

# Preparation and Properties of a Carboxyl-Terminated Butadiene Acrylonitrile Toughened Epoxy/Montmorillonite Nanocomposite

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**ABSTRACT:** The influence of the montmorillonite type and concentration on the mechanical properties and morphology of a carboxyl-terminated butadiene acrylonitrile toughened epoxy/montmorillonite nanocomposite has been studied. Modified montmorillonite can be well dispersed in a carboxyl-terminated butadiene acrylonitrile toughened epoxy/montmorillonite nanocomposite. Jeffamine, a curing agent, contributes to the intercalation of

sodium montmorillonite, allowing the loss of the ordered layered structure in the nanocomposite. The preparation method of the nanocomposite has a slight effect on the mechanical properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 685–692, 2009

**Key words:** mechanical properties; morphology; nanocomposites; organoclay; rubber

## INTRODUCTION

Polymer layered silicates such as montmorillonite (MMT) nanocomposites are used for various products because of their improved mechanical and barrier properties, chemical resistance, and thermal stability even with a small amount of MMT.<sup>1–10</sup> MMT has a high aspect ratio typically ranging from 100 to 1500 and unique intercalation/exfoliation characteristics.<sup>11,12</sup> To obtain a high degree of intercalation/exfoliation of the layered silicate in the polymer matrix, it is essential that the cations present in the layered silicate be exchanged with organic cations.<sup>13–19</sup> The desire to prepare epoxy nanocomposites exists because a reinforcing effect of less than 10 times can be achieved with an MMT loading of only 7.5 vol %.<sup>20</sup> Wang and Pinnavia<sup>21</sup> prepared an epoxy nanocomposite containing organomodified clay and suggested that the curing rate and the type of organomodifier should be severely controlled to acquire an exfoliated nanocomposite because acidic onium ions in MMT galleries promote intragallery polymerization rather than extragallery polymerization. In several studies, researchers have attempted to use polyoxypropylene (Jeffamine), the usual curing agent for epoxy resins, as an organic modifier.<sup>18,21</sup> Jang et al.<sup>19</sup> showed that exfoliation is achieved with a polymer matrix with a high solubil-

ity parameter because of the strong electrostatic attractions between the intergallery cations and polymer chain. This result also demonstrates that *in situ* polymerization is a more efficient process than conventional melt blending for the desired morphology.

In a series of investigations, we examined how a low loading of organically modified MMT yields a carboxyl-terminated butadiene acrylonitrile (CTBN) toughened epoxy resin with improved impact strength and toughness. We also confirmed that this result is consistent with observations of a CTBN-toughened epoxy resin including sodium montmorillonite (Na-MMT).<sup>22</sup>

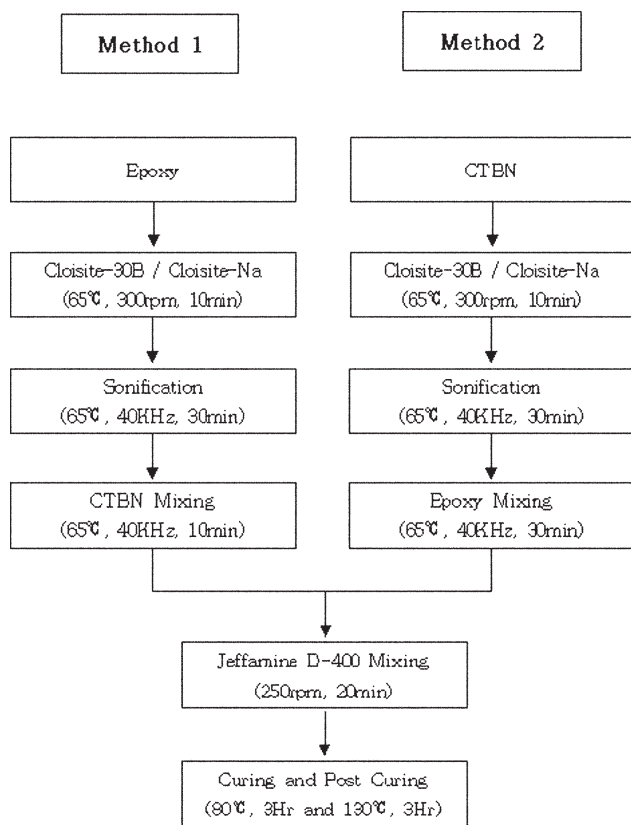
In this study, CTBN-toughened epoxy/MMT nanocomposites were prepared to explore the influence of chemical properties of CTBN on the mechanical properties of the polymer and the possibility of exfoliated nanocomposites with Na-MMT in *in situ* polymerization.

## EXPERIMENTAL

### Materials

A bisphenol A epoxy resin (YD-128) was purchased from Kukdo Chemical (Seoul, Korea). The toughening and curing agents were CTBN (Hycar 1300×8, B.F. Goodrich, Greenville, SC) and Jeffamine D-400 (Huntsman Co., USA). Organically modified MMT (Cloisite 30B) with an ion-exchange capacity of 90 mequiv/100 g and Na-MMT (Cloisite-Na) were obtained from Southern Clay Co. (Gonzales, TX).

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**Figure 1** Preparation of the CTBN-toughened epoxy/MMT nanocomposite.

### Preparation of the CTBN-toughened epoxy/MMT nanocomposites (Fig. 1)

#### Method 1

Two methods of nanocomposite preparation were investigated. Method 1 used an epoxy resin including MMT, whereas method 2 used MMT dispersed in CTBN rubber as possible.

In method 1, MMT was mixed with the epoxy resin at 65°C for 10 min with a mechanical stirrer. Before the mixing, the epoxy resin was heated to 120°C to ensure an effective viscosity. The mixture was then sonicated for 30 min at 65°C. CTBN (30 phr) was added, and the mixture was stirred again. The curing agent (53.5 g) was added with stirring. Finally, the mixture was degassed for 30 min at 50°C. The well-mixed system was poured into a Teflon-coated mold, and then the mixture was cured at 80°C for 3 h and postcured at 130°C for 3 h.

#### Method 2

CTBN (30 g) was initially heated at 65°C and mixed with MMT with a mechanical stirrer for 10 min. The mixture was then sonicated at 65°C for 30 min. The epoxy resin (100 g) was added, and this was followed by agitation at 65°C for 10 min. The curing

agent (53.5 g) was then added, and the mixture was stirred at 50°C for 20 min. The bubble was removed with a vacuum oven for 30 min.

### Characterization

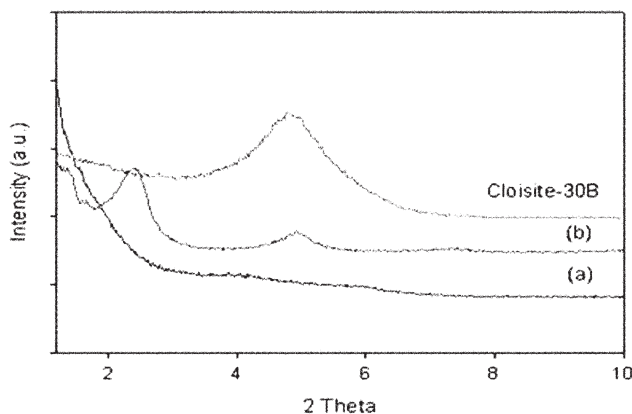
X-ray diffraction (XRD) measurements of the cured sample were performed with a X'Pert-APD diffractometer (Philips) equipped with Cu K $\alpha$  radiation ( $\lambda = 1.54$ ). The dispersion of CTBN and the type of fracture were examined with scanning electron microscopy (SEM; S-570, Hitachi, Japan). The structure of the nanocomposite was determined with transmission electron microscopy (TEM; EM 109, Karl Zeiss, Germany).

## RESULTS AND DISCUSSION

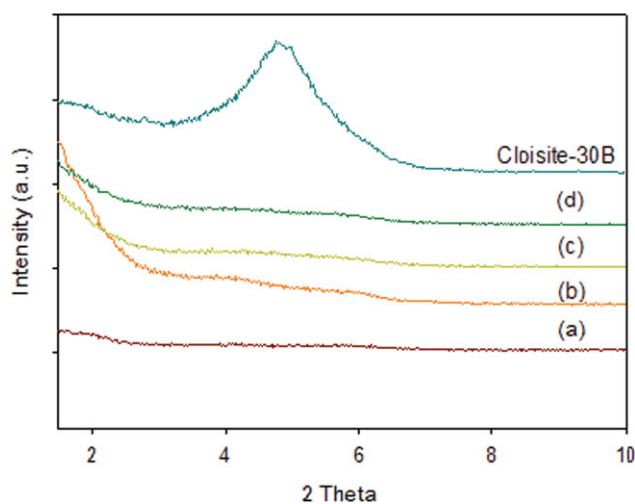
### Dispersion of MMT in the epoxy nanocomposites

The XRD patterns of the epoxy/Cloisite 30B mixture with a 5 phr MMT loading are shown in Figure 2. The  $d_{001}$  reflection has disappeared for the CTBN-containing sample, and this indicates a positive effect of CTBN on the MMT dispersion. It is assumed that the chemical interaction of CTBN with MMT is higher than that with the epoxy resin. Figure 3 shows the XRD patterns of the epoxy/Cloisite 30B mixture before curing with different MMT contents. When the content of MMT increases, a weak  $d_{001}$  reflection can be observed in the epoxy/MMT nanocomposite; however, no characteristic peak can be observed in the CTBN-toughened epoxy resin.

In the case of the CTBN-toughened epoxy/Na-MMT mixture, the same trend can be observed, as shown in Figure 4. A weak peak at  $2\theta = 6.2^\circ$  appears in the case of 10 and 15 phr loadings. XRD patterns of the CTBN-toughened epoxy/Na-MMT nanocomposites prepared by methods 1 and 2 are



**Figure 2** XRD patterns [ $d_{(001)}$  reflection] of epoxy/Cloisite 30B (5 phr) mixtures: (a) CTBN-toughened and (b) no CTBN.

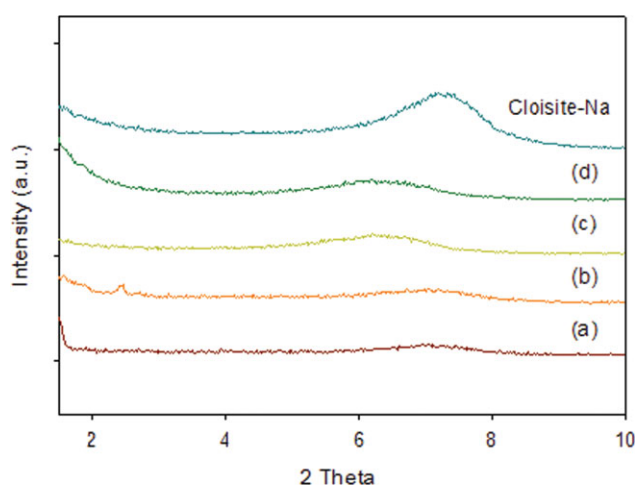


**Figure 3** XRD patterns [ $d_{(001)}$  reflection] of CTBN-toughened epoxy/Cloisite 30B mixtures with different MMT contents: (a) 3, (b) 5, (c) 10, and (d) 15 phr. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

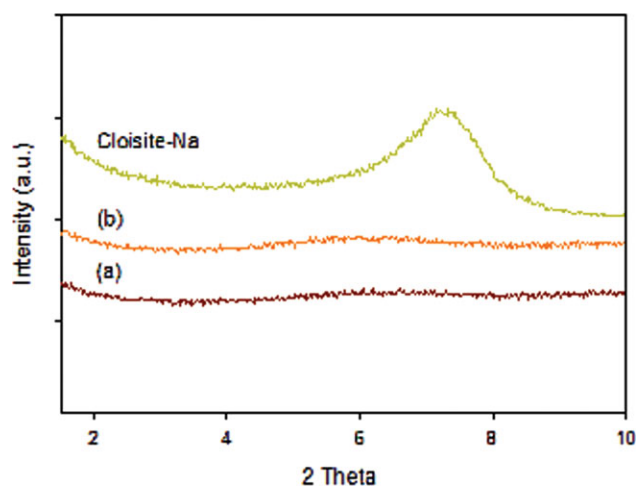
shown in Figures 5 and 6. No peaks can be observed at the 3 and 5 phr loadings, and this indicates an intercalated morphology for the nanocomposite prepared by method 1.

Figure 6 shows the XRD patterns of CTBN-toughened epoxy/Na-MMT nanocomposites prepared by methods 1 and 2. The absence of XRD peaks indicates that the interaction between MMT and CTBN leads to an increase in the  $d$ -spacing. Uhl et al.<sup>23</sup> reported that Na-MMT-modified films exhibited an enhancement of mechanical properties due to the intercalated structure.

To examine the presence of Jeffamine in MMT galleries, the CTBN-toughened epoxy/MMT nanocom-



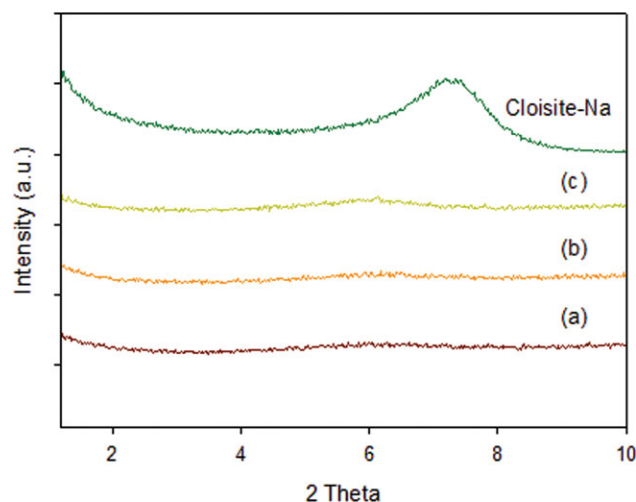
**Figure 4** XRD patterns [ $d_{(001)}$  reflection] of CTBN-toughened epoxy/Na-MMT mixtures with different MMT contents: (a) 3, (b) 5, (c) 10, and (d) 15 phr. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



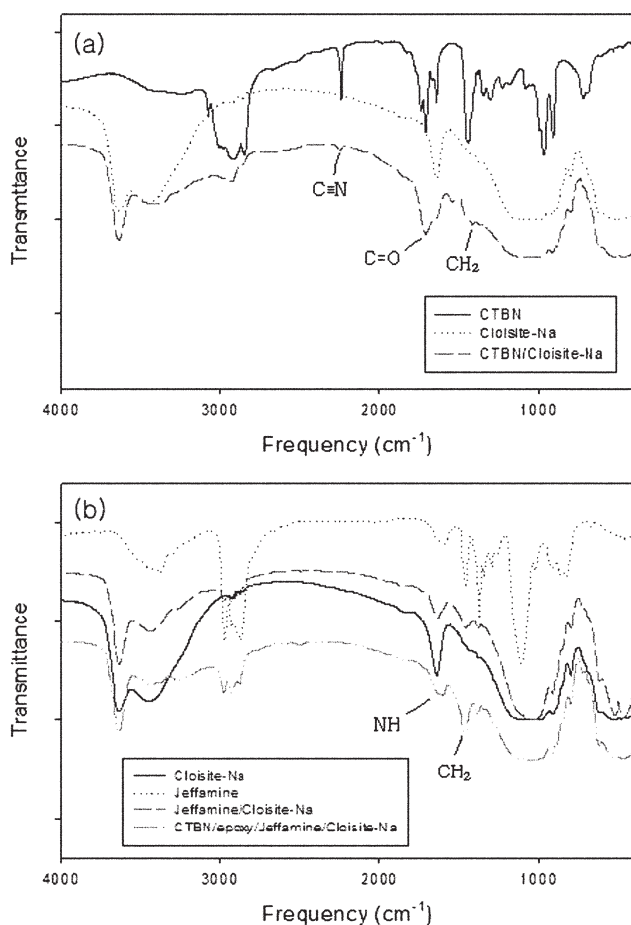
**Figure 5** XRD patterns [ $d_{(001)}$  reflection] of CTBN-toughened epoxy/Na-MMT nanocomposites prepared by method 1: (a) 3 and (b) 5 phr. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

posite was washed with toluene to eliminate Jeffamine and dried for 1 day. Plots of Fourier transform infrared (FTIR) data obtained for toluene after washing are shown in Figure 7. There is no characteristic peak except for toluene, and this indicates that the most of that remaining on the MMT surface was removed. In the FTIR data for the washed nanocomposite with Cloisite 30B, we monitored 1710 and 1470  $\text{cm}^{-1}$  for  $-\text{NH}$  and  $-\text{CH}_2$  to determine the intercalation of Jeffamine into MMT galleries.

The effect of Jeffamine on the expansion of MMT galleries can also be seen in XRD patterns of washed nanocomposites, as shown in Figure 8. This can be attributed to the interaction between Na-MMT and



**Figure 6** XRD patterns [ $d_{(001)}$  reflection] of CTBN-toughened epoxy/Na-MMT nanocomposites prepared by method 2: (a) 3, (b) 5, (c) 10, and (d) 15 phr. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

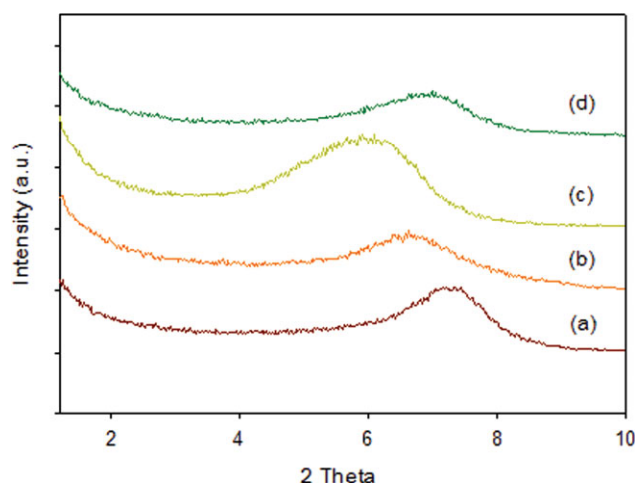


**Figure 7** (a) FTIR data for Na-MMT, CTBN, and CTBN-toughened epoxy/Na-MMT nanocomposites and (b) FTIR data for Na-MMT, Jeffamine, Jeffamine/Na-MMT, and CTBN-toughened epoxy/Na-MMT nanocomposites.

Jeffamine, which allows better intercalation into MMT galleries. The mixing temperature also influences the nanocomposite because of the increased molecular mobility of Jeffamine.

### Mechanical properties

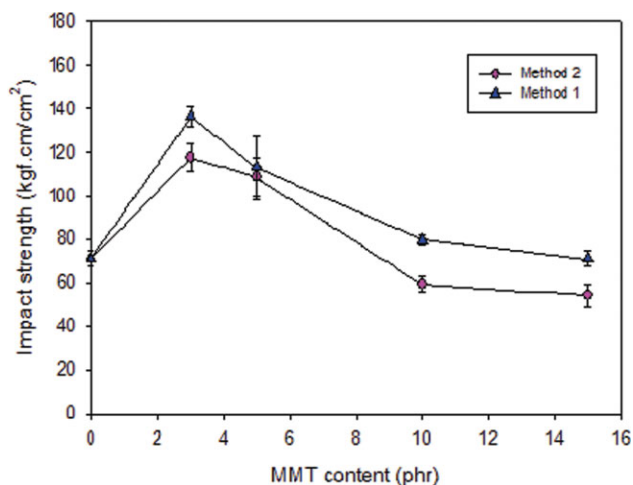
A comparison of the mechanical properties of the CTBN-toughened epoxy nanocomposites prepared by methods 1 and 2 is shown in Figure 9. The impact strength of the nanocomposite prepared by method 1 is higher than that of the nanocomposite prepared by method 2 because of the effect of MMT dispersed in the epoxy matrix on energy dissipation when external stress is applied. Figure 10 shows typical stress-strain curves for the CTBN-toughened epoxy nanocomposites according to the preparation method. For the nanocomposite prepared by method 1, there is no significant increase in the tensile properties, but there is a slight increase in the elongation with the MMT content. However, an increase of 1.2



**Figure 8** XRD patterns [ $d_{(001)}$  reflection] of CTBN-toughened epoxy nanocomposites with different compositions: (a) Na-MMT, (b) Jeffamine/Na-MMT, (c) Jeffamine/Na-MMT (mixed at 80°C), and (d) CTBN/Na-MMT. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

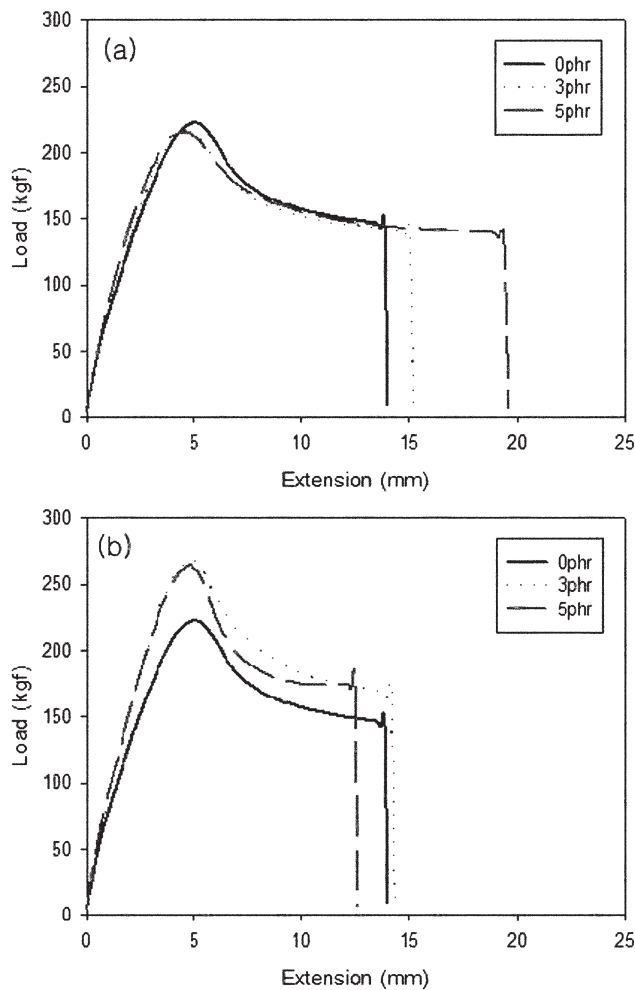
times with 5 phr MMT in the tensile strength can be seen for the nanocomposite prepared by method 2. This can be attributed to the fact that the dispersion of MMT in the rubber phase is better for the improvement of the tensile properties than that in the epoxy matrix. A recent study by Zilg et al.<sup>23</sup> concluded that the enhancement of mechanical properties is more obviously shown in a rubber-containing nanocomposite, and this is similar to our results.<sup>23</sup>

Figure 11 shows Young's modulus of a CTBN-toughened epoxy nanocomposite prepared by different methods. Similar to the tensile properties, Young's modulus of the nanocomposite prepared by



**Figure 9** Impact strength of CTBN-toughened epoxy/Cloisite 30B nanocomposites with various MMT contents. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

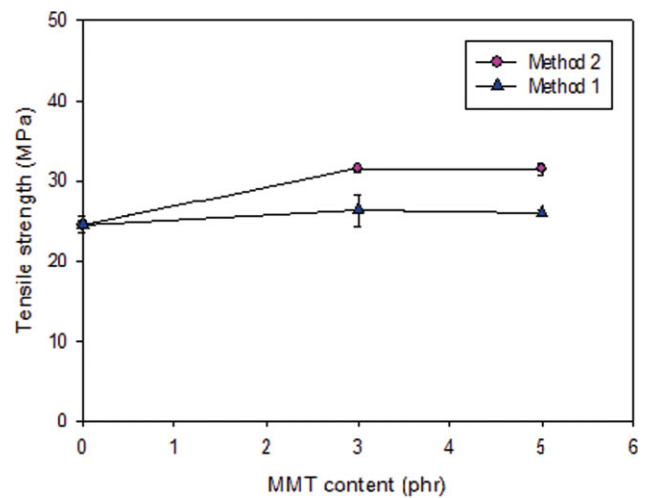




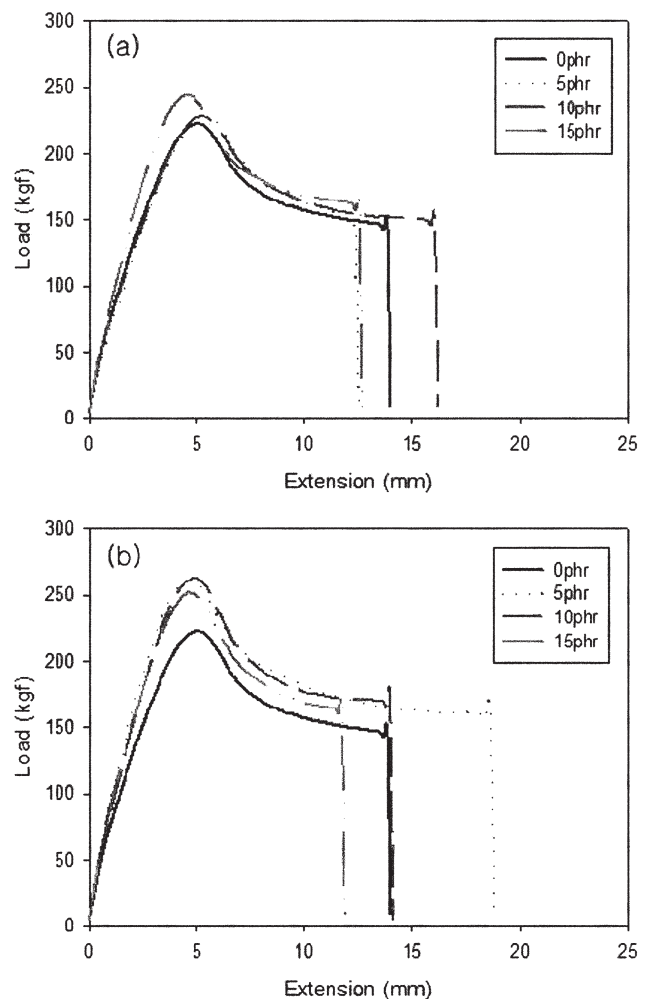
**Figure 10** Stress-strain curves of CTBN-toughened epoxy/Cloisite 30B nanocomposites with various MMT contents: (a) method 1 and (b) method 2.

method 2 is higher than that of the nanocomposite prepared by method 1. The presence of MMT in the rubber phase may compensate for the decrease in the modulus of the nanocomposite.

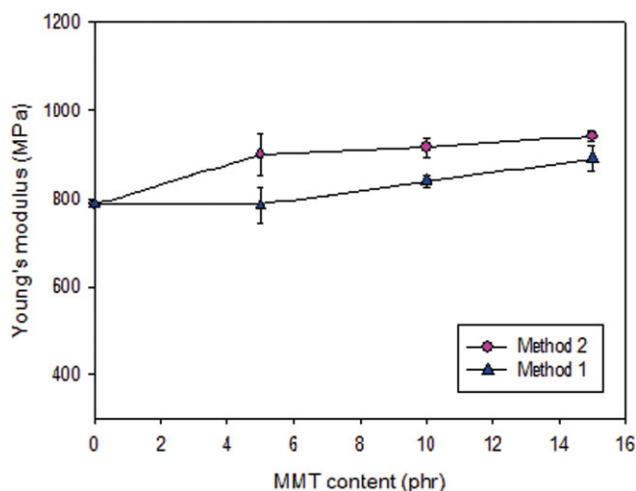
The stress-strain curves for the epoxy nanocomposites with unmodified MMT (Na-MMT) prepared by different methods is shown in Figure 12. The nanocomposite prepared by method 2 shows an enhancement of the tensile properties at a 5 phr MMT loading, in contrast to the nanocomposite prepared by method 1. Similar results can be also observed for Young's modulus of the nanocomposite, as shown in Figure 13. It can be suggested that unmodified MMT can also improve the mechanical properties. This may be due to the presence of a large amount of Jeffamine in the MMT galleries before the curing reaction, which may form intercalated nanocomposites. From this investigation, it is thought that a polar curing agent such as Jeffamine can result in an effective degree of intercalation of the nanocomposite.



**Figure 11** Young's modulus of CTBN-toughened epoxy/Cloisite 30B nanocomposites with various MMT contents. (a) method 1 and (b) method 2.



**Figure 12** Stress-strain curves of CTBN-toughened epoxy/Na-MMT nanocomposites with various MMT contents: (a) method 1 and (b) method 2.



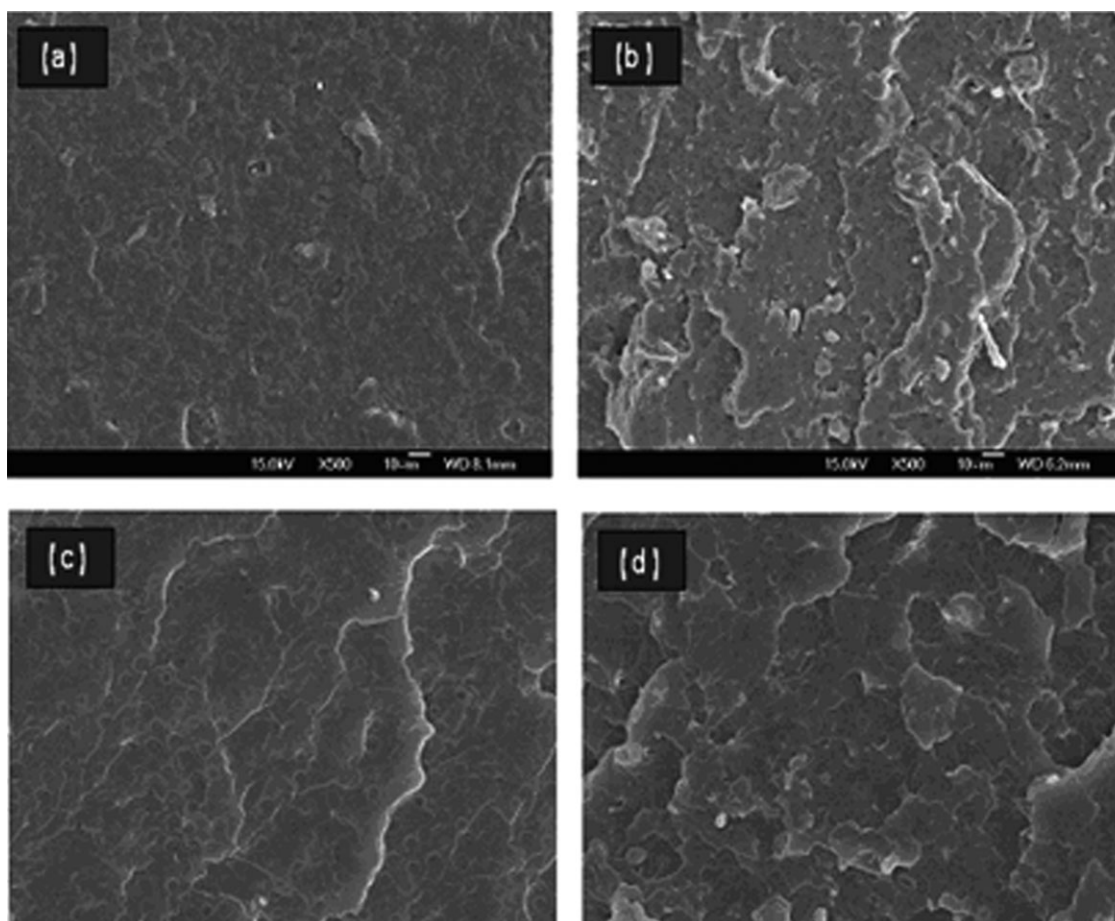
**Figure 13** Young's modulus of CTBN-toughened epoxy/Na-MMT nanocomposites with various MMT contents: (a) method 1 and (b) method 2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Morphology

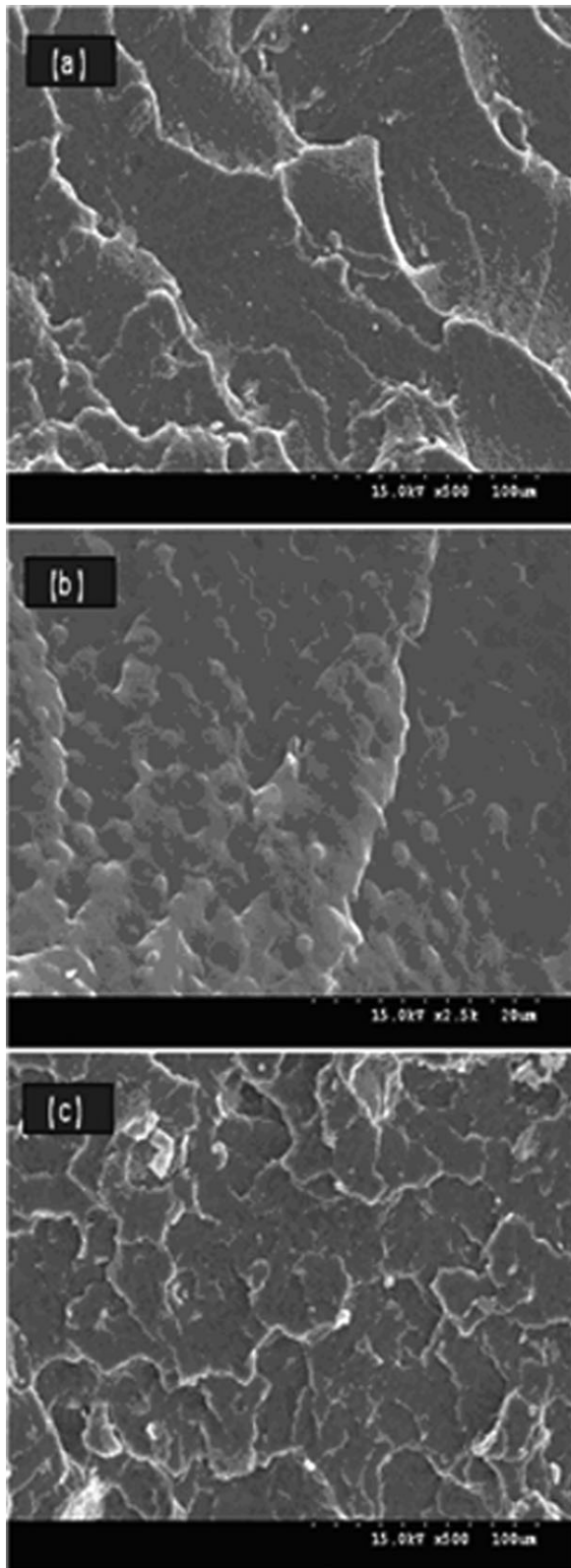
The fractured surface of the CTBN-toughened epoxy/Na-MMT nanocomposite was examined with

SEM, and the results are shown in Figures 14 and 15. A rough surface morphology can be observed in the nanocomposite with a high MMT loading. Moreover, the CTBN particles are well dispersed in the epoxy matrix, being less than 2  $\mu\text{m}$  in diameter. Moreover, the preparation of the nanocomposite has an effect on the fracture surface morphology because of the difference in the reinforcing effect of dispersed MMT in the matrix or CTBN phase.

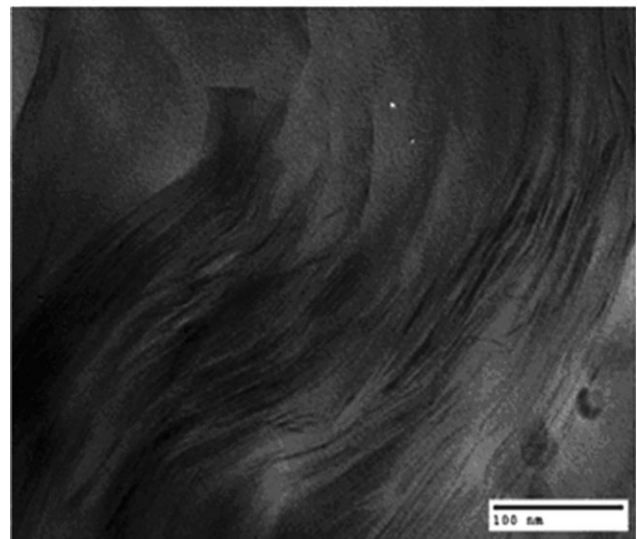
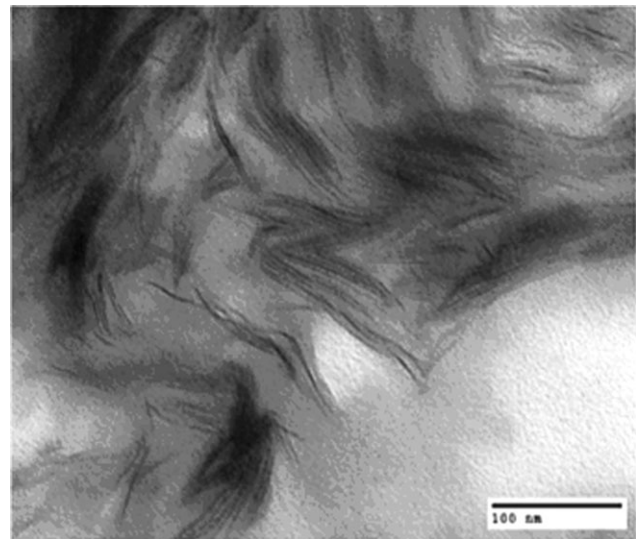
The loss of organization of MMT layers was confirmed by TEM, and the results are shown in Figure 16. Only a few stacked layers can be observed, indicating a well-dispersed morphology of the CTBN-toughened epoxy/Cloisite 30B nanocomposite, regardless of the preparation method. The less disordered morphology of the nanocomposite prepared by method 1 may be related to the elongation in fracture. Figure 17 shows a TEM image of the CTBN-toughened epoxy/Na-MMT nanocomposite. The absence of ordered layer stacks indicates the intercalated morphology of the nanocomposite. This result confirms that Jeffamine may have contributed to the formation of the intercalated nanocomposite.



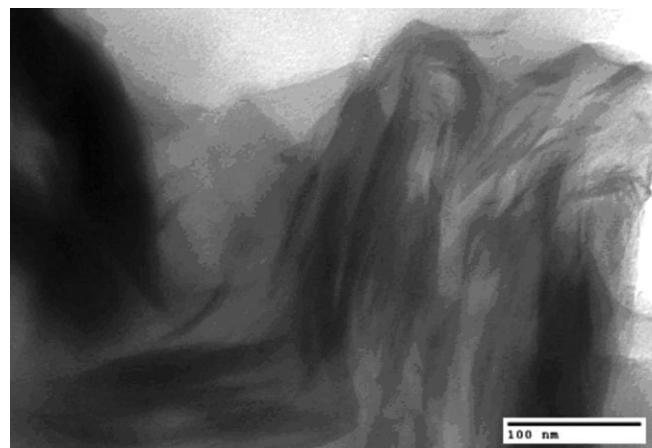
**Figure 14** SEM images of the fracture surface morphology of CTBN-toughened epoxy/Na-MMT nanocomposites with various MMT contents prepared by method 1. (a) 5 ( $\times 500$ ), (b) 15 ( $\times 500$ ), (c) 5 ( $\times 2000$ ), and (d) 15 phr ( $\times 2000$ ).



**Figure 15** SEM images of the fracture surface morphology of CTBN-toughened epoxy/Na-MMT nanocomposites with various MMT contents prepared by method 2: (a) 5 (×500), (b) 5 (×2500), and (c) 15 phr (×500).



**Figure 16** TEM images of CTBN-toughened epoxy/Cloisite 30B nanocomposites: (a) method 1 and (b) method 2.



**Figure 17** TEM image of a CTBN-toughened epoxy/Na-MMT nanocomposite prepared by method 2.

## CONCLUSION

A CTBN-toughened epoxy/MMT nanocomposite was prepared, and the effects of the type and amount of MMT on the properties of the nanocomposite were studied. From XRD patterns and IR data, we found that modified MMT can be well dispersed in CTBN rubber and epoxy resin. This can also be observed in the CTBN-toughened epoxy/MMT nanocomposite. Jeffamine, a curing agent, behaves like a compatibilizer with Na-MMT, increasing the degree of intercalation of Na-MMT in the nanocomposite. This highly intercalated Na-MMT in the nanocomposite can enhance the mechanical properties of the nanocomposite. The preparation method of the nanocomposite has a slight effect on the mechanical properties. Method 2, in which MMT is mainly dispersed in the CTBN rubber phase, is more effective in improving the tensile strength and modulus. The rough structure of the fractured surface of the nanocomposite was observed by SEM, and this indicated the reinforcing effect of dispersed MMT.

## References

1. Blumstein, A. *J Polym Sci* 1965, 3, 2665.
2. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
3. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 983.
4. Okada, A.; Kawasumi, M.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *Polym Prep* 1987, 28, 447.
5. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 1755.
7. Bourbogot, S.; Gilman, J. W.; Wilkie, C. A. *Polym Degrad Stab* 2004, 84, 483.
8. Okada, A.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Kamigaito, O. *Mater Res Soc Symp Proc* 1990, 171, 45.
9. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 983.
10. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1993, 49, 1259.
11. Giese, R. F. *Clay Miner* 1978, 26, 51.
12. Gilman, J. W.; Award, A. W.; Davis, R. D.; Shields, J.; Harris, R. H., Jr.; Davis, C.; Morgan, A. B.; Sutto, T. E.; Callahan, J.; Trulove, P. C.; Delong, H. C. *Chem Mater* 2002, 14, 3776.
13. Zhu, J.; Morgan, A. B.; Lamelas, F. J.; Wilkie, C. A. *Chem Mater* 2001, 13, 3774.
14. Wang, D.; Wilkie, C. A. *Polym Degrad Stab* 2003, 82, 307.
15. Zhang, J.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 301.
16. Vaia, R. A.; Teukosky, R. K.; Giannelis, E. P. *Chem Mater* 1994, 6, 1017.
17. Hackett, E.; Manias, E.; Giannelis, E. P. *J Chem Phys* 1998, 108, 7410.
18. Fornes, T. D.; Yoon, P. J.; Hunter, D. L.; Keskkula, H.; Paul, D. R. *Polymer* 2002, 43, 5915.
19. Jang, B. N.; Wang, D.; Wilkie, C. A. *Macromolecules* 2005, 38, 6533.
20. Lan, T.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 468.
21. Wang, M. S.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 2216.
22. Uhl, E. M.; Webster, D. C.; Davuluri, S. P.; Wong, S. H. *Eur Polym J* 2006, 42, 2596.
23. Zilg, C.; Mulhaupt, R.; Finter, J. *J Macromol Chem Phys* 1999, 200, 661.