

Nanoclay and Long-Fiber-Reinforced Composites Based on Epoxy and Phenolic Resins

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ABSTRACT: In this study, high-performance thermoset polymer composites are synthesized by using both long fibers and nanoclays. Epoxy and phenolic resins, the two most important thermoset polymers, are used as the polymer matrix. The hydrophobic epoxy resin is mixed with surface modified nanoclay, while the hydrophilic phenolic resin is mixed with unmodified raw nanoclay to form nanocomposites. Long carbon fibers are also added into the nanocomposites to produce hybrid composites. Mechanical and thermal properties of synthesized composites are compared

with both long-fiber-reinforced composites and polymer-layered silicate composites. The optimal conditions of sample preparation and processing are also investigated to achieve the best properties of the hybrid composites. It is found that mechanical and thermal properties of epoxy and phenolic nanocomposites can be substantially improved. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3720–3726, 2008

Key words: nanoclay; carbon fiber; epoxy resin; nanoclay; nanocomposites; phenolic resin

INTRODUCTION

Among various thermoset polymers, epoxy resins provide the best overall performance, such as good mechanical properties, chemical resistance, and low shrinkage. They are high-performance materials used in coating, as adhesive, in civil engineering, structural, electronic, and composite applications.¹

Phenolic resins were the first thermoset resins to be synthesized commercially in 1907. These resins are not only low-cost and easy to produce, but also exhibit excellent fire performance, good dimensional stability, excellent thermal insulation properties, and good chemical and corrosion resistance. These features enable phenolics to be used in myriad applications, such as household appliances, business equipment, wiring devices, and electrical systems.²

Fiber-reinforced plastics (FRPs) are the most widely used composites. In general, fibers are the principal load-carrying members, while the surrounding matrix keeps the fibers in the desired location and orientation. It acts as a load transfer medium and protects the fibers from environmental damage because of exposure to elevated temperature and humidity. Fiber-reinforced composites have low

specific gravity, high internal damping, high strength-to-weight ratio, and high modulus-to-weight ratio. There are numerous applications based on FRPs.^{3,4}

Nanocomposites are a type of composite in which the scale of the dispersed phase is less than 100 nm, in at least one dimension. Because of the nanoscale dispersion and the high aspect ratios of the inorganic clays, polymer-layered silicate nanocomposites (PLSNs) exhibit light weight, dimensional stability, heat resistance, high stiffness, barrier properties, and improved toughness and strength with far less reinforcement loading than conventional composite counterparts.^{5–11} The synthesis and characterization of PLSNs has become one of the frontiers in materials science.

In general, PLSNs can be divided into two categories: intercalated and exfoliated composites.^{5–8} In an intercalated nanocomposite, a few polymer chains diffuse into the silicate galleries with fixed interlayer spacing. In contrast, an exfoliated nanocomposite is formed when the silicate nanolayers are delaminated and well dispersed in the continuous polymer matrix. The exfoliated state may maximize interfacial contact between the organic and inorganic phases, and as a result, nanocomposites with optimum performance properties can be achieved.

Although FRPs have good mechanical properties, cohesive failure of the polymer matrix may occur under tension, compression, or impact. If water or other small molecules diffuse into the interface between the matrix and fibers, interfacial strength may drop substantially and adhesive failure may occur in the interfacial region. On the other hand,

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the loading of clay often cannot reach a very high level (< 10 wt %) due to difficulty in dispersion. Thus, mechanical properties of PLSNs are relatively low compared with those of highly loaded FRPs (> 50 wt %).

In this study, we try to combine the advantages of both FRPs and PLSNs to synthesize high-performance thermoset polymer composites based on epoxy and phenolic resins.

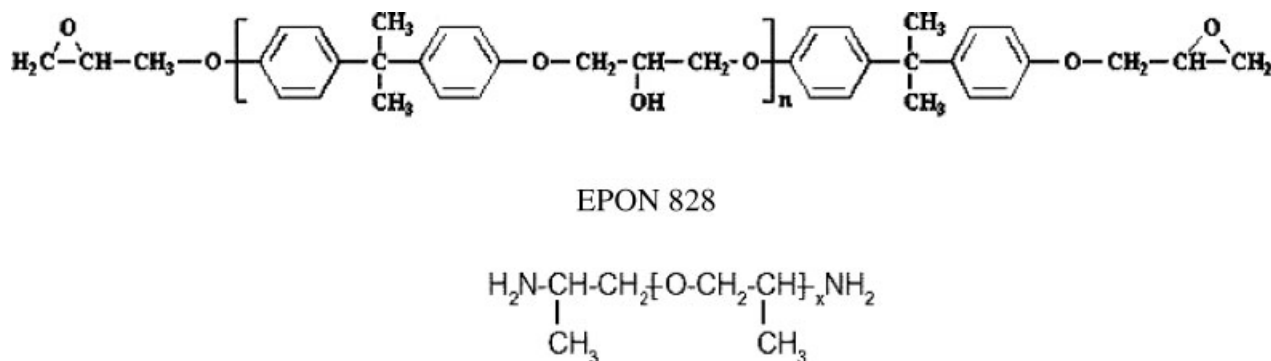
EXPERIMENTAL

The epoxide resin used for the synthesis of the neat epoxy polymer, the epoxy-clay nanocomposites, and the epoxy-clay-carbon fiber composites is EPON 828 (provided by Resolution Performance Products), a diglycidyl ether of bisphenol-A (DGEBA). It has an epoxy equivalent weight of ~ 187 . The curing agent is polyoxypropylene diamine, Jeffamine D230 with a molecular weight of ~ 230 provided by Huntsman Chemicals. The clay used is an industrially purified and organically treated montmorillonite, Cloisite[®] 10A, provided by Southern Clay. The carbon fiber is a 25.4 mm chopped fiber, Zoltek XP3304815R-X19, obtained from Ashland Chemical Company.

The neat epoxy polymer was formed by mixing the epoxy monomer (EPON 828) with the curing agent (Jeffamine D230). The mixture was degassed at 50°C for 30 min, cured in a silicone rubber mold at 65 and 120°C for 1 h each, and then postcured at 180°C for an additional 2 h. The two stage initial curing is for releasing the stress buildup during the cure process. The post curing process modifies and strengthens the three dimensional cross-linked structure due to rearrangement reactions. It also ensures complete conversion of the monomers.

The preparation of epoxy-clay nanocomposites was similar to the formation of the pure epoxy resin. In one method (a), EPON 828 and the clay were mixed for 30 min and sonicated for another 30 min at room temperature. The curing agent D230 was then added into the mixture and degassed at 50°C for 30 min. In the second method (b), the clay was initially mixed with D230. The mixture was sonicated for 30 min at room temperature, and then EPON 828 was added.

The epoxy-clay-carbon fiber prepregs were prepared by the hand lay-up method. The prepregs were compression molded under a pressure of 3.45×10^6 Pa at 120°C for 1 h and postcured at 180°C for additional 2 h. The content of carbon fiber was 25 wt %.



Both phenol and formaldehyde solution were obtained from Fischer Scientific. The curing agent hexamethylenetetramine (HMTA), was obtained from ICN Biomedicals Incorporated. The clay used is an industrially purified montmorillonite, Cloisite[®] Na⁺ clay from Southern Clay. A type of 1.27 cm chopped PAN-based carbon fiber, Zoltek XP3304815R-X19, was provided by Ashland Chemical Company.

Phenolic-clay nanocomposites were prepared by *in situ* condensation. In a typical reaction, phenol (1.0 mol), 37% formaldehyde solution (0.85 mol), and the desired amount of Na⁺-clay were added into a 500-mL three-neck flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. A small amount of hydrochloric acid (~ 0.005 mol) was

added as the catalyst. The mixtures were heated at 95°C with stirring for 3 h and then dehydrated under reduced pressure at 120°C for another 3 h to obtain phenolic-clay composites. Cured phenolic-clay composites were obtained by mixing the uncured mixtures (1.8 g) with HMTA (0.2 g), cured at 120°C for 2 h, and postcured at 180 and 200°C for additional 2 h respectively.

To prepare phenolic-clay-carbon fiber composites, phenolic-clay mixtures were dissolved in ethyl alcohol (weight ratio = 1 : 1) with a desired amount of HMTA. The resin solution is mixed with carbon fiber. Then the mixture was dried at room temperature for 24 h, compression molded under a pressure of 3.45×10^6 Pa at 120°C for 2 h, and postcured

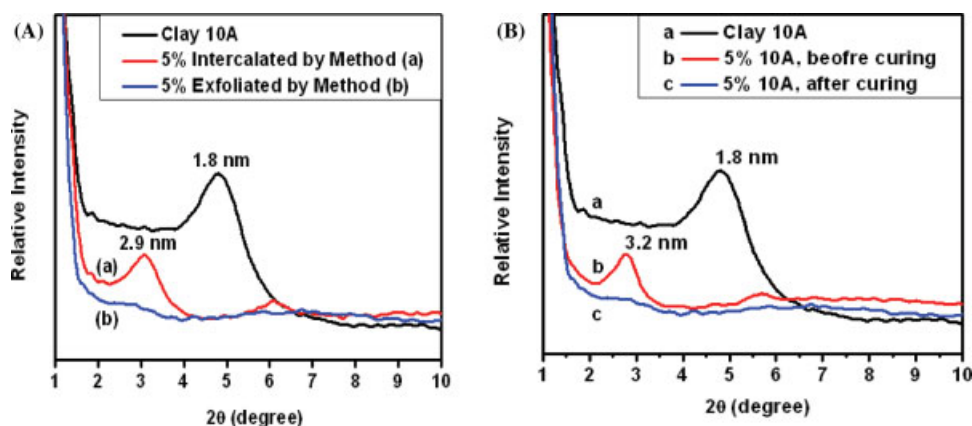


Figure 1 A: XRD patterns of Clay 10A, (a) intercalated 5% and (b) exfoliated 5% epoxy nanocomposite. B: XRD patterns of (a) Clay 10A, (b) 5% epoxy nanocomposite at gel point prepared by method (b), and (c) 5% epoxy nanocomposite after postcuring. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

at 180 and 200°C for additional 2 h, respectively. Although the T_g of phenolic resin is about 200°C, the use of cure accelerator in the Novalac cure reaction (acid) makes this temperature sufficient for post curing.¹² Moreover, the use of a higher temperature would also lead to thermal degradation of the nano-clay particles.

X-ray diffraction (XRD) patterns were obtained on a Scintag XDS-2000 X-ray diffractometer equipped with Cu $K\alpha$ X-ray radiation at 45 kV and 20 mA. All samples were scanned from 1° to 10° at a scanning rate of 1°/min.

Thermal mechanical analysis (TMA) was performed on a TA 2940 thermal mechanical analyzer to measure glass transition temperature (T_g) and coefficients of linear thermal expansion (α). The heating rate was 5°C/min. For each sample, three specimens were tested.

Tensile tests were carried out with an Instron 8511 Testing Machine under a strain rate of 5 mm/min at either 25 or 80°C. All test specimens were made according to ASTM D638-01. Five specimens were tested for each sample.

Flexural properties were tested with an Instron 8511 Testing Machine according to ASTM D790-03.

TABLE I
The Coefficient of Linear Thermal Expansion of Epoxy Prepared by Method (b)

Samples	Neat epoxy resin	3% Clay nanocomposite	5% Clay nanocomposite
α_1 ($\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$) ^a	70.6	65.9	49.6
α_2 ($\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$) ^b	258.9	242.6	232.9

^a α_1 is the coefficient of linear thermal expansion in the temperature range of 30–60°C (below T_g).

^b α_2 is the coefficient of linear thermal expansion in the temperature range of 90–120°C (above T_g).

The support span of the 3-point bending tests was 50.8 mm. Five specimens were tested for each composite sample. The strain rate was 50 mm/min.

Water absorption tests were carried out according to ASTM D570-98. The specimens were 76.2 mm long, 25.4 mm wide, and 3.2 mm thick. Two specimens were tested for each sample.

RESULTS AND DISCUSSION

Epoxy composites

Clay dispersion in the composites was verified using XRD. The typical XRD patterns of the clay 10A and composites are shown in Figure 1(A). The XRD pattern of the clay 10A powder exhibits a strong silicate diffraction peak at $2\theta = 4.81^\circ$ corresponding to a basal spacing of 1.8 nm. For the composite obtained by method (a), the diffraction peak shifts to 3.07° corresponding to a spacing of 2.9 nm. This indicates an

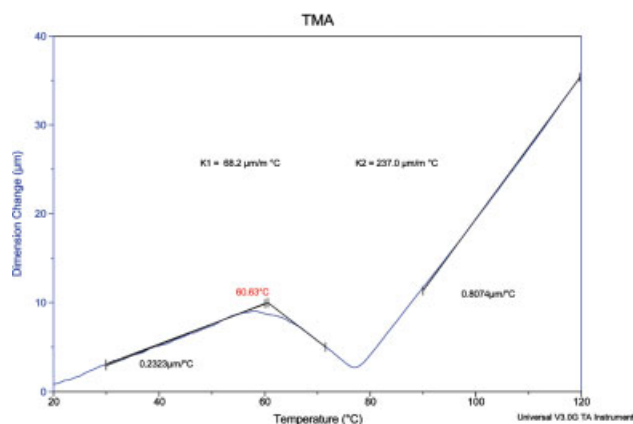


Figure 2 A typical TMA curve of epoxy-clay nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

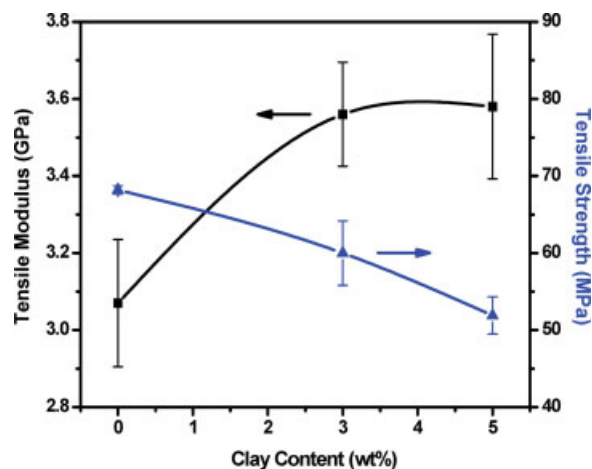


Figure 3 Dependence of tensile modulus (■) and strength (▲) of intercalated epoxy-clay nanocomposites on clay loading at ambient temperature (25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

intercalated structure in the composites. The diffraction peak of the clay disappears completely in the composite prepared by method (b), implying that an exfoliated epoxy-clay nanocomposite was obtained. This is probably because the diamine molecules are smaller and more flexible than epoxy molecules. It is much easier for diamine monomers to diffuse into the gallery of clay. In method (b), D230 was mixed with clay first, which provided more time for the diamine molecules to diffuse into the gallery of clay. The polymerization occurring between the amine group and the epoxy group on the silicate layer surface led to the propagation of polymer chains, causing the spacing of the clay layers to increase gradually. Finally, the clay was delaminated by polymer

molecules. This is demonstrated by the change of the diffraction peak in the composite during curing of a resin-clay mixture prepared by method (b) as shown in Figure 1(B).

Table I shows the results from the TMA tests. A typical TMA curve of epoxy-clay nanocomposite is shown in Figure 2. When the clay loading increases, the coefficient of linear thermal expansion of nanocomposites declines. The reason is that the dispersed clay layers can restrict the movement of polymer chains and help hold the structure of the composites. This means that adding the clay can improve the thermal stability of composites.

The tensile strength and modulus of two kinds of epoxy-clay nanocomposites were measured to assess the reinforcement effect of the clay in both glassy and rubbery states of the polymer matrix. As shown in Figure 3, the modulus of the intercalated nanocomposite (5% clay loading) increased by 17%, but the strength reduced by 24% in the glassy state (25°C), compared with the pure epoxy. However, in the rubbery state (80°C), both modulus and strength increased substantially, especially for exfoliated nanocomposites [Fig. 4(A,B)]. With 5% clay loading, the tensile modulus and strength of the exfoliated nanocomposites improved by 80% and 64%, respectively. The reason is that the mobility of polymer chain can be restricted by the presence of the clay layers in the polymer matrix in the rubbery state. In exfoliated nanocomposites, the crystal structure of clay is destroyed and the clay layers are uniformly dispersed in the matrix. Therefore, the interaction between the polymer and the clay is much stronger than that in intercalated nanocomposites. In addition, platelet alignment under strain may also contribute to improved performance of clays in a

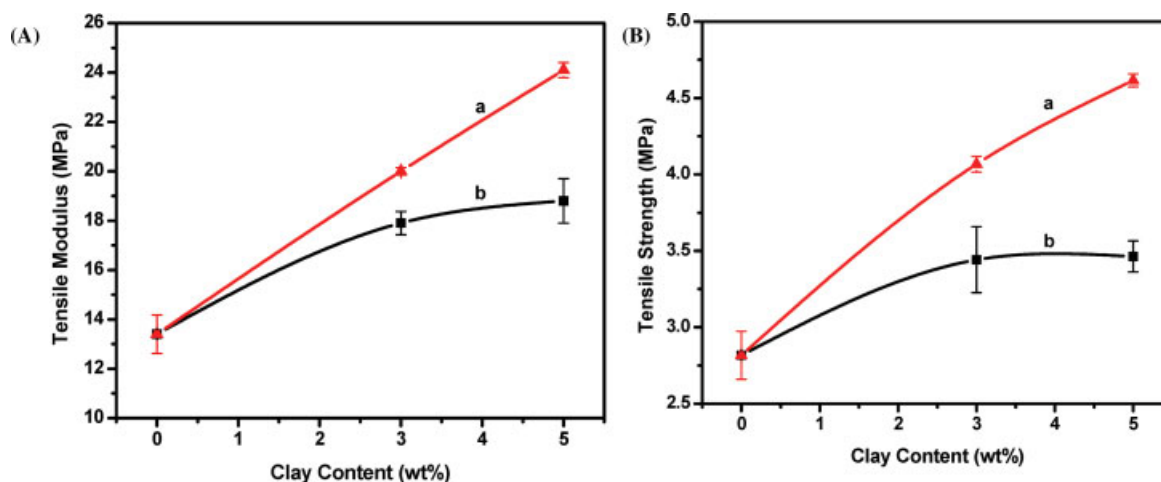


Figure 4 A: Dependence of tensile modulus of epoxy-clay nanocomposites on clay loading at 80°C, (a) exfoliated and (b) intercalated epoxy nanocomposites. B: Dependence of tensile strength of epoxy-clay nanocomposites on clay loading at 80°C, (a) exfoliated and (b) intercalated epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

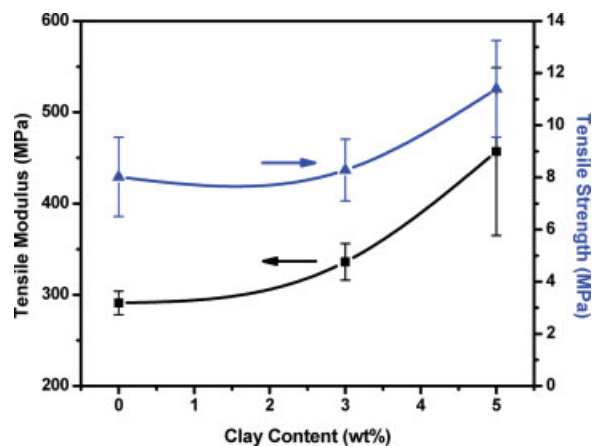


Figure 5 Dependence of tensile modulus (■) and strength (▲) of epoxy-clay-carbon fiber composites on clay loading at 80°C (25 wt % carbon fiber). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rubbery matrix when compared to a glassy matrix. The induced alignment of the clay layers can block the propagation of fracture in the polymer matrix.¹³ Similar results were also observed for the intercalated epoxy/clay nanocomposites reinforced by 25 wt % carbon fiber, as shown in Figure 5.

The barrier property of nanoclay is evaluated through the water absorption tests. From Figure 6(A,B), it can be seen that the amount of water absorbed by the composites and the rate of water absorption decreased with an increase of clay content in the composites. After 168 h (7 days), the water absorbed by the composite with 5% clay is about 15% lower than that in the composite without

clay. Because of the presence of clay in the polymer matrix, the diffusion path of water molecules increases, and the rate of water absorption becomes smaller. This lowers the permeability of water or other small molecules in and out of the composites, improving the water resistance of composites and extending the longevity of long-fiber-reinforced composites.

Phenolic composites

Clay dispersion in the composites was verified using XRD. The typical XRD patterns of the clay and composites are shown in Figure 7. The XRD pattern of the Na⁺-clay powder exhibits a strong silicate (001) diffraction peak at $2\theta = 7.15^\circ$ corresponding to a basal spacing of 1.1 nm. For both uncured and cured phenolic composites, the (001) diffraction peak of clay disappears completely, implying that the phenolic-clay exfoliated nanocomposites can be readily prepared during the sample preparation stage and retained in the curing processes. It is known that pristine Na⁺-clay mainly contains hydrated sodium ions to counterbalance the layer charge, making the nanoclay hydrophilic.¹⁴ Although, it is difficult for organic monomer or polymer molecule to intercalate into the silicate layers directly, the nanoclay can easily exfoliate in water. Since the polycondensation of phenol and formaldehyde is carried out in an aqueous system and a large number of sodium ions exist in the galleries of Na⁺-clay, phenol and formaldehyde molecules can readily intercalate into the galleries by polar-polar and charge interactions.¹⁵ Moreover, the protons (H⁺) in the reaction system

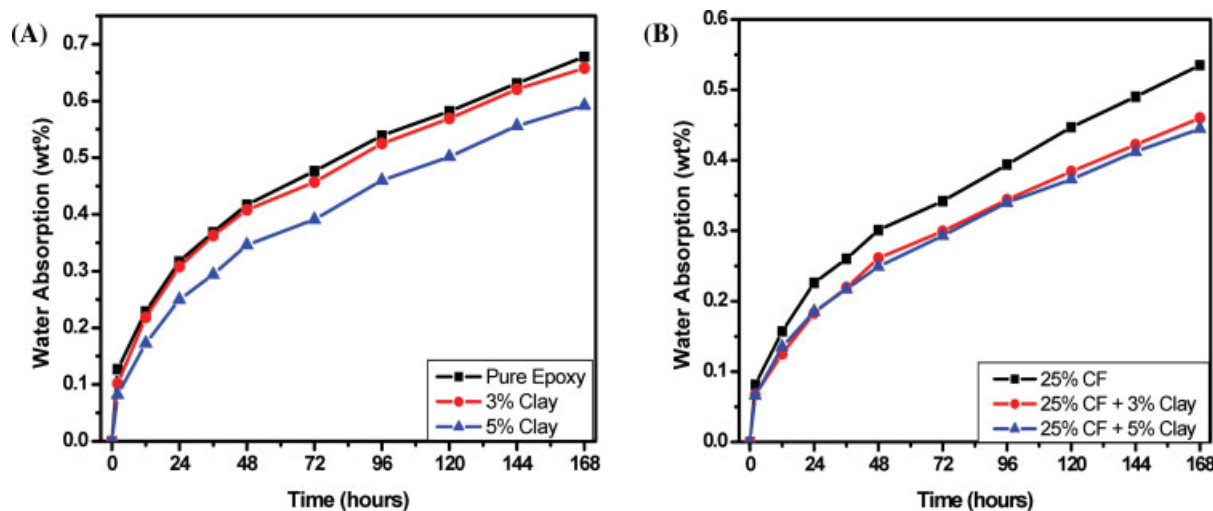


Figure 6 A: Water content of (■) pure epoxy resin, (●) epoxy-3% clay nanocomposite, and (▲) epoxy-5% clay nanocomposite when immersed in DI water at room temperature. B: Water content of (■) epoxy-25 wt % carbon fiber composite, (●) epoxy-3 wt % clay-25 wt % carbon fiber composite, and (▲) epoxy-5 wt % clay-25 wt % carbon fiber composite when immersed in DI water at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

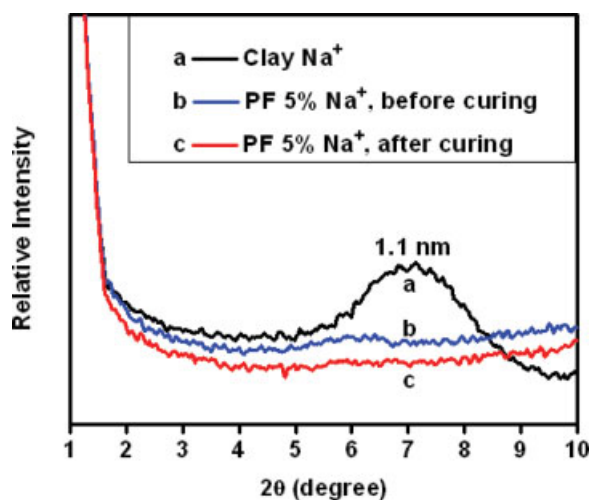


Figure 7 XRD patterns of (a) Cloisite Na⁺, 5% phenolic nanocomposites, (b) before curing, and (c) after curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

can easily exchange the sodium ions of Na⁺-clay and diffuse into the galleries of clay.¹⁶ These protons can catalyze the condensation reaction of phenols and formaldehydes. The growth of polymer chains can expand the silicate galleries, and finally the nanoclay can exfoliate completely. Therefore, during the polymerization of phenolic resins, Na⁺-clay can delaminate entirely with the formation of high-molecular-weight phenolics. Even with dehydration and curing, the exfoliated state of clay remains in the crosslinked structure of phenolic nanocomposites.

The flexural properties of phenolic composites are shown in Figure 8(A,B). It can be seen that the incorporation of long carbon fibers and nanoclay can improve the flexural properties of phenolic resins. For example, when adding 25 wt % carbon fibers into phenolic resins, both flexural strength and mod-

ulus are more than doubled. The additional 5 wt % nanoclay can contribute another 17% and 10% improvement in the flexural strength and modulus, respectively. In the phenolic-carbon fiber-nanoclay composites, the carbon fibers with high strength and modulus provide the main enhancement of the mechanical properties, and the exfoliated nanoclays may reinforce the resin-rich area in the composites, preventing crack generation and crack propagation in the polymer matrix between the carbon fibers. The synergic effects of long fiber and nanoparticles lead to the largest improvement of the flexural properties of phenolic composites.

Comparison of epoxy and phenolic composites

From earlier results, it can be found that organically modified clays need to be used in the epoxy system to obtain an exfoliated structure. For the phenolic system, raw clays without any organic surfactant can delaminate easily during *in situ* polymerization. This is because epoxy resin is hydrophobic and phenolic resin is hydrophilic. In addition, the synthesis of phenolic resin takes place in an aqueous solution in which Na⁺-clay particles can be readily exfoliated by water molecules.

From the results shown in Figure 9, it can be seen that the introduction of nanoclay shifts the T_g of phenolic resins to a considerably higher temperature. This, however, is not the case for epoxy systems. The T_g of phenolic resin rises from 207°C (for the pure phenolic resin) to 247°C (for the phenolic-5% clay nanocomposite). On the other hand, the T_g of the epoxy nanocomposites increases by less than 10°C with the same clay loading. This difference may be explained by the interactions between the polymer matrix and nanoclays. In general, the nanoclays in the epoxy system may cause an increase of

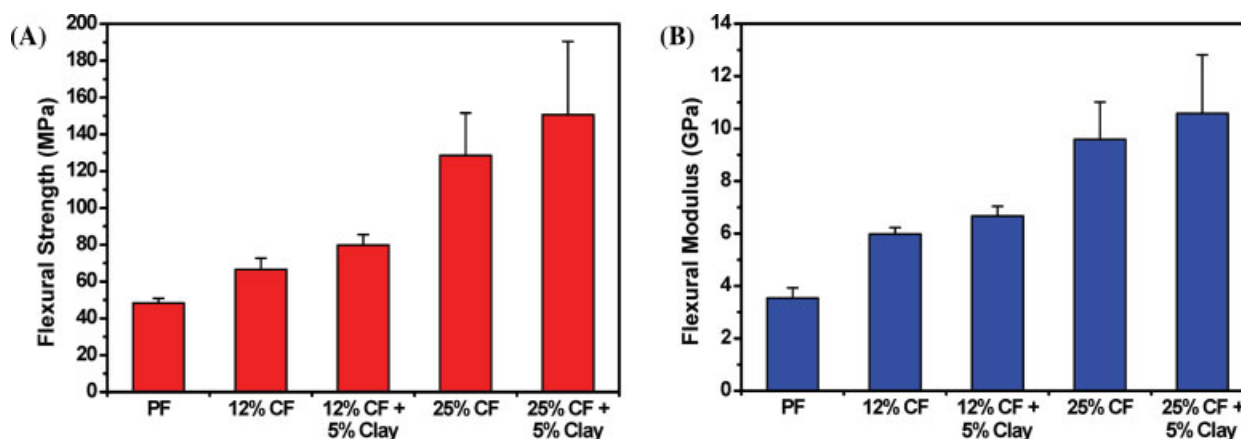


Figure 8 A: Flexure strength of phenolic-carbon fiber-Na⁺ clay composites at ambient temperature (25°C). B: Flexure modulus of phenolic-carbon fiber-Na⁺ clay composites at ambient temperature (25°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

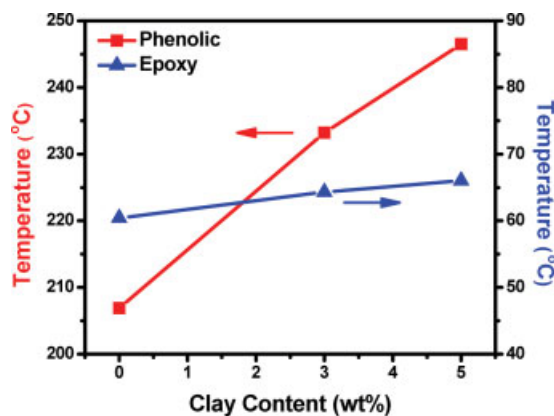


Figure 9 Dependence of glass transition temperature of phenolic and epoxy nanocomposites on the nanoclay loading. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

T_g because of the molecular interactions at the epoxy-clay interface, resulting in restricted motions of polymer segments near the organic-inorganic interface.^{7,17} It has been also found that the presence of nanoclays may decrease the crosslinking of epoxy resins.^{18,19} This would lead to higher free volume and longer soft segments in the polymer chains, resulting in a decline of T_g . The T_g of epoxy-clay nanocomposites is determined by the competition of these two factors. For phenolic resins, the dramatic increase of the T_g is due to the strong interfacial interaction between the silicate nanolayers and phenolic matrix, which reduces the molecular mobility of the matrix molecules. In addition, the structure of phenolic resin is quite different from that of epoxy resin. Every phenol ring can be a crosslinking site because it is a tri-functional molecule. Therefore, a large number of crosslinks exist in the phenolic resin, resulting in a rigid structure. Even though the presence of nanoclays may affect some crosslinks in the phenolic resin, there are still a lot of crosslinks left in the system. Consequently the T_g may not be affected significantly by a slight decrease of crosslinks.

CONCLUSIONS

A series of epoxy-clay and epoxy-clay-carbon fiber composites were prepared. Adding nanoclay into the epoxy resin can substantially improve the tensile strength and modulus of materials above the glass transition temperature. It also enhances the thermal

stability and lowers the water permeability when compared to the neat epoxy resin. The dispersion state of nanoclay in the polymer matrix is affected by the mixing sequence. Both intercalated and exfoliated nanocomposites can be obtained.

Phenolic-raw clay nanocomposites and phenolic-carbon fiber-raw clay hybrid composites were also prepared. Exfoliated nanocomposites were obtained by *in situ* polymerization. Adding nanoclay into the phenolic matrix can enhance the flexural properties and T_g substantially. This study examined a method for manufacturing multifunctional hybrid nanocomposites for various high end applications in the structural and aerospace industries.

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