Preparation, Characterization, and Nanostructural Evolution of Epoxy Nanocomposites

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ABSTRACT: Epoxy nanocomposites were prepared from the different organoclays with aerospace epoxy resin. A series of organoclays treated with alkylammonium chloride with different alkyl groups of different carbon chains were prepared, including SC4, SC6, SC8, SC10, SC12, SC16, SC18, and NC8, NC12, NC18. All of these organoclays, except for SC4, are very compatible with the aerospace Epon 862/curing agent W. The characterization from wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) confirms the exfoliated nanostructure. The six-carbon chain length of the ammonium cation is enough to wet the surface of the clay gallery to make the organoclay compatible with epoxy resin. The clay with lower cation exchange capacity is more favorable for the polymer penetration inside the gallery and is dispersed better in the polymer matrix. The structural evolution of the aerospace epoxy nanocomposite was monitored by *in situ* SAXS. The 3% SC18/Epon 862/W, 3 and 6% SC8/Epon 862/W showed exfoliated nanostructure, while there is no exfoliation taking place for 3% S30B/Epon 862/W and 3%S25A/Epon 862/W up to 200°C. The acidity from the pendent group in SC18 and SC8 has a catalytic effect for the polymerization inside the gallery, while the organic pendent group of S30B and S25A does not. The faster reaction of the intragallery epoxy resin produced extra thermal heat inside the gallery to expand the gallery and is favorable for the migration of epoxy resin outside the gallery into the gallery where exfoliation took place. The exothermal heat of curing inside the gallery is an important factor for nanosheets exfoliation. Although exfoliation took place for both 3% SC18/Epon 862/W and 3% SC8/Epon 862/W, the detailed morphology development during the curing is different. For 3% SC8/Epon 862/W, the interplanar spacing between the layers is increased gradually, while 3% SC18/Epon 862/W experienced the disappearance of the ordered structure of the layered silicate in the beginning of the curing process and reappearance of the ordered structure of the silicate later. The glassy and rubbery moduli of the polymer-silicate nanocomposites were found to be greater than the unmodified resin because of the high aspect ratio and high stiffness of the layered silicate filler. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2276–2287, 2003

Key words: nanocomposites; clay; morphology; SAXS

INTRODUCTION

Since Toyota researchers began comprehensive research on the polymer clay nanocomposite,[1] the research on polymer layered-silicate nanocomposites has attracted a great deal of attention.[2–8] New nanocomposite materials satisfying the ever-demanding requirements for high-technology application are being developed. Nylon-based nanocomposites have even been commercialized.[9]

Polymer layered-silicate nanocomposites are new hybrid polymeric materials with layered silicates in the form of sheets of one to several nanometers thick and hundreds of nanometers long. Due to the unique nanometer-size dispersion of the layered silicates with high aspect ratio, high surface area, and high strength in the polymer matrix, nanocomposites generally exhibit improvements in properties of polymeric materials even at very low volume fraction loading (1 to 5%) of layered silicates in contrast to the high volume fraction loading (~ 50%) in the traditional advanced composites. These properties can include mechanical performance, ablation performance, thermal stability, barrier performance, and flame retardancy.[2–8] The low loading of inorganic particles maintains polymeric clarity and cost and also allows for conventional polymer processing.

Several types of morphology can occur when the polymer is mixed with layered silicates,[3,10] as follows: (1) immiscible, the polymer and layered silicate are completely separated, and no polymer chain is penetrated inside the gallery of the layered silicate; (2) intercalated, the polymer is compatible with the layered silicates, and the polymer chains penetrate inside the gallery and expand the nanosheets to some extent, while the layered structure of the silicate is still in

registry; and (3) exfoliated, the expansion of the layered silicate is so large that the interaction between the layers is not strong enough to keep the stack-like registry and association; and ideally the individual silicate layers are completely separated and dispersed in a continuous polymer matrix.

Layered silicates are abundant and important minerals in geological environments at or within roughly 20 km of the earth surface.[11] There are many types of sheet silicates, including clay mineral. The most widely used layered silicate for nanocomposites is montmorillonite. Montmorillonite is constructed of repeating triple-layer structure composed of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of alumina.[10] The dimensions for these silicate sheets are 0.96 nm in thickness and approximately 100 to several hundred nanometers in length. The hydrophilic layered silicates have a stack-like registry structure that makes them incompatible with the hydrophobic organic polymer. Generally the surface of the clay needs to be modified to improve the wettability and dispersibility of hydrophilic clay. Because of the isomorphic substitution by low covalent atoms, sheet backbone produces some negative charges counterbalanced by some cations in the gallery. These cations can be easily exchanged with surfactants such as alkyl ammonium cations. The pendent organic group in the surface of the silicate sheets lowers the surface energy of silicate layers and makes the layered silicate compatible with the polymer matrix.

Epoxy resin is widely used in adhesives, coatings, integrated circuit packaging, printed circuit boards, and composite materials. The introduction of the nanoclay into the epoxy resin is expected to improve the thermal and mechanical properties of the polymeric materials. Up to now, extensive research on the epoxy layered-silicate nanocomposites has been carried out[2,12–30] since the pioneering work of Pinnavaia's group.[2,12,14,15] Recently, the mechanism for exfoliation has also been of great interest but not well understood.[15,16,24–26,28–30] This research is focused on the nanocomposites with aerospace epoxy [high glass transition temperature (T_g): $\sim$ 150°C] as the matrix. A series of aerospace epoxy nanocomposites with organoclays with a long alkyl chain or short alkyl chain, and the nanocomposites from the organoclays with different cation exchange capacities, were prepared: their morphologies were characterized; their morphology development during processing was monitored; and their differential scanning calorimetry (DSC) and rheology were studied. The exfoliation mechanism was discussed.

EXPERIMENTAL

Materials

The materials used were as follows: Epon 862 (a bisphenol F epoxy), EpiCure curing agent W were pur-

chased from Miller-Stephenson Chemical Company, Inc. (Danbury, CT). *n*-Butylamine, *n*-hexylamine, *n*-octylamine, *n*-decylamine, *n*-dodecylamine, *n*-hexadecylamine, and *n*-octadecylamine were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). Hydrochloric acid was obtained from Fisher Scientific (Lawn, NJ). SNA, S30B, and S25A were obtained from Southern Clay Products (Gonzale, TX). PGW was supplied by Nanocor (Arlington Heights, IL).

Organoclays

SC18, SC16, SC12, SC10, SC8, SC6 and SC4 were prepared from Closite Na (CEC: $\sim$ 92 meq/100 g) treated with HCl and primary amines with different carbon chains, including *n*-octadecyl amine, *n*-hexyldecylamine, *n*-dodecylamine, *n*-decylamine, *n*-octylamine, *n*-hexylamine, and *n*-butylamine, respectively, by using the following procedure. SNA was added to the mixed aqueous and ethanol solution of amine and aqueous hydrochloric acid (1N). The mixture suspension was stirred at $\sim$ 65°C for 6 h. The suspension was filtered, and the solid was washed with a mixture of warm water and ethanol and dried in a vacuum oven overnight. NC18, NC12, and NC8 were made by the sodium montmorillonite (PGW) from Nanocor with Cation exchange capacity (CEC: $\sim$ 145 meq) treated with HCl and primary amines octadecyl amine, dodecylamine, and octylamine, respectively, by using a similar procedure.

Processing

The desired amount of organoclay was added to the epoxy resin. The mixture was stirred at elevated temperature, while stoichiometric curing agent was added to the mixture. The resulting mixture was cast in the mold and cured. The curing cycle for Epon 862 with curing agent W was as follows: heat the cast in the oven to 121°C over 30 min, hold at 121°C for 2 h, then heat to 177°C over 30 min and hold for another 2 h at 177°C, and finally cool to ambient temperature.

Characterization

WAXD was performed in the Rigaku X-ray powder diffractometer. The generator power was 40 kV and 150 mA; the scan mode was continuous with a scan rate of 0.8°/min, and the 2θ scan range was from 2° to 10°. Small-angle X-ray scattering (SAXS) was performed at the National Synchrotron Light Source at the Brookhaven National Laboratory on Beamline X27C utilizing a one-dimensional detector (λ = 1.366 Å). The *in situ* SAXS experiment was also performed at the National Synchrotron Light Source at the Brookhaven National Laboratory (Beamline X27C with a one-dimensional detector). The mixture of the organoclay with

TABLE I
Summary of Composition, WAXD Characterization and Optical Appearance of the Organoclays and Nanocomposites

Materials	WAXD characterization	Optical appearance
SNA (Southern Clay, CEC 92 meq)	11.1 Å	Powder
PGW (Nanocor, CEC: 145 meq)	12.2 Å	Powder
SC4	12.9 Å	Powder
3.0% SC4/Epon 862/W	No intercalation/exfoliation	Opaque
6.0% SC4/Epon 862/W	No intercalation/exfoliation	Opaque
SC6	13.0 Å	Powder
3.0% SC6/Epon 862/W	Exfoliated	Transparent
6.0% SC6/Epon 862/W	Exfoliated	Transparent
SC8	13.2 Å	Powder
3.0% SC8/Epon 862/W	Exfoliated	Transparent
6.0% SC8/Epon 862/W	Exfoliated	Transparent
8.0% SC8/Epon 862/W	Exfoliated	Transparent
12.0% SC8/Epon 862/W	Exfoliated	Translucent
NC8	14.4 Å	Powder
3.0% NC8/Epon 862/W	Exfoliated	Transparent
6.0% NC8/Epon 862/W	Exfoliated	Transparent
SC10	13.4 Å	Powder
3.0% SC10/Epon 862/W	Exfoliated	Transparent
6.0% SC10/Epon 862/W	Exfoliated	Transparent
SC12	15.5 Å	Powder
3.0% SC12/Epon 862/W	Exfoliated	Transparent
6.0% SC12/Epon 862/W	Exfoliated	Transparent
NC12	17.5 Å	Powder
3.0% NC12/Epon 862/W	Exfoliated	Transparent
6.0% NC12/Epon 862/W	Exfoliated	Transparent
SC18	18.0 Å	Powder
3.0% SC18/Epon 862/W	Exfoliated	Transparent
6.0% SC18/Epon 862/W	Exfoliated	Transparent
NC18	28.0 Å	Powder
3.0% NC18/Epon 862/W	Exfoliated	Transparent
6.0% NC18/Epon 862/W	Exfoliated	Transparent

epoxy and curing agent was mounted in a copper cell with Kapton™ tape windows and placed in a programmable oven cell within the X-ray beam. The sample was heated up at 2°C/min., and the data were recorded every minute. The samples for TEM were microtomed in a Reichert-Jung Ultracut Microtome and mounted on 200-mesh copper grids. TEM was performed by using a Philips CM200 TEM with a LaB_6 filament operating at 200 kV. The DMA was performed by using a Rheometrics ARES dynamic spectrometer with the use of torsion bar geometry at a frequency of 100 rad/s, a strain of 0.1%, and a heating rate of 2°C/min, whereas the viscosity test was carried out on a Rheometrics ARES dynamic spectrometer by using 50-mm-diameter parallel plates geometry at a frequency of 10 rad/s, a strain of 3%, and a heating rate of 2°C/min. DSC was performed by using a TA Instruments differential scanning calorimeter 2920 modulated DSC at 2°C/min with air sweep gas.

RESULTS AND DISCUSSION

Preparation and WAXD characterization

The aerospace epoxy studied here is made from Shell Epon 862 (diglycidylbisphenol-F) with EpiCure curing agent W (diethyltoluenediamine). This epoxy system has high T_g (~ 150°C), good epoxy performance characteristics, and involves non-MDA aromatic amines, and its low viscosity made it suitable for resin transfer modeling. Sodium montmorillonite was modified

TABLE II
Composition and SAXS Characterization of Nanocomposites

Composition	d (Å)
3% SC6/Epon 862/W	140
6% SC6/Epon 862/W	135
3% SC8/Epon 862/W	156
6% SC8/Epon 862/W	131
3% SC10/Epon 862/W	136
6% SC10/Epon 862/W	125
3% SC12/Epon 862/W	137
6% SC12/Epon 862/W	127
3% SC18/Epon 862/W	135
6% SC18/Epon 862/W	108
3% NC8/Epon 862/W	147
6% NC8/Epon 862/W	130
3% NC12/Epon 862/W	118
6% NC12/Epon 862/W	90.5/46
3% NC18/Epon 862/W	111
6% NC18/Epon 862/W	82.9/42.0
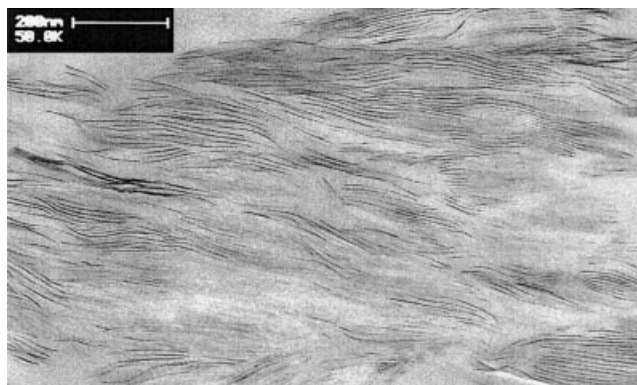
Figure 1 Transmission electron microscopy image of 3% SC8/Epon 862/W nanocomposites.

with HCl and primary amines with different carbon chains, including octadecyl amine, hexyldecylamine, dodecylamine, decylamine, octylamine, hexylamine, and butylamine to make SC18, SC16, SC12, SC10, SC8, SC6 and SC4. WAXD (Table I) studies indicated that the interplanar spacings of these organoclays were logically increased, and the organic modification of the sodium clay was successful. These organoclays were also mixed with Epon 862 at elevated temperatures by stirring. All of the organoclay/Epon 862 mixtures except SC4 appear homogeneous and clear. After mixing them with curing agent W, the mixture was transferred into the mold and cured in the programmed blue oven. All samples except SC4/Epon 862/W appear to have good optical quality with a transparent appearance. WAXD can only detect up to 2° for 2θ. So if there is no peak in the WAXD, the interplanar spacing between the silicate layers is larger than 44 Å compared with the original 13 to 18 Å for the organoclay. It is assumed that the epoxy-silicate nanocomposites are exfoliated from WAXD characterization. The detailed data are given in Table I.

The compatibility of SC8 with Epon 862 appears the best in all these organoclays. Even with the SC8's loading as high as 12%, WAXD still shows no peak in the low-angle region. This is in contrast to the general concept that more and longer alkyl chains are better for the organoclay's compatibility with the polymer matrix. This is perhaps related to the structure of the epoxy resin. Although the epoxy resin contains some aromatic group and alkyl group, it also contains a cycle-oxygen group, which is a polar group, and changes into very polar OH when cured. So, perhaps, the alkyl group with medium length in the organoclay is a good balance for the organoclay's compatibility with epoxy resin. The organoclay (SC6) with a short alkyl chain (six-carbon chain) can still form exfoliated nanocomposites with 3 and 6% organoclay loading. However, the organoclay (SC4) with an even shorter alkyl chain (four-carbon chain) was not compatible with epoxy resin and could not disperse well in the

epoxy resin. The WAXD demonstrates that the organoclay particle is precipitated in the bottom of the sample with almost no change of the interplanar spacing of the organoclay (SC4), while the upper section of the sample shows no diffraction from the organoclay (SC4). It appears that the four-carbon chain is not large enough to cover and wet the surface of the silicate backbone and lower the surface energy to make the organoclay compatible with the epoxy resin.

Another sodium montmorillonite from Nanocor with CEC of ~ 145 meq was modified with HCl and primary amines with different carbon chains, including octadecyl amine, dodecylamine, and octylamine, to make NC18, NC12, and NC8. WAXD analysis indicated that the interplanar spacings of these organoclays were logically increased, and the interplanar spacings of the NC organoclays are larger than the corresponding SC organoclays. This is as expected because the NC clay has larger CEC and more organic group can be exchanged into the gallery. These organoclays were also mixed with Epon 862 at elevated temperature by stirring. All of these organoclay/Epon 862 mixtures appear homogeneous. After mixing them with curing agent W, the mixture was transferred into the mold and cured. All samples appear to have good optical quality. The detailed data are shown in Table I.

Small-angle X-ray scattering

As indicated above, WAXD can only detect interplanar spacing of less than 44 Å. To further characterize the morphologies of these nanocomposites, SAXS was performed at Brookhaven National Laboratory. A summary of the SAXS of these nanocomposites is listed in Table II. Most interplanar spacing of the nanocomposites is larger than 100 Å, and the weakness of the peak demonstrates the existence of the disordered structures. So the silicate nanosheets are
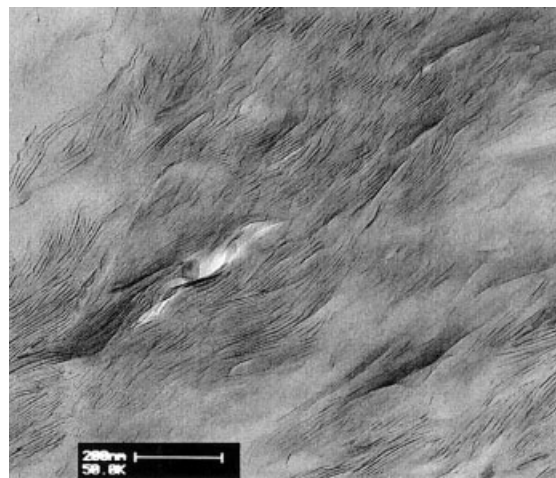
**Figure 2** Transmission electron microscopy image of 6% SC8/Epon 862/W nanocomposites.
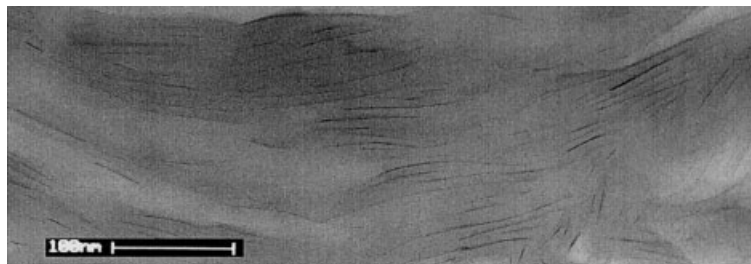
Figure 3 Transmission electron microscopy image of 6% SC18/Epon 862/W nanocomposites.

well dispersed, and these types of morphology can be considered to be exfoliated nanocomposites. It is clearly seen that the low loading of the organoclay generally shows much larger interplanar spacing. This is perhaps partly because the low loading of organoclay in the nanocomposites allows relatively more epoxy resin to enter the clay gallery. More importantly, the low concentration of the organoclay in the epoxy matrix makes the general distance farther between the neighboring organoclay clusters. When the gallery of the organoclay expands, interaction between the neighboring organoclay clusters should still be much smaller, and the expansion of the gallery can be continued more freely. So the interplanar spacings were much larger for the nanocomposites with low loading of organoclays. On the other hand, the morphology of the nanocomposites is also related to the CEC of the original clay. The nanocomposite made from Southern Clay Products (CEC: 92 meq/100 g) generally shows greater interplanar spacing than that made from Nanocor (CEC: 145 meq/100 g), although the original interplanar spacing of the organoclay is generally larger for those made from Nanocor than those made from Southern Clay Products, which appears controversial. The reason for this is because too much pendent group in the gallery of the organoclay created some hindrance to prevent the epoxy resin from migrating inside the gallery, and therefore less epoxy

resin can penetrate inside the gallery and interplanar spacing is smaller. The SAXS data are also consistent with the observation of compatibility during processing. The most compatible organoclays with epoxy resin are SC8 and NC8. The SAXS indicated that nanosheets of 3% SC8/Epon 862/W and 3% NC8/Epon862/W nanocomposites are better dispersed with the interplanar spacings of 156 and 147 Å. The incompatibility of SC4, good compatibility of SC6, SC12, NC12, SC16 and SC18, and the best compatibility of SC8 and NC8 with epoxy resin (Epon 862/W) demonstrate that the alkyl group of medium length in the organoclay perhaps is a good balance for the compatibility with epoxy resin, which contains both nonpolar groups such as aromatic and aliphatic alkyl groups and polar cycle-oxygen groups or strong polar OH when cured. These results can be combined with some theoretical work, such as solubility parameters, to get some semiquantitative analysis.

Transmission electron microscopy

TEM provides direct observation and direct evidence of the detailed features of the morphology of the polymer layered-silicate nanocomposites. Several layered-silicate epoxy nanocomposites were microtomed and TEM images were taken. The TEM images of 3% SC8/Epon 862/W, 6% SC8/Epon 862/W, and 6% SC18/
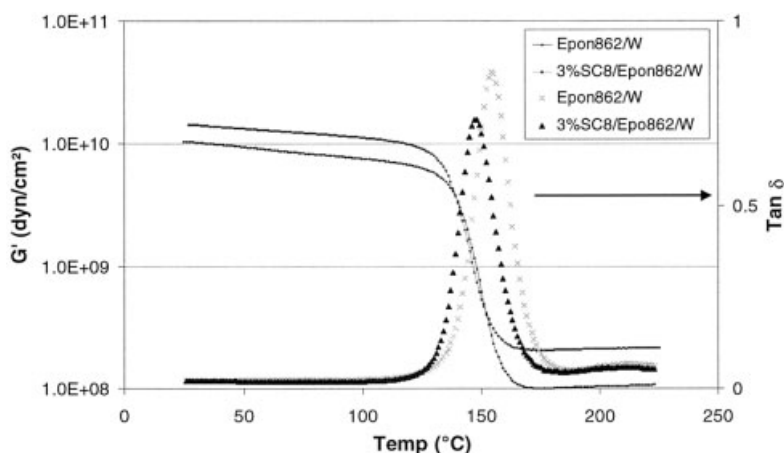
Figure 4 Dynamic storage modulus and tan δ curve versus temperature of Epon 862/W (control) and 3% SC8/Epon 862/W.

TABLE III
Storage Moduli and Glass Transition Temperatures (T_g) of the Nanocomposites and Their Pristine Polymer

| | G' (dyne/cm^2) | | |
Composition	Glassy (30°C)	Rubber (180°C)	T_g (°C)
Epon 862/W	1.03E10	1.00E8	154
6.0%SC6/Epon 862/W	1.41E10	2.49E8	149
3.0%SC8/Epon 862/W	1.42E10	2.06E8	149
6.0%SC10/Epon 862/W	1.29E10	2.41E8	147
3.0%SC12/Epon 862/W	1.32E10	1.76E8	148
6.0%SC12/Epon 862/W	1.39E10	2.88E8	147
1.0%SC16/Epon 862/W	1.20E10	1.16E8	154
3.0%SC16/Epon 862/W	1.18E10	1.63E8	153
6.0%SC16/Epon 862/W	1.60E10	2.55E8	147
6.0%SC18/Epon 862/W	1.30E10	2.14E8	153
10.0%SC18/Epon 862/W	1.56E10	2.82E8	144

Epon 862/W are shown in Figures 1, 2 and 3. The images show the typical morphology of the exfoliated layered-silicate epoxy nanocomposites. The dark lines are cross sections of the silicate sheets of 1-nm thickness. The original aggregates of the silicate sheets were disrupted, and each individual sheet with nanometer-thickness was well dispersed in the epoxy resin. Some sheets are disordered, whereas others still preserve the ordered structure in a registry with more than 10 nm separations between the nanosheets. This is consistent with the SAXS results in Table II.

Dynamic mechanical analysis (DMA)

DMA was used to study the dynamic modulus. The dynamic storage modulus and tan δ curve versus temperature of Epon 862/W (control) and 3% SC8/Epon 862/W are shown in Figure 4. The storage modulus of 3% SC8/Epon 862/W nanocomposite is increased about 40% in the glass state and about 100% in the

rubber state. Based on the tan δ curve, the T_g is close to the pure resin (149°C versus 154°C). More storage moduli of the nanocomposites with different organoclays or different concentrations are listed in Table III. The nanocomposite generally shows higher storage modulus than that of the pristine epoxy resin (from 15 to 55% higher in the glass state and 15 to 180% higher in the rubber state). This is attributed to the high aspect ratio and high stiffness of the organoclay filler. Generally, the nanocomposites show more significant improvement of storage modulus in the rubber state than that in the glassy state. This perhaps is caused by the extra reinforcement from further nanosheet alignment in the rubber state.[13,14] The T_g of the nanocomposites with different organoclays or different concentrations based on tan δ curve is also listed in Table III. It indicated that the glass temperature of the nanocomposites is decreased to a very small extent (from 0 to 10°C). The small decrease of the glass temperature of the nanocomposites perhaps is caused by the effect of plasticizer from the organoclay.

DSC studies

Some DSC studies were taken for epoxy resin with organoclay loading. The DSC spectra of Epon 862/W (control), 3% SC8/Epon 862/W and 3% SC18/Epon 862/W; Epon 862/W (control), 3% S30B/Epon 862/W; and 3% S25A/Epon 862/W at 2°C/min are shown in Figures 5 and 6. The onset temperature of the curing and the temperature of the exothermal heat peak for the control resin Epon 862/W are 121 and 159°C, respectively, whereas they are 80 and 142°C for 3% SC8/Epon 862/W, and 100°C and 152°C for 3% SC18/Epon 862/W. This demonstrates that both the onset temperatures for curing and the temperatures in the exothermal heat peak for 3% SC8/Epon 862/W and 3% SC18/Epon 862/W are shifted to lower tempera-
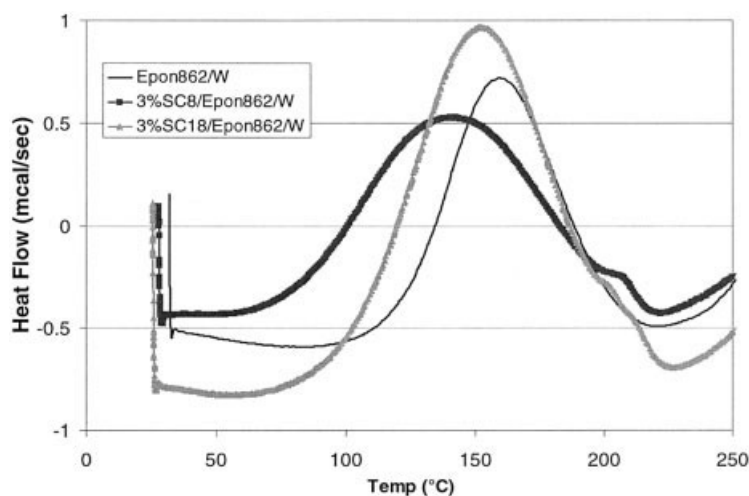
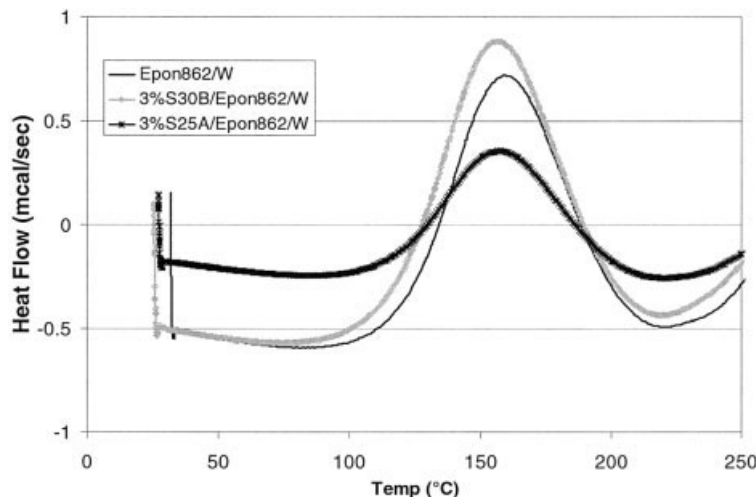**Figure 5** DSC of Epon 862/W (control), 3% SC8/Epon 862/W, and 3% SC18/Epon 862/W at 2°C/min.

Figure 6 DSC of Epon 862/W (control), 3% S30B/Epon 862/W, and 3% S25A/Epon 862/W at 2°C/min.

tures. This is caused by the catalytic effect from the acidic RNH_3^+ group in the gallery of the organoclay.[15,16] The epoxy resin inside the gallery of the organoclay should have lower onset temperature for curing. This exothermal peak will overlap with the exothermal peak from the pure epoxy resin outside the gallery of the organoclay. Therefore, the peak is shifted to lower temperatures. Compared with the data for SC8 and SC18, the onset temperature of curing for the mixture with SC8 is lower than that with SC18. This is caused by the fact that there are smaller organic pendent groups in the SC8 than those in the SC18, and therefore more epoxy resin can easily migrate inside the gallery. This is verified from the SAXS data. The interplanar spacing is ~ 82 Å for the 3% SC8/Epon 862/W, whereas it is ~ 38 Å for 3% SC18/ Epon 862/W. So more curing takes place in the gallery at lower temperature for 3% SC8/Epon 862/W than that for 3% SC18/Epon 862/W. Simultaneously, the onset temperatures for curing and the temperatures of the exothermal heat peak are 116 and 157°C for 3%

S30B/Epon 862/W, and 116 and 156°C for 3% S25A/ Epon 862/W, which are very close to those of the control Epon 862/W. This demonstrated that there is no catalytic effect for the epoxy polymerization from these two organoclays. This is related to the composition of these two organoclays. S30B is montmorillonite modified with a ternary ammonium salt [(methyl)(tallow)(bis-2-hydroxyethyl)ammonium], and S25A is montmorillonite modified with a ternary ammonium salt [(dimethyl)(hydrogenated tallow)(2-ethylhexyl)ammonium]. The organic pendent groups in both S30B and S25A are ternary ammonium, which has no catalytic effect for the epoxy polymerization.[15,16]

Rheology

The viscosity study of Epon 862/W (control), 3% SC18/Epon 862/W, 3% SC18/Epon 862/W, 3% S30B/ Epon 862/W, and 3% S25A/Epon 862/W at 2°C/min was performed by DMA (Fig. 7). At room temperature the viscosity of the Epon 862/W with organoclays is a
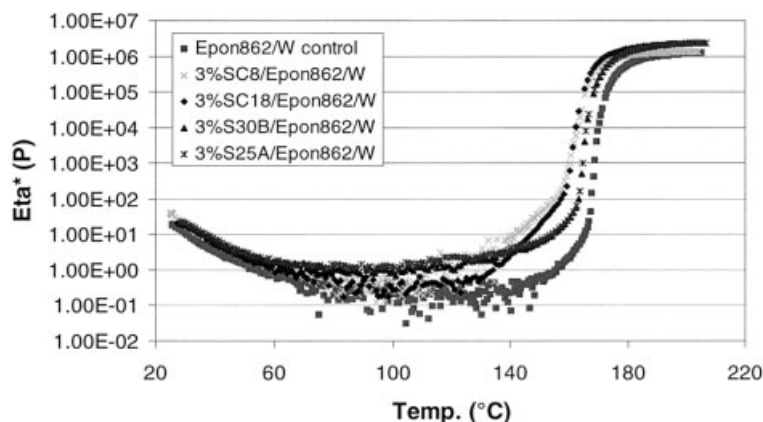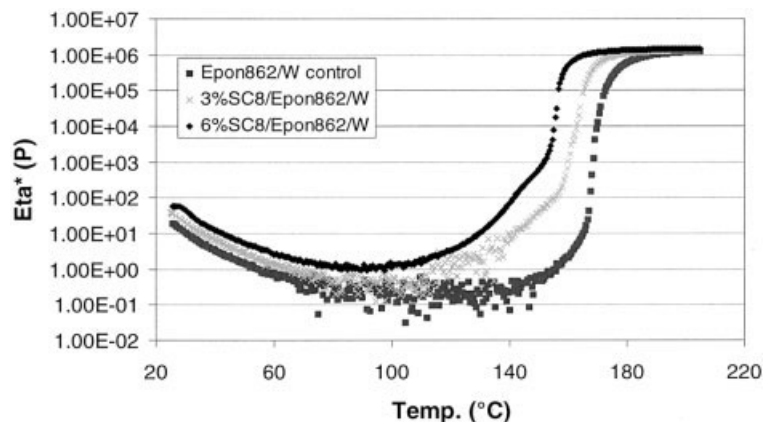

Figure 7 Viscosity of Epon 862/W (control), 3% SC8/Epon 862/W, 3% SC18/Epon 862/W, 3% S30B/Epon 862/W, and 3% S25A/Epon 862/W at 2°C/min.

Figure 8 Viscosity of Epon 862/W (control), 3% SC8/Epon 862/W, and 6% SC8/Epon 862/W at 2°C/min.

little larger than that of Epon 862/W, as expected. However the increase is limited and the processible window is still very wide for resin transfer modeling. As the temperature increases, the crosslinking polymerization takes place. After the polymerization took place, the viscosity was increased. For the sample with 3% SC18 loading, the gelling takes place more quickly, and the viscosity is increased more rapidly from 120 to 160°C. This is ascribed to the catalytic effect of the SC18 for the polymerization. The viscosity increase for 3% SC8/Epon 862/W is generally a little more than that for 3% SC18/Epon 862/W. This is because of the early polymerization occurring for 3% SC8/Epon 862/W as DSC indicated above. For 3% S30B/Epon 862/W and 3%S25A/Epon 862/W, their viscosity curves were almost the same, and their viscosities are always higher than that of pure resin because of the introduction of the nanoclays. Because there is no catalytic effect from the S30B or S25A, the viscosity increase is not as fast as SC18 and SC8. The 3% SC8/Epon 862/W and 6% SC8/Epon 862/W with control one (Epon 862/W) is also shown in Figure 8. As expected, the higher loading of the organoclay increased the viscosity, but the processible window is still wide.

In situ small-angle X-ray scattering

The in situ SAXS can provide information on the morphology development of the nanocomposite during processing. The 3% SC18/Epon 862/W mixture was mounted in a copper cell and heated up at 2°C/min. The SAXS data of the nanocomposite during heating were recorded every minute. For clarity purposes, some key X-ray scattering lines were chosen and are shown in Figure 9. The first line of the SAXS data shows that the interplanar spacing of the mixture was 38 Å, while the original interplanar spacing of the organoclay was 18 Å. The 20 Å increase of the interplanar spacing is due to the compatibility of the Epon 862 with the surface of the gallery of the organoclay,

and therefore the penetration of Epon 862 into the gallery of the organoclay and the expansion of the gallery of the organoclay. When the temperature was elevated from 60 to 98°C, the peak corresponding to the interplanar spacing between the nanosheets had a gradual shift to a lower angle but was very limited. The interplanar spacing was shifted from 38 to 42 Å. The small expansion of the gallery is due to the mobility increase and some migration of the Epon 862 and curing agent W caused by temperature increase. Until 104°C, the peak almost disappeared. This indicated that the ordered structure was almost collapsed and exfoliation took place. At 110°C, a new, but very broad and very weak, peak appeared again with interplanar spacing of about 90 Å. With the increase in temperature from 116 to 160°C, the peak shifted gradually from ~ 108 to ~ 140 Å. The intensity of the peaks was increased gradually but was still weak and broad. Later the peak became more intense with the increasing temperature, and eventually the interplanar spacing between the nanosheets was around 150 Å at 200°C. The change in the SAXS data is related to the
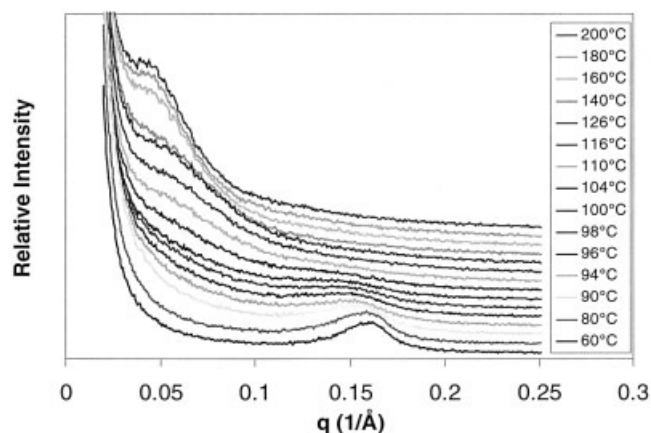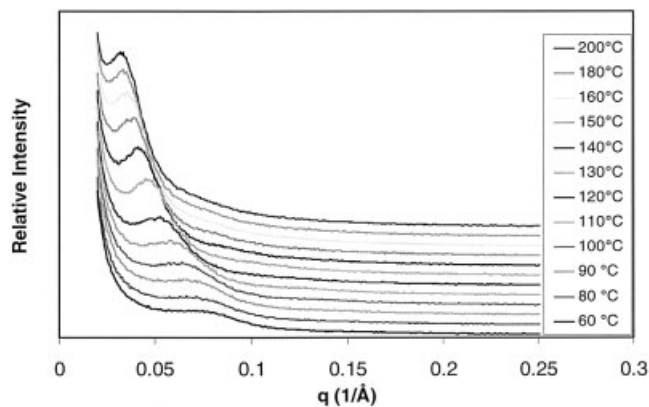

Figure 9 In situ small-angle X-ray scatterings of 3% SC18/Epon 862/W at 2°C/min.

structural evolution of the nanocomposite during the curing. Based on DSC studies, the onset temperature for curing of the SC18/Epon 862/W nanocomposite is ~ 100°C. Before this onset temperature of curing, there is little cure taking place. The increase in the temperature just helps expand the gallery of the organoclay to a very limited extent. When the temperature is higher than 100°C, the curing takes place for the epoxy resin inside the gallery of organoclay. The exothermal heat from curing at ~ 100°C provides extra energy to help the nanoclay sheets expand. Simultaneously, there is no curing taking place for the epoxy resin outside the gallery of the organoclay, and the epoxy resin is in a liquid state with very low viscosity (~ 0.2 poise, Fig. 7) at 100°C. Thus the epoxy resin outside the gallery penetrates inside the gallery of the organoclay. The viscosity of epoxy resins migrated from the outside gallery, and the viscosity inside the gallery is still very low because the curing inside the gallery just started. So this is a very flexible environment for the silicate nanosheets, and the energy from heating and exothermal heat makes the nanosheets move flexibly. So the ordered structure of the layered silicate is distorted, and there is almost no peak from SAXS at ~ 104°C. With the increase in the temperature from 116 to 160°C, more and more curing takes place for the epoxy resin inside the gallery. The crosslinking outside the gallery began after 120°C; the viscosity is still pretty low (0.3 poise at 120°C, 0.6 poise at 130°C, 2.7 poise at 140°C, 15 poise at 150°C, 134 poise at 158°C, Fig. 7), and more and more epoxy resin outside the gallery migrates inside the gallery. The viscosity of the epoxy resin is increased, and the flexibility of the nanosheets of the silicate is reduced gradually; therefore, the ordered structure of the layered silicate will be in more order, so the intensity of the peak is increased gradually. The interplanar spacing of the gallery is still increased, and the ordered structure of the layered silicate will be in more and more order. The intensity of the peak in the SAXS is more intense, and interplanar spacing is increased until the epoxy is almost fully cured, and the epoxy surrounding the nanosheets of the layered silicate is rigid and has a fixed ordered structure.

The morphology development for the 3% SC8/Epon 862/W appears different from that of 3% SC18/Epon 862/W, as shown in Figure 10. The first line of the SAXS data shows that the interplanar spacing of the mixture was ~ 82 Å with a broad weak peak, whereas the original interplanar spacing of the organoclay is 13.2 Å. The ~ 70 Å increase is due to the penetration of Epon 862 into the gallery of the organoclay and the expansion of the gallery. Compared with the increase of 20 Å for the 3% SC18/Epon 862/W system, the increase of the interplanar spacing for 3% SC8/Epon 862/W is much larger. This is because there are less organic pendent groups in the original gallery

Figure 10 *In situ* small-angle X-ray scatterings of 3% SC8/Epon 862/W at 2°C/min.

of SC8 (d: 13.2 Å) than SC18 (d: 18.0 Å), which makes the penetration of the epoxy resin easier. With the increase in temperature, there is no collapse of the ordered layered structure as SC18/Epon 862/W did. Both the interplanar spacing and the intensity of the peak was increased gradually when the temperature was elevated. From 60 to 80°C, the interplanar spacing is increased from 82 to 87 Å. The temperature increase is 20°C, and the increase of the interplanar spacing is ~ 5 Å. When the temperature increased from 80 to 100°C, the increase of the interplanar spacing was ~ 10 Å with this 20°C increase in temperature. When the temperature increased from 100 to 120°C, the increase of the interplanar spacing was ~ 20 Å. When the temperature increased from 120 to 140°C, the increase of the interplanar spacing was ~ 35 Å. When the temperature increased from 140 to 160°C, the increase of the interplanar spacing was ~ 20 Å. When the temperature increased from 160 to 180°C, the increase of the interplanar spacing was ~ 10 Å. When the temperature increased from 180 to 200°C, there was almost no increase of the interplanar spacing. Based on DSC studies, Figure 5, from 60 to 80°C, there is a small amount of polymerization; the small amount of polymerization inside the gallery and neat temperature increase the mobility and the migration of the epoxy inside the gallery is limited. So the interplanar spacing increase is around 5 Å. When the temperature reached the onset temperature of curing at 80°C, more polymerization inside the gallery took place, the extra exothermal heat inside the gallery will expand the nanosheets, and the epoxy resin can migrate from outside into the inside gallery, and thus the interplanar spacing was increased more. Although the polymerization started at ~ 80°C, the polymerization just started and the viscosity becomes lower with the increase in temperature. So with the increase in temperature, more and more epoxy resins are migrating inside the gallery and the interplanar spacing increases quickly. Until more and more crosslinking takes place
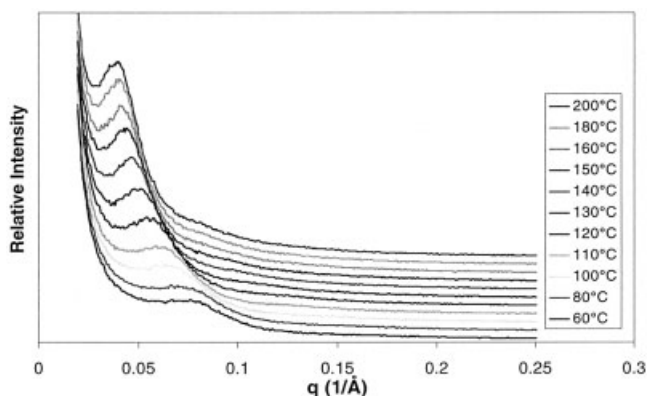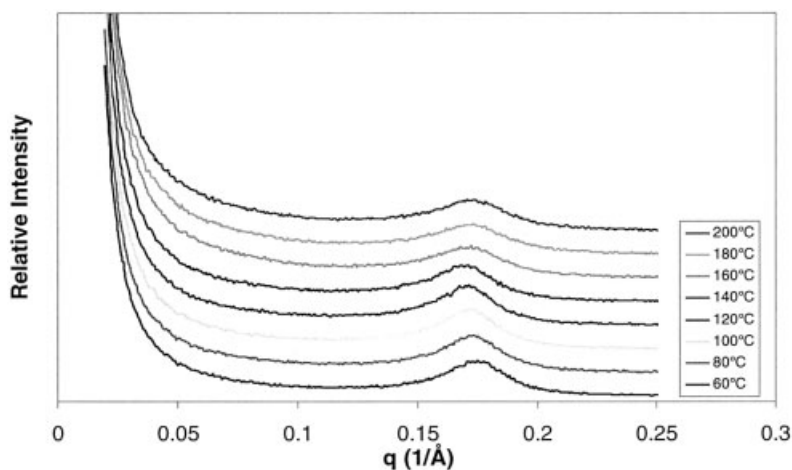
Figure 11 *In situ* small-angle X-ray scatterings of 6% SC8/ Epon 862/W at 2°C/min.

at 140°C, the increase of the interplanar spacing will be reduced. At 180°C most crosslinking is finished, and the matrix surrounding the layered silicate is almost fixed. So the increase in the temperature from 180 to 200°C almost did not have an effect on the morphology of the nanocomposites. The final interplanar spacing for 3% SC8/Epon 862/W is about 190 Å.

The morphology development for the 6% SC8/ Epon 862/W was very similar to that of 3% SC8/ Epon 862/W, as shown in Figure 11. The first line of the SAXS data shows that the interplanar spacing of the mixture was ~ 81 Å with a broad weak peak, whereas the original interplanar spacing of the organoclay is 13.2 Å. Again with the increase in the temperature, there is no collapse of the ordered layered structure as in SC18/Epon 862/W. From 60 to 120°C, the morphology development is almost the same as 3% SC18/Epon 862/W. From 120 to 180°C, the increase of the interplanar spacing is not as fast as 3% SC8/Epon 862/W. This is perhaps related to the farther distance between the neighboring organoclay clusters in the low concentration of the organoclay in the epoxy matrix. When the expan-

sion of the gallery of the organoclay started, interaction between the neighboring organoclay clusters should still be much smaller, and the expansion of the gallery can be continued more freely. With the increase of the temperature and the expansion of the gallery, the interaction between the neighboring organoclay clusters should be increased in the higher loading of the organoclay, and therefore the expansion of the gallery is relatively slower than that with lower loading of organoclay. Again from 180 to 200°C, there is almost no change in the interplanar spacing. The final interplanar spacing for 6% SC8/ Epon 862/W is about 160 Å.

Our previous studies showed that the S30B and S25A from Southern Clay Products just form intercalated nanocomposites with Epon 862/W.[27] The *in situ* SAXS of 3% S30B/Epon 862/W and 3% S25A/Epon 862/W are shown in Figures 12 and 13. The interplanar spacing is ~ 36 Å when S30B is mixed with Epon 862. With the increase in the temperature, there is almost no change of the interplanar spacing. At 200°C the interplanar spacing is still 36 Å. The reason is that there is no migration of the epoxy resin from outside the gallery into the gallery. S30B does not have any catalytic effect as DSC indicated. So the polymerization outside and inside the gallery took place at the same time, or even the polymerization outside the gallery took place earlier than the epoxy resin inside the gallery, because the curing agent W is not very compatible with the organoclay gallery, and the migration of curing agent W needed time. The situation is almost the same in the S25A case. The starting interplanar spacing for 3% S25A/Epon 862/W is about 32 Å, and the final interplanar spacing is about 31.5 Å at 200°C. Again DSC also demonstrated that S25A has no catalytic effect on the polymerization. So both S30B and S25A with Epon 862/W gave the intercalated nanocomposites rather than the exfoliated nanocomposites.

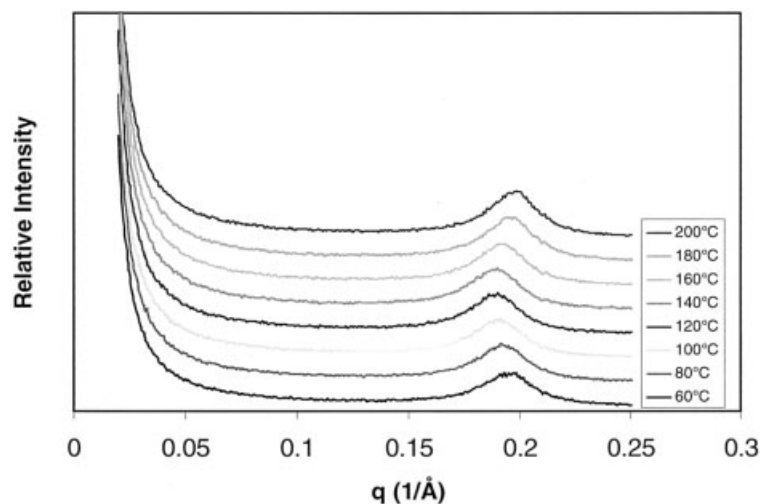**Figure 12** *In situ* small-angle X-ray scatterings of 3% S30B/Epon 862/W at 2°C/min.

Figure 13 *In situ* small-angle X-ray scatterings of 3% S25A/Epon 862/W at 2°C/min.

CONCLUSION

A series of organoclays modified with alklyammoniumchloride with different alkyl groups of different carbon chains, from a 4-carbon chain to an 18-carbon chain, were prepared, including SC4, SC6, SC8, SC10, SC12, SC16, SC18, and NC8, NC12, NC18. All of these organoclays except for SC4 are very compatible with the aerospace epoxy resin (Epon 862/W). Characterizations from WAXD, SAXS, and TEM confirm the exfoliated nanostructure. The six-carbon chain length of the ammonium cation is enough to wet the surface of the clay gallery to make it compatible with Epon 862/W. The morphology of the nanocomposites is closely related to the CEC of the montmorillonite. The clay with lower CEC is more favorable for the polymer penetration. The dynamic storage modulus of the nanocomposites was increased as expected.

Rheological characteristics showed that the addition of clay to the resin did not significantly change the viscosity or cure kinetics, and that the modified resin would still be suitable for resin transfer molding. The morphological development of the aerospace epoxy nanocomposite was monitored by *in situ* SAXS. The 3% SC18/Epon 862/W, 3 and 6% SC8/Epon 862/W showed exfoliation occurring, whereas there was no exfoliation occurring for 3% S30B/Epon 862/W and 3% S25A/Epon 862/W when the mixture was heated up to 200°C. The reason for this is because SC18 and SC8 contain acidic RNH_3^+, which has a catalytic effect on the polymerization inside the gallery, whereas the organic pendent group of S30B and S25A do not have a catalytic effect on the epoxy polymerization as DSC indicated. The faster reaction of the intragallery epoxy resin is important for the migration of epoxy resin outside the gallery into the gallery and gives rise to exfoliation. Even for the exfoliation of the 3% SC18/Epon 862/W and 3% SC8/Epon 862/W, the morphology development is different. For 3% SC8/Epon 862/W, the initial interplanar spacing in increased from 13.5 to ~ 80 Å, and the interplanar spacing between the layers is increased gradually to 190 Å until at 200°C. However, for 3% SC18/Epon 862/W, the initial interplanar spacing is increased from 13.5 to ~ 38 Å, and it experienced the disappearance of the ordered structure of the layered silicate in the beginning of the curing process, and reappearance of the ordered structure of the silicate later, which is related to the epoxy resin curing process surrounding the silicate nanosheets. Rheology, DSC, and *in situ* SAXS studies showed that organoclays (SC8 and SC18) has some catalytic effect on polymerization, and that the exothermal heat of curing inside the gallery is a key factor for nanosheets exfoliation.

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