water solution and stirred vigorously for 1 h at 80°C. An orange precipitate formed and was isolated by filtration and washed several times with a hot water/EtOH (50/50) mixture until no chloride was detected in the filtrate by one drop of 0.1N AgNO$_3$ solution, The exchanged montmorillonite (Mont–DMP) was then dried several days at 75°C, ground with a mortar and a pestle, and the <53-μm fraction was collected. A similar procedure was followed to prepare DDM exchanged montmorillonite (Mont–DDM).

Preparation of epoxy–clay nanocomposites

Epoxy resin (50 g) was mixed with 2 g of organophilic clay at 75°C and stirred for 6 h. A stoichiometric amount of five different curing agents was added separately to the epoxy–clay composites. Based on the chemical properties of different curing agents,[16] composites were cured at different suitable temperatures for certain periods of time until all the samples were fully cured. In principle, composites were cured at low temperature for a relatively long time, but cured at high temperature for a short time.

X-ray diffraction (xrd)

Powder XRD analyses were performed using a Siemens D5000 diffractometer (Siemens, South Iselin, NJ) with Cu radiation (40 kV, 40 mA). The scanning speed and step size were 0.08°/min and 0.02°, respectively. The crude clay and organophilic clay were mounted on a sample holder with a large cavity and a smooth surface was obtained by pressing the powders with a glass plate. The organoclay swollen in the epoxy resin was analyzed by spreading the mixture on a slide. The fully cured samples cut from the mold were directly analyzed by XRD.

Transmission electron microscopy (TEM)

The TEM specimen was cut from an exfoliated block. The TEM was recorded on a Hitachi-800 (Hitachi, Ibaraki, Japan), at an acceleration speed and low electron value of 100 kV and <10 mA, respectively.

IR measurement

IR spectra of clay/epoxy composites were recorded on a Bruker Vector 22 (Bruker Instruments, Billerica, MA). The curing degree of epoxy (CD%) was calculated according to the following equation:

$$CD\% = \left(1 - \frac{A'_{913}/A'_{1610}}{A_{913}/A_{1610}}\right) \times 100$$

where A_{913} and A_{1610} are the absorbance of epoxy resin at 913 and 1610 cm^{-1}, respectively; and A'_{913} and A'_{1610} are the absorbance of epoxy/clay composites at 913 and 1610 cm^{-1}, respectively.

RESULTS AND DISCUSSION

Synthesis of organoclays

Modification of the hydrophilic Na$^+$–MMT surface layers to become hydrophobic is the initial stage of dispersing MMT uniformly into the epoxy resin matrix. The Na$^+$ cations of the MMT can be easily exchanged by organic cations, thus rendering the clay organophilic. It then becomes easy for epoxy resin to diffuse between the clay layers and eventually intercalate into the layers. Many studies have cited that epoxy resin intercalated into the clays is easy when the interlamellar spacing is large enough. In this study, two types of organophilic clays were prepared. One organoclay, designated Mont–DMP, was treated with the organophilic agents of DMP, the curing agents for epoxy resin. The other, designated Mont–DDM, was treated with the organophilic agents of DDM, whose curing speed is extremely low. Figure 1 presents the XRD curves of the crude clay and the two organoclays. The interlamellar spacing of the clay, corresponding to the (001) plane peak, increases from 12.5 Å for the purified Na$^+$–MMT to 14.5 Å for the Mont–DMP and 16.5 Å for the Mont–DDM. This shows that the organophilic ions have been intercalated between the layers during the cation-exchanged process, adopting a lateral bilayer structure.

Epoxy resin intercalated into organoclays

The clay treated with organophilic agents becomes hydrophobic. The interaction between organophilic clay and epoxy resin induces migration of the polymer molecular into the organoclay layers, which makes the interlamellar spacing increase further (Fig. 2). Almost all studies show that epoxy resin intercalating the organoclay is easy and is stable enough not to separate out from the organoclay layers after an extended time.
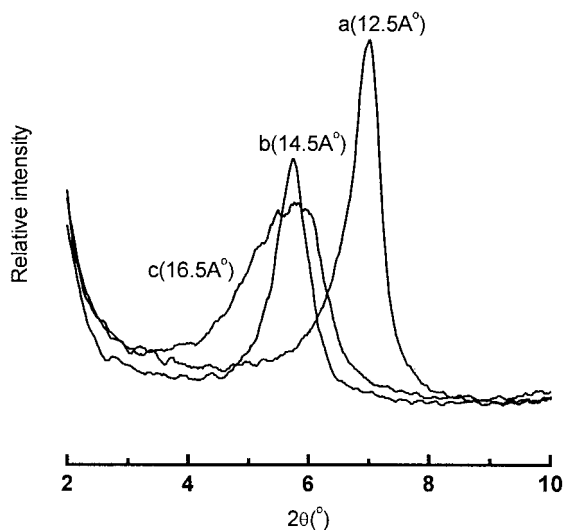
Figure 1 XRD patterns of (a) Na$^+$–Mont, (b) Mont–DMP, (c) Mont–DDM.

Influence of the organophilic agents of the organoclay in cured epoxy resin

Stable intercalation of epoxy–clay is easily obtained, but to form nanocomposites, exfoliation during the curing process is the most important factor. In this study, the intercalated epoxy–clays were cured by five different curing agents at different temperatures. The five curing agents selected are 2,4,6-tris[(dimethylamino)methyl]phenol (DMP, **1**), diethyltriamine (DETA, **2**), copolymer of DETA with acrylonitrile (Amine 1, **3**), copolymer of DETA with thiourea (Amine 2, **4**), and p,p'-diaminodiphenylmethane (DDM, **5**). Their curing speeds are in the order of $\mathbf{1 > 2 > 3 > 4 > 5}$.[16]

Figure 3 shows the XRD patterns of two types of organophilic clay/epoxy intercalation cured with five different agents at 35°C for 60 h. For Mont–DMP clay,
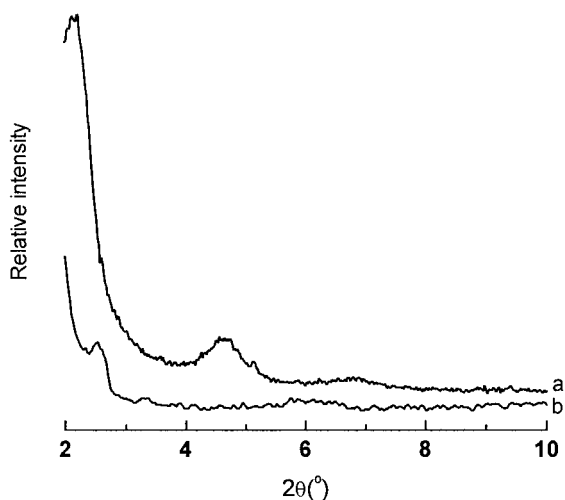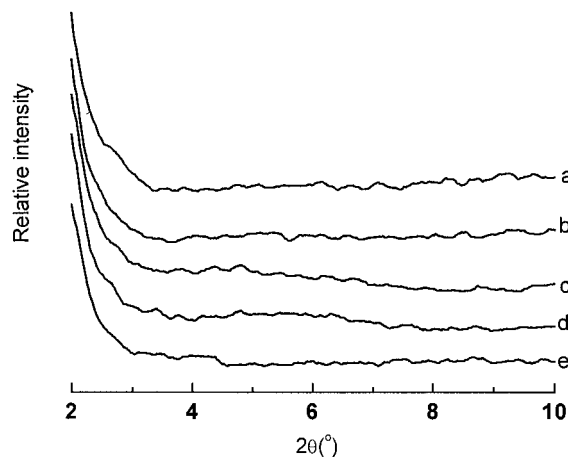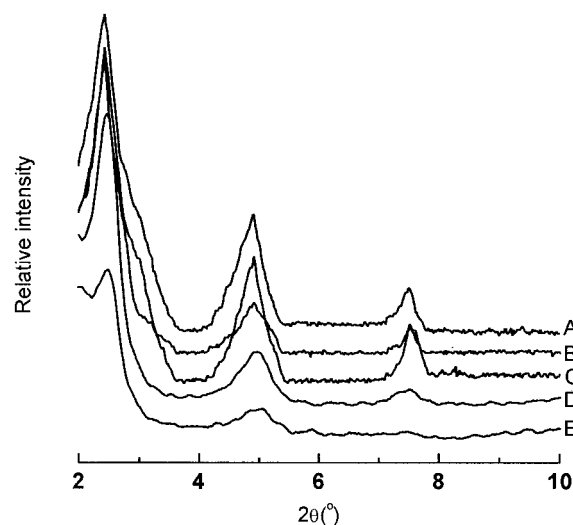

Figure 3 XRD patterns of epoxy–organoclay composites cured with different curing agents at 35°C for 60 h. Upper panel (Mont–DDM): (A) DETA; (B) modified amine 1; (C) modified amine 2; (D) DDM; (E) DMP. Lower panel (Mont–DMP): (a) DMP; (b) DDM; (c) DETA; (d) modified amine 1; (e) modified amine 2.

the interlamellar spacing of the clay, corresponding to the (001) plane peak, disappeared completely after curing with different curing agents, which shows the clays were completely exfoliated, whereas for Mont–DDM clays, the (001) plane peak remained constant after curing by different agents.

Higher curing temperatures were also investigated. Figures 4, 5, and 6 present the XRD curves of two kinds of intercalated organoclay/epoxy cured with the same five curing agents at 70, 120, and 150°C, respectively. For Mont–DMP clay, exfoliated clay/epoxy can be prepared by curing with different curing agents at three temperatures, whereas such nanocom-
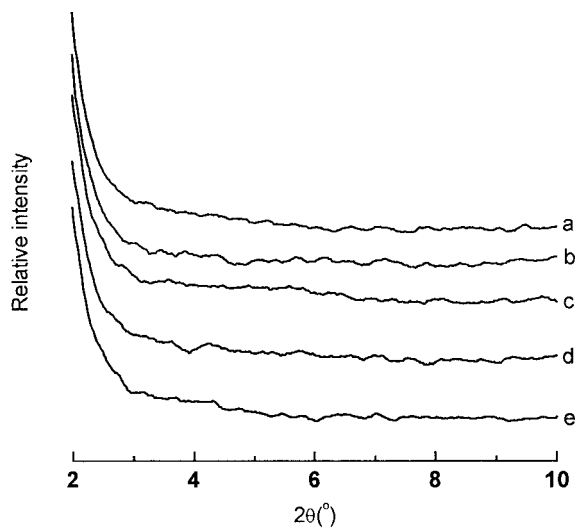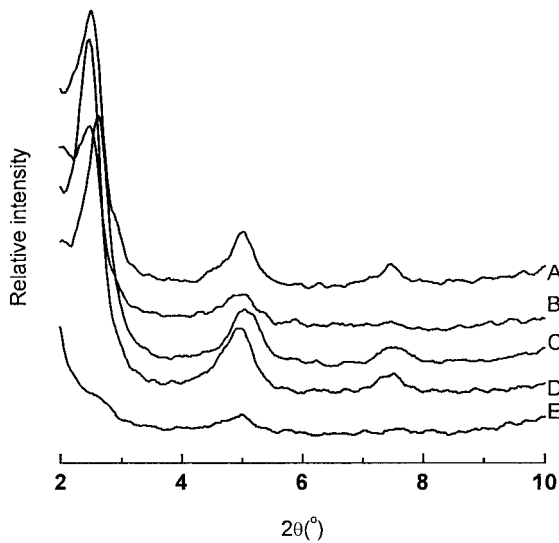

Figure 2 XRD patterns of organoclay–epoxy complex: (a) Mont–DDM/epoxy; (b) Mont–DMP/epoxy.

and in the epoxy matrix at the same time. The exfoliation process requires that additional epoxy migrates among the clay layers. When the curing speed of the interlayer is higher than that of the extralayer, additional epoxy can migrate within clay layers, given that the total viscosity is not very high and the increment of spacing among clay sheets will not meet strong resistance derived from solidification of the matrix. Therefore the exfoliation process can be finished before complete curing of the matrix. DMP is a facilitated curing agent for epoxy resin. When it is exchanged to the clays, it will remain in the interlayer of clay. When the curing agent was added to the clay/epoxy, the interlayer epoxy resin curing speed will be accelerated and therefore becomes faster than that of
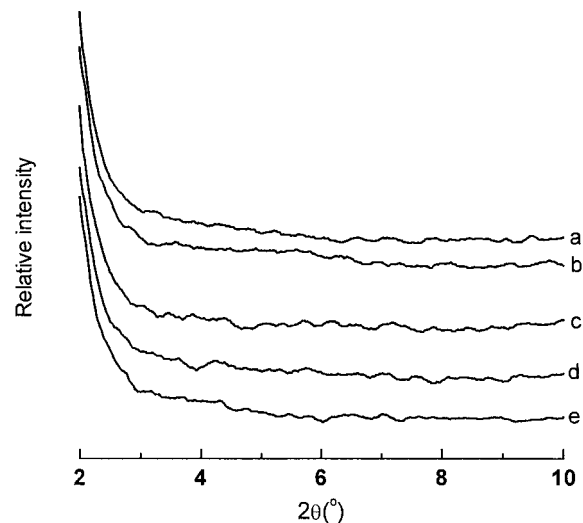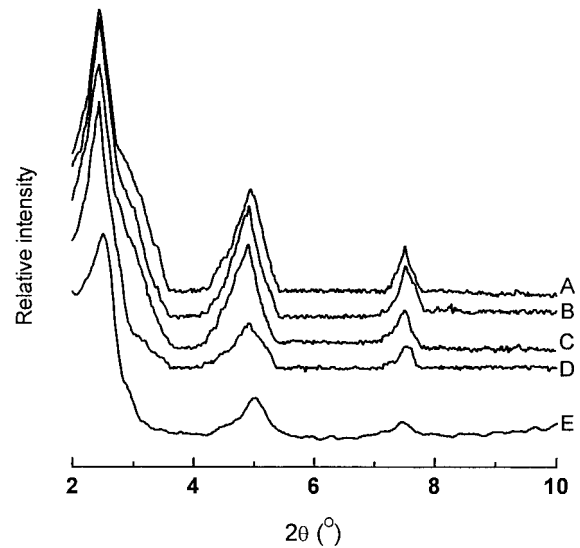

Figure 4 XRD patterns of epoxy–organoclay composites cured with different curing agents at 70°C for 24 h. (Designations are the same as in Fig. 3.)

posites cannot be generated at three different temperatures for Mont–DDM clays.

To examine the dispersion of the clay layers in the exfoliated composites, TEM studies were carried out. Figure 7 is a typical TEM micrograph for the exfoliated composites. From the TEM, the distance between the silicate layer ranged from 9 to 20 nm, which are much larger than that of the original silicate. This shows that clay has been exfoliated and the clay layers have been fully enclosed by the epoxy matrix. The flexibility of the layer is attributed to the extremely small thickness and very large aspect ratio of the clay sheets, as shown in TEM images by Krishmamoorti et al.[18]

Concerning the curing course of intercalated epoxy resin, the curing process takes place among clay layers

Figure 5 XRD patterns of epoxy–organoclay composites cured with different curing agents at 120°C for 8 h. (Designations are the same as in Fig. 3.)
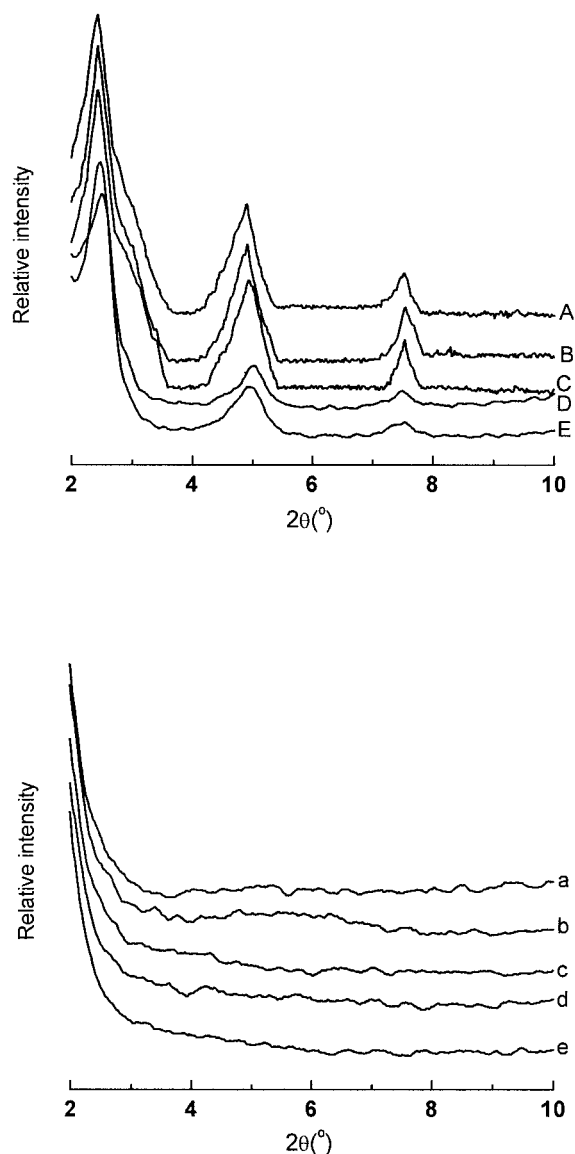
curing agents were dispersed in the matrix of epoxy, or in other words, another curing agent was distributed in the extralayer. The curing speed of DDM is minimal compared to that of the other four curing agents selected in this investigation. Therefore the curing speed of the interlayer of Mont–DDM must always be slower than that of the extralayer. No exfoliated nanocomposites were prepared by Mont–DDM precursor with different extra curing agents and temperatures according to XRD measurement. Furthermore, when Mont–DDM is cured at different temperatures, the XRD curves indicate a slight difference. When Mont–DDM was cured at low temperature (e.g., 35 and 70°C), exfoliation took place to a certain degree when DMP was used as an extra curing agent. This result is most probably caused by the different relative curing speeds of interlayer and extralayer. At high temperature the curing speed of the extralayer must be much higher than that of the interlayer, so the exfoliation will occur to the least degree. At low-temperature curing, the difference of curing speed between interlayer and extralayer is minimized; thus exfoliation might occur to some degree for some curing agents, a result that is also consistent with the proposed mechanism of exfoliation.

IR spectroscopy is one useful method to study the curing speed of epoxy. Two typical examples were selected for such an investigation. Figure 8 presents the spectra of MMT/epoxy prepared by curing Mont–DDM with DETA at 35 and 150°C, respectively. There were two kinds of curing agents within and outside the clay. Thus it is possible to deduce the different curing degrees from IR spectra of composites. For both
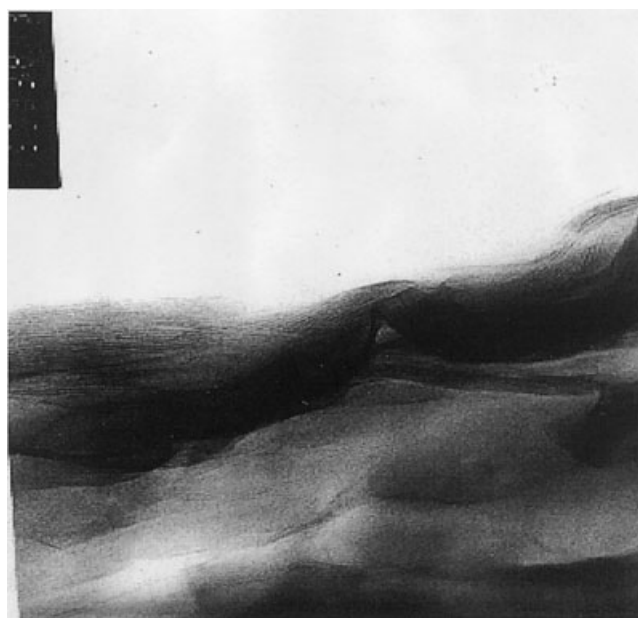

Figure 6 XRD patterns of epoxy–organoclay composites cured with different curing agents at 150°C for 2 h. (Designations are the same as in Fig. 3.)

the extralayer. Our results demonstrate that exfoliation occurs for all Mont–DMP precursors cured with different chemicals at different temperatures.

When the curing speed of the interlayers of clay is less than that of the extralayer, two resultant effects will halt the exfoliation process. First is the mass transport. High viscosity resulting from the curing process of matrix will prevent epoxy resin from moving toward the interlayers. Second is the mechanical force generated during curing. When the epoxy matrix is cured to a certain degree, the mechanical strength will halt the expansion of the intercalated epoxy. Both effects will stop the undergoing exfoliation process. The Mont–DDM system, which contains two different curing agents, was designed for such a purpose. DDM is located on the interlayer of clay, and five different

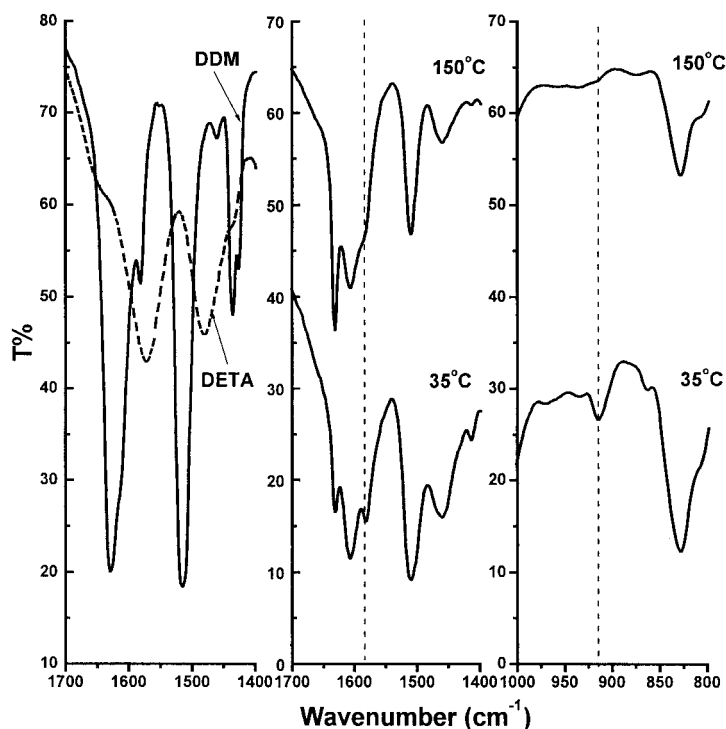**Figure 7** TEM micrograph of exfoliated clay/epoxy composites (×150,000).

Figure 8 IR spectra of Mont–DDM cured with DETA at 35°C and 150°C. Left: pure DDM and DETA; middle and right: epoxy/MMT.

curing temperatures, the absorption band at 1482 cm^{-1} corresponding to NH$_2$ of DETA disappeared, which indicates the reaction degree of DETA is very high; whereas the intensity of absorption bands at 1582 and 913 cm^{-1}, corresponding to the amino group of DDM and epoxy bond, respectively, were different
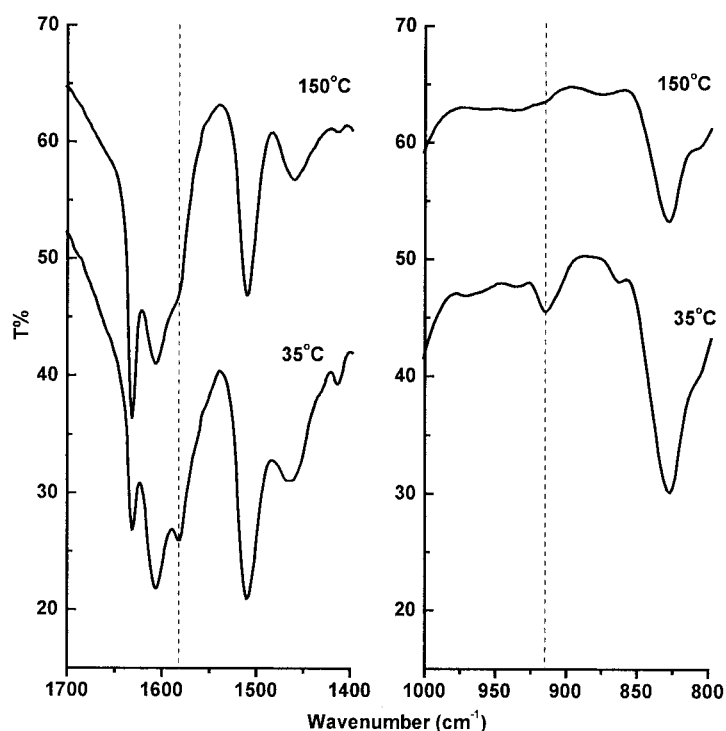

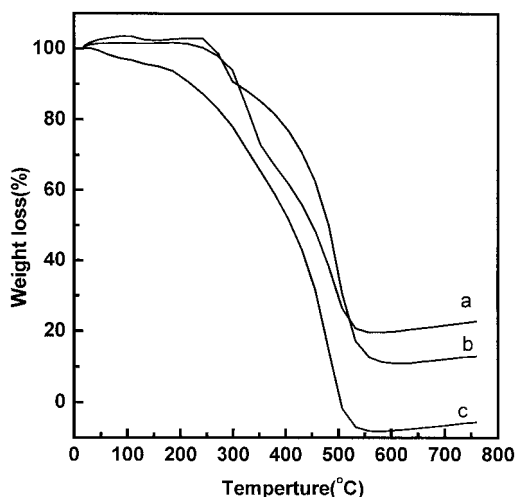**Figure 9** IR spectra of Mont–DMP cured with DETA at 35 and 150°C.

Figure 10 TGA thermograms of (a) pristine epoxy, (b) exfoliated clay/epoxy, and (c) intercalated clay/epoxy.

when Mont–DDM was cured at the same two temperatures. The reaction degree of both NH_2 and epoxy of Mont–DDM cured at 150°C was higher than that of Mont–DDM cured at 35°C. The curing degrees were 52 and 76% when Mont–DDM was cured with DETA at 35 and 150°C, respectively. Such a result indicates that exfoliation hardly occurs when the curing speed of the extralayer of clay is higher than that of the interlayer; even the curing degree of epoxy can reach a significantly high level. It could not discriminate the curing speed of extralayer and interlayer of the Mont–DMP system, given that only a single curing agent was employed. However, IR spectra of clay/epoxy prepared by Mont–DMP cured with DETA at 35 and 150°C can offer additional evidence from an alternative viewpoint as well. As shown in Figure 9, when Mont–DMP was cured at 35°C, there were still free epoxy and amino groups in the composites, such that even an exfoliated nanocomposite was produced.

Our results proved that the curing speeds of interlayer and extralayer are key factors to determine whether exfoliation will occur. The other factors such as organophilic agent of clay, the kind of curing agents, curing temperature, and procedure have less to do with such exfoliation.

Thermal stability of epoxy resin/clay

Figure 10 shows TGA thermograms of pristine epoxy, exfoliated clay/epoxy, and intercalated clay/epoxy.

The exfoliated composites have only slightly increased thermal stability and the intercalated composites have slightly decreased thermal stability compared to that of the neat epoxy resin. These differences are attributed to dispersion of the clay layers. Under exfoliation, the silicate layers disperse well in the epoxy resin and act as barriers when heated. When not exfoliated, however, the clay layers keep their original structure, and the extra- and interlayer epoxies have different characteristics, thus probably accelerating the decomposition.

CONCLUSIONS

The curing speed of inter- and extralayer intercalated epoxy/clay is a key factor for synthesis of exfoliated nanocomposites. The exfoliation occurs when the curing speed of the interlayer is faster than that of the extralayer. The other factors such as organophilic agent of clay, the kind of curing agents, curing temperature, and procedure have less relationship with such exfoliation.

References

1. Carter, L.W.; Hendricks, J. G.; Bolley, D. S. U.S. Pat. 2,531,396, 1950.
2. Okada, O.; Kawasumi, M.; Usuki, A.; Kurauchi, T.; Kamigaito, O.Mater Res Soc Symp Proc 1990, 171, 45.
3. Wang, Y.; Suna, A.; Mahler, W.; Kawoski, R. J Chem Phys 1987, 87, 7315.
4. Pinnavaia, T. J.; Lan, T.; Wang, Z.; Shi, H.; Kavaratna, P. D. ACS Symp Ser 1996, 622, 250.
5. Messersmith, P. B.; Giannelis, E. P. Chem Mater 1994, 6, 1719.
6. Kelly, P.; Akelah, A.; Qutubuddin, S.; Moet, A. J Mater Sci 1994, 29, 2274.
7. Vaia, R. A.; Ishii, H.; Giannelis, E. P. Chem Mater 1992, 5, 1694.
8. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 2493.
9. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A.J Appl Polym Sci 1997, 63, 137.
10. Ke, Y.; Long, C.; Qi, Z. J Appl Polym Sci 1999, 71, 1139.
11. Wang, Z.; Pinnavaia, T. J. Chem Mater 1998, 10, 3769.
12. Usuki, A. U.S. Pat. 4,889,885, 1989.
13. Messersmith, P. B.; Giannelis, E. P. Chem Mater 1994, 6, 1719.
14. Lan, T.; Pinnavia, T. J. Chem Mater 1994, 6, 2216.
15. Lan, T.; Kaviratna, P. D.; Pinnavia, T. J. Chem Mater 1995, 7, 2144.
16. Wang, D. Z. Epoxy Resin Production and Application; Chemical Engineering Press: Beijing, China, 1985.
17. Kornmann, X.; Lindberg, H.; Berglund, L. A. Polymer 2001, 42, 1303.
18. Krishmamoorti, R.; Vaia, R. A.; Giannelis, E. P. Chem Mater 1996, 8, 1728.