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Chemorheology and properties of epoxy/layered silicate nanocomposites

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Abstract

The effect of the organoclay nanoparticles on the rheology and development of the morphology and properties for epoxy/organoclay nanocomposites has been studied. The interlayer spacing increases with the temperature of cure resulting in intercalated morphologies with varying degrees of interlayer expansion, depending on the cure temperature used. Rheological studies of the curing process indicate that intergallery diffusion before curing is essential for exfoliation, before the morphology is frozen in by gelation and vitrification. The maximum increase in modulus was observed for the 2 wt% clay loading. Viscoelastic behavior and mechanical properties of the cured samples were correlated with the morphological and rheological study.
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1. Introduction

Nanocomposites based on organically modified layered silicates represent an area of research which has shown explosive growth in the past decade [1–7]. This has been due in large part to the potential to achieve property enhancements significantly greater than that attainable using conventional fillers or polymer blends. Polymer/layered silicates typically are defined with respect to the state of dispersion of the silicate layers within the polymer matrix. For example, when the polymer chains are ordered between the silicate layers, the morphology of the system is referred to as intercalated, and an exfoliated morphology results when layers are highly separated and are well dispersed and usually disordered within the polymer. It is more common that layered silicate nanocomposites exhibit combinations of these two morphologies. While thermoplastic polymer nanocomposites have been studied extensively, thermoset polymer nanocomposites are beginning to receive considerable attention as well [8–25]. For both systems, the precise mechanism(s) by which the property enhancements reported are achieved remains a matter of ongoing debate.

The ability to process thermoset nanocomposites into useful forms depends upon the ability to control the interplay of the thermoset composition (e.g. resin, curing agent, catalyst, nanoparticles, etc.) and its effect on the state of cure (cure kinetics, crosslink density) and the morphology development. (int. vs. ex; partitioning; heterogeneity) [16]. These issues are also dependent upon processing variables such as method of dispersal and cure temperature. Thus, understanding and controlling the various factors that govern the synthesis of exfoliated thermoset/layered silicate nanocomposites is rather complex. Several researchers have recently made contributions to understanding some of these issues [16,18–21]. Lan et al. have reported that balancing the intra- and extragallery polymerization rates is a key to obtaining exfoliated thermoset/layered silicate nanocomposites [16,18]. This has been determined to depend on several other factors, including the polarity difference between the polymer and the silicate surface, the cationic exchange capacity, as well as the length of the organic modifier used [22,23]. Interestingly, preaging an intercalated epoxy/layered silicate pepolymer mixture before curing has been shown to result in exfoliated nanocomposites and enhancement in toughness [23].

In our laboratory, we have developed a series of layered

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silicate/thermoset nanocomposites using several thermoset polymers (di- and tetra-functional epoxies, cyanate esters and PMR-type polyimides) and studied the effect of the nanoparticles on the rheology, morphology development and properties. For many of the systems we have studied, significant improvements in mechanical and thermal properties have been achieved. For example, enhancements of ca. 30% in modulus, 10% in strength and 25° increase in T_g have been observed in the best cases [8,16].

For the cyanate esters in particular, controlling the final morphology has been found to depend on the rate of intergallery diffusion of the prepolymer and subsequent gelation and vitrification, as well as the intra and extragallery cure kinetics [21]. This leads to morphological heterogeneity in the systems, however the effect on the crosslink topology is still unclear. These effects seem to arise from catalysis of the curing reaction by the clays (as shown by gel times and cure kinetics). Time–temperature transformation diagrams were developed to assist in developing a phenomenological model of the effect of silicate particles on curing behavior. In this study, we present recent studies on the effect of organically modified layered silicates on the cure behavior, morphology development and properties of epoxy resin nanocomposite. In particular, we have utilized rheological methods to examine and extend our study beyond the cyanates reported on in a previous study [21].

2. Experimental

Epon 828 Epoxy resin and EpicureW curing agent were kindly supplied by Shell Chemical Company. The resin and curing agent were mixed in the ratio of 5:1 as suggested by the manufacturer. Nanocomposites were prepared by heating the epoxy resin to 60 °C using a hot plate. The appropriate weight percentage of the clay, Cloisite 30-B, montmorillonite clay organically modified with a ternary ammonium salt (Southern Clay Co.) was added, followed by stirring with a magnetic stir bar for 30 min. The curing agent was heated to 60 °C in a separate beaker and added to the resin/clay dispersed mixture. The nanodispersed prepolymer was stirred at 60 °C for an additional 30 min. The sample was poured into Teflon molds, and degassed under vacuum for 40 min, followed by curing in an oven at temperatures ranging from 120 to 170 °C for 2 h.

Rheological experiments of the uncured samples were conducted on an AR 2000 rheometer, (TA Instruments Inc., Delaware) using the parallel plate mode. A strain of 1% was used. The glass transition temperatures (T_g), storage modulus and loss modulus values for cured samples were obtained using the AR 2000 in the torsion rectangular mode. A frequency of 1 Hz, strain of 0.10% and a scan rate of 3 °C/min was used. Multiple scans were conducted to ensure reproducibility. Wide-angle X-ray scattering (WAXS) measurements were performed using a Rigaku D/MAX-

2200 diffractometer with Cu K$_\alpha$ ($\lambda = 1.54$ Å) radiation. An accelerating voltage of 40 kV/30 mA was maintained. The scanning speed was 1.0°/min. Small angle X-ray scattering (SAXS) studies were conducted using a Rigaku RU200 rotating anode generator with an accelerating voltage of 40 kV/30 mA. The data was collected on phosphor image plates at a sample-to-film distance of 40 cm. The data was digitized using a Molecular Dynamics scanner. Flexural properties were measured using an RSI Mimimat materials tester. The tests were performed in the 3-point bending mode using crosshead speed of 0.5 mm/min using a span-to-depth ratio of 7:1.

3. Results and discussion

3.1. Morphological characterization

Fig. 1 shows the X-ray scans as a function of clay loading for the pure organically modified silicate clay, Cloisite 30-B and the nanocomposites cured at 150 °C. The Cloisite 30-B shows a single, intense reflection at ca. 4.7° 2θ. The sample containing 2% clays exhibits no visible peak, suggestive of complete loss of order [1–3]. The samples containing higher clay loadings are highly disordered as shown by the significant loss of intensity and broadening of the peak due to the basal spacing of the silicate.

The d-spacing associated with this peak is 18.5 Å, and corresponds to the interlayer or intergallery spacing of the silicate. Diffusion of the prepolymer into the layers and subsequent curing results in expansion of the layers and a loss of order to varying degrees, depending on the cure temperature. These changes are manifested by shifting of the peaks to lower angles and an increase in the peak width.

The intergallery spacings for the samples cured at 150 and 170 °C were correlated with spacings measured by SAXS. These spacings, as well as those for samples cured at other temperatures, are displayed in Fig. 2. The d-spacing for the pure clay which is not shown on the graph, is 18.5 Å;
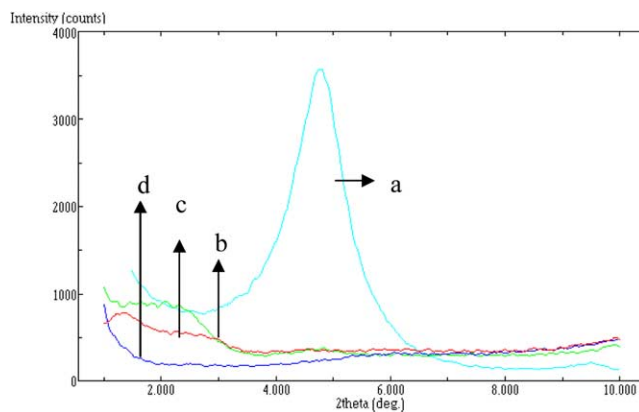

Fig. 1. Comparison of XRD scans for (a) modified silicate (Cloisite 30B) and epoxy/silicate nanocomposites containing (b) 6%, (c) 4% and (d) 2% silicate, respectively. The samples were cured at 150 °C.
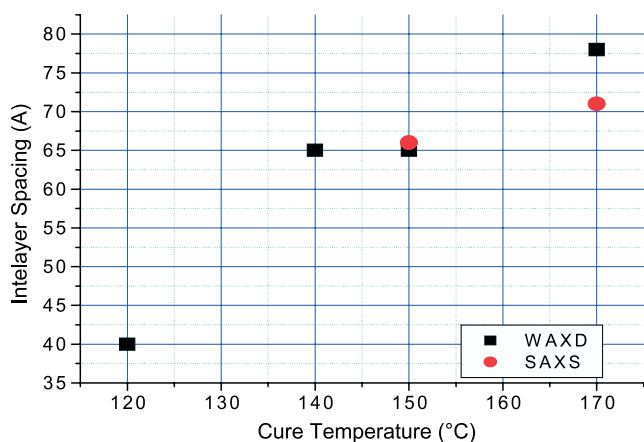
Fig. 2. Effect of cure temperature on the intergallery spacing for epoxy resin/silicate nanocomposite. The weight percentage of clay is 4%.

this spacing increases to 29 Å, when the clay is swelled with uncured epoxy resin. Wang and Pinnavaia showed that heating pure DGEBA epoxy resin in the presence of clay, without curing agent, results in homopolymerization of polyether nanocomposites [6]. They found that the protonated primary amine cations on the exchanged sites of the montmorillonites acted primarily as acid catalysts rather than as curing agents. Our interest is in thermoset systems and the effect of the silicates on their cure behavior. We examined the d-spacings for the epoxy-curing agent-silicate systems as a function of cure temperature. The d-spacing increases to 40 Å for the 120 °C cure, followed by an expansion to 65 Å, which remains constant from 140 to 150 °C, followed by further expansion to 78 Å when cured at 170 °C.

Thus, increasing the cure temperature increases the interlayer spacing [8,10]. All of the samples exhibit an intercalated morphology, although the higher cure temperatures result in significant interlayer expansion. Interlayer diffusion and subsequent curing and delamination require that the viscosity be sufficiently low. The cure temperature of 120 °C is presumably too low to allow sufficient mass diffusion into the layers before gelation and vitrification locks in the morphology [16,18,21]. This may also be coupled with bridging of the silicate layers caused by reactions at their edges [7]. On the other hand, at the higher temperatures, the combination of a lower prepolymer viscosity and faster intergallery curing are sufficient to yield more significant expansion of the layers.

3.2. Rheological characterization

Rheological characterization of the curing process was undertaken to corroborate the morphological findings. While thermoset based nanocomposites hold much promise for a range of applications including electronics, aerospace and recreation industries, they also have some unique attributes, which makes a study of their process–property

relationships highly relevant. The ability to process these materials will depend on the ability to control the interplay of the thermoset composition (resin, curing agent, catalyst (if any), nanoparticles, etc.) and its effect on the state of cure (cure kinetics, crosslink density) and the morphology development (int. vs. ex; partitioning; heterogeneity) of the dispersed nanoparticles. All of this has to be accomplished within the time frame of the resin gelation and vitrification. Once the sample has cured past this point, the morphology will be essentially locked in by the crosslinked structure [16,18,21]. Thermoset polymers are usually cured using isothermal cure cycles. Several studies have investigated the effect of isothermal curing on the intergallery spacings of similar epoxy/layered silicate nanocomposites using X-ray diffraction and have shown that, once the clay is swelled with the epoxy-curing agent prepolymer, no further expansion occurs until the temperature of cure is increased to the onset of cure [15,19,20–23]. In other words, after mixing, the curing process is responsible for intergallery expansion. Correlation of the chemorheology (viscosity, gelation, vitrification and activation energies) of these systems with morphological studies discussed in Section 3.1 provides insight into the morphology development process which is the goal of this study.

Representative isothermal (150 °C) cure plots for uncured nanocomposites with varying amounts of clay are shown in Fig. 3. The scattered data of the neat resin relative to the nanocomposites may be due to its very low initial viscosity at this temperature. The general shape of the curves, which show the storage modulus versus time, show a gradual increase in the modulus, followed by a rapid increase at gelation and a leveling as vitrification occurs.

The viscosity values at 100 s are 7, 50, 80 and 130 P for the neat resin, 2, 4 and 6% clay loadings, respectively. In an earlier study, we showed that the addition of silicates changed the flow behavior of cyanate ester prepolymers from Newtonian to psuedoplastic [18]. The gelation and vitrification regions correspond to regions of steady state interlayer expansion and the cessation of interlayer expansion, respectively as defined by X-ray diffraction studies by Chen et al. [15]. This correlation is reasonable, because extensive interlayer expansion will have to occur before the onset of gelation and vitrification. Intergallery expansion ceases in the vitrification region, presumably because the modulus of the extragallery polymer, G'_{ex} becomes equal to or greater than that of the intragallery polymer, G'_{intra}.

The effect of the silicates on the gel times can be seen more clearly by plotting the storage (G') and loss moduli (G'') as a function of time at 150 °C for the nanocomposite with 4% clay, as shown in Fig. 4. This plot is representative of the other silicate loadings. The G'/G'' crossover is taken as the gel points for these systems and is displayed as a function of silicate loadings, in Fig. 5 [21]. The catalytic effect by the clays is manifested as a decrease in gel times with clay loadings, as well as an increase in the slopes of the curves in the region before gelation. Presumably, during the
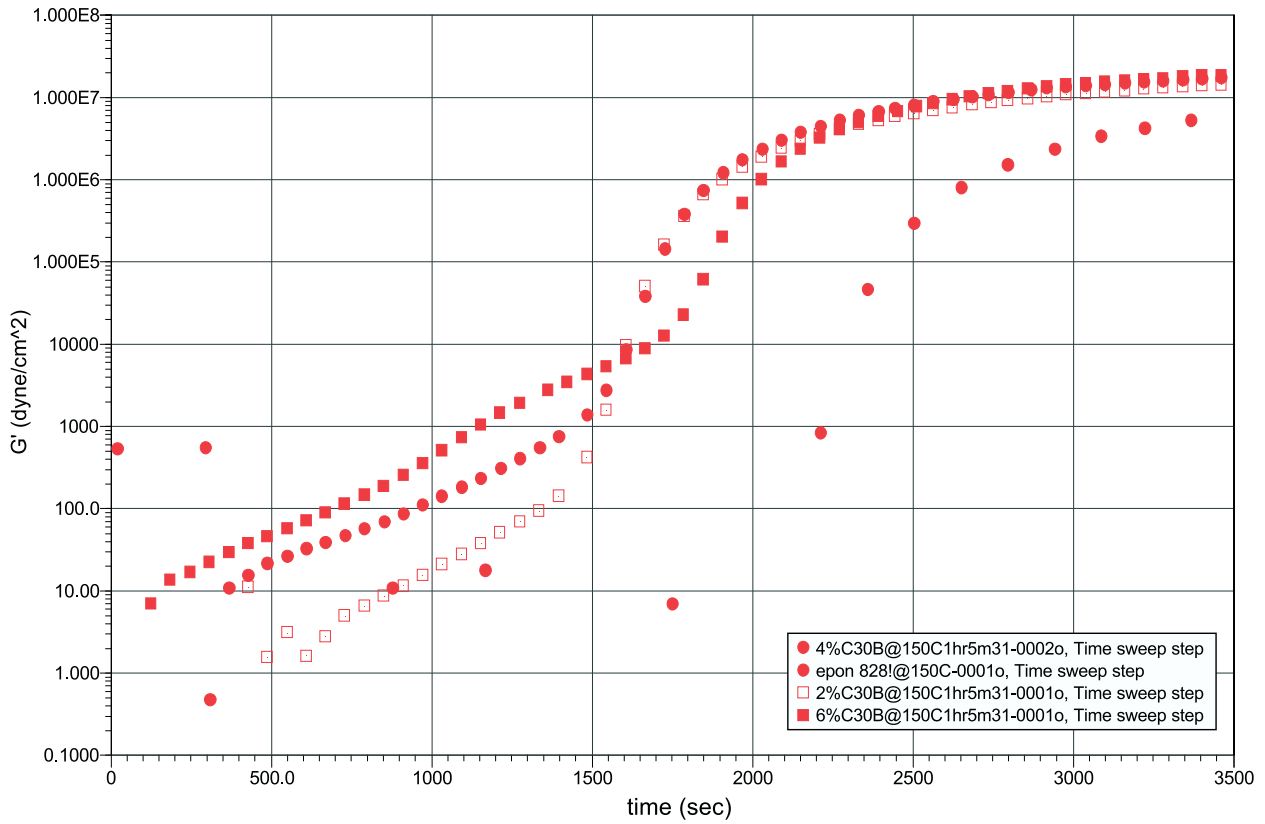
Fig. 3. Effect of clay loading on gel times at 150 °C for epoxy nanocomposites (closed circles—neat resins; open squares—2%; dark circles—4%; dark squares—6%).
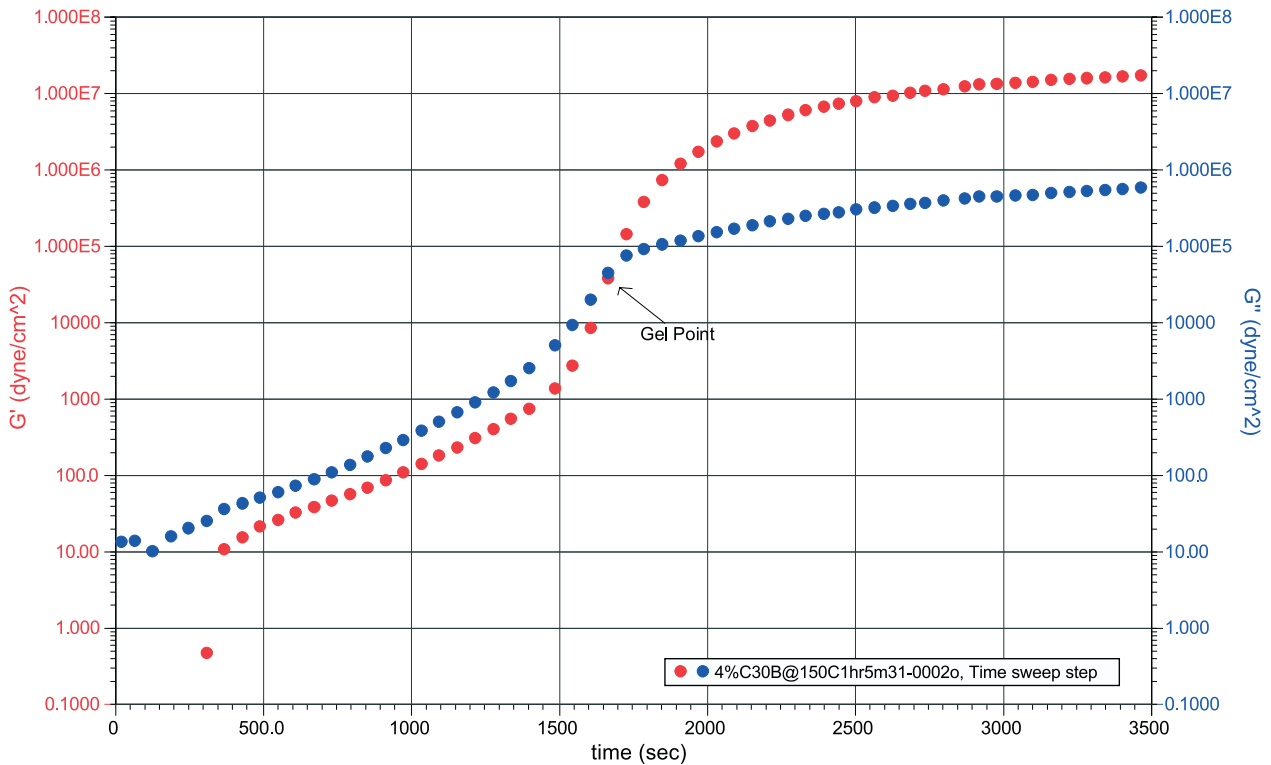

Fig. 4. Storage (*G'*) and loss moduli (*G''*) as a function of cure time at 150 °C for the nanocomposite with 4% clay.
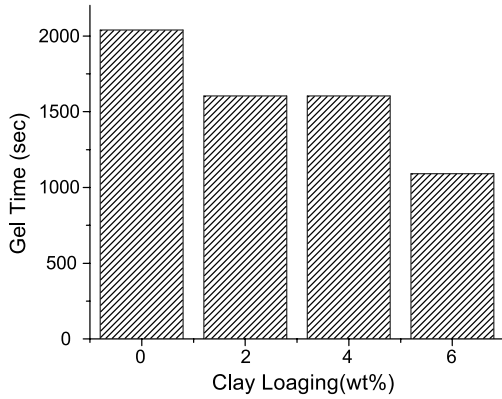
Fig. 5. Gel times versus clay loadings for epoxy/silicate nanocomposites cured at 150 °C.

Fig. 7. Natural log of the gel times versus $1/T$ for the neat resin (circles) and nanocomposite with 4% clay (squares).

curing process, unreacted prepolymer will diffuse into the intergallery regions and polymerize. It has been suggested that in order to obtain an exfoliated system, the relative rate of extragallery and intergallery polymerization must be balanced [6,14–15]. This balance depends on several factors, including prepolymer viscosity and the nature of the silicate (i.e. the CEC, intergallery polarity) [19,21–22].

The effect of cure temperature on the rheology is shown for the 4% nanocomposite in Fig. 6. An Arrhenius plot of this data along with that for the neat resin, shown in Fig. 7, gives activation energies of 70 and 31.5 kJ/mol for the neat resin and nanocomposite, respectively.

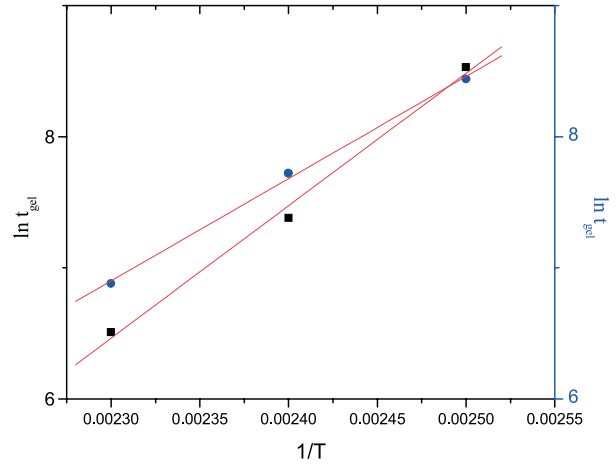The trend in the data agrees with similar data obtained

from time resolved, high temperature X-ray diffraction data by Chen, which showed that the activation energy associated with interlayer expansion is less that the activation energy for the curing process and is a necessary requirement for obtaining exfoliated samples [15].

3.3. Viscoelastic and mechanical behavior of cured samples

Dynamic mechanical analysis of the cured samples is shown in Figs. 8 and 9. The plot of storage modulus versus temperature as shown in Fig. 8 shows that the
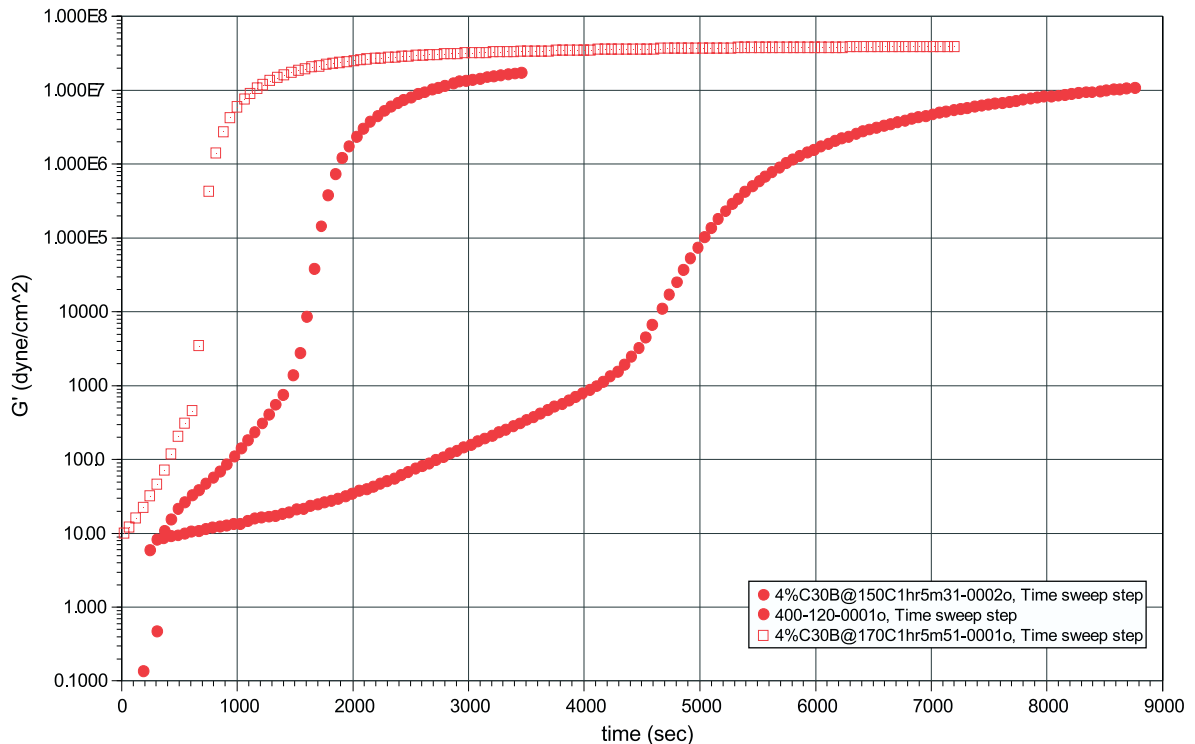

Fig. 6. The effect of temperature on the gelation and vitrification behavior for the 4% clay/epoxy nanocomposite.
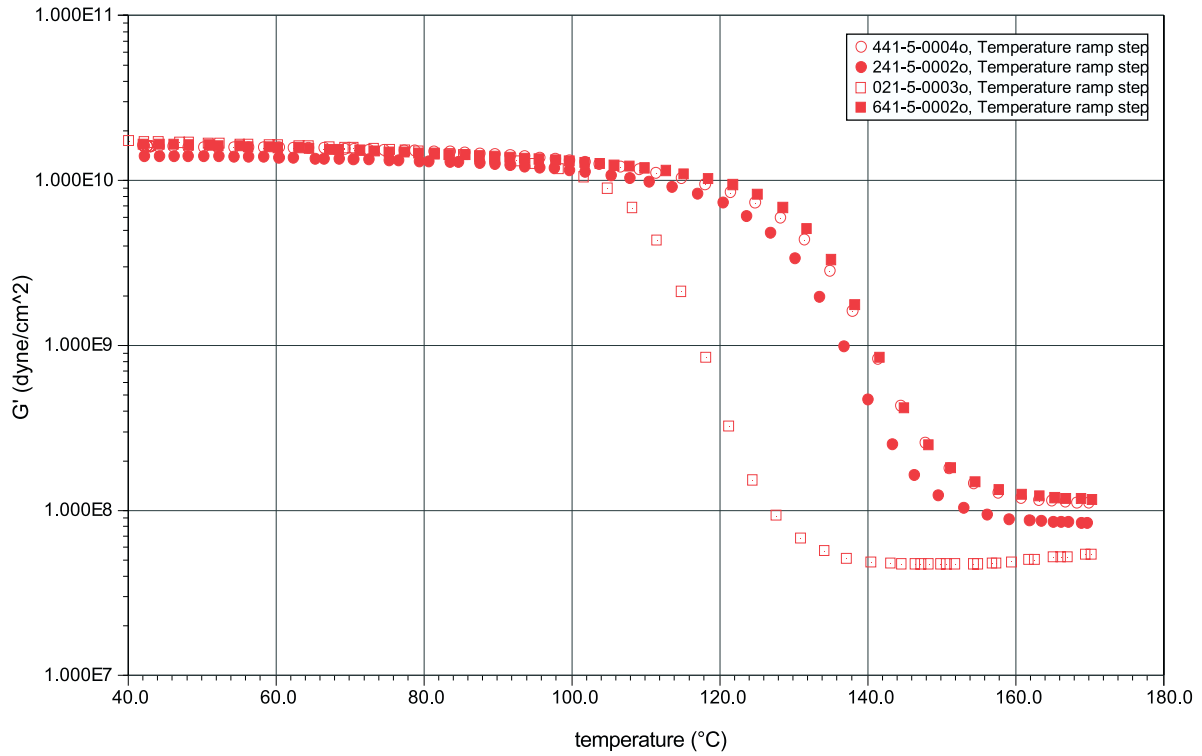
Fig. 8. Storage modulus versus temperature, depicting the viscoelastic behavior of the neat resin (open squares), 2% (solid circles), 4% (open circles) and 6% (solid squares) nanocomposites, respectively.
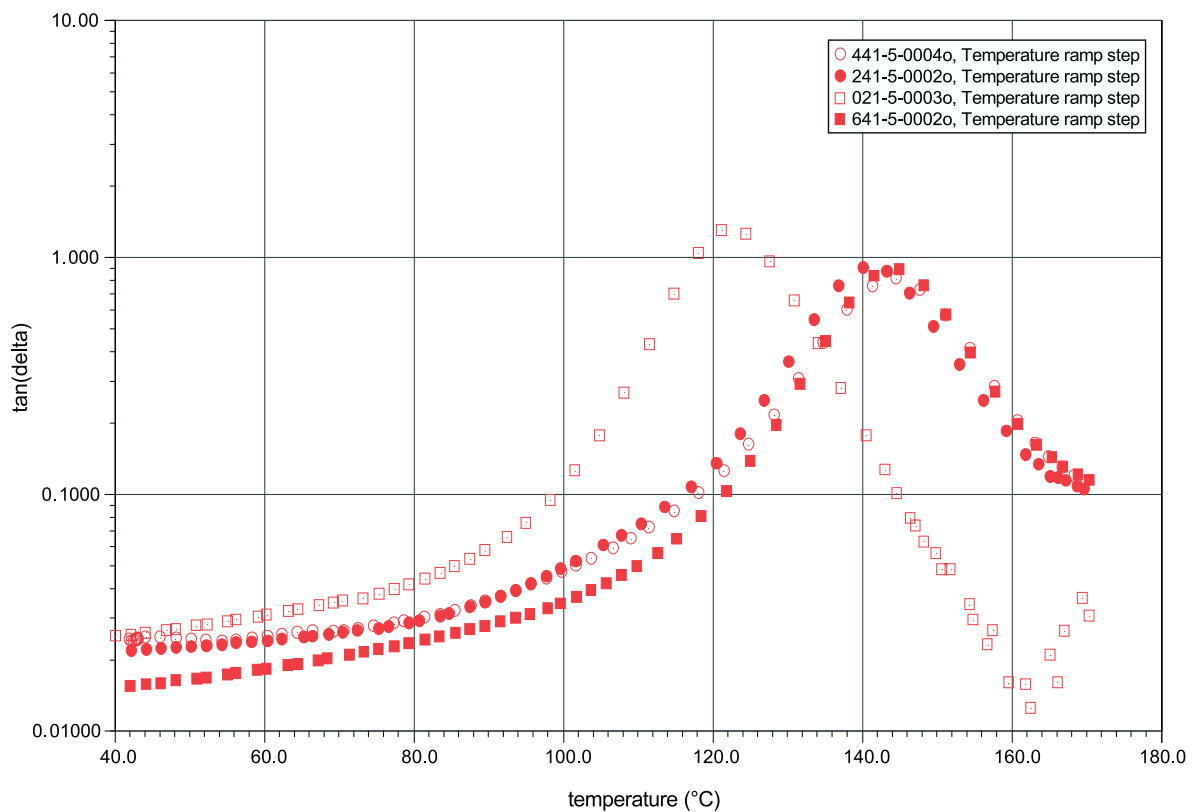

Fig. 9. Tan δ versus temperature for neat resin (open squares), 2% (solid circles), 4% (open circles) and 6% (solid squares) nanocomposites, respectively.

Table 1
Flexural properties of epoxy nanocomposites as a function of clay loading

Sample	Modulus (GPa)	Strength (MPa)
Neat resin	4.0 ($\pm$4%)	223 ($\pm$7%)
2% Clay	5.4 ($\pm$5%)	211 ($\pm$6%)
4% Clay	4.6 ($\pm$3%)	133 ($\pm$4%)
6% Clay	5.7 ($\pm$5%)	180 ($\pm$3%)

The samples were cured at 150 °C.

nanocomposites retain a significantly higher modulus in the rubbery region, due to the constrainment effects of the clays [7,8,16]. The T_g can be clearly discerned from the tan δ curves in Fig. 9, which shows a T_g of 124 °C for the neat resin and 143 °C for each of the nanocomposites.

3.4. Mechanical properties

Representative data for the mechanical properties (flexural) of some epoxy nanocomposites cured at 150 °C is shown in Table 1 below. The data represents the average of at least five data points. As the clay loading increases, the modulus increases by 35% for the 2% sample, 15% for the 4% sample, and 30% for the 6% sample, respectively. The strength values show a decrease with clay loading, as others have seen. Variations in crosslink topology as well as homopolymerization may give rise to plasticiation and hence lower strength [3,14–16,18]. However, loss and tan δ plots for these systems give no evidence (e.g. lower modulus or T_g) to support either of these effects, thus they are likely due to the dispersion quality.

4. Conclusions

The effect of the organoclay nanoparticles on the rheology and development of the morphology and properties for epoxy/organoclay nanocomposites has been studied. While intercalated structures were obtained in all cases, the interlayer spacing increases with the temperature of cure. Rheological studies of the cure process suggest that integallery diffusion and catalyzation of the curing process are essential for exfoliation of the silicate layers. This study shows the utility of rheological studies in understanding the effect of nanoparticles on the overall curing process in thermoset polymer nanocomposites. Questions remain, concerning the nature of the crosslink topology on a scale not discernable by the techniques presented in this study. We are currently investigating this question along with others, with the goal of preparing exfoliated thermoset nanocomposites with a well defined, reproducible morphology.

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