

High Compatibility of the Poly(oxypropylene)amine-Intercalated Montmorillonite for Epoxy

Jiang-Jen LIN,[†] I-Jein CHENG, and Chien-Chia CHU

Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan

(Received October 21, 2002; Accepted March 17, 2003)

ABSTRACT: The poly(oxypropylene)amine (POP-amine) intercalated montmorillonite (MMT) was found to have a high organophilicity and compatibility with epoxy materials. The 2000 g mol⁻¹ molecular weight POP-amine modified MMT, analyzed to have 63 w% organics and 58.0 Å X-ray diffraction (XRD) *d*-spacing, was compounded with a curing agent (Jeffamine[®] D2000) and an epoxy resin (diglycidyl ether of bisphenol A). With 1–10 w% organoclay additions, the cured epoxies exhibited an exfoliated characteristic and significant improvements in thermal stability, solvent resistance and mechanical properties. The tensile strength (2.8 vs. 0.3 Mpa), flexural modulus (9.6 vs. 3.1 Mpa), and elongation (81.2 vs. 25.3%) were observed for the improved epoxy polymer.

KEY WORDS Nanocomposites / Organophilic / Poly(oxypropylene)amine / Clay / Epoxy /

In recent years, organic/inorganic nanocomposites have attracted a great deal of interests due to their proven industrial applications.^{1–3} Most potential composite systems are hybrids of organic polymers and inorganic mineral clays consisting of layered silicates.^{4–10} Mainly due to the high aspect ratio and plate-like morphologies¹¹ of the silicates, the nanocomposites have exhibited unique properties including mechanical strength,^{12–16} thermostability,^{17,18} chemical resistance,^{19,20} gas barrier properties,^{21,22} solvent resistance,²⁰ etc. However, the naturally abundant silicate clay is hydrophilic in nature and lacks the affinity for hydrophobic organic polymers. To improve its miscibility with polymers, the layered silicate must be modified to become organophilic by widening the interlayer space with surfactants. The modification generally involves swelling the layered silicate lattice and also exchanging the interlayer metal cations with organic surfactant salts.²³ The widened interlayer spacing can then be incorporated by polymers, in which the layered silicates are exfoliated and well-dispersed. In literature, this key intercalating process has been well studied by using alky ammonium salts or amino acids as the intercalating agents.^{5,12,23} The enlargement of the basal spacing to a maximum of 28 Å has been achieved. Previously, we found that further widening up to 92 Å was possible by employing the poly(oxypropylene)-backboned diamines.²⁴ The modified clays become highly organophilic and dispersible in hydrophobic toluene. The observation impels us to investigate their compatibility with the polymer matrix. In this paper, the epoxy system of diglycidyl ether of bisphenol A and a polyetheramine is chosen to study its compatibility with organic polymers. By simple mixing

in the curing process, the modified organoclay is introduced into the epoxy matrix and their improving mechanical, thermal, and solvent resistant properties are demonstrated.

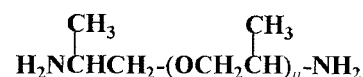
EXPERIMENTAL

Materials

Sodium montmorillonite, supplied by Kunimine Ind. Co. (Japan), is a Na⁺ form of layered clay with a cationic exchange capacity of 1.15 meq g⁻¹. Liquid diglycidyl ether of bisphenol-A (DGEBA, trade name BE-188) with an epoxide equivalent weight (EEW) of 188 was obtained from Nan-Ya Chemicals (Taiwan). Hydrophobic poly(oxypropylene)amine (POP-amine) of 400, 2000, and 4000 *M_w*, namely Jeffamine[®] D400, D2000, and D4000 respectively, were purchased from Huntsman Chemical Co. or Aldrich Chemical Co. Chemical structures of these compounds are illustrated in Figure 1.

Preparation of Organophilic Clay (MMT/D2000)

General procedures for the POP-amine intercalation



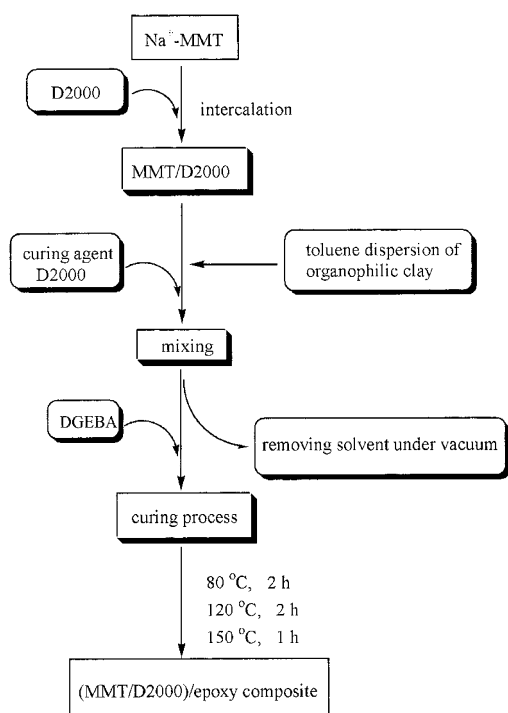
$$n = 5 - 6 \quad (\text{D400}, M_w = 400)$$

$$n = 33 \quad (\text{D2000}, M_w = 2000)$$

$$n = 68 \quad (\text{D4000}, M_w = 4000)$$

Figure 1. Chemical structures of POP-diamines (Jeffamine[®] amines).

[†]To whom correspondence should be addressed (Tel: +886-4-2285-2591, Fax: +886-4-2287-1787, E-mail: JLin@dragon.nchu.edu.tw).



Scheme 1. Process flow chart for clay/epoxy composite preparation.

have been reported previously²⁴ and an example is described below. Sodium montmorillonite (Na^+ -MMT, 1.15 meq g^{-1} , 10 g,) was dispersed in 1 L of deionized water at 80°C by vigorously mixing. The POP-amine of 2000 M_w (Jeffamine[®] D2000, 23.0 g, 11.5 meq) and aqueous hydrochloric acid (37 w%, 1.2 g) were dissolved in 30 mL ethanol to form quaternary ammonium salts at room temperature and then poured into a Na^+ -MMT slurry in water. The mixture was continuously stirred at $70\text{--}75^\circ\text{C}$ for 5 h. A white precipitate was filtered, collected, and washed thoroughly with 400 mL of hot water/ethanol several times. The product was characterized by using X-ray diffraction (XRD) and thermal gravimetric analyses (TGA).

General Procedures for Dispersing POP-Amine-Modified MMT with Epoxy (MMT/D2000/epoxy)

A process flow chart for preparing the MMT/D2000/epoxy composites is depicted in Scheme 1. Different weight fractions of MMT/D2000 were dispersed in Jeffamine[®] D2000 curing amine. A designated amount of DGEBA (BE-188), based on a 1:1 equivalent ratio of epoxide/N-H, was then added. The mixture was thoroughly stirred, degassed and poured into a 1/8 inch-thick aluminum mold. The curing conditions were programmed to be 80°C for 2 h, 120°C for 2 h, and 150°C for 1 h.

Measurements

The X-ray diffraction patterns of MMT/D2000/epo-

xy composites were recorded on an Shimadzu SD-D1 diffractometer (XRD) with Cu target ($k = 1.5405 \text{ \AA}$). The basal spacing ($n = 001$) was calculated according to Bragg's equation ($n\lambda = 2d \sin \theta$) through the observed peaks of $n = 002, 003$, etc. Differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) were performed on a Seiko SII model SSC/5200. A heating or cooling rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere was used for DSC. TGA was measured by heating the samples from 40°C to 800°C at $20^\circ\text{C min}^{-1}$. Fourier transform infrared spectroscopy (FT-IR) absorption was recorded by using a PerkinElmer spectrometer. Tensile properties were measured according to ASTM D638-86 at a testing rate of 5 mm min^{-1} , and flexural properties were measured according to ASTM D790 at a testing rate of 2.6 mm min^{-1} using an Instron machine. Solvent absorption percentage ($S\%$) was obtained by using the equation $S\% = [(W_1 - W_0)/W_0] \times 100\%$, where W_0 is the initial weight of MMT/D2000/epoxy and W_1 represents the weight after solvent saturation.

RESULT AND DISCUSSION

Preparation of Organophilic Clays

The organophilic clays were prepared by the intercalation of Na^+ -MMT and POP-amine quaternary salts. The intercalation can be viewed as an ionic exchange reaction between Na^+ ions in MMT and amine salts. Using D400, D2000, and D4000 as the intercalating agents, three modified clays with different organophilicity were prepared and characterized by X-ray diffraction (XRD). The silicate interlayer space is generally widened to be larger than the pristine 12.4 \AA (Na^+ -MMT). In Figure 2, the patterns of d -spacing for MMT/D400, MMT/D2000, and MMT/D4000 are shown to be 19.4, 58.0, and 92.0 \AA , respectively, according to Bragg's equation. Particularly, the MMT/D2000 hybrid exhibited a pattern of Bragg peaks from $n = 1$ to 5, indicating a highly ordered gallery pattern. The intercalating agents of different molecular weights not only affect the MMT basal spacing but also the amount of incorporated organics. The TGA data indicates a POP fraction of 26 w% in MMT/D400, 63 w% in MMT/D2000, and 75 w% in MMT/D4000. Structurally, the hybrids consist of stacked hydrophobic POP-amine and hydrophilic silicate plates in an alternating manner, as illustrated in Figure 3. In the case of MMT/D2000, the POP-amine occupies 47 \AA in space width and 10 \AA in silicate plate thickness, which represents the amphiphilic arrangement and high affinity for organic compounds. The pristine Na^+ -MMT is comprised of only hy-

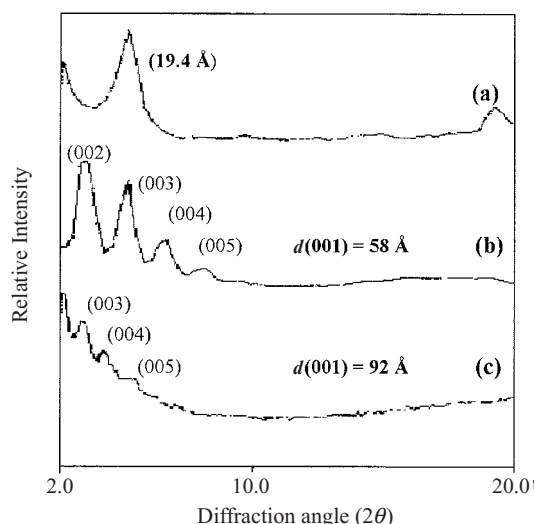


Figure 2. X-Ray diffraction patterns of (a) MMT/D400 (b) MMT/D2000 (c) MMT/D4000.

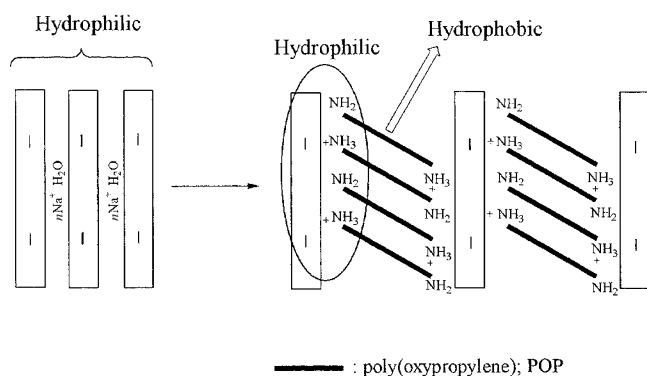


Figure 3. Conceptual illustration of stacking hydrophobic POP and hydrophilic silicate structure.

Table I. Compositions of MMT/D2000 compounding epoxy curing materials

Organoclay w% ^a	MMT/D2000 ^b (g)		Curing agent (D2000, g)	DGEBA ^c (g)
	D2000	MMT		
0	0	0	72.7	27.3
1	0.63	0.37	72.0	27.0
3	1.89	1.11	70.5	26.5
5	3.15	1.85	69.0	26.0
10	6.30	3.70	65.4	24.6

^a w%: MMT/D2000 hybrid in epoxy. ^b MMT/D2000: Na⁺-MMT modified by Jeffamine[®] D2000. ^c Liquid diglycidyl ether of bisphenol-A (DGEBA).

drophilic silicate ions and sodium counter ions, while D400 contributes not enough and D4000 too much hydrophobicity in the modified clays. It was found that MMT/D2000 was dispersible in organic solvents such as toluene and ethanol.

Preparation of Clay/Epoxy Nanocomposites

The MMT/D2000 hybrid, consisting of 63 w% organics and 37 w% silicates, was selected to study its

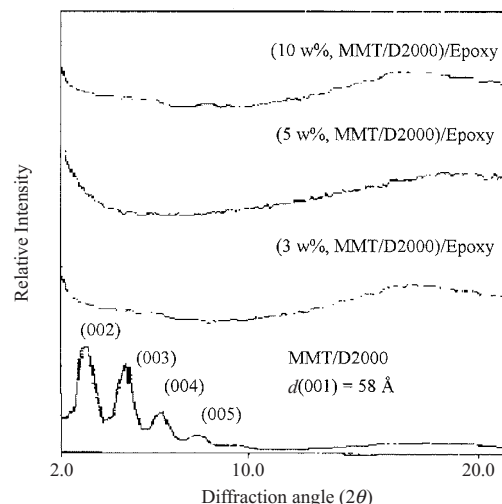


Figure 4. X-Ray diffraction patterns of MMT/D2000 in the DGEBA/D-2000 epoxy matrix.

compatibility with epoxy materials. The chosen epoxy system is comprised of two components, Jeffamine[®] D2000 amine and diglycidyl ether of BPA (DGEBA) at 1:1 molar ratio of epoxy/N-H or weight fraction of 72.7 w% and 27.3 w%, respectively. The detailed composition of the modified clay in the epoxy system is summarized in Table I. The cured epoxy materials with 3, 5, and 10 w% of MMT/D2000 in the system were examined by using XRD analyses. The 10 w% is the maximum loading, above which the viscosity becomes too high for mixing in the process. Shown in Figure 4, none of diffraction peaks are observed in the range of $2\theta = 2-10^\circ$ for cured epoxy polymers with the MMT-D2000 addition up to 10 w%. By contrast, the parent MMT/D2000 exhibits a pattern of peaks from $n = 2$ to 5 with the calculated 58.0 Å for $n = 1$. The results implicate the silicates are well dispersed and possibly exfoliated in the epoxy matrix.

FT-IR Analysis

Examples of FT-IR absorptions are shown in Figure 5. In Figure 5a, the peak at 1038 cm^{-1} can be associated with Si-O stretching vibrations, 3624 cm^{-1} with -OH stretching of the lattice water, and between 600 to 400 cm^{-1} with Al-O stretching and Si-O bending. Figure 5b showed the absorptions at $3000-2900\text{ cm}^{-1}$ (CH_3 stretching), $1625-1430\text{ cm}^{-1}$ (aromatic C=C stretching), 1100 cm^{-1} (polyoxyalkylene, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$), and weak absorptions between $950-750\text{ cm}^{-1}$ (epoxide ring vibration) for DGEBA/D2000 epoxy polymer. Nevertheless, there was no evidence of new absorption peaks in Figure 5c for interactions between silicates and polymer.

Mechanical Properties

The mechanical properties of MMT/D2000 dispers-

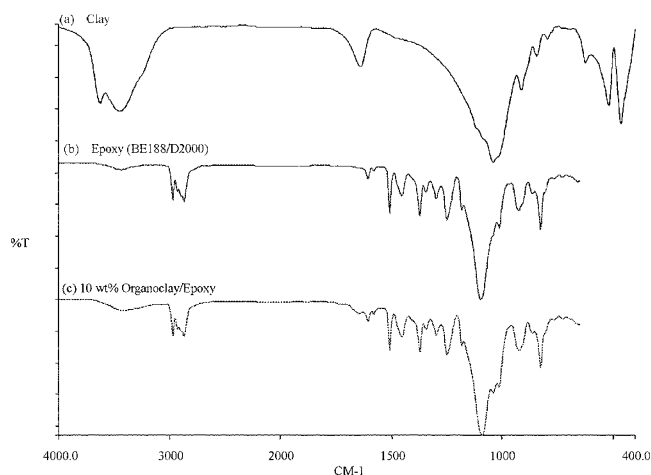


Figure 5. FT-IR spectra of (a) Na⁺-MMT (b) DGEBA/D2000 epoxy (c) 10 wt% MMT/D2000 in DGEBA/D2000.

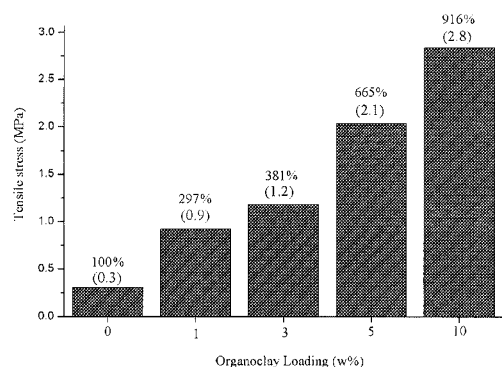


Figure 6. Tensile strength of MMT/D2000 dispersed in DGEBA/D2000 epoxy matrix.

ed in the cured epoxies were measured by using an Instron machine. The tensile properties for various MMT/D2000 (37 w% silicates) loadings from 1, 3, 5, and 10 w% are compared in Figure 6. The tensile strengths dramatically increased with increasing silicate loadings. The tensile strength of 1 w% organoclay in the system was almost three times that of the pristine epoxy polymer. The improvement was attributed to the presence of well-dispersed and exfoliated silicates in the epoxy matrix. However, the flexural modulus, shown in Figure 7, displayed only moderate improvements. For the elongation performance, the increasing organoclay addition from 1 to 5 w% resulted in improvements of nearly four times (Figure 8). The significant increase in elongation may be due to the strong interaction between the silicate plates and D-2000 poly(oxypropylene) backbone through a polar ion/(O-C-C)- non-covalent bonding. However, the trend of elongation increase is off-set at the extremely high clay loading, perhaps from the balance of the high hardness and flexural modulus properties. In general, these mechanical properties were improved significantly upon adding the organophilic MMT.

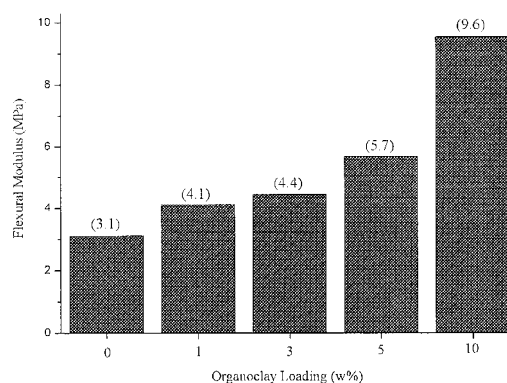


Figure 7. Flexural modulus of MMT/D2000 dispersed in DGEBA/D2000 epoxy matrix.

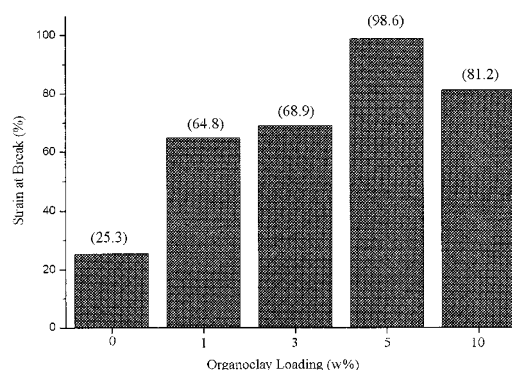


Figure 8. Elongation properties of MMT/D2000 dispersed in DGEBA/D2000 epoxy matrix.

Thermal Properties

The thermal properties of these epoxies were characterized by using a differential scanning calorimeter. During the curing process, the presence of MMT/D2000 hybrid had enhanced the epoxy curing process. The comparison of the curing behavior in DSC (Figure 9), a lower curing temperature profile was observed for the addition of 10 w% MMT/D2000 to the BE188/D2000 system. The D2000 cured epoxies were polymeric materials with low cross-linking due to the high molecular weight of the curing Jeffamine[®] amine used. With increased MMT/D2000 hybrid loadings, the composite exhibited a higher glass transition temperature (T_g), from 19.0 °C up to 36.9 °C (Figure 10). This observation can be interpreted in terms of the exfoliated silicate plates interacting with the epoxy polymer chains, resulting in low mobility of the matrix. The thermal stability of the cured materials was examined by using a TGA (Figure 11). In this epoxy matrix, the poly(oxypropylene) ether segments are less stable functionality which can be degraded at a lower temperature compared to the BPA portions. The MMT/D2000/epoxy had a slightly lower decomposition temperature than the pristine epoxy, due to presence of the additional D2000 from the MMT/D2000. However, beyond the 50 w% decomposition tempera-

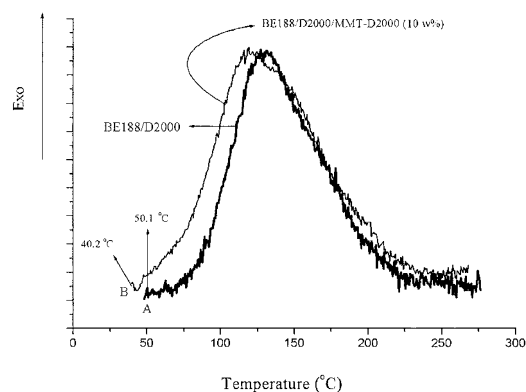


Figure 9. DSC thermograms of the curing process with and without clay.

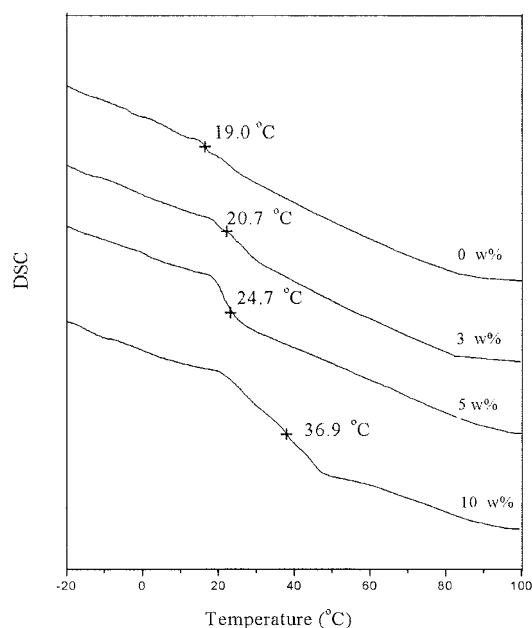


Figure 10. DSC thermograms of MMT/D2000 dispersed in epoxy at various loadings.

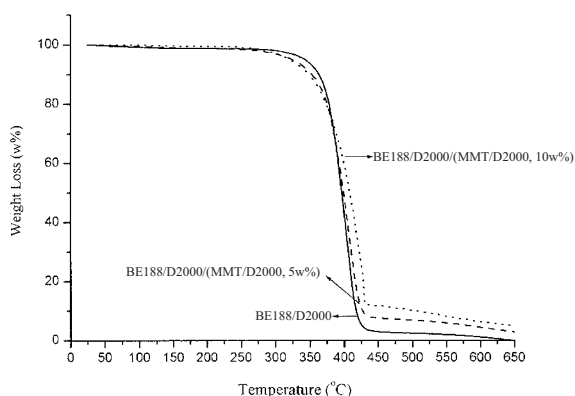


Figure 11. TGA of silicates dispersed epoxies.

ture (approximately at 400 °C), the organoclay started to play a role for stabilizing the epoxy matrix and displayed a higher decomposition temperature as well as char residue (approximately 10 w% at 550 °C). The presence of silicate plates appeared to affect the decom-

Table II. Solvent absorption (S%) of epoxy composites

	H ₂ O	EtOH	Toluene (S%) ^a	DMAc	THF
Epoxy	4.1	88	170	160	210
Epoxy/(MMT/D2000 (10 w%))	4.1	64	98	110	160

^aS% = $[(W_1 - W_0)/W_0] \times 100\%$. Absorption conditions: 1.5 g samples in solvents for 5 d.

position of epoxy materials because of the shielding effect.²⁵

Solvent Resistance Property

The effect of silicate plates on solvent resistance is demonstrated by comparing the weights of solvent absorption. The introduction of silicate plates into epoxies has led to an obvious decrease in the solvent absorption (Table II). For instance, at the organoclay loading of 10 w%, the solvent absorption is translated to be only 72% in ethanol, 56% in toluene, 72% in *N,N*-dimethylacetamide, and 75% in THF of the original absorptions by the epoxy without clay. Due to the hydrophobic nature, both epoxies with and without organoclay absorb low amounts of water. The decrease of solvent absorption is rationalized by the presence of delaminated silicate plates dispersed randomly in the epoxy matrix. A representative micrograph of transmission electronic microscopy (TEM) of 5 w% MMT/D2000 in epoxy material has exhibited the well dispersion of layered silicates in the matrix. The pictures represent the fine dispersion in a macroscopic view (Figure 12a) and an averaged 1–3 aligned silicate plates in a exfoliated mode from a microscopic view (Figure 12b). The well dispersed silicate plates in the polymer matrix contributed the reduction of solvent absorption and other physical properties of these epoxy materials.

CONCLUSIONS

A highly organophilic MMT, prepared from the intercalation of 2000 M_w POP-amine, has been used to demonstrate the compatibility with epoxy materials. The modified clay of 58.0 Å *d*-spacing is highly dispersible in toluene. In mixing with Jeffamine[®] D2000 cured epoxy, the resultant polymer is optically transparent and displays improved mechanical properties such as increased tensile strength, flexural modulus, and elongation. The thermal stability and solvent resistance are also improved.

Acknowledgment. We acknowledge the financial support from the National Science Council (NSC) of Taiwan.

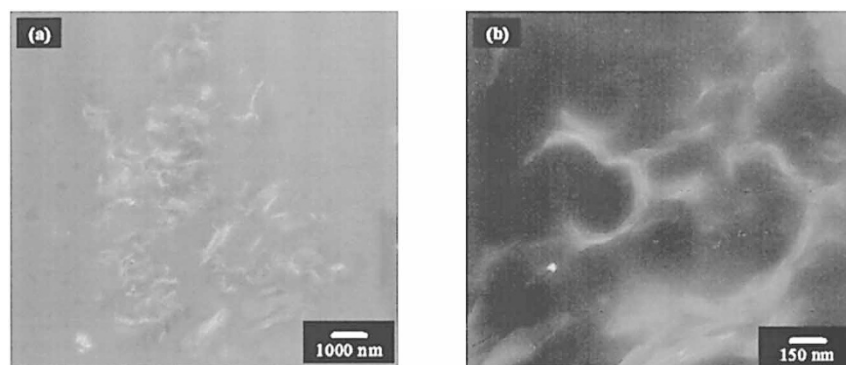


Figure 12. TEM of 5 w% MMT/D2000 dispersed in the epoxy.

REFERENCES

1. A. Okada and A. Usuki, *Mater. Sci. Eng.*, **C3**, 109 (1995).
2. P. C. Lebaron, Z. Wang, and T. J. Pinnavaia, *Appl. Clay Sci.*, **15**, 11 (1999).
3. E. P. Giannelis, *J. Adv. Mater.*, **8**, 29 (1996).
4. Z. Wang and T. J. Pinnavaia, *Chem. Mater.*, **10**, 1820 (1998).
5. M. S. Wang and T. J. Pinnavaia, *Chem. Mater.*, **6**, 468 (1994).
6. T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, *J. Phys. Chem. Solids*, **57**, 1005 (1996).
7. H. Ishida, S. Campbell, and J. Blackwell, *Chem. Mater.*, **12**, 1260 (2000).
8. X. Fu and S. Qutubuddin, *Polymer*, **42**, 807 (2001).
9. C. D. Muzny, B. D. Butler, H. J. M. Hanley, F. Tsvetkov, and D. G. Peiffer, *Mater. Lett.*, **28**, 379 (1996).
10. A. Akelah, N. S. El-Deen, A. Hiltner, E. Baer, and A. Moet, *Mater. Lett.*, **22**, 97 (1995).
11. A. Akelah and A. Moet, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, **55**, 153 (1994).
12. M. Kato, A. Usuki, and A. Okada, *J. Appl. Polym. Sci.*, **66**, 1781 (1997).
13. H. L. Tyan, Y. C. Liu, and K. H. Wei, *Chem. Mater.*, **11**, 1942 (1999).
14. T. Agag and T. Takeichi, *Polymer*, **41**, 7083 (2000).
15. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada, *Macromolecules*, **30**, 6333 (1997).
16. N. Hasegawa, H. Okamoto, M. Kawasumi, and A. Usuki, *J. Appl. Polym. Sci.*, **74**, 3359 (1999).
17. N. Ogata, S. Kawakage, and T. Ogihara, *Polymer*, **38**, 5115 (1997).
18. J. W. Gilman, *Appl. Clay Sci.*, **15**, 31 (1999).
19. J. Konta, *Appl. Clay Sci.*, **10**, 275 (1995).
20. J. C. Huang, Z. K. Zhu, J. Yin, X. F. Qian, and Y. Y. Sun, *Polymer*, **42**, 873 (2001).
21. K. Yano, A. Usuki, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2493 (1993).
22. P. Frisk and J. Laurent, U. S. Patent 5,972,448 (Oct. 26, 1999).
23. A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1174 (1993).
24. J. J. Lin, I. J. Cheng, R. Wang, and R. J. Lee, *Macromolecules*, **34**, 8832 (2001).
25. K. Yano, A. Usuki, T. Kurauchi, and O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2493 (1993).