New Method for the Synthesis of Clay/Epoxy Nanocomposites

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ABSTRACT: A new liquid–liquid method for the synthesis of epoxy nanocomposites was developed. This new method improved the dispersion and exfoliation of the organoclay in the polymer matrix, thus improving the end-use properties. The microstructure and physical properties of the clay/epoxy nanocomposite synthesized by the new method were studied. Rheological tests of the uncured epoxy–organoclay system demonstrated that this method resulted in a great increase in viscosity, much more than the most commonly used direct-mixing method. The Krieger–Dougherty model successfully described the dispersion of the clay layers in the uncured epoxy. In the 5 wt % organoclay nanocomposite, compressive tests on the cured samples showed that there was a 45% increase in the maximum strength, a 10% increase in the yield strength, and a 26% increase in the modulus over the pure epoxy–amine cured system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4286–4296, 2006

Key words: nanocomposites; epoxy; organoclay; clay exfoliation; clay dispersion

INTRODUCTION

The science and technology of nanocomposites has created great excitement and expectations in the last decade. Research in this area has been focused on the nanoscale second phase embedded in the polymeric matrix that gives physical and chemical properties that cannot be achieved by ordinary material synthesis methods. With new methods of synthesis and tools for characterization and manipulation, nanocomposite science and technology is now experiencing explosive growth.[1,2]

In 1993, researchers from the Toyota research group in Japan successfully synthesized organoclay/polyamide 6 nanocomposites[3] that showed great improvements in the mechanical properties and thermal stability when only 4 wt % clay was introduced into the polymer matrix.

Many researchers then expanded the use of organoclay to different polymer matrix nanocomposites, including epoxy, polypropylene, polystyrene, polyimide, polyurethane, and dendritic polymers. Their results have shown that the mechanical properties, physical/chemical properties, and fire resistance of the composites have been improved at very low clay contents.

Many aspects of clay/epoxy nanocomposites, which are regarded as one of the most promising new materials for industrial applications, have been studied. Areas such as the effect of curing processes,[4] promoters (catalysts),[4,5] choice of clays,[6] choice of curing agents,[7] choice of intercalating agents with alkylammonium ion with different alkyl chain lengths and different head groups (primary, secondary, tertiary and quaternary alkylammonium),[8] and corresponding morphological, mechanical, chemical, thermal, and rheological properties have been researched.

After nearly 10 years of the extensive study of clay/epoxy nanocomposites, there are still many problems that need to be solved. The dispersion and exfoliation of clay layers in an epoxy matrix are not sufficient for improving the mechanical and physical properties of nanocomposites to a reasonable degree.

There are many ways to improve the final mechanical, physical, and chemical properties of clay/epoxy nanocomposites. One of the most important ways is to disperse the clay into the matrix evenly to reach the maximum of clay exfoliation. The method of mixing clay with an epoxy resin was considered in this study.

The direct mixing (DM) method, in which organoclay is mechanically mixed with epoxy with or without solvents,[5–7,9,10] is the most common method in the synthesis of clay/epoxy nanocomposites (Fig. 1). Commercial clay, such as organoclays from Nanocor and Southern Clay Product, is usually used. The solvents (e.g., acetone, ethanol, isopropyl alcohol) needs to have a low boiling point.[9] A common laboratory-
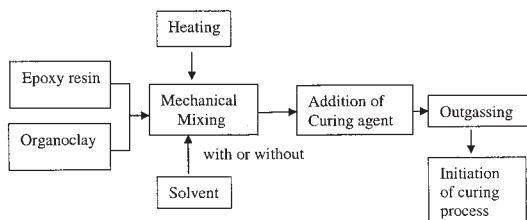
Figure 1 Illustration of the DM process for the preparation of the clay/epoxy nanocomposites.

type mixer with speed range under 9000 rpm with light duty is used.

The synthesis of epoxy nanocomposites by the DM method without solvent includes the following steps:

1. Mixing the desired amount of organoclay with epoxy resin under mechanical stirring and heating (the heating temperature varies with the resins).
2. Adding the curing agent to the previous mixture and then degassing in a vacuum oven.
3. Pouring the mixture into the mold and curing it at an elevated temperature.

It is easy to prepare epoxy nanocomposites and save laboratory time when this method is applied. The problem is that the dispersion of the organoclay is not good, and lots of large particles above 10 μm exist in the whole system.[6] The reason for this is that the dry organoclay are agglomerated, and the epoxy molecules are difficult to insert into the layers because of the existence of van der Waals force between the layers and particles.

A solvent is used to improve the basic DM method. The solvent can lower the force between the layers and facilitate the movement of epoxy molecules into the clay galleries. So an extra degassing step is added to the common DM method to eliminate the solvent before the addition of the curing agent in the synthesis of epoxy nanocomposites.

In summary, the DM method has the following advantages: (1) it makes it easy to synthesize clay/epoxy nanocomposites, (2) there is less void in the final cured samples because of the low viscosity of the clay/epoxy mixture, and (3) it is suitable for use with commercial organoclays. The biggest disadvantage of the method is the agglomeration of organoclays because of the low shear force due to the limitation of

mechanical stirring, even with the use of solvent in DM method.

The most difficult problem in the preparation of epoxy nanocomposites and the solution to this problem were considered in this study. The agglomeration between clay layers and between particles should be the most important factor affecting the final properties of the epoxy clay nanocomposites. There are two methods that give answers to the problem: the use of extremely high shear forces and the avoidance of any stage when clay is in the dry state.

The use of an extremely high shear force can effectively break the particles under control. With organoclay in the solvent, high shear force is applied to the clay particles and layers and tears particles and layers apart, and the solvent prevents the small size particles and clay layers from agglomerating again. However, high shear forces break the clay plates and lower the aspect ratio of the clay layers (α), which may reduce the final mechanical/physical properties of the epoxy nanocomposites.

When Na^+ clay is put in water, a suspension mixture is formed, and this is stable because of the chemical structure of the primary clay. In the synthesis of epoxy nanocomposites, one needs to use an intercalating agent to modify the Na^+ clay to make it to be organophilic. The problem occurs the organoclay dries after successful synthesis. If we can avoid this dry organoclay stage, the clay agglomeration phenomenon can be minimized because the solvent offers the most efficient atmosphere for keeping the clay layers separated.

In contrast to the DM method, a new liquid–liquid (L–L) method for the synthesis of nanocomposites was developed in our laboratory. This new method improved the dispersion and exfoliation of the organoclay in the polymer matrix, thus improving the mechanical and physical properties of the final materials.

EXPERIMENTAL

Materials

Epoxy

The epoxy resin used was diglycidyl ether of bisphenol A, EPON 828, provided by Resolution Performance Products (Shell Chemicals, TX, USA), with an average molecular weight of 377 and an average epoxide equivalent weight of 189 (Fig. 2).
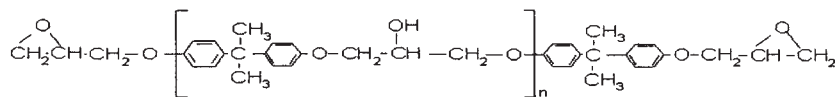
Figure 2 Chemical structure of Epon 828. $n = 0$ (88%); $n = 1$ (10%); $n = 2$ (2%).

Curing agent

Epi-Cure 3046, an aliphatic diamine with an average equivalent weight of 90, was used as the curing agent. It was provided by Resolution Performance Products.

Clay

New organoclay (triclay) synthesis. The primary clay was a natural Na$^+$-rich montmorillonite (Cloisite Na+) purchased from Southern Clay Products (TX, USA). Its cation exchange capacity was 92.6 mequiv/100 g of clay. Jeffamine T-403 polyoxypropylenetri-amine, supplied by the Huntsman Corp. (TX, USA), was used to synthesize the intercalating agent. We used this acidified T-403 intercalating agent to improve the interface between the clay layers and matrix because there were two extra amine groups in T-403, which had the ability to chemically react with epoxide groups from the epoxy resin to produce a better interface. Figure 3 illustrates the chemical structure of Jeffamine T-403 polyoxypropylenetriamine.

Chemical-grade HCl (2N) was reacted with T-403 to prepare the intercalating agent and was provided by Daigger & Co., IL, USA) Chemical-grade AgNO$_3$ (0.1N) was also purchased from Daigger.

Commercial organoclay. Organoclay I.30E, a surface-modified commercial montmorillonite used with epoxy to make the nanocomposites and for comparison with our laboratory-synthesized Triclay, was provided by Nanocor, Inc. (IL, USA).
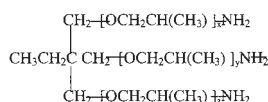
Nanocomposite preparation

### I.30E/epoxy nanocomposite preparation

I.30E/epoxy nanocomposites were prepared by the DM method. The desired amount of I.30E powder was added to the epoxy solution at 80°C with a quantity of ethanol and stirred for 2 h. Then, 35 phr Epi-Cure 3046 was added, which was followed by outgassing, and then, the mixture was cast into a preheated silicone mold and cured in an oven at 125°C.

Triclay/epoxy nanocomposite preparation

Synthesis of the triclay powder . The primary clay (9.473 g of Cloisite Na+) was dispersed into 750 mL of H$_2$O at 60°C at 300 rpm and stirred for about 30 min. The intercalating agent was prepared by the titration of

CH$_2$—[OCH$_2$CH(CH$_3$)]$_x$NH$_2$

CH$_3$CH$_2$C　CH$_2$—[OCH$_2$CH(CH$_3$)]$_y$NH$_2$

CH$_2$—[OCH$_2$CH(CH$_3$)]$_z$NH$_2$

Figure 3 Chemical structure of Jeffamine T-403 polyoxypropylenetriamine. $x + y + z \approx 5.3$.
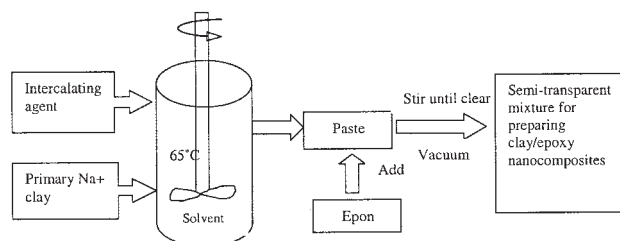
Figure 4 L–L method for the preparation of the organo-clay/epoxy mixture.

0.013 mol of T-403 with 6.5 mL of 2N HCl in 100 mL of distilled water. The mixture was then poured into the primary montmorillonite hot-water suspension and stirred for another hour at the same temperature. The precipitate, Triclay, was filtered and washed several times with a hot ethanol/water solution (50/50) until no Cl$^-$ could be detected by one or two drops of 0.1N AgNO$_3$. After the powder was dried, it was ground and passed through a #325 sieve.

Triclay/epoxy nanocomposites prepared by the DM method. The whole process was same as that described for the preparation of the I.30E/epoxy nanocomposites, but Triclay powder was used instead of the I.30E commercial organoclay.

Triclay/epoxy nanocomposites prepared by the L–L method. This method combined Triclay synthesis with the Triclay/epoxy mixture preparation. The process is illustrated in Figure 4.

Primary clay (10.0 g of Cloisite Na+) was dispersed into 750 mL of H$_2$O at 60–65°C at 300 rpm mechanical stirring for about 30 min. Then, the intercalating agent was poured into the suspension and stirred for another hour. The precipitate was filtered and washed thoroughly. Then, a suitable amount of the paste and epoxy were mixed under rapid mechanical stirring at about 600 rpm until a clear, high-viscosity suspension was obtained. This suspension was outgassed at 120°C for 16 h. Solid Triclay/epoxy nanocomposites were prepared by the addition of 35 phr Epi-Cure 3046 curing agent, and the curing temperature was set to 125°C.

Characterizations

X-ray diffraction (XRD)

XRD was performed on a Philips (Eindhoven, The Netherlands) PW1710 diffractometer with Cu irradiation (λ = 1.54 Å). Samples were scanned at diffraction angles (2θ's) from 2–10° at a scanning rate of 1°/min.

Scanning electron microscopy (SEM)

We used a Jeol (Tokyo, Japan) JSM-840 scanning electron microscope equipped with a LINK energy disper-
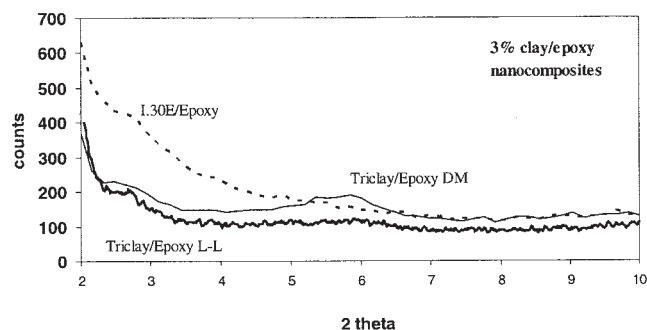
Figure 5 XRD of the clay/epoxy nanocomposites prepared by different methods: (1) DM method with 3 wt % organoclay (I.30E and Triclay)/Epon 828/Epi-Cure 3046 and (2) L–L method with 3 wt % Triclay/Epon828/Epi-Cure 3046.

sive spectrometer. The images were taken at 12 kV, and the probe current was set at 1×10^{-10} A. Magnification scales of 1200× and 8000× were used. The backscattered electron image, mapping, which gave chemical information, was taken at 12 kV, and the probe current was set at 1×10^{-8} A.

Compression tests

The tests were done on an MTS (TN, USA) Servo hydraulic testing machine, according to ASTM D 695. The crosshead speed was 1.3 mm/min, the size of the specimens was 12.7 mm × 12.7 mm × 25.4 mm. Five specimens were tested for each weight percentage of clay/epoxy nanocomposites. Compressive modulus, yield strength, and maximum compressive strengths were measured.

Rheological properties

A Brookfield (Essex, UK) CAP2000+ viscometer with a #6 spindle was used. The set temperature was 25°C, and a time of 3 min was allowed a temperature balance between the sample and spindle to be reached. The shear rate was set from 33 to 2600/s.

RESULTS AND DISCUSSION

XRD results

XRD analysis is commonly regarded as a convenient tool for judging the clay layer exfoliation in the clay/polymer nanocomposites, and the Bragg equation is used to calculate the gallery space between the adjacent layers.

The differences in the nanocomposites prepared by the DM and L–L methods are shown in Figure 5. For the 3 wt % Triclay/Epon 828/Epi-Cure 3046 nanocomposites, there was no obvious peak in the curve of the samples prepared by the L–L method, only a weak peak at a 2θ of 2.7°. The Triclay/epoxy nanocomposite

sample prepared by the DM method had an obvious peak at $2\theta = 5.8$°. With the commercial organoclay I.30E used to prepare the clay/epoxy nanocomposites by the DM method, there was a weak peak at $2\theta = 2.7$°. Our conclusion is that the nanocomposites prepared by the L–L method showed an advantage in their ability to disperse the clay layers evenly in the matrix and make the clay layers more exfoliated.

Also, the XRD method was used to judge the dispersion and exfoliation of the clay layers in the matrix before and after the curing process. For the Triclay/epoxy mixture prepared by the L–L method (before curing), the X-ray signal count and peak were close to the curve of the cured Triclay/epoxy nanocomposite (Fig. 6).

The clay exfoliation process can be explained as (1) an intercalating agent treatment that changes the primary clay from hydrophilic to hydrophobic and also increases clay gallery distance, (2) a swelling of the clay by epoxy monomers (epoxy migration) that provides an environment for the curing agents to migrate into the clay interlayer region, and (3) a temperature-controlled curing process that results in the final nanocomposite.[9] The observation in Figures 5 and 6 can be attributed to the effective migration of the epoxy monomers into the organoclay layers, and the clay layers were further exfoliated under the curing process.

SEM results

Two different amounts of the Triclay/Epon 828/Epi-Cure 3046 nanocomposites prepared by the L–L method were studied by SEM (Fig. 7). The spots for scanning were randomly chosen. At first, we studied the nanocomposites' microstructure at a lower magnification times (1200×), and then, we enlarge the images to 8000×. On these four images, only very few particles with a diameter of about 2 μm were found. If samples are prepared by the DM method, the size of
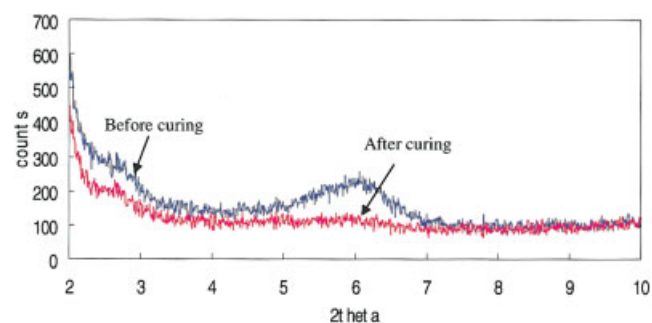
Figure 6 XRD curves of the 3% Triclay/Epon 828 nanocomposites prepared by the L–L method before curing (upper line) and after curing (lower line). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
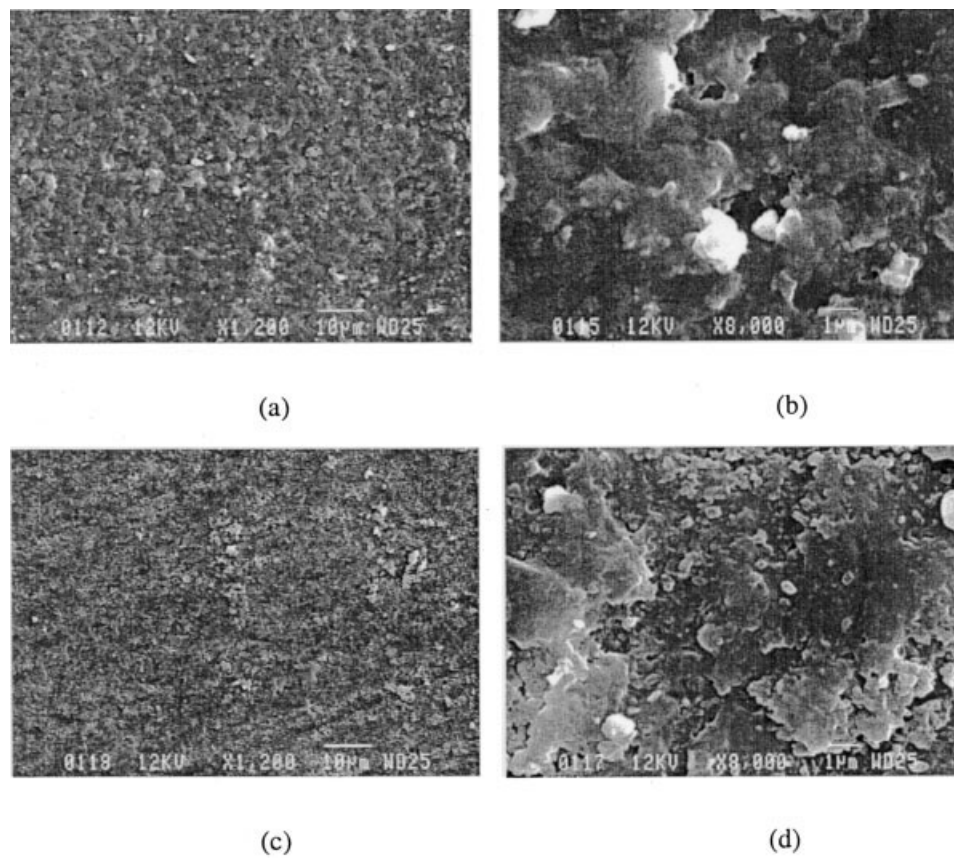
Figure 7 SEM of the Triclay/epoxy nanocomposites prepared by the L–L method: 1 wt % Triclay at (a) 1200× and (b) 8000× and 5 wt % Triclay at (c) 1200× and (d) 8000×.

the scattered particles is usually larger than 10 μm.[10] This observation suggests that the L–L method can effectively disperse the clay into the matrix and prevent the agglomeration of the clay particles.

Element mapping is a technology with X-rays in SEM to analyze element distribution, so one can separate the clay from the matrix. In the mapping of the Triclay/epoxy nanocomposites, dark color areas represent the carbon element from the epoxy matrix, and the light color areas represent the silicon and aluminum elements from the clay.
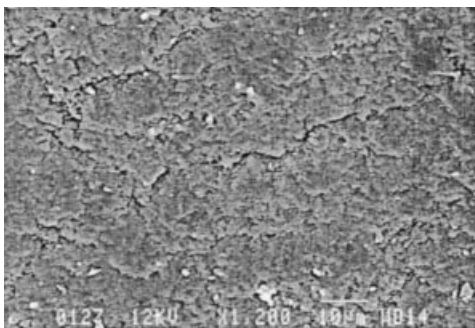
Figure 8 Mapping of the 5%Triclay/Epon 828/Epi-Cure 3046 nanocomposites prepared by the L–L method (1200×).

As shown in the mapping graph, the organoclay was dispersed well into the resin, with only very few small clay particles (Fig. 8). These small particles were agglomerated organoclay that were formed during the filtration of the Triclay/solvent solution on the glass wall side of the beaker and fell into the organoclay/ solvent solution.

In the mapping, the electron beam was focused on the dark spot that represented matrix. When we performed elemental analysis of the reflected electrons, we found strong existence of the clay (Fig. 9). We made the same observation in the clay spot where the existence of carbon (epoxy) was found.

From SEM analysis, it was clear that the clay was dispersed well in the matrix of the epoxy, and the epoxy monomers successfully migrated into the clay galleries to expend the clay layers.

Rheological properties

To produce clay/epoxy nanocomposites of the highest quality, it is necessary to improve the dispersion of clay in the matrix, especially to achieve maximum exfoliation in the clay layers. Therefore, it is very important to understand the clay dispersion status in

the matrix. In this section, the clay even-dispersion theory and rheological tests are used to discuss the dispersion.

Clay dispersion analysis

If one assumes that a single clay layer is a circular disk that occupies a cubic diameter as same as the disk's diameter (D), the disk thickness is t, and the average number density of this type disk in the system is n (Fig. 10).

In this case, the volume fraction (V) is[6]

$$V = \frac{\pi D^2 t}{4D^3} = \frac{\pi^* t}{4D} \tag{1}$$

Let $\alpha = D/t$. Every randomly exfoliated clay layer occupies a volume of D^3. So the critical volume fraction (V_C) is

$$V_c = \frac{\pi^* t}{4D} = \frac{\pi}{4\alpha} \approx \frac{0.8}{\alpha} \tag{2}$$

This is a useful equation for understanding the dispersion of particle-filled polymers.

Here are some cases we discuss:

1. Natural clay has α's distributed between 100 and 1000.[11] If we took the average of this distribution, $\alpha = 200$,[12] and assumed that few clay layers were
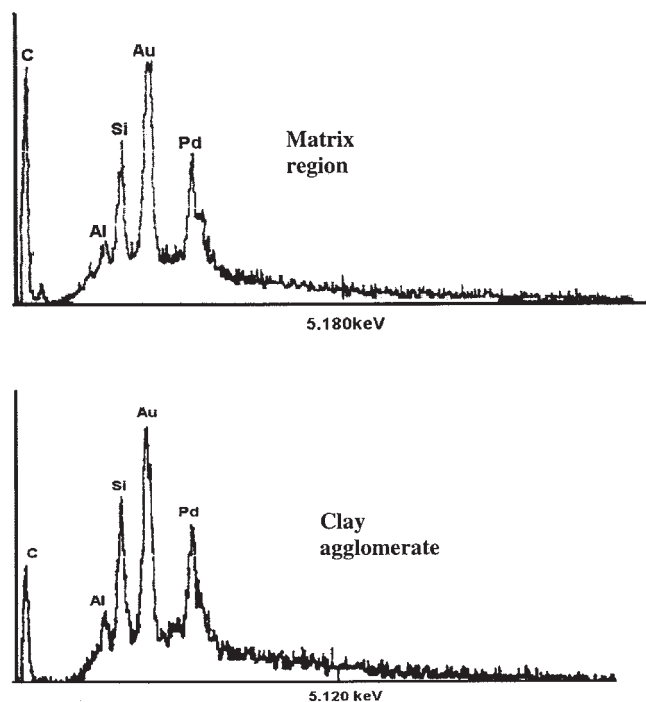
Figure 9 SEM element analysis of the matrix and clay particles.
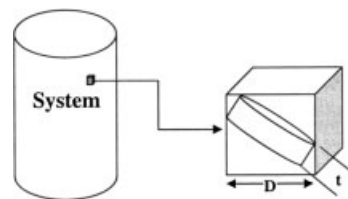
Figure 10 Illustration of a circular disk in a cubic matrix.

broken under intercalating agent treatment, the clay content for even dispersion under complete exfoliation was around 0.4%. Beyond this point, the viscosity of the uncured epoxy nanocomposites should have increased dramatically.
2. If more clay is added to the system, some clay layers must transform to a clustered (layered) structure and adopt a lower α.
3. When the clay is mixed with a polymer, if only the gallery height increases and no exfoliation takes place (a kind of intercalated state), the α is low, which leads to a low viscosity. For example, for a typical stack of 100 layers, which results in a low α of around 2, the system viscosity will be lower.

It is clear that ideal exfoliated clay/epoxy nanocomposites can only exist in a system with less than a 0.4% volume fraction of clay. Increasing the content of clay will lead to a lower exfoliation state, such as an intercalating and/or conventional filled composite.

Viscosity of the organoclay/uncured epoxy mixtures

Shown in Figure 11 are the following rheological characteristics of Triclay/epoxy mixture:

1. The Triclay/Epon 828 mixture prepared by the L–L method had a much higher viscosity.
2. The even dispersion point for the Triclay/uncured epoxy appeared to be at a point higher than 1% because the viscosity–shear rate behavior of this system did not show a dramatic viscosity increase seen in the curves of the 3 and 5% Triclay/uncured epoxy mixtures. In the 3 and 5% Triclay/uncured epoxy mixtures, the systems' apparent viscosities showed a faster increase in viscosity when the apparent shear rate decreased, which was different from the 1% Triclay/uncured epoxy mixture system with slow increasing at decreasing shear rates. Our theoretical calculations indicated that even dispersion of the clay should have occurred at 0.4% Triclay if the assumptions that we made about the geometry of the layers were correct. In particular, a somewhat lower α could explain the behavior observed.
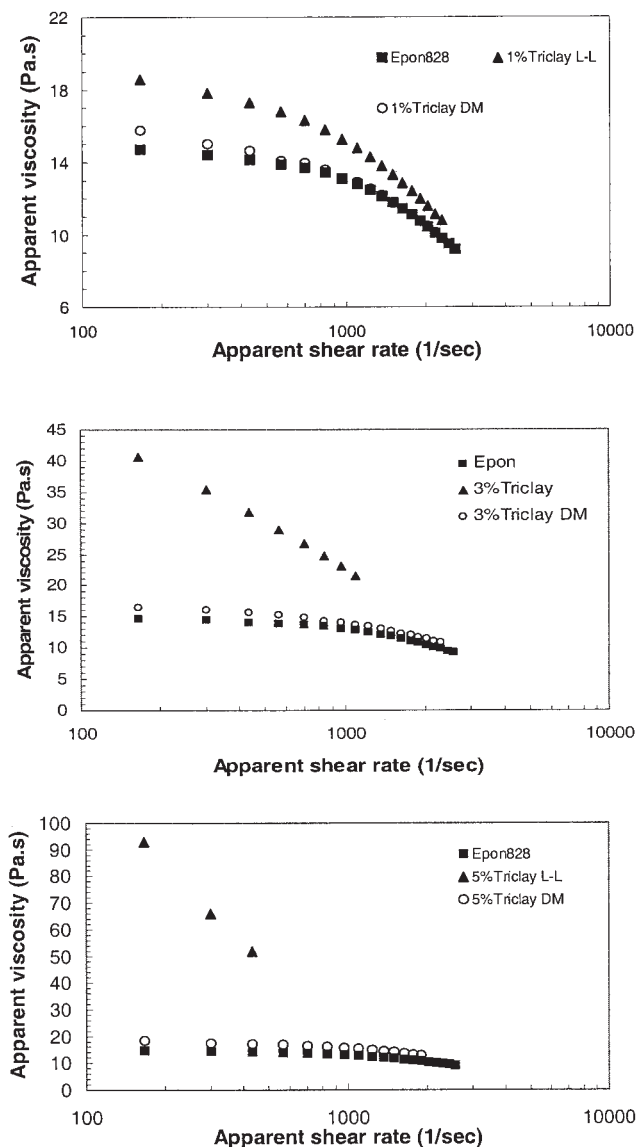
Figure 11 Viscosity of the Triclay/epoxy mixtures prepared by different methods.

3. All clay/epoxy mixtures exhibited shear thinning behavior, which meant that the viscosity decreased with increasing shear rate. This is common for filled polymer systems.

The great increase in the viscosity may be explained by two major reasons: the first is the good dispersion and exfoliation of the organoclay, and the second possible cause is the increase in the matrix viscosity due to the reaction between the epoxy and the functional intercalating agent (acidified T403), water, and ethanol.

To investigate the influence of the functional intercalating agent on the increase in system viscosity, we designed the following two experiments:

1. We determined the effect of free amine groups from the intercalating agent on the surface of the

Triclay. The free amines had the ability to react with the epoxide group to increase the system's viscosity.

2. We investigated the effect of residual water and ethanol because water/ethanol may change the reaction of free amine groups with the epoxide groups, which would thus affect the final system's viscosity.

Effect of the amine groups on the intercalating agent. For this experiment, a desired amount of T403 was added to Epon 828, and then, we studied its effect on the system's viscosity with and without heating. We calculated the amount of free amine in the intercalating agent and mixed that amount of amine in T403 with Epon 828. We assumed that the amount of intercalating agent on the surface of the organoclay was about 20% and that two out of three amine groups had the ability to react with the epoxide group. The following equation was used:

$$\text{Equivalent T403(wt \%)} = \text{Triclay (wt \%)}$$
$$\times\ 20\% \times \frac{2}{3} \quad (3)$$

For our experiments, 0.667, 0.4, and 0.133 wt % T-403 was mixed with Epon 828, which represented the amount of free amine in 5, 3, and 1% Triclay, respectively, in the Triclay/Epon 828 mixture.

The results are that there was less than a 40% viscosity increase in 0.667 wt % T-403/Epon 828 (corresponding to the 5 wt % Triclay/Epon 828 mixture) compared with pure Epon 828 (Fig. 12). We also found that heating conditions at 120°C or room temperature had almost no effect on the final viscosity properties.

Effect of residual water and ethanol. The existence of the water/ethanol molecules can affect the curing process of epoxy–amine systems, so it was necessary to investigate their effects at different contents.

We investigated six samples of the Epon828–T403–H_2O system: three samples of 0.667% T403 in Epon 828 with various water amounts (1, 2, and 3%) and three samples of 0.4% T403 in Epon 828 with various water amounts (1, 2, and 3%). Another set of samples of Epon828–T403–ethanol was three samples of 0.667% T403 in Epon 828 with various ethanol amount (1, 3, and 5%) and three samples of 0.4% T403 in Epon 828 with various ethanol amounts (1, 3, and 5%). All of these samples were heated to 120°C for 16 h and then conditioned at room temperature for 72 h. The results are shown in Figure 13.

The increase in viscosity was independent of the amount of H_2O. The curves of all three samples with 0.667% T403 were very close to each other, and the curves of the three samples with 0.4% T403 fell into
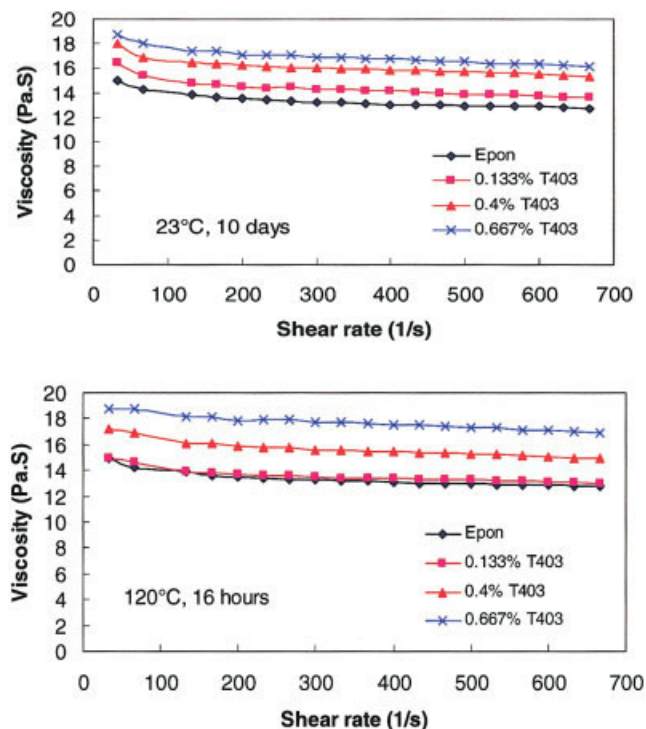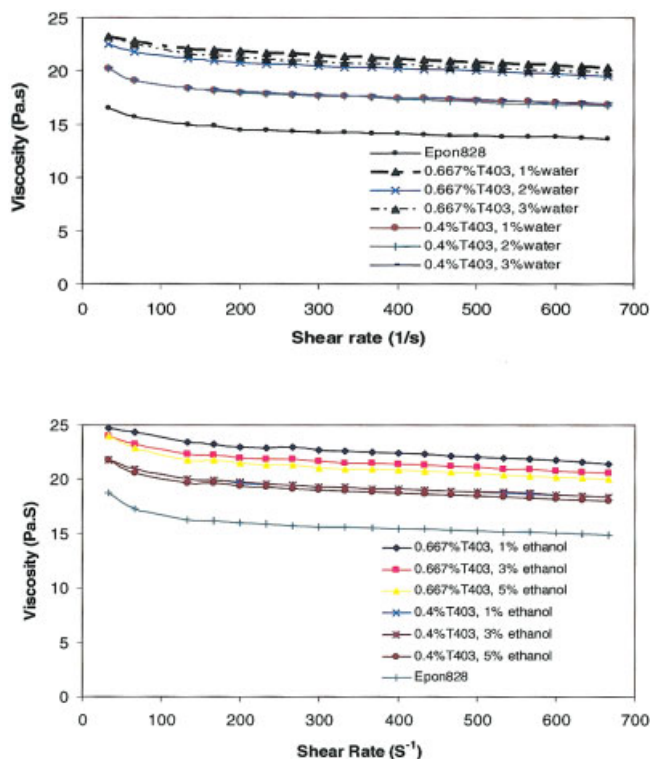
Figure 12 Effect of free amines from T-403 on the final viscosity of the system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 13 Effect of residual water (1, 2, and 3%) and ethanol (1, 3, and 5%) on the viscosity of the Epon828–T403 systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

almost one curve. For 0.667% T403/Epon 828 with 1, 2, and 3% H$_2$O, the viscosities were almost 40–50% higher than pure Epon 828. This increase was only 10% higher than that of the Epon 828/T403 without water, shown in Figure 12. The samples of 0.4% T403 with 1, 2, and 3% H$_2$O showed a 25% increase in viscosity compared with pure Epon 828, which was close to the change in the viscosity of Epon828 with 0.4% T403 without water (Fig. 12).

The case for the effect of residual ethanol in the Epon828–T403 system was very similar to Epon828–T403–H$_2$O (Fig. 13). The increase in the viscosity was mainly decided by the amount of amine T403, and the introduction of ethanol slightly decreased the viscosity of Epon828–T403.

We concluded that in the Epon828–T403 system, residual water and ethanol in the system did not greatly affect the system's viscosity. In the L–L method, the amount of water was usually from the water in the solvent, and it migrated out of the Epon 828/Triclay system with ethanol when it was heated at 120°C.

Combining the effect of amine groups from the intercalating agent and the effect of residual water, we concluded that the largest increase in the viscosity of the Triclay/Epon 828 mixture prepared by the L–L method was due to two reasons: (1) an increase in interactions between the clay and epoxy mole-cules and (2) an increase in the clay–clay friction; this increase in viscosity was not from the introduction of free amine groups or even the existence of H$_2$O.

We also measured the Triclay/Epon 828 mixture at lower shear rates, and the curve showed that the vis-
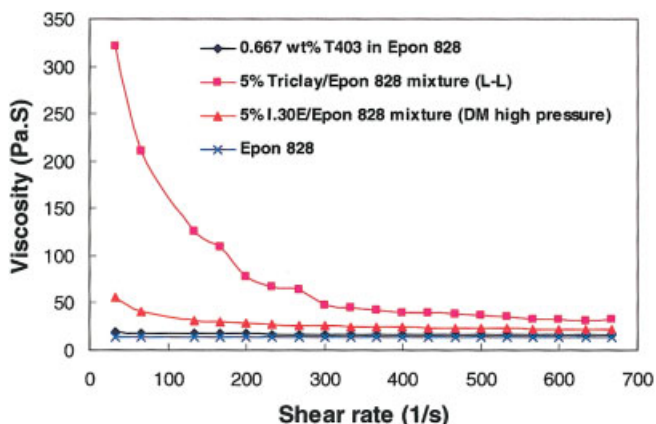
Figure 14 Comparison of the viscosities of the Triclay/Epon828 mixture prepared by the L–L method, the I.30E/Epon 828 mixture prepared by DM with high pressure, and Epon with 0.667 wt % of T-403. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Best-Fit Parameters for the KD Model

	Shear rate					
	ϕ_m (s^{-1})			$[\eta]$ (s^{-1})		
	167	300	433	167	300	433
Triclay/Epon 828 L-L	0.08	0.11	0.2	22	22	22
Triclay/Epon 828 DM	0.1	0.1	0.1	3	3	3

cosity of the 5 wt % Triclay/Epon 828 mixture prepared by the L–L method at a shear rate of 33 s^{-1} was about 7 times higher than that of the I.30E/Epon 828 mixture and 18 times higher than that of pure Epon 828 (Fig. 14).

Rheological model

There are two models that can describe viscosity of particle-filled polymers: the Krieger–Dougherty (KD) model and the Einstein model. We describe these models next.

KD model[13]. This model indicates that there is an increase in the viscosity when particles are added. This increase depends on the concentration of the particles:

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \qquad (4)$$

where the intrinsic viscosity ($[\eta]$) is equal to 2.5 for spheres and is determined by the shape of the particle and clay–clay and clay–matrix interactions,[14] ϕ is the volume fraction of the particles, ϕ_m is the volume fraction at maximum packing that occurs when the rotational diffusion freezes and the viscosity diverges at a certain density, η is the viscosity of the suspension, and η_0 is the viscosity of the medium.

ϕ can be calculated from the clay weight ratio (w), clay density (ρ_c), and matrix density (ρ_m):

$$\phi = \frac{w/\rho_c}{[w/\rho_c + (1 - w)/\rho_m]} \qquad (5)$$

where η and η_0 are as defined above for Eq. (4).

Einstein model. For a dilute solution, only pair interactions (e.g., collisions) are considered. At low shear rates, the increase in viscosity can then be described as

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 6.2\phi^2 \qquad (6)$$

where η and η_0 are as defined above for Eq. (4).

The KD model described the clay/uncured epoxy mixture system better. The parameters for the KD model that best fit the data are shown in Table I.

Figure 15 illustrates the use of the KD model and the Einstein model to reveal some properties of the clay/uncured epoxy mixtures. First, the KD model described the organoclay/uncured epoxy mixtures very well. The fitted $[\eta]$'s were 22 and 3 for the mixtures prepared by the L–L method and DM, respectively, and these value were almost not affected by the apparent shear rate. Interestingly, $[\eta]$ of the Triclay DM system was very close to 2.5, which represented the spherical particle shape. Therefore, we concluded that DM could not disperse the clay layers evenly into the matrix, and the clay particles were still agglomerated in an almost spherical geometry. With the L–L method, $[\eta]$ increased greatly, which revealed that the clay layer dispersion was improved, and thus, we produced better nanocomposites due to better exfoliation of the clay layers.

Compression testing

From the compression tests, we obtained the maximum strength (or ultimate strength), yield strength, and modulus values. In the clay/epoxy nanocomposites' mechanical properties tests, the compres-
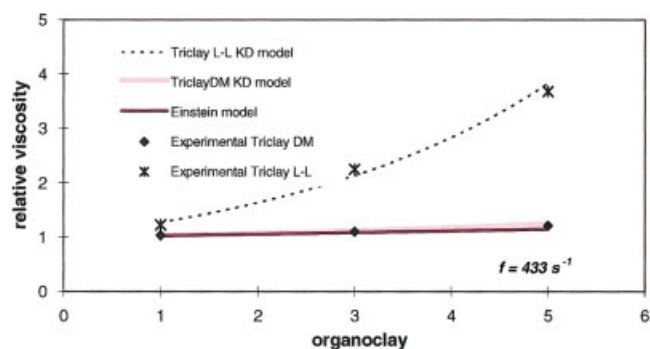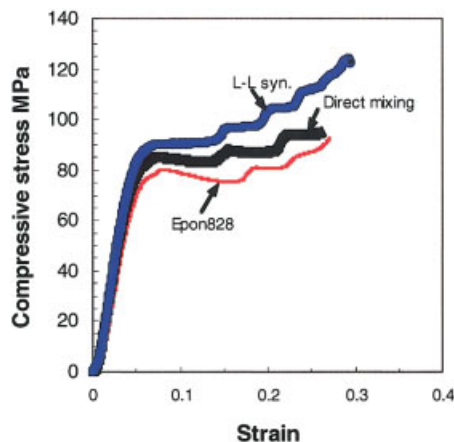

Figure 15 KD model for the clay/uncured epoxy mixture. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 16 Compression test results of the 5% Triclay/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sion tests better showed the effect of the organoclay than tensile strength tests because compression test results were less sensitive to voids in the material. Voids generated during the mechanical mixing of a curing agent with an organoclay/epoxy mixture can seriously lower void-sensitive properties like tensile tests and fracture tests. The mixture of Triclay/Epon 828 prepared by the L–L method had an especially high viscosity, and many air bubbles were generated when the Epi-Cure 3046 curing agent was mixed to make solid clay/epoxy nanocomposites.

Figure 16 shows the compression stress–strain curves for the 5% Triclay/epoxy nanocomposites. Here, the effect of two preparation methods, the L–L method and the DM method, are compared. Table II shows the details of the compressive properties of the Triclay/epoxy nanocomposites.

The nanocomposites prepared by the L–L method showed advantages. There was a 20% increase in maximum strength, a 5% increase in yield strength, and a 10% increase in modulus with only 1 wt % Triclay. The best improvement was in the 5 wt % clay, which gave a 45% increase in maximum strength, a 10% increase in yield strength, and a 26% increase in modulus. Liu

et al.[15], with DM with high pressure for 6 wt % I.30E/Epon 828, demonstrated a 29% increase in maximum strength, a 5.8% increase in yield strength, and a 25% increase in modulus.

These increases in strength and modulus may be attributed to the fact that the exterior force was transferred to the clay layers, like in glass fiber/polymer composites. The high strength and high modulus of the clay layers reinforced the materials' mechanical and physical properties. The 45% increase in maximum strength showed the advantage of the L–L method in the synthesis of the Triclay/Epon 828/Epi-Cure 3046 nanocomposites and exerted the advantage of clay layers in reinforcement effects.

CONCLUSIONS

The L–L method produced better result than the conventional method because it effectively dispersed the organoclay into the matrix and prevented the conglomeration of dry clay particles. The good dispersion resulted in a high viscosity in the uncured system and gave the nanocomposites better mechanical properties. However, the high viscosity generated a lot of voids in the final solid samples, which resulted from the process of mixing the curing agent with organoclay/epoxy mixture.

The KD model successfully described the dispersion of the clay layers in the uncured epoxy. $[\eta]$ was 22 for Triclay/Epon 828 mixtures prepared by L–L method and 3 for the mixture prepared by DM. These results hint that the organoclay was dispersed well in the matrix using L-L method.

The compressive properties of the Triclay/Epon 828/Epi-Cure 3046 nanocomposites prepared by the L–L method were greatly improved over those of the cured epoxy. The 5% Triclay nanocomposites exhibited a 45% increase in maximum strength, a 10% increase in yield strength, and a 26% increase in modulus.

TABLE II
Compressive Test Results of the Triclay/Epoxy Nanocomposites

Triclay (wt %)	Maximum strength (MPa)		Yield strength (MPa)		Modulus (MPa)	
	L–L	DM	L–L	DM	L–L	DM
0	89.02	89.02	82.18	82.18	1831	1831
1	107.67	101.82	86.13	85.36	2011	2028
5	129.22	97.66	90.90	87.13	2298	2109

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