# Thermoset-Layered Silicate Nanocomposites. Quaternary Ammonium Montmorillonite with Primary Diamine Cured Epoxies

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The role of various quaternary ammonium-modified montmorillonites in epoxy/diamine nanocomposite formation is examined to further refine the criteria for selection of organic modifiers necessary to enable fabrication of thermoset resins containing nanoscale dispersions of inorganic phases. Utilization of a hydroxyl-substituted quaternary ammonium modifier affords flexibility to combine both catalytic functionality, which increases the intragallery reaction rate, with enhanced miscibility toward both reagents. The rheological implications of these processing techniques are discussed with regards to using thermoset nanocomposites as a matrix in conventional fiber reinforced composites. The use of a low-boiling solvent to enhance mixability and processability of the initial mixtures is shown not to alter the structure or properties of the final nanocomposite. Also, the use of autoclave techniques enabled fabrication of high-quality specimens containing up to 20 wt % organically modified layered silicate (OLS). Finally, exfoliated and partially exfoliated epoxy/diamine nanocomposites were produced with enhanced heat-distortion temperature and increased flammability resistance.

## Introduction

Over the past decade, the utility of inorganic nanoparticles as additives to enhance polymer performance has been established.[1−9] Of particular interest are polymer layered silicate nanocomposites because of demonstrated improvements, relative to an unmodified resin, of a large number of physical properties, including mechanical (modulus, strength, thermal expansion coefficient),[1−5] barrier,[2−3] flammability resistance,[6] ablation performance,[7] environmental stability,[8] and solvent uptake.[9] These enhancements are all achieved with less than 4 vol % addition of a nanoscale dispersion (exfoliated) of 1 nm thick aluminosilicate layers with diameters between 20 and 500 nm. Thus, cost, clarity, and a degree of polymeric processability are maintained. This is in stark contrast to conventional polymer fillers, such as talc, mica, silica, and carbon black, which require high concentrations (>30 wt %) and thus incur processing difficulties, to provide a fraction of these enhancements.[10]

The enhanced modulus, decreased coefficient of thermal expansion, and potential rigid-phase toughening afford thermoset-layered silicate nanocomposites opportunities in polymer matrix composites (PMCs). The vast majority of thermoset-layered silicate research has focused on epoxy-based chemistries.[3,5,11,12] Aliphatic amine, aromatic amine, anhydride, and catalytic curing agents have been examined, yielding systems with a broad range of glass-transition temperatures. These studies indicate that a critical balance between the relative rate of reagent intercalation, chain formation, and network cross-linking must be maintained in order to achieve exfoliation before network formation and matrix gelation.[11] Critical is the ability to enhance intragallery polymerization rate catalytically to be comparable or greater than extragallery polymerization. For example, Wang and Pinnavaia proposed that the acidic primary ammonium ion acted as an intragallery catalyst for primary amine−epoxy polymerization, accounting for the ability to achieve exfoliated structures for primary ammonium-modified layered silicates and not for secondary, tertiary, or quaternary ammonium-modified layered silicates.[11] Not withstanding these accomplishments, many issues associated with the generality of synthetic approaches, choice of interlayer surfactant, processing, and control of morphology are still unresolved. For example, in multicomponent systems, functionality of the inorganic surface should not

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favor preferential segregation of one reagent but enhance miscibility in the interfacial region. Also, the competing factors of network gelation via cross-linking and layered silicate exfoliation lead to process-history-dependent, hierarchical morphologies containing mixed structures (both exfoliated, partially exfoliated, and intercalated layers), which for establishment of structure–property relationships, need to be characterized carefully.

This report examines the role of various quaternary ammonium surfactants in the epoxy/diamine nanocomposite formation as well as processing techniques, which are necessary in ultimately fabricating PMC with a nanocomposite matrix resin. In brief, utilization of a hydroxyl-substituted quaternary ammonium modifier affords flexibility to combine both catalytic functionality, which increases the intragallery reaction rate, and enhanced miscibility toward both components. Balancing these two factors is necessary to maintain rheological properties that are compatible with PMCs. Additionally, the use of low-boiling-point processing aids minimizes viscosity and advancement during mixing, enabling fabrication of exfoliated and partially exfoliated epoxy nancomposites containing up to 20 wt % layered silicate.

## Experimental Section

**Materials.** Organically modified layered silicates (OLS) utilized in this study are bis(2-hydroxy-ethyl)methyl tallow ammonium montmorillonite (S30A, Southern Clay Products, Inc.), dimethyl ditallow ammonium montmorillonite (B34, Rheox, Inc.), and dimethyl tallow benzylammonium montmorillonite (B24, Rheox, Inc.). The quaternary ammonium surfactants are derived from natural tallow, which contains a mixture of alkanes ($C_{18}/C_{16}/C_{14}$ of 0.66:0.31:0.03). These OLS represent the three general types of quaternary ammonium surfactants, relative to interactions with the matrix, currently commercially available: strong specific interactions (H-bonding, S30A), dipolar (aromatic, B24), and van der Waals (alkyl, B34). The OLSs were used as received with no additional purification steps. Commercial ion exchange processes often result in a small excess of ammonium surfactant. Soxlet extraction to remove this excess may lead to changes in behavior of the OLS, but extracted materials were not examined in this study.

Diamine cured epoxies were formed from Epon 828 ($M_w \sim 377$, Shell Chemical Co., low-molecular-weight diglycidyl ether of bisphenol A (DGEBA) monomer with $n = 0, 1, 2$ at 0.88, 0.10, 0.02) and polyoxyproplyene diamine (Jeffamine D2000 ($M_w \sim 2000$, $n \sim 33.1$), Jeffamine D400 ($M_w \sim 400$, $n \sim 5.6$), Huntsman Chemical Co.). Since OLS/epoxy/diamine form a three-component system, substantially different materials may result from the order of mixing of the starting materials, processing conditions, and cure temperatures. Iterations on the fabrication procedure are discussed in detail below. An example procedure follows. OLS was suspended, 3:1 by weight, in acetone, and an epoxy/acetone solution (3:1 by weight) was prepared. The epoxy solution was added to the OLS suspension and stirred for 30 min. Acetone was subsequently allowed to evaporate at ambient conditions and then vacuum-dried at 90 °C for 1 h to remove remaining acetone (verified by FTIR). Stoichiometric quantities of the diamine were added to the epoxy/OLS mixture at 75 °C via stirring. Plaques were cast in RTV rubber molds. A typical cure cycle consisted of 2 h at 75 °C followed by 2.5 h at 125 °C.

**Characterization.** Thermal data was obtained on a Thermal Instruments differential scanning calorimeter 2820 at 10 °C/min with nitrogen. Dynamic mechanical analysis from −150 to +100 °C was obtained in torsion rectangular mode on a Rheometrics RDS−II at 1 Hz and 0.1% strain. Samples were dried in a vacuum oven for 12 h at 50 °C prior to testing. Dynamic rheology data was obtained in a Rheometrics ARES and RAA in the linear strain region (1−2% strain) using 25 or 50 mm parallel plates with a forced-air oven equilibrated at experimental temperature prior to performing frequency sweeps.

Scanning electron microscopy (SEM) data was obtained on a R. J. Lee personal scanning electron microscope (PSEM). Samples were coated with a thin (1−5 nm) gold film prior to viewing to prevent charging. Transmission electron micrographs were obtained on microtomed and cryomicrotomed samples using a Reichert-Jung ultracut microtome equipped with a 45° diamond knife and mounted on 200 mesh copper grids. Bright-field transmission electron images were obtained using low-dose techniques[13] on a Phillips CM200 transmission electron microscope with a $LaB_6$ filament operating at 200 kV.

Wide-angle X-ray was performed with $\Theta-2\Theta$ Rigaku diffractometer (rotating anode, 45 kV, 40 mA, Cu K$\alpha$) with a scan speed of 2°/min on films cast on glass. The smallest source slits (0.5°) were used to minimize beam spread, decrease parasitic scatter from the sample holder, and enable lowest possible $2\theta$ resolution.

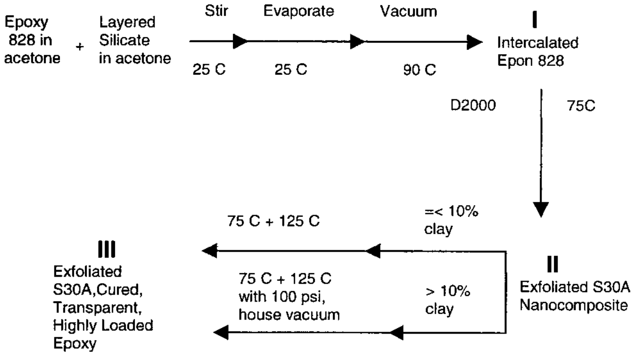

**Figure 1.** Generalized processing scheme.

**Table 1. Basal Spacing of OLS/Epon 828/D2000 Systems**

| | WAXD: basal reflections (nm) | | |
|---|---|---|---|
| OLS | I[a] | II[a] | III[a] |
| B34 | 3.40, 1.70 | 3.40, 1.70 | 3.68, 1.84 |
| B24 | 3.25, 1.64 | 3.40, 1.70 | 3.40, 1.73 |
| S30A | 3.16, 1.60 | exfoliated | exfoliated |

[a] I, II, III, see Figure 1. Basal reflections: $d_{001}$, $d_{002}$.

## Results

**Fabrication.** Initially, the effect of various processing steps on nanocomposite formation is examined. The generalized processing procedure is outlined in Figure 1. Relative dispersion of the OLSs at various stages during processing was determined by monitoring the position, breadth, and intensity of the basal reflections by wide-angle X-ray diffraction.[13] The results are summarized in Table 1.Multicomponent thermoset systems require preloading of the inorganic into one component or incorporation of the inorganic into the component mixture. High viscosity and component reactivity nominally inhibit incorporation of the inorganic into the component mixture. On the other hand, preloading requires excessive concentration of inorganic in one component, compounding processing difficulties. For example, since the weight ratio of Epon 828 to D2000 is 1:3, an initial silicate loading of greater than 30 wt % in the Epon 828 is necessary to yield a final nano-

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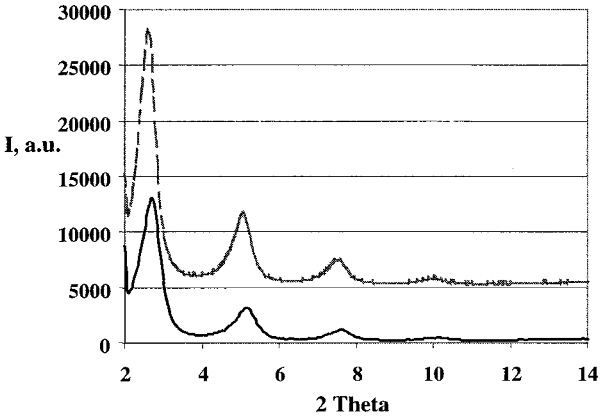

**Figure 2.** X-ray diffraction of Epon 828 intercalated into S30A through an acetone medium (top, dashed) or as a melt (bottom, solid).

composite with 10 wt % layered silicate. Similar preloading issues are encountered with fabrication of rubber-modified and thermoplastic-modified thermosets. Here, low-boiling-point solvents, such as acetone, are used to enhance mixability by lowering viscosity.

Comparable processing strategies were found to be amenable to the organically modified layered silicates. Premixing components with a low-boiling-point solvent created a low-viscosity medium in which intimate, homogeneous mixing of the components could be achieved at temperatures much lower than that at which reactions between reagents occur. For example, combining 90% Epon 828 and 10% S30A in acetone at room temperatures and subsequent removal of acetone by evaporation and vacuum stripping lead to intercalated systems comparable to those created by combining S30A directly with Epon 828 at 90 °C. Figure 2 shows the X-ray diffraction spectra of S30A/Epon 828 mixtures with and without use of acetone as a processing aid. These approaches were amenable to all of the OLS examined (Table 1). In contrast to neat processing, OLS/epoxy mixtures approaching 48% were possible using the solvent-assisted approach, leading to nanocomposites containing as much as 25% OLS. Most importantly, there was no observed change in curing reaction, morphology, or final mechanical properties. Note though that residual amounts of small molecule polar activators have been previously observed to modify OLS−polymer and OLS−solvent interactions, altering the swelling characteristics of the OLS.[9,14]

For all of the OLSs considered, only intercalation of DGEBA was observed, Table 1. The differences in the organic modification on the montmorillonite manifested upon the addition of the diamine to the OLS/epoxy mixture at 75 °C. B34/Epon 828 and B24/Epon 828 mixed easily with D2000 diamine at 75 °C and resulted in intercalated structures comparable to the original OLS/Epon828 structures. In contrast, the addition of the D2000 diamine at 75 °C to the S30A/Epon 828 mixture lead to a drastic viscosity increase and corresponding delamination of the OLS as indicated by the absence of basal reflections in X-ray diffraction.

Similar differences are observed if the diamine is combined directly with the OLS. B34/D2000 yielded an intercalated structure ($d_{00l}$ = 4.0, 2.0, 1.3 nm). In contrast, mixing S30A with D2000 results in a marked viscosity increase and a highly disordered morphology represented by a very weak, broad basal reflection centered around 2.0 nm (a gradually sloping low-angle background probably conceals the 001 reflection around 4.0 nm). The larger gallery spacing associated with the B34/D2000 intercalate relative to the initial B34/Epon828 intercalate or the B34/Epon828 intercalate with D2000 implies that in the latter system, reagent concentration in the interlayer is Epon828-rich. Once intercalated, Epon828 preferentially resides in the interlayer and is not displaced by the diamine, indicating the order of reagent addition is critical. In this instance, substantially greater intragallery reactivity is necessary to create a gradient to drive reagents from the exterior regions into the interlayer. The strong affinity of the diamine for the OLS, as in S30A, leads to layer separation, and thus a more uniform reagent mixture between the layers is anticipated.

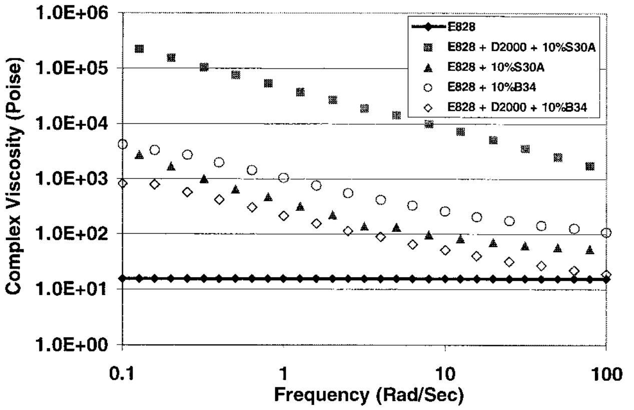

**Figure 3.** Complex viscosity of 10 wt % S30A and B34 in Epon 828 with and without diamine.

Complex viscosity measurements verify structural changes upon addition of the diamine. Figure 3 summaries the change in the complex viscosity during different stages of processing for Epon 828 and Epon 828/D2000 (1:3) mixtures at 40 °C containing 10 wt % B34 and S30A. Relative to the Newtonian response of the Epon 828 ($\eta_{\text{Epon 828,40C}} = 15$ P), the systems containing OLS exhibited classic shear-thinning behavior associated with particulate suspensions and weakly flocculated particulate gels.[15] For 10 wt % OLS in Epon 828, the relatively large increase in the low-shear-rate-plateau viscosity (approximately 100 times) is associated with the anisotropic nature of the intercalated OLS particulate (primary particles).[13,16] The lower viscosity of S30A reflects the smaller layer size, and thus primary particle and aggregate size, of the base montmorillonite used for the S30A relative to that used for B34. These size differences are documented in the microscopy discussed below.

Addition of the less-viscous D2000 ($\eta_{0,\text{D2000,40C}} = 1-2$ P) ostensibly lowers the medium's viscosity. This is observed for the Epon 828/D2000 mixture containing 10 wt % B34. The shear-rate dependence of the suspension viscosity is unchanged, indicating that the addition

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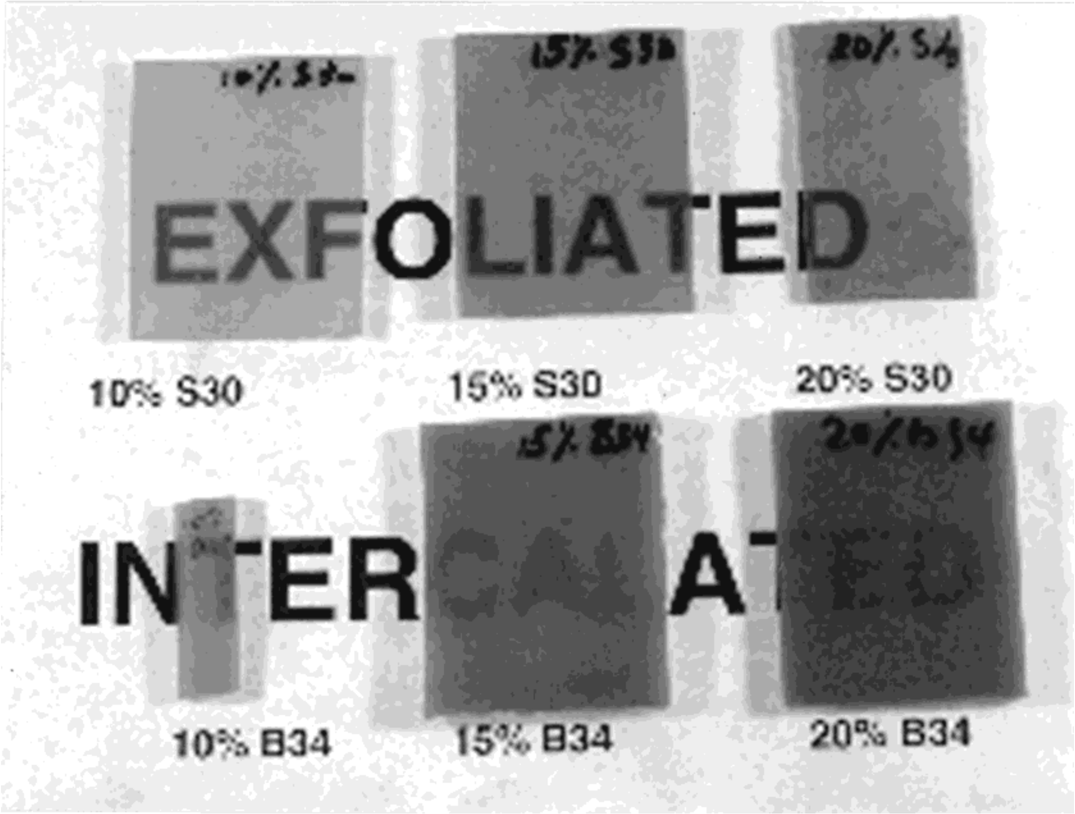

**Figure 4.** Optical image of 5 mm thick plaques of Epon 828/D400 containing 10, 15, and 20% (left-to-right) S30A or B34. Epon 828/D2000 plaques appear similar.

of D2000 did not effect the suspension of the intercalated B34 particles, but only altered the magnitude of the Newtonian response of the medium (now consisting of a 1:3 mixture of Epon 828/D2000). In contrast, addition of the D2000 to the S30A/Epon 828 mixture increases the viscosity by 2-orders of magnitude. Disruption of the intercalated S30A, resulting in an increased number density of higher aspect ratio particles, as well as possible increased OLS-medium interactions through direct amine−hydroxyl hydrogen bonding at the OLS surface increases the low-shear-rate-plateau viscosity, shifting it to lower frequencies (outside experimental range), as well as increasing the shear-rate dependence of the complex viscosity.[15]

Thermal cure (125 °C, 3 h) of the OLS/Epon 828 mixtures in which diamine was added did not alter the general distribution of the OLS, as determined by X-ray diffraction (Table 1:III). In the B34/Epon 828 and B24/Epon 828 systems, intragallery reactivity was not sufficient to delaminate the layers. This is in agreement with previous studies of quaternary modified montmorillonite.[3,5,11,12] Thermal cure of OLS/diamine mixtures in which Epon 828 was added resulted in turbid plaques with poor mechanical properties. For S30A, this is attributed to the difficulty in achieving uniform mixture of the viscous S30A/diamine exfoliate with Epon 828.

Autoclave processing (evacuated bag with 100 psi hydrostatic pressure) was useful in producing bubble-free, uniform plaques, especially for systems containing greater than 10 wt % OLS. Figure 4 shows optical micrographs of optically transparent plaques of autoclaved nanocomposites containing up to 20 wt % S30A in Epon 828/D400 resin and turbid plaques containing up to 20 wt % B34 in Epon 828/D400 resin.

Detailed transmission electron microscopy (TEM) verified the intercalated structure of B34-containing resins, Figure 5a,b. Individual layers, oriented perpendicular to the sample surface, appear as dark lines, with lateral size around 500 nm. Primary particles consisting of groupings of parallel layers are larger with large dimensions from 0.5 to 1.5 $\mu$m. Although the S30A nanocomposites were deemed exfoliated by X-ray diffraction and the plaques were optically clear, a mixture of partially intercalated as well as exfoliated layers exist, Figure 6a,b. The mesoscopic arrangement (10 nm and greater) is reminiscent of the original crystallites (stack of layers), indicating that the morphology of these "exfoliated" nanocomposites consist of hierarchical distribution of layers on numerous length scales.[17] Thus by TEM, the S30A systems are more properly described as containing a mixed morphology or as partially exfoliated where the descriptor exfoliated is reserved for systems in which the layer−layer distance is maximized and related to the volume fraction of OLS in the resin.[17] Note, because the base montmorillonite used for S30A is from a different mineralogical deposit than that used for B24 and B34, the lateral dimension of the aluminosilicate layer (100−200 nm) as well as the size of the primary particles (200−500 nm) is smaller.

**Properties.** Parts a and b of Figure 7 compares the temperature dependence of the dynamic shear moduli (1 Hz) from torsional bar measurements for unmodified

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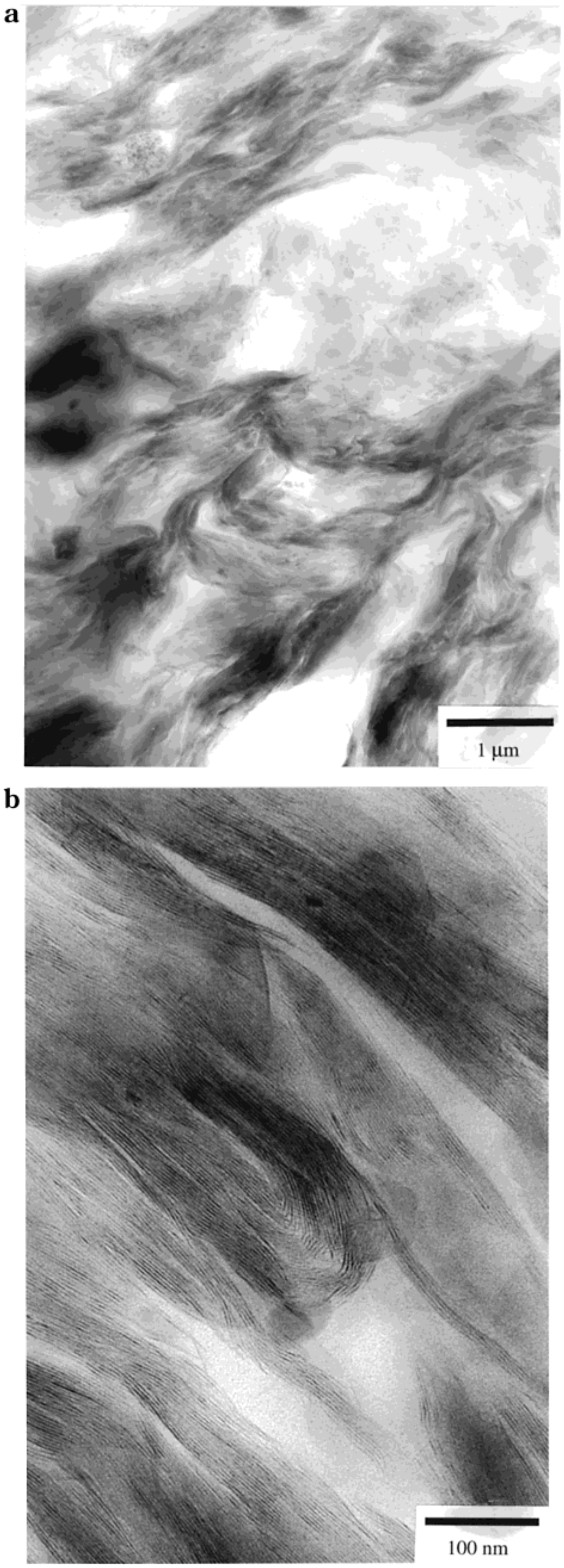

**Figure 5.** Bright-field transmission electron micrographs of 10% B34 in Epon 828 cured with D2000: (a) low magnification of large aggregate and (b) high magnification within aggregate.

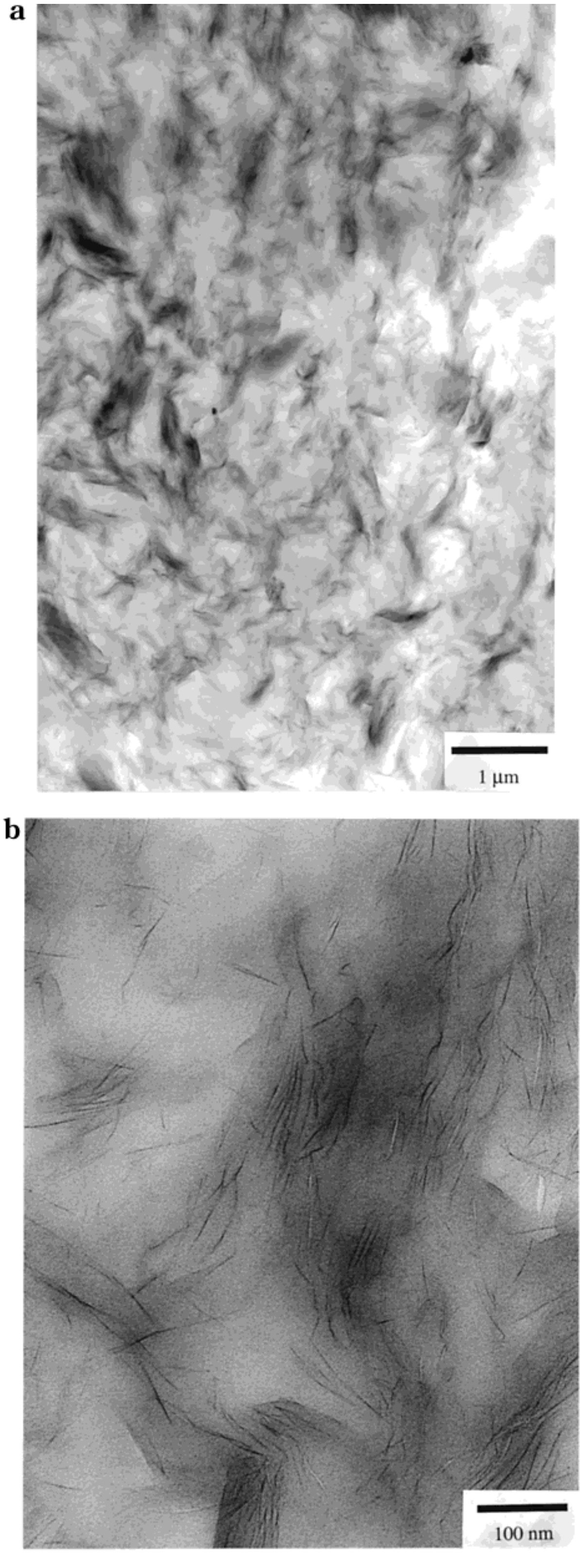

**Figure 6.** Bright-field transmission electron micrographs of 10% S30A in Epon 828 cured with D2000: (a) low and (b) high magnification.

Epon 828/D2000 with nanocomposites containing 10 wt % OLS. Parts a−d of Figure 8 compares the temperature dependence of the dynamic shear moduli at various concentrations of intercalated B34 and partially exfoliated S30A in Epon 828/D2000. Table 2 summarizes the glass-transition temperatures (temperature at tan $\delta_{max}$) and dynamic shear moduli at various temperatures.

Irrespective of the distribution of OLS, only a minor increase in $T_g$ (α-transition) is observed, which increase

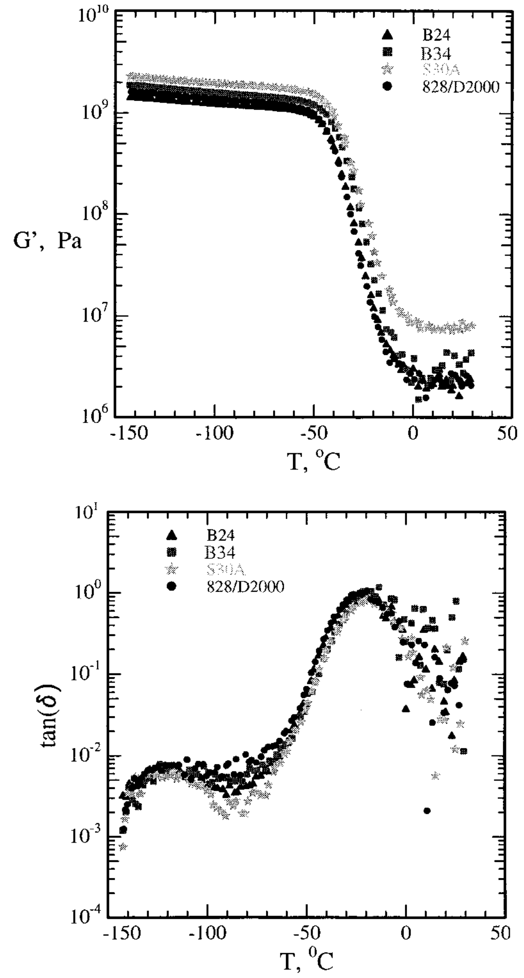

**Figure 7.** Temperature dependence of the (a) dynamic shear moduli and (b) tan(δ) from torsional bar measurements (0.1% strain, 1 Hz) for unmodified Epon 828/D2000 and nanocomposites containing 10 wt % OLS.

**Table 2. Dynamic Mechanical Summary for OLS/Epon828/D2000**

| | wt % OLS | $T_g$[a] | $G'$ (±25%) | | | |
|---|---|---|---|---|---|---|
| | | | −140 °C[b] | −60 °C[b] | −25 °C[c] | 0 °C[c] |
| 828/D2000 | | −24 | 1.6 | 1.1 | 31 | 2.4[d] |
| B34 | 2.5 | −18 | 1.7 | 1.3 | 35 | 1.2[d] |
| | 5.0 | −18 | 1.8 | 1.3 | 52 | 2.5[d] |
| | 10 | −18 | 1.9 | 1.4 | 80 | 3.1 |
| S30A | 2.5 | −18 | 1.7 | 1.3 | 90 | 2.5[d] |
| | 5.0 | −22 | 1.8 | 1.3 | 50 | 1.0[d] |
| | 10 | −15 | 2.3 | 1.7 | 120 | 8.0 |
| | 15 | −12 | 2.4 | 1.9 | 270 | 23 |
| B24 | 10 | −22 | 1.4 | 1.1 | 28 | 2.9[d] |

[a] Plus or minus 3 °C. [b] In GPa. [c] In MPa. [d] Lowest resolution for transducer ~1−2 MPa.

slightly in magnitude with increasing OLS content (e.g., $\Delta T \sim 10$ °C for 10 wt %). Moduli below $T_g$ (glassy region) increase slightly with increased OLS concentration and enhanced dispersion; quantification though is difficult since the changes are within the uncertainty associated with modulus determination via DMA (~50%). Interestingly, the $\gamma$-relaxation temperature of the matrix ($T_\gamma \sim -122$ °C), which is conventionally associated with local crankshaft motion within $(CH_2)_n$ segments,[18] is unaffected by the addition of the OLS. However, a decrease in the loss tangent between the $\gamma$- and $\alpha$-transitions (~ −85 °C) occurs with increased concentration of partially exfoliated S30A. A $\beta$-transition, attributed to the motion of flexible side chains (e.g., $-(CH_2-CH(OH)CH_2O)-$), is sometimes observed around −60 °C in these resin systems.[18] This solid-state relaxation mechanism is associated with stress relaxation processes and contributes to the toughness of the resin. The decrease in tan $\delta$ indicates that the presence of the exfoliated layers (and associated increase in internal interfacial area) modifies the network structure, effecting the relaxation mechanisms on a submonomer length scale, potentially decreasing resin toughness. Further investigations are necessary.

The dominant mechanical effect of OLS addition is observed in the modulus and distribution of relaxation (tan($\delta$)) around and above $T_g$. Intercalated morphologies (B34 and B24) results in a small enhancement in shear modulus around $T_g$, however precipitous decay, similar to the unmodified resin, is observed with increased temperature. In contrast, increased exfoliation of the layered silicate results in enhanced shear modulus around $T_g$ as well as above $T_g$. This results in an increased heat-distortion temperature and substantially stiffer elastomer at room temperature.

The mechanical properties of various Epon828/diamine nanocomposites have previously been reported. However, different mechanical characterization techniques (room-temperature tensile testing (modulus, strength, and strain to break[5,11,19]) and dynamical mechanical testing (3-point bend,[12,20] tensile,[3] and torsional)) and uncertainty in the global orientation of the layered silicate reinforcement in the test specimens makes qualitative comparison of results difficult. In general, the modulus of unfilled resin is approximately 1−3 GPa below $T_g$ and 1−3 MPa above $T_g$. Previous room temperature (~25 °C) tensile testing by Pinnavaia et al.[5,11,18] of nanocomposite Epon 828/D2000 indicated a 4−5-fold increase in rubbery modulus with the addition of 10 wt % montmorillonite ($E_{0\ \mathrm{wt\ \%}} = 2.5-3$ MPa; $E_{10\ \mathrm{wt\ \%}} = 13-14$ MPa) in agreement with observations herein. Comparable increases in the rubbery region have been reported for other DGEBA diamine cured nanocomposites.[3,12] Modulus enhancement in the glass region ($T < T_g$) is generally much less, only 1.25−2.0-fold for 5−10 wt % loading.[3,12] Subambient mechanical response of rubbery matrixes containing dispersed layered silicates has not previously been reported.

Incorporation of the layered silicate into the epoxy resulted in enhanced flammability[6] and ablation resistance.[7] By use of an open flame, unmodified Epon 828/D2000 burns, leaving an oily, tacky residue. In contrast, resin containing intercalated B34 burns but produces a rigid graphitic char. However, increased exfoliation of the layers, as in the S30A-containing resins, resulted in a self-extinguishing behavior upon removal of the flame. Additionally, the resulting char exhibited a highly uniform microcellular microstructure consisting of 10−20 $\mu$m diameter cells separated by 1−2 $\mu$m struts

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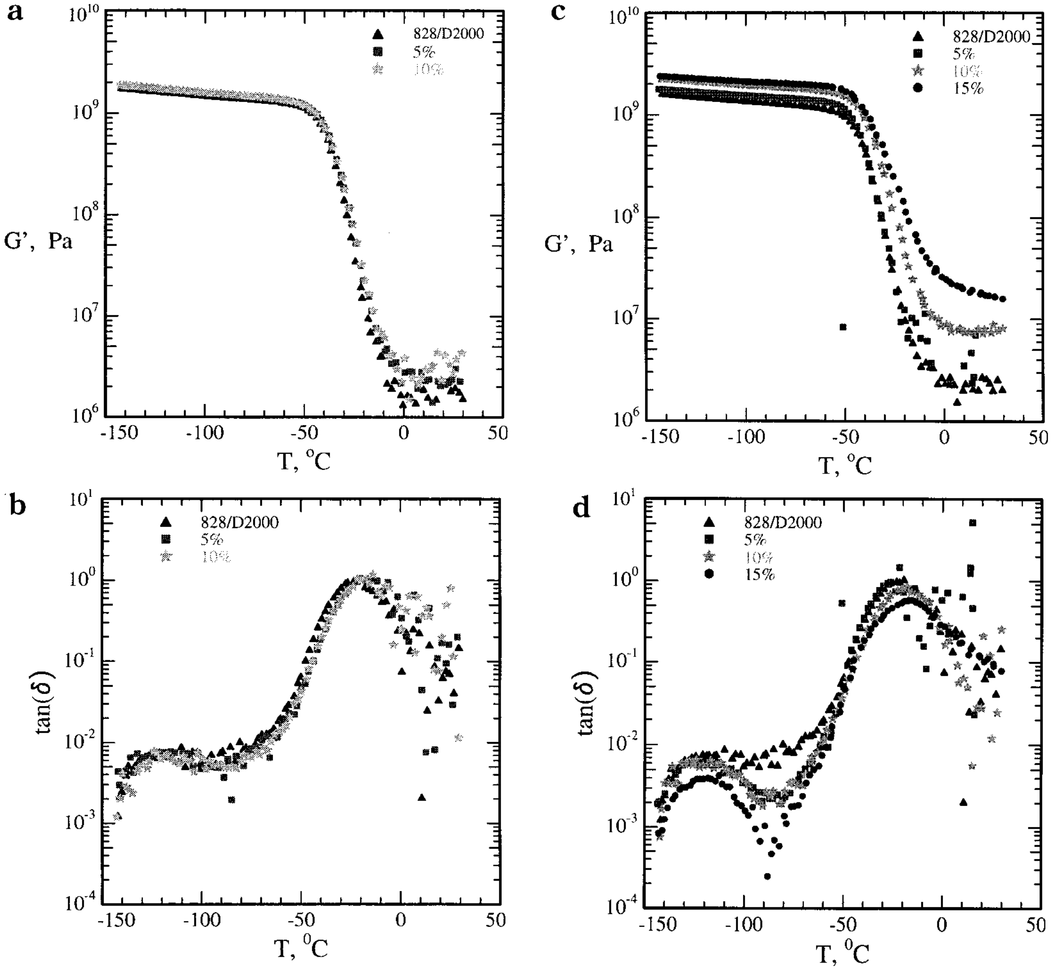

**Figure 8.** Temperature dependence of the dynamic shear moduli and tan(δ) from torsional bar measurements (0.1% strain, 1 Hz) for various concentrations of (a), (b) intercalated B34 and (c), (d) partially exfoliated S30A in Epon 828/D2000.

of silica−alumina−oxycarbide (Figure 9) as determined by microprobe analysis. This cellular structure is reminiscent of the original hierarchical distribution of inorganic in the nanocomposite (Figures 6). Removal of the organic and subsequent retention of the original hierarchical structure of the layered silicate may yield new routes to structured ceramics foams produced from calcination or graphitization of exfoliated layered silicate polymer nanocomposites.

## Discussion

For multicomponent thermoset systems, a balance between the rate of layer separation and network formation must be considered in fabricating exfoliated nanocomposites. At the gel point associated with network formation of the epoxy matrix, the distribution of the inorganic phase will be frozen. Two alternative processes for dispersion of the OLS exist. First, uniform dispersion may be achieved before the network-forming reaction. This, however, results in unwanted viscosity increases and processing difficulties of the unreacted system. Alternatively, dispersion may occur coincident with network formation. In this case, layer separation must occur at a sufficiently rapid rate that the desired distribution is achieved before complete network formation. This approach requires an enhanced reaction rate between the layers relative to that in the bulk. Thus the organic surface modifiers need to combine both catalytic functionality to increase the intragallery reaction rate and enhanced miscibility toward both components to ensure stoichiometric ratio of reactants between the layers.

The differences in B34, B24, and S30A indicate that the hydroxy-ethyl pendant of the S30A acts to decrease the overall organophilicity of the interlayer and thus enhance the compatibility with the diamine. This manifests in an increase in viscosity and lack of basal reflections. Specific amine-hydroxyl association has been observed using FTIR for urea, amides, and amines intercalated into kaolinite.[21−23] In contrast, the all-aliphatic B34 organic modifier and the aromatic/aliphatic B24 modifiers do not sufficiently modify interlayer interactions to enable miscibility to both components as indicated by intercalated structures for epoxy and diamine. Note that although the base montmorillonite for these OLSs differ in lateral dimensions, previous efforts in melt processing,[24] rheological additives,[14,25] and thermoset nanocomposite synthesis[24] indicate that the dominate influence of exfoliation

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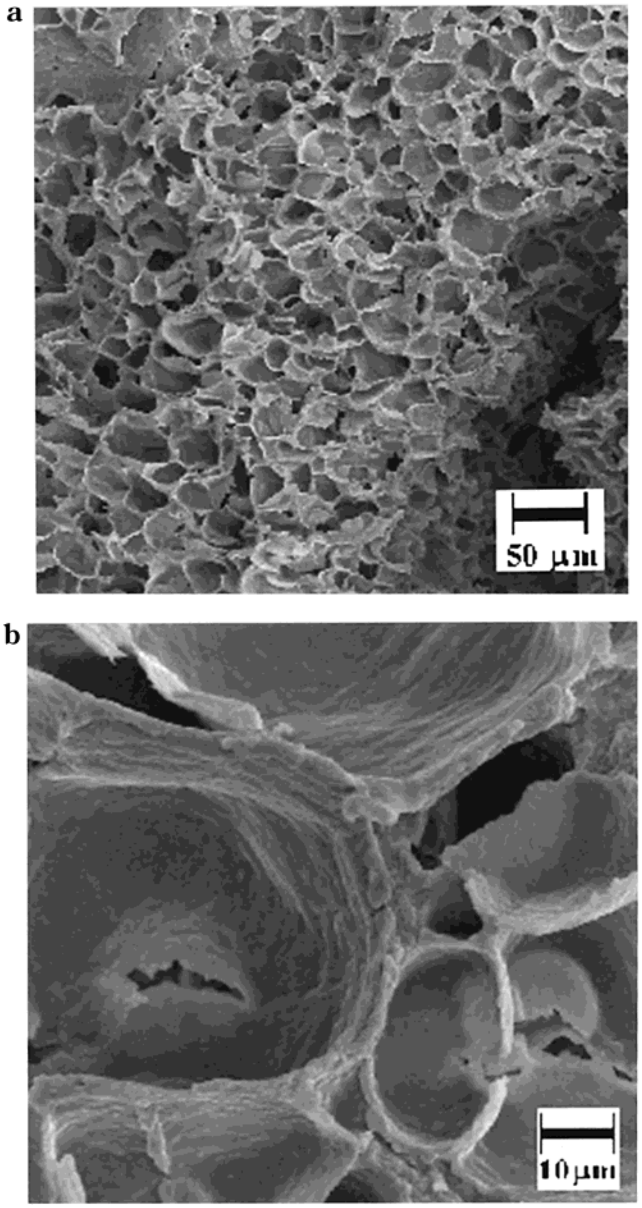
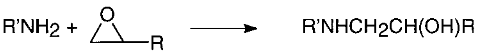


**Figure 9.** Scanning electron micrograph of char produced by burning 10% S30A/Epon 828/D2000 in air.

behavior for system of this general size and type is the surface modifiers.

In addition to the increased miscibility, the hydroxyl (once available) on the S30A surface is expected to catalyze network formation between the epoxy and diamine, thus enhancing the intralayer reaction rate. The cure of epoxies with primary diamines and the catalytic effects of hydroxyl containing materials on the reaction rate have been well-documented in the literature.[18] Generalized epoxide reaction with a diamine, resulting in chain extension, is



(1)

(2)

The hydroxyls produced in the epoxy/amine reaction are *autocatalytic* to the epoxy/amine reaction, increasing the rate substantially. This effect is observed by the addition of water or alcohol to the reaction.[18] Proposed mechanisms for this rate increase include hydrogen bonding of the epoxy to the alcohol in the transition state, hydrogen transfer from the donor to the epoxy, or hydrogen bonding of both the epoxy and the amine. Whatever the mechanism, considerable interaction of the hydroxyl containing material with the reactants accelerates the epoxy/diamine cure.

**Table 3. DSC Data for Epon828/D2000/OLS Mixtures**

| variation | $T_{onset}$ (°C) | $T_{max}$ (°C) | $\Delta H_{rxn}$ (cal/g) |
|---|---|---|---|
| Epon 828 Homopolymerization (no diamine) | | | |
| neat Epon 828 | 265 | 340 | *a* |
| 10% B34 | 316 | 329 | *a* |
| 10% S30A | 304 | 315 | 56[b] |
| Epon 828 with D2000 | | | |
| cold mix | 132 | 190 | 29 |
| 75 °C mix | 128 | 188 | 25 |
| 10% B34 | 125 | 190 | 21 |
| 10% S30A | 98 | 166 | 16 |

[a] Difficult to integrate due to homopolymerization and degradation at same time. [b] Sharp, crisp, homopolymerization peak.

Table 3 summarizes differential thermal calorimetry (DSC, 10 °C/min) of the curing reaction in the absence and presence of B34 and S30A. The onset of the primarily reaction between a stoichiometric mixture (1:3) of Epon 828 and D2000 mixed at room temperature is approximately 131 °C with a maximum at 189 °C. Combining the epoxy and the diamine at 75 °C slightly lowers the onset temperature and heat of reaction, indicating that partial reaction occurs during the hot mixing. When the epoxy is initially combined with B34, and the amine is added at 75 °C, only minor changes in the cure reaction is observed ($\Delta H$ normalized to inorganic content is ~23 cal/g). The slight decrease may be attributable to inconsistencies in temperature and time of the 75 °C mixing or a minor catalytic effect of the acid hydrogens (Si−OH and Al−OH) on the montmorillonite edge.

In contrast, more substantial effects are observed when the mixture contains 10% exfoliated S30A. The onset decreases by 30 °C, raising the possibility that substantial chain extension may occur during the 70−75 °C mixing step. Since the epoxy is initially intercalated into S30A, the epoxide is associated with the internal hydroxyls, enabling a catalytic effect in accord with the anticipated mechanisms mentioned above. A intralayer/near-surface reaction faster than that which occurs in the bulk is anticipated. Since the layer order is sufficiently disrupted during addition of the diamine to suppress basal reflections in WAXD, further small-angle scattering studies are necessary to evaluate additional morphological changes during curing.

In addition to catalyzing chain extension, hydroxyls are also capable of reacting with the oxirane ring. This effect was utilized by Messersmith et al. to tether the epoxy network to the silicate surface using an aromatic amine catalyst (benzyldimethyl amine) to not only catalyze homopolymerization of DGEBA but also catalyze the reaction between surfactant hydroxyl groups and the oxirane rings[3]. However, unless a catalyst is present, this etherification reaction does not occur until 225–275 °C.[18] Additionally, homopolymerization of Epon 828 (potentially along with degradation) occurs above 265 °C. Table 3 summarizes additional DSC data that indicates that these higher temperature reactions are also modified by S30A. Little change is observed between homopolymerization of Epon 828 and 10 wt % addition of B34 to Epon 828. However upon addition of 10% S30A, the exothermic peak associated with this higher temperature reaction sharpens. The presence of the bis(2-hydroxy-ethyl)methyl tallow ammonium surfactants on the external surfaces of the aggregates, degradation products of bis(2-hydroxy-ethyl)methyl tallow at $T > 200$ °C,[26] or the increased concentration of acidic hydrogens on the layer edges arising from the smaller primary particle size is sufficient to alter the curing chemistry. Note though that for the reaction temperatures used in this study (up to 125 °C), only the catalytic effect of the hydroxyls in the S30A on the epoxy/diamine chain extension reaction occurs, and participation in homopolymerization is not anticipated.

These results, along with the viscosity and X-ray, indicate that the bis(2-hydroxy-ethyl)methyl tallow surfactant serves two roles: (1) to compatibilize the diamine/epoxy mixture resulting in exfoliation of the montmorillonite and concomitant exposure of the surface hydroxyls to a uniform mixture of reactants, and (2) to catalyze the epoxy/diamine reaction. Similar catalytic behavior attributed to the presence of an exposed surfactant has been previously discussed for other thermoset nanocomposite systems. Pinnavaia and co-workers attributed the ability to achieve exfoliated systems with alkyl primary ammonium-modified montmorillonite and the inability to achieve similar results with alkyl quaternary ammonium-modified montmorillonite with the availability of hydrogens on the ammonium group to enhance the intragallery reaction rate.[11] Extending these previous studies to a general methodology of incorporating a catalyst for thermoset formation directly into the surfactant, as demonstrated here, provides new flexibility to achieve high-performance thermoset nanocomposites. These concepts parallel recent efforts to developed surface-initiated polymerization of thermoplastics by tethering initiation groups to colloidal particles.[27,28]

## Conclusions

Exfoliated and partially exfoliated epoxy/diamine nanocomposites can be produced utilizing a hydroxyl-substituted quaternary ammonium-modified layered silicate. The organic modifier serves as a compatibilizer for the monomers as well as act as a catalyst for the epoxy/diamine cure. Furthermore, the use of a low-boiling solvent to enhance mixability and processability of the initial OLS/epoxy mixtures does not alter the structure or properties of the final nanocomposite. Finally, the use of autoclave techniques enabled fabrication high-quality specimens containing up to 20 wt % OLS.

In general, this study and others indicate that surface modifiers should include a catalyst to enhance reactivity within the OLS crystallites. However, a critical balance must be maintained for use with PMCs. If miscibility between the OLS and thermoset mixture is great, unacceptably large viscosity increases and potential gelation of the system will occur though impingement of exfoliated sheets. On the other hand, if miscibility toward both components is insufficient, a nonstoichiometric mixture of reagents will be present in the interlayer and enhanced interlayer reactivity will not produce the desired network formation. Thus, optimal methodology for multicomponent thermosets would entail a choice of an OLS modification that (1) partially compatibilizes the mixture leading to a disordered intercalate containing both components and separation of the OLS aggregates into individual crystallites (slight viscosity increase) and (2) catalyzes interlayer reactivity to enable rapid layer separation before matrix gelation. The use of smaller lateral dimensions of the aluminosilicate layer should decrease mass transport of reagents from the medium into the interlayer, further enhancing the ability to exfoliate layers as well as decreasing viscosity. Overall, this further refines the criteria for organic modifiers necessary to fabricate blends of nanoscopic inorganic phases and ultrahigh performance resins.

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