

# Reinforcing Effect of Organoclay in Rubbery and Glassy Epoxy Resins, Part 1: Dispersion and Properties

T.-D. Ngo,<sup>1</sup> M.-T. Ton-That,<sup>2</sup> S. V. Hoa,<sup>1</sup> K. C. Cole<sup>2</sup>

<sup>1</sup>Department of Mechanical and Industrial Engineering, Concordia University, Montreal, Quebec, H3G 1M8 Canada

<sup>2</sup>National Research Council Canada, Industrial Materials Institute, Boucherville, Quebec, J4B 6Y4 Canada

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**ABSTRACT:** The reinforcing effect of organoclay in two epoxy matrices, one rubbery and one glassy, was studied. The rubbery and glassy epoxy matrices were chosen to have a very similar chemistry to minimize its impact on the comparison of properties. The epoxy resin was EPON<sup>TM</sup> 828, and the two hardeners were amine-terminated polyoxypropylene diols, having different average molecular weights (MW) of 2000 and 230 g/mol, namely Jeffamine<sup>®</sup> D-2000 and Jeffamine<sup>®</sup> D-230, respectively. The nanocomposites were prepared with the organoclay Cloisite<sup>®</sup> 30B from Southern Clay Products. The quality of dispersion and intercalation/exfoliation was analyzed by means of X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEGSEM), and transmission electron microscopy (TEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the curing reactivity and the thermal stability of the epoxy resin systems, respectively. Tensile properties and hardness of epoxy resin and epoxy nanocompo-

sites were measured according to ASTM standards D638-02 and D2240-00, respectively. Fracture surfaces were also analyzed by FEGSEM. These two epoxy systems as well as their nanocomposites display totally different physical and mechanical behavior. It is found that the quality of clay dispersion and intercalation/exfoliation, and the mechanical behavior of the glassy and rubbery epoxy nanocomposites are distinct. The results also indicate that the presence of the clay does not significantly affect the  $T_g$  of either the rubbery or the glassy epoxy; however, the fracture surface and mechanical properties were found to be influenced by the presence of nanoclay. Finally, several different reinforcing mechanisms are proposed and discussed for the rubbery and glassy epoxy nanocomposites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1154–1162, 2008

**Key words:** nanocomposites; nanolayers; rubbery; glassy; dispersions

## INTRODUCTION

Polymer–clay nanocomposites are materials consisting of a polymer matrix and nanometer-size clay particles. During the past 10 years, a lot of fundamental and applied research has been carried out in the field of polymer–clay nanocomposites. They exhibit significant improvements in tensile modulus and strength and reduced permeability to gases and liquids when compared with the pure polymer. These property improvements can be realized while retaining clarity of polymer without any significant increase in density, because the typical clay loading is 2–5 wt %.

Epoxy resin reinforced with nanoscopic-layered silicates has received increasing attention recently because of the possibility of obtaining improved properties in terms of stiffness, strength, fire resistance, dimensional stability, etc.<sup>1–5</sup> Interfacial interaction, platelet aspect ratios, chemistry, and layer charge densities of the nanoclay have a direct impact on the quality of clay dispersion and clay intercalation/exfoliation, and thus on the mechanical properties of epoxy nanocomposites.<sup>2,3</sup> However, it is not clear what mechanism governs the reinforcing effect of organoclay in epoxy resins, and whose characteristics can vary over a broad range from rubbery to highly glassy. Improvement in mechanical properties has been reported in several epoxy systems, mostly rubbery ones,<sup>2,6–8</sup> while no or almost insignificant improvement has been found in other epoxy systems, mostly glassy ones,<sup>9,10</sup> but not all. Liu et al.<sup>11</sup> showed an improvement in fracture toughness of the TGDDM-DDS system at low nanoclay loading (about 1.5 phr). However, there is a slight decrease in  $T_g$  of nanocomposites compared to neat epoxy. Wang et al.<sup>8</sup> studied the effect of clay on properties of both rubbery and glassy epoxy resins. They pointed out that the exfoliated forms of the silicate

Correspondence to: M.-T. Ton-That (Minh-Tan.Ton-that@imi.cnrc-nrc.gc.ca).

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nanolayers in both rubbery and glassy epoxy matrixes provided effective reinforcement. There are variations in chemistry of materials and the mixing method used to fabricate these nanocomposites, and it is not yet clear how these parameters affect the nanocomposite performance.

The results reported here pertain to an attempt to understand the influence of organoclay on the dispersion and the intercalation/exfoliation in rubbery and glassy epoxy resins, and thus on their mechanical properties. To simplify the problem, the nanoclay Cloisite<sup>®</sup> 30B, which undergoes no chemical reaction with the matrix at the temperatures used in the study, was used. The rubbery and glassy epoxy matrixes were also carefully chosen to minimize the difference in chemistry between them, thus minimizing their effect on the interaction with clay. They are based on the same epoxy resin. The two hardeners are of the same type but have different molecular weights. In addition, all the fabrication steps of the two nanocomposites, such as dispersing clay in the epoxy resin, mixing this mixture with hardener, and curing, were kept exactly the same. Furthermore, the study also includes the effect of nanoclay on  $T_g$  and fracture surface of the two materials. Several different reinforcing mechanisms are proposed and discussed for the rubbery and glassy epoxy nanocomposites. The aim is to better understand the dispersion of clay into two epoxy systems, which show completely different behavior at room temperature, as well as the effect of clay on  $T_g$  and their mechanical properties.

## EXPERIMENTAL

### Materials

The resin selected for this study was EPON<sup>™</sup> 828, from Resolution Performance Products LLC (Houston, TX). The two hardeners were amine-terminated polyoxypropylene diols having different average molecular weights of 2000 and 230 g/mol, namely Jeffamine<sup>®</sup> D-2000 and Jeffamine<sup>®</sup> D-230, respectively, from Huntsman. An organonano clay recommended for use with amine-cured epoxy systems was used, namely Cloisite 30B (montmorillonite treated with methyl tallow *bis*-(2-hydroxyethyl) quaternary ammonium) from Southern Clay Products (Gonzales, TX). Henceforth, the hardeners and clay will be designated in shortened form as D2000, D230, and C30B, respectively.

### Sample preparation

A masterbatch of epoxy resin and 23.6 phr clay was prepared using a conventional mechanical mixer at 120°C for 1 h, and the mixture was mixed thor-

oughly until cooled down to room temperature and then stored at room temperature. For curing, the required amounts of masterbatch, epoxy resin, and hardener(s) to obtain 6 wt % organoclay in the final products were mixed at room temperature for 5 min and then subjected to vacuum for another 30 min at 50°C. Samples were then cured at 120°C for 2 h, with subsequent postcure at 140°C for another 2 h.

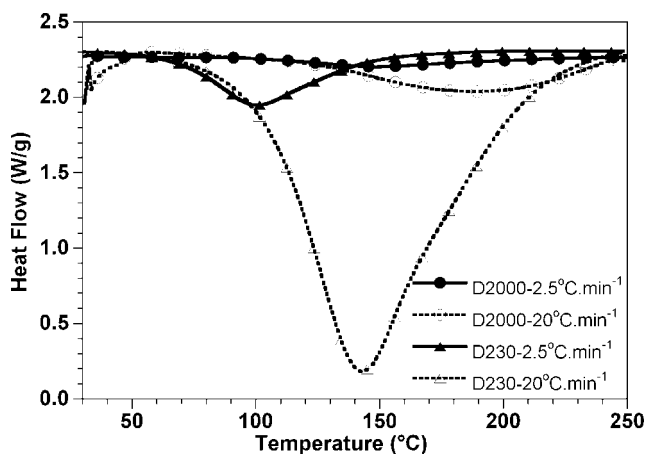
### Measurements

To evaluate the intercalation/exfoliation of the nanoclay in the polymer matrix, X-ray diffraction (XRD) patterns were obtained from the surface of the samples with a Bruker Discover 8 powder X-ray diffractometer with Cu K $\alpha$  radiation. The experiments were conducted on the exposed surface of specimens prepared by casting. A Hitachi-S4700 field emission gun scanning electron microscope (FEGSEM) was used to observe the dispersion of clay in the epoxy matrix at the microlevel as well as the fracture surface of the samples after tensile testing. For clay dispersion at the nanolevel, ultrathin (50–80 nm) sections of nanocomposite samples were prepared with a Leica EMFCS cryo-ultramicrotome and supported on a copper 200-mesh grid for observation with a Hitachi H9000 TEM. To determine the  $T_g$  and to confirm the absence of any residual curing, the cured samples were heated in a PerkinElmer Pyris 1 DSC instrument using helium atmosphere from –100°C to 150°C at 20°C min<sup>-1</sup> and then cooled to –100°C at 20°C min<sup>-1</sup> to minimize the enthalpy relaxation in the second heating scan, which involved reheating to 150°C at 20°C min<sup>-1</sup>. TGA data were obtained on a TA-Q50 instrument using nitrogen atmosphere. The samples were heated from 30 to 1000°C at a heating rate of 20°C min<sup>-1</sup>. The tensile properties of the epoxy system with and without clay were determined at room temperature according to ASTM D638-02 on an MTS Instron machine with crosshead speed of 5 mm/min. The hardness of epoxy and epoxy nanocomposites was determined at room temperature and relative humidity of 50% according to ASTM D2240-00 using a Shore Conveloader Instrument.

## RESULTS AND DISCUSSION

### Curing reactivity

To clarify the effect of curing rate on structure of epoxy and its nanocomposites, the curing reactivity of these two epoxy systems was investigated. Figure 1 shows the DSC results of D2000 and D230 systems at two different heating rates of 2.5 and 20°C min<sup>-1</sup>. In general, with lower heating rate, epoxy and hardener have more time to react with each other. Because of this, the curing of the same epoxy system

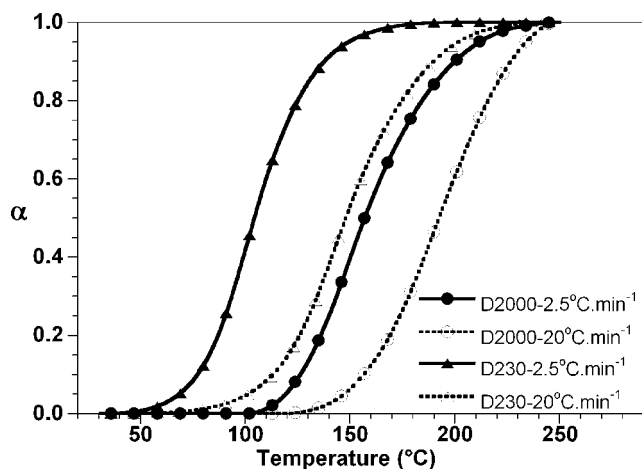


**Figure 1** DSC curves of the EPON828-D2000 and EPON828-D230 systems at two different heating rates of  $2.5^{\circ}\text{C min}^{-1}$  and  $20^{\circ}\text{C min}^{-1}$ .

happens at lower temperature for low heating rate compared with the high heating rate. The epoxy system cured with D230 shows a higher initial slope and lower onset temperature for both low heating rate ( $2.5^{\circ}\text{C min}^{-1}$ ) and high heating rate ( $20^{\circ}\text{C min}^{-1}$ ) relative to the epoxy system cured with D2000. This can be explained by the lower concentration of reactive groups in the D2000 system. From the transformation curves (Fig. 2), it can be observed that the slopes of the D230 systems are greater than those of the corresponding D2000, thus indicating that the curing in the D230 system took place faster than in the D2000 system.

### Dispersion

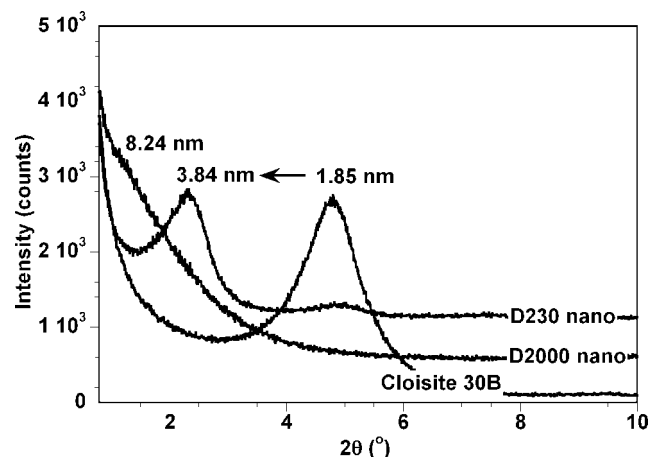
X-ray diffraction curves of the clay C30B and its nanocomposites are illustrated in Figure 3. The clay layer separation (degree of intercalation) in the nano-



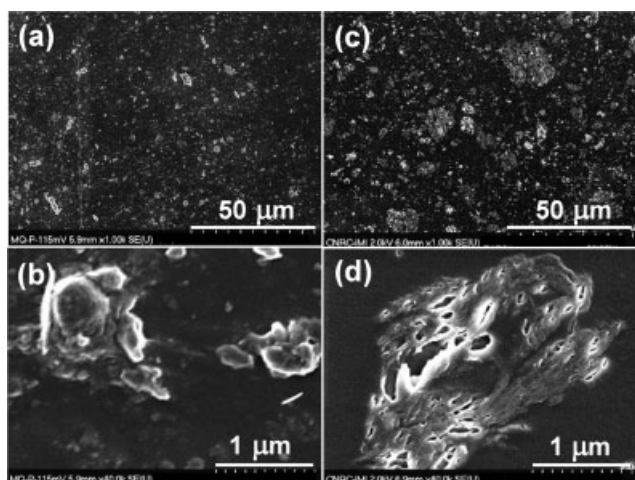
**Figure 2** Transformation curves of the EPON828-D2000 and EPON828-D230 systems at two different heating rates of  $2.5^{\circ}\text{C min}^{-1}$  and  $20^{\circ}\text{C min}^{-1}$ .

composite samples is more than twice as large as in the original C30B, showing that the clay has been further intercalated by the epoxy matrix. It is also noticed that D2000 leads to a much greater clay gallery distance compared to D230. The molecular weight of D230 is smaller than that of D2000, and so D230 would be expected to diffuse into the clay galleries more easily during curing, and hence to increase further the clay gallery distance. However, the curing rate of the D2000 system is slower compared to the D230 system (Fig. 2). As a consequence, it is reasonable to believe that D2000 and possibly EPON 828 would have more time to diffuse into the clay galleries to exfoliate the clays. Comparing the results in Figures 2 and 3, there is a correlation between the reactivity of the epoxy system and the intercalation/exfoliation of clay in the corresponding nanocomposites. Thus, the lower is the curing reactivity of the epoxy system, the greater is the clay intercalation in the nanocomposites. This observation is in good agreement with the literature.<sup>12</sup> Moreover, it is also believed that the size of the D2000 molecules contributes significantly to the intercalation/exfoliation of clay C30B in epoxy matrix. With a larger size compared to D230, D2000 can push the clay platelets apart and expand the clay galleries more than D230. It is worth stressing here that in thermoset systems, the intercalation and exfoliation process can continue during curing and is controlled not only by the rate of diffusion of organic molecules (in this case, the curing agent and the epoxy molecules) into the clay gallery but also by the curing rate of the epoxy system and by the size of epoxy and hardener molecules.

The XRD results can only provide the average *d*-spacing of the crystalline (001) plane of the clay, but it cannot describe well the level of dispersion of the clays in the systems, and so the microscopy studies were carried out. The microstructures of nanocom-



**Figure 3** X-ray diffraction curves of epoxy-nanocomposites based on C30B.



**Figure 4** FEGSEM micrographs of C30B nanocomposites cured with D2000 (a, b) and D230 (c, d).

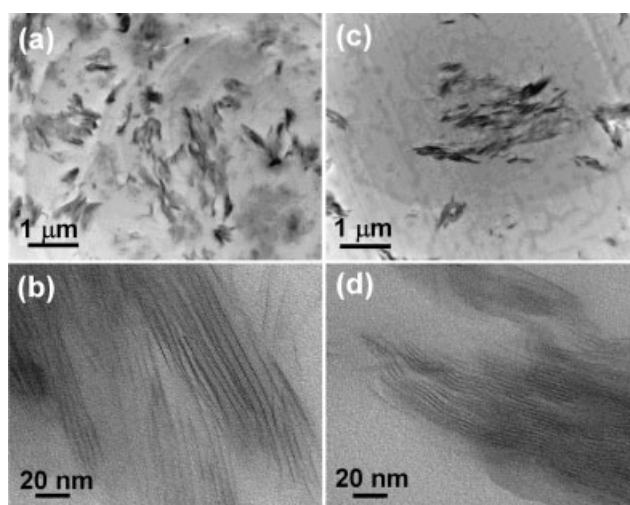
posite samples observed by FEGSEM are shown in Figure 4. The bright spots on the backscattered images correspond to clay aggregates. Apparently, a portion of the clay remains at the microscale level with different size populations depending on the type of hardener. As can be seen in Figure 4(a,c), there is a greater density of small particles with size below 2  $\mu\text{m}$  in the D2000 system than in the D230 system. This means that the clay has been dispersed better in the nanocomposite cured with D2000 than in the one cured with D230. This indicates that the longer hardener molecule and the lower curing rate of the D2000 epoxy system have a positive effect not only on the intercalation (as identified by XRD) but also on the dispersion of the clay at the microlevel in the epoxy.

TEM micrographs for these two nanocomposites at different magnifications are shown in Figure 5. It is clear that the clay particles were not completely exfoliated into individual platelets. However, epoxy matrix has entered into the clay galleries, as an increase in the clay gallery distance can be seen for the two nanocomposites. Figure 5(a,c) confirm that the clay has been dispersed better in nanocomposite cured with D2000 than in nanocomposite cured with D230 (as identified by FEGSEM). From Figure 5(b,d), the  $d$ -spacing is estimated to be around 7 nm and 3 nm for the D2000 and the D230 systems, respectively, which is in fairly good agreement with the XRD results. Again it is confirmed that D2000 leads to greater clay intercalation compared to D230. However, it is surprising that, although the gallery distance in the D2000 is fairly large (to an extent often considered as full exfoliation), the platelets still remain ordered into stacks. This may be due to the fact that the clay concentration is rather high, so that the platelets tend to pack in a highly ordered state as governed by thermodynamic rules (to minimize

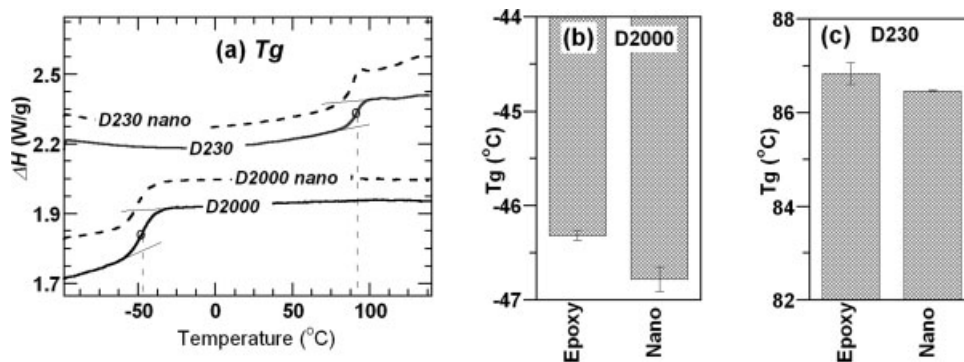
the Gibbs free energy). Another reason is related to the fact that the intercalation took place in the absence of shear forces, and hardener and epoxy molecules diffused into the galleries very gradually with time. So far, the results from XRD, SEM, and TEM combined indicate that in this particular case a longer chain length of curing agent and a lower curing rate of the epoxy system has a positive effect on the dispersion and intercalation/exfoliation of clay in the epoxy system.

### Properties of nanocomposites

The  $T_g$  of epoxy and epoxy nanocomposites was determined by DSC, and the results are shown in Figure 6. The  $T_g$  values of samples (with and without clay) cured with D2000 are much lower than those of samples cured with D230. After curing at 120°C, the epoxy matrix prepared with D2000 is a soft rubbery material with  $T_g = -46.3^\circ\text{C}$ , whereas the one prepared with D230 is hard and glassy with a high  $T_g = 86.8^\circ\text{C}$ . As a result of the difference in molecular weights, the distance between crosslinks in EPON828-D2000 is expected to be greater than in EPON828-D230. This explains the difference in the  $T_g$  of the two samples. It was also observed that the presence of nanoclay C30B does not significantly affect the  $T_g$  of the epoxy systems. The  $T_g$  values of nanocomposite samples cured with D2000 and D230 are  $-46.8^\circ\text{C}$  and  $86.5^\circ\text{C}$ , respectively. C30B, a montmorillonite treated with methyl tallow *bis*-(2-hydroxyethyl) quaternary ammonium, might be expected to undergo some interaction (for example, hydrogen bonding) with the epoxy resin at the temperatures used in the study. Such interaction should increase the  $T_g$  of the system significantly, but this is not the case, probably because the hydroxyethyl groups



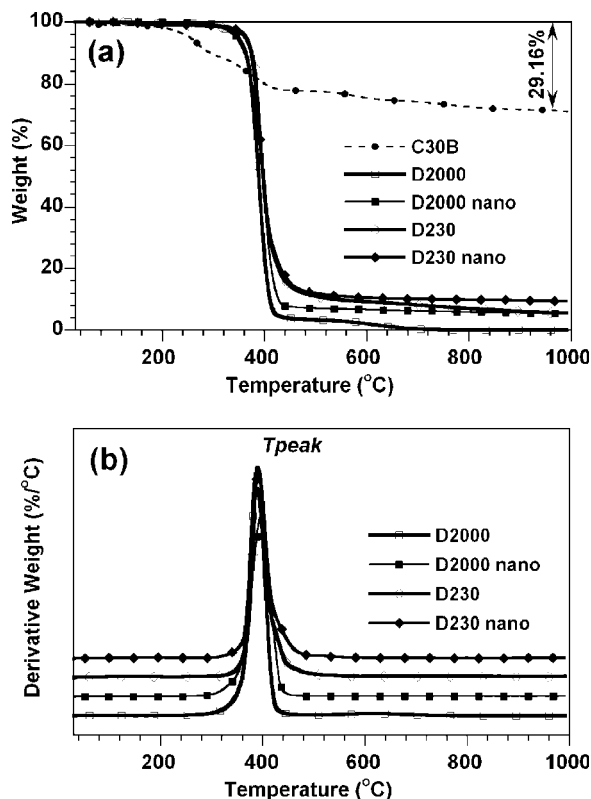
**Figure 5** TEM micrographs of C30B nanocomposites cured with D2000 (a, b) and D230 (c, d).



**Figure 6**  $T_g$  for materials cured with D2000 and D230: (a) DSC curves, (b)  $T_g$  values for the D2000 system and its nanocomposite, and (c)  $T_g$  values for the D230 system and its nanocomposite.

are “hidden” under the long hydrocarbon chains of the tallow, thus inhibiting a direct interaction between these groups and the epoxy resin. It was also observed that there was only one transition step in the DSC curves for the two systems, and the transition step was quite narrow and identical, indicating that there is only one phase in the system. This excludes the possibility that the curing is different inside and outside the clay galleries.<sup>12</sup>

Thermogravimetric analysis data of C30B, EPON828-D2000, EPON828-D230, and their nanocomposites are shown in Figure 7 and Table I. Figure 7(a)



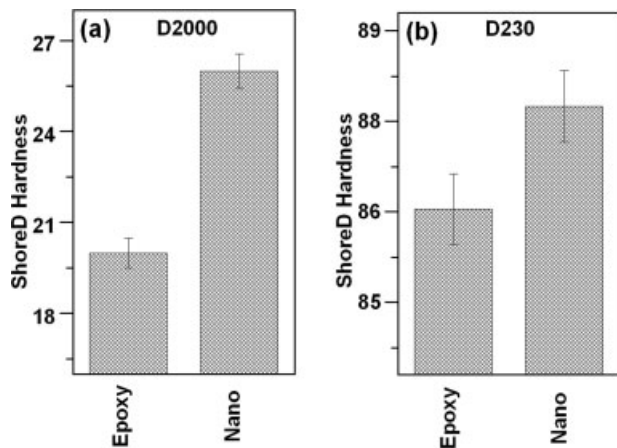
**Figure 7** TGA results of C30B and its nanocomposites cured with D2000 and D230.

shows typical TGA weight loss plots. It can be seen that there is 29.16% of weight loss in C30B up to 1000°C, which leaves 70.84 wt % representing the inorganic silicate in C30B. It can also be seen in Figure 7(a) and Table I that the EPON828-D230 system is more thermally stable than the EPON828-D2000 system; its  $T_{\text{onset}}$  temperature is higher and the temperature corresponding to any given weight loss is higher. This can be attributed to the shorter polyoxypropylene links, resulting in a lower overall polyoxypropylene content. Such groups would be expected to decompose at a lower temperature than the more stable bisphenol A units of the epoxy resin. The presence of clay C30B does not have a significant influence on the TGA results of these two epoxy systems. For the D2000 systems, at the same weight loss, the nanocomposite shows a slightly higher temperature compared with the neat epoxy. For the case of systems cured with D230, at lower temperatures, there is a slight decrease of degradation temperature for the nanocomposite compared to neat epoxy. However, above about 390°C, the nanocomposite shows a higher degradation temperature. Typical DTG thermograms (the first derivative curves of TGA) of the rubbery and glassy epoxy systems and their nanocomposites are shown in Figure 7(b). They reveal that the thermal degradation of these systems consisted of only one step. The maximum degrada-

**TABLE I**  
Summary of TGA Results for D2000, D230 Epoxy Systems, and Their Nanocomposites

Materials	Temperature (°C)			
	D2000	D2000 nano	D230	D230 nano
$T_{\text{onset}}$	367.7	369.3	375.1	370.9
$T_{\text{peak}}$	388.9	396.8	389.4	389.2
$T_5$	347.3	347.4	363.3	363.9
$T_{10}$	363.1	363.2	375.1	373.4
$T_{20}$	374.1	375.9	383.6	381.4

$T_x$  is the temperature of  $x$  percent of weight loss.



**Figure 8** Surface hardness of epoxy and its C30B nanocomposites cured with (a) D2000 and (b) D230.

tion rate temperatures  $T_{\text{peak}}$  from Figure 7(b) are shown in Table I. The presence of clay increases  $T_{\text{peak}}$  for the D2000 system but not for the D230 system. This may be due to the effect of intercalant and the level of dispersion, intercalation/exfoliation of C30B in these two systems.

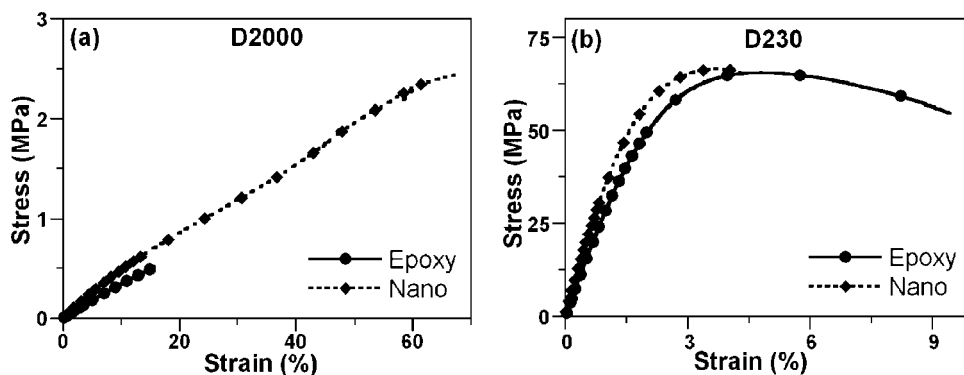
The surface hardness of the samples with and without clay was determined at room temperature, and the results are shown in Figure 8. As expected, adding nanoclay increases the surface hardness for both rubbery and glassy epoxy. However, the level of increase in the hardness for the rubbery system (D2000) is greater than for the glassy system (D230). Clay has a much greater surface hardness because of its ceramic nature. Therefore, at the same clay concentration, the contribution of clay to the hardness is greater for the rubbery epoxy system than for the glassy epoxy system. Furthermore, the better dispersion and better intercalation/exfoliation of the clay in the D2000 system may also be a contributing factor.

Typical stress-versus-strain curves for the epoxy systems and their nanocomposites are shown in Figure 9. The response of the materials to applied stress

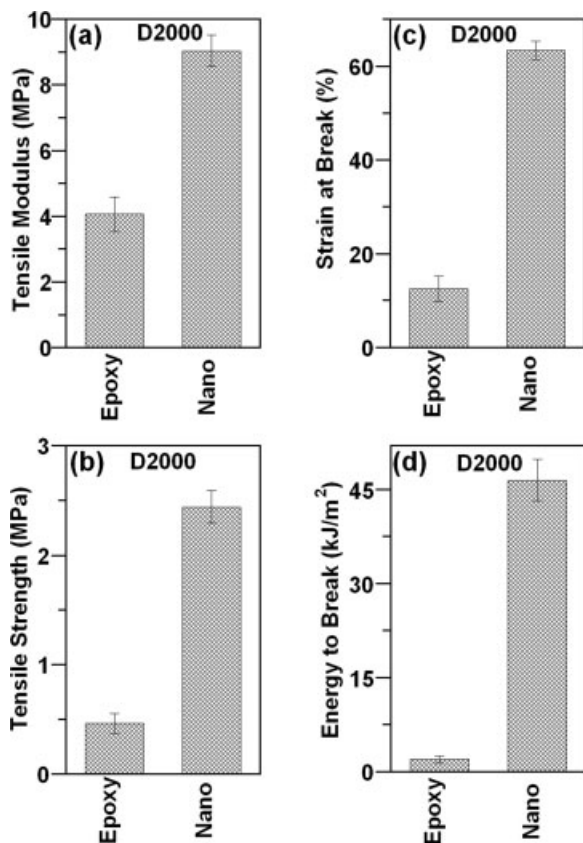
is described as ductile to brittle depending on the curing agent used. It is clear that the toughness of the EPON828-D2000 nanocomposite is significantly improved compared to the neat epoxy [Fig. 9(a)], whereas the reverse is true for the glassy Epon828-D230 nanocomposite [Fig. 9(b)].

The tensile properties of the epoxy systems and their nanocomposites are shown in Figures 10 and 11. The presence of C30B results in a significant increase in modulus, whether the epoxy matrix is rubbery or glassy. A similar effect was also reported by other researchers.<sup>2,5,6,9</sup> Because the modulus of clay is superior to that of the matrix, this improvement can be simply explained by the rule of mixtures. Figure 10 also illustrates an important increase in strength and toughness for the nanocomposite cured with D2000, which is representative of soft and weak materials. The presence of 6 wt % of nanoclay substantially increases the tensile modulus [more than two times, Fig. 10(a)], the strength [more than five times, Fig. 10(b)], the strain at break [five times, Fig. 10(c)], and the energy to break [more than 22 times, Fig. 10(d)] relative to the pristine elastomeric polymer.

On the other hand, for the glassy epoxy system with the same clay content, the tensile modulus increases by only 21% for the nanocomposite relative to the neat epoxy system [Fig. 11(a)]. Although the strength remains almost unchanged [Fig. 11(b)], the strain at break and energy to break decrease significantly [Figs. 11(c,d)]. This means that for high- $T_g$  epoxy thermoset, the presence of organoclay does not lead to an improvement of the tensile strength but rather makes the materials more brittle.<sup>13,14</sup> Clearly, the reinforcing effect of nanoclay is strongly dependent on the nature of the neat polymer, and the nanoclay has a more positive effect on mechanical properties of the rubbery material than on the glassy one. First, a better reinforcing effect of nanoclay in the rubbery system can be expected based on the rule of mixtures. Because its strength and modulus are many times smaller than those of the glassy one, the



**Figure 9** Typical stress-strain curves for epoxy and its C30B nanocomposites cured with (a) D2000 and (b) D230.



**Figure 10** Tensile properties of epoxy and its C30B nanocomposite cured with D2000: (a) modulus, (b) strength, (c) strain at break, and (d) energy to break.

positive impact of the organoclay becomes more important. Second, the improvement can be explained by the fact that, owing to the ability of nanoparticles to dissipate energy because of their mobility under applied stress,<sup>15,16</sup> the nanoclay can provide temporary physical crosslinks between polymer chains, providing localized regions of enhanced strength. There is also the possibility that the looser structure of the nanoclay in the rubbery structure can allow a better realignment of clay layers according to the stress direction, thus resulting in a greater reinforcing effect.<sup>2</sup> In addition, the better dispersion and intercalation/exfoliation in the rubbery system can also be of importance.

Table II summarizes the change in mechanical properties of the nanocomposites compared with the neat resin. It confirms that nanoclay has a more significant effect on the properties of soft rubbery materials (typical of material in the rubbery region above  $T_g$ ), namely the system cured by D2000.

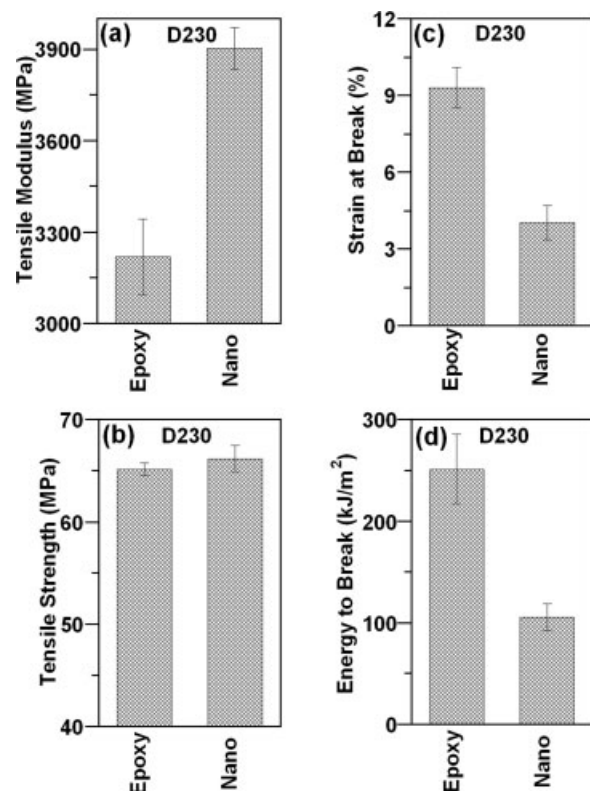
From the results, we can see that the quality of dispersion and intercalation/exfoliation of clay into rubbery and glassy epoxy systems are clearly different. The effect of clay on mechanical behavior of the glassy and rubbery epoxy nanocomposites is also distinct. It is interesting to try to further understand

the reinforcing effect of nanoclay on the mechanical properties of the two epoxy systems. The prediction of increase in modulus is one target issue, which will be described in a forthcoming paper (Part 2).

### Fracture surface

To further understand the reinforcing mechanism of C30B on rubbery and glassy epoxy systems, the fracture surfaces of tensile-tested specimens were observed by FEGSEM (Fig. 12). It can be seen that neat epoxy resin exhibits a relatively smooth fracture surface. The difference in the fracture of rubbery and glassy states of the neat epoxy can be seen clearly in Figure 12(a,d). There is yielding behavior on the fracture surface of the rubbery-state epoxy, which is a typical fractography feature of soft fracture behavior [Fig. 12(a)]. When compared with rubbery epoxy, the fracture surface of glassy epoxy is rougher and there are more cracks in different planes but almost parallel to the crack-propagation direction, indicated by a white arrow [Fig. 12(d)]. This is a typical fractography feature of brittle fracture behavior, thus accounting for the low fracture toughness of the unfilled epoxy.

The failure surface of the nanocomposites containing 6 wt % C30B is shown in Figure 12(b,c,e,f). Gen-



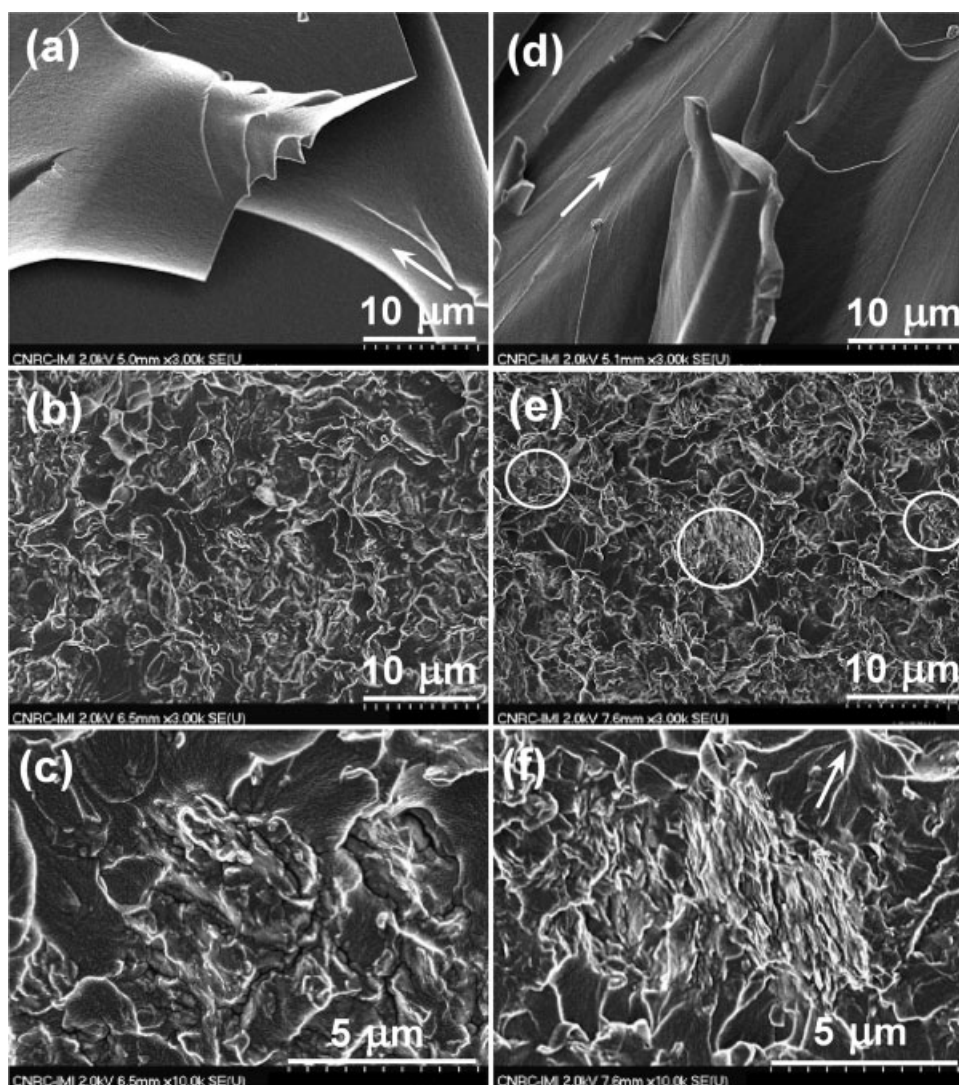
**Figure 11** Tensile properties of epoxy and its C30B nanocomposite cured with D230: (a) modulus, (b) strength, (c) strain at break, and (d) energy to break.

**TABLE II**  
**Summary of the Reinforcing Effect of Nanoclay on Mechanical Properties of Rubbery and Glassy Epoxy**

Nanocomposite	Properties change (%)				
	Shore D hardness	Tensile modulus	Tensile strength	Tensile strain at break	Energy to break
D2000	+30	+123	+430	+407	+2225
D230	+1.7	+21	+1.6	-57	-58

erally, a much rougher fracture surface is seen upon adding nanoclay into the epoxy matrix for both rubbery and glassy states of epoxy. In addition, although the roughness of the fracture surface is similar in both nanocomposites, the extent of increase in roughness is more evident for the case of soft material [Fig. 12(a,b)] compared to rigid material [Fig. 12(d,e)]. The increased surface roughness implies that the path of the crack tip is distorted because of the clay platelets, making crack propaga-

tion more difficult. More precisely, the clay is able to interact with the growing crack front. Therefore, the presence of clay particles or aggregates would cause perturbations along the crack front, thus altering the path of the propagating crack from the straight unperturbed growth seen in the neat resin (as evidenced by an incline relative to the initial crack propagation direction that is indicated by a white arrow). Consequently, the cracks are deflected by the clay particles into the rougher regions surrounding



**Figure 12** Fracture surfaces for epoxy systems and their C30B nanocomposites: (a) EPON828-D2000; (b, c) EPON828-D2000 with 6 wt % C30B; (d) EPON828-D230; (e, f) EPON828-D230 with 6 wt % C30B.



them. The crack deflection observed is responsible for the increase of strength and toughness observed on incorporating clay into the epoxy matrix. On the other hand, clay particles are also very likely to act as stress concentration sites [Fig. 12(c,f)], thus usually resulting in (1) clay-matrix debonding and (2) cleavage of clay tactoids, consequently producing micro- or nanovoids and finally reducing the performance. Figure 12(e) proves that many clay aggregates are observed on the fracture surface of the glassy system (several distinct agglomerations are indicated by circles). Figure 4 also demonstrates a poorer microdispersion of the glassy system. Therefore, it can be believed that the negative effect of the latter aspect plays a more important role in the fracture toughness of this system, which is not the case for the rubbery system. Furthermore, for the rubbery system, owing to the much greater elongation due to loading above the  $T_g$ , the improved performance of rubbery nanocomposite may largely be due to shear deformation,<sup>2</sup> in which nanoclay under strain may align as discussed earlier thus further contributing to the improved performance.

### CONCLUSIONS

Epoxy resins can display totally different behavior at room temperature, depending upon whether their glass transition temperature occurs above or below room temperature. The reinforcing effect of nanoclay in rubbery and glassy epoxy resin was evaluated. Although the presence of C30B does not influence the  $T_g$  of either the rubbery or the glassy epoxy, it significantly affects the mechanical properties of both materials. Tensile strength, modulus, and toughness improve significantly in the rubbery system with the presence of C30B. However, in the glassy system, the presence of clay does not lead to an improvement of the tensile strength and reduces the toughness and ductility. The fracture surface was also found to be influenced by the presence of nanoclay. In this particular study, the organoclay is better dispersed and better intercalated/exfoliated in the rubbery epoxy system than in the glassy one, mainly

because of its lower curing rate and the longer hardener molecule. A better reinforcing effect of organoclay in the rubbery system can involve different contributions: (1) better microdispersion, (2) better intercalation/exfoliation, (3) a greater relative contribution of the clay mechanical properties because of the lower matrix properties compared with the glassy one, and (4) alignment ability of clay in response to the applied stress.

Further work is underway to quantify the clay reinforcing effect on the mechanical behavior of epoxy nanocomposites, whose characteristics can vary over a broad range from rubbery to glassy. In addition, investigations of the influence of different types of clay as well as mixing procedures on the dispersion and properties of nanocomposites are in progress.

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