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AEROSPACE COMPOSITE MATERIALS

Delivery Order 0003: Nanocomposite Polymeric Resin Enhancements for Improved Composite Performance

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Epoxy nanocomposites were successfully prepared using different montmorillonite-based organoclays with an epoxy resin system including several added to fiber preforms. The cation exchange capacity of the clays was the most important factor affecting the clay exfoliation. The addition of clays does not significantly alter the viscosity or cure kinetics so that the modified resin will still be suitable for liquid composite molding techniques such as resin transfer molding. The cure and morphology were examined using differential scanning calorimetry and in situ small-angle x-ray scattering (SAXS). The morphology was also examined by wide-angle x-ray diffraction, SAXS, and transmission electron microscopy. The exfoliation process requires excess energy available only when the resin exothermic reaction takes place or the temperature is very high. The moduli of the polymer-silicate nanocomposites increased over the unmodified resin. The oxygen plasma erosion rates, solvent absorption in methanol and acetone, and the solvent diffusion coefficients of the nanocomposites were all reduced for the nanocomposites. The thermal oxidative properties of the nanocomposites, however, were not enhanced. Additional work is underway examining covalently bonded organic modifiers to the inorganic clays.

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FOREWORD

This report was prepared by the University of Dayton Research Institute under Air Force Contract No. F33615-00-D-5006, Delivery Order No. 0003. The work was administered under the direction of the Nonmetallic Materials Division, Materials and Manufacturing Directorate, Air Force Research Laboratory, Air Force Materiel Command, with Karla L. Strong (AFRL/MLBCO) as Project Engineer.

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EXECUTIVE SUMMARY

Epoxy nanocomposites were prepared from the different organoclays with a high T_g epoxy resin (Shell Epon 862 and curing agent W). These organoclays are montmorillonites treated with a different organic group. Results indicate that the carbon chain length of the ammonium cation has no direct effect on the exfoliation of nanoclay in the epoxy resin, and the acidic alkyl ammonium ions play an important role for the exfoliation of epoxy resin. The clay with lower cation exchange capacity (CEC) is more favorable for the polymer penetration into the clay gallery.

Investigation of the rheological characteristics showed that the addition of clay to the resin did not significantly alter the viscosity or cure kinetics and that the modified resin would still be suitable for liquid composite molding techniques such as resin transfer molding. Differential scanning calorimetry (DSC) was performed to study the kinetics of the curing reactions in the modified resin. An *in situ* small-angle x-ray scattering (SAXS) experiment was used to try to understand the structural development during cure. Based on the *in situ* SAXS data, structural evolutions were monitored in real time during cure and analyzed. Wide-angle x-ray diffraction (WAXD), SAXS, and transmission electron microscopy (TEM) of the polymer-silicate-nanocomposites were used to characterize the morphology of the layered silicate in the epoxy resin matrix. The DSC data and *in situ* SAXS data correlate well for the morphological development. The kinetics study shows that the exfoliation takes place at the curing onset temperature, where the released cure energy is necessary for the initiation of exfoliation.

The glassy and rubbery moduli of the polymer-silicate nanocomposites were found to be greater than the unmodified resin due to the high aspect ratio and high stiffness of the layered silicate filler. The oxygen plasma erosion rates were also reduced for the nanocomposites. The solvent absorption of the exfoliated aerospace epoxy-organoclay nanocomposite in methanol and acetone was examined, and the diffusion coefficients of the nanocomposites were reduced. However, the addition of layered silicate into an epoxy matrix did not enhance the thermal oxidative stability. This is perhaps caused by the poor thermal oxidative stability (TOS) of the surfactants in the organoclays. Much effort in this reporting period was devoted to making the organoclays, which can form strong interfacial bonding.

1. INTRODUCTION

Conventional composite materials consist of a macroscopic combination of two or more distinct materials, having a recognized interface between them *[1]*. They have been widely used in construction, transportation, electronics and consumer products. Composites with at least one solid phase of a dimensional range of 1 to 100 nm can be defined as nanocomposites *[2]*. Polymer-layered silicate nanocomposites are new hybrid composite materials with only one dimension in the nanometer size for the dispersed particle filler. The filler in this class of material is in the form of sheets, which are one to several nanometers thick and hundreds of nanometers long. As a result of the layered silicates' high aspect ratio and high surface area, these nanocomposites can exhibit increased modulus, increased thermal stability, improved flame retardancy, improved ablation performance, increased solvent resistance, reduced gas permeability, and decreased thermal expansion coefficients compared to the original polymers *[3-6]*. Since Toyota researchers began comprehensive research on the polymer clay nanocomposite *[7]*, the research on polymer layered silicate nanocomposites has attracted great attention *[3-6]*. New nanocomposite materials satisfying the ever-demanding requirements for high-technology application are being developed. Nylon-based nanocomposites have even been commercialized.

Layered silicates are abundant and important minerals in geological environments at or within roughly 20 km of the Earth surface *[8]*. There are many types of sheet silicates, including clay mineral. The most widely used layered silicate for the nanocomposites is smectite clays such as montmorillonite. They offer a high aspect ratio and a high surface area. Sodium montmorillonite is 2:1 phyllosilicate, constructed of repeating tetrahedron-octehedrontetrahedron layers with two silica tetrahedral sheets fused to an edge-shared octahedral sheet of alumina.

The individual sheets in the silicates are generally stacked together and hydrophilic. Thus montmorillonite is compatible with water-soluble polymers such as poly(vinyl alcohol) *[9,10]* and poly(ethylene oxide) *[11]*. However they are not compatible with most hydrophobic organic matrix polymers. Therefore, the challenge is to produce a layered silicate system compatible with the matrix polymer. Fortunately, some silicon atoms in the silica tetrahedral layer and some alumina atoms in the octahedral layer are isomorphically substituted by alumina and magnesium, respectively. This generates negative charges that are counterbalanced by some cations, such as Na^+, K^+ or Ca^{2+}, 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 improves the wettability and dispersibility of hydrophilic clay in hydrophobic polymer matrix or monomer to make the layered silicate compatible with the polymer matrix or monomer. When the organoclays are dispersed in the polymer matrix, there are two types of nanostructures: intercalated and exfoliated. Although most organoclay nanocomposites reported so far are intercalated (polymer within the galleries), the exfoliated structure (galleries completely opened up) is more desirable for property improvement of the polymeric materials. Up to now, extensive research on the polymer layered silicate nanocomposites is being carried out and most of the research is focused on the preparation of the nanocomposite *[3-6]*. Recently, the mechanism for the exfoliation has also been of interest *[12-14]*. In this research work, the emphasis is placed on aerospace epoxy-silicate nanocomposites. The aerospace epoxy studied here is made from Shell Epon 862 (a low viscosity bis-phenol F/epichlorohydrin-based liquid epoxy resin) and Epi-Cure curing agent W (diethyltoluenediamine) with a weight ratio of 100:26. This epoxy system has high T_g (155 °C) and low viscosity, which is suitable for resin transfer modeling and has excellent and balanced mechanical properties. Thus far we have investigated the morphological development and exfoliation mechanism during processing and barrier properties in solvents and in oxygen plasma. To understand the factors affecting the exfoliation and properties of the nanocomposites, the organoclays with different surfactants ($C_{18}H_{37}NH_3^+Cl^-$, $C_{16}H_{33}NH_3^+Cl^-$, $C_{12}H_{25}NH_3^+Cl^-$) containing a different carbon chain or different original clays (SNA, Nancor) with different CEC were prepared to make epoxy nanocomposites.

For most organoclays, such as SC18, SC16, or SC12, the interfacial interaction between the organoclay and epoxy matrix is a weak Van der Waals interaction. Much effort in this reporting period was spent attempting to make organoclays which can form strong interfacial bonding. These organoclays include those modified with $HOOCC_{10}H_{20}NH_3^+$, D400/HCl, and $H_2N(CH_2)_{12}NH_2$/HCl. Although the interfacial interaction in this type of organoclay with epoxy is strong, the interaction between the backbone clay and organic pendent group is an ionic interaction, which is moderate. This interaction can become stronger with covalent bonding. Therefore, some effort to make reactive organoclays with covalent bonding between montmorillonite backbone was also tried.

Polymer nanocomposites have great potential to enhance the performance of polymers used for composite matrices. The reported performance improvements in polymers modified with low loading of organo mica-type silicates offer promise of economically improving the performance of the fiber reinforced composite. In this research, an epoxy resin suitable for use as a composite matrix (Epon 862 and Curing Agent W) modified with various modified clays (I.30E) will be introduced into the carbon fiber IM7 to make an advanced composite *[15]*.

2. EXPERIMENTAL DETAILS

2.1 MATERIALS

The resin, cure agent, chemical modifiers, clay, and organoclay used in this research include Shell Epon 862 (a bis-phenol F epoxy), Epi-cure curing agent W, carbon fiber IM7G-12K tow (Hexcel), *n*-dodecylamine (Aldrich), *n*-hexadecylamine (Aldrich), *n*-octadecylamine (Aldrich), $HOOCC_{10}H_{20}NH_2$ (Aldrich), Quat188 ($ClCH_2CH(OH)CH_2N(CH_3)_3^+Cl^-$, Dow Chemical), hydrochloric acid (Aldrich), Jeffamine D400 (Huntsman), and clays SNA (Southern Clay Products) and I.30E (Nanocor).

2.2 PREPARATION

The organoclays prepared were similar to those previously reported *[16]*. They were prepared from Closite Na (CEC: ~92 meq/100g) treated with *n*-dodecylamine and hydrogen chloride, *n*-hexadecylamine and hydrogen chloride, *n*-octadecylamine and hydrogen chloride, $HOOCC_{10}H_{20}NH_2$/HCl, D400/HCl, $H_2N(CH_2)_{12}NH_2$/HCl using the procedure described in reference *[16]*. For example, SC18 was prepared as follows: 21.1 g of *n*-octadecylamine in 750 mL of ethanol and water mixture solvent (v:v, 1:1) were added with aqueous hydrochloric acid (HCl, 1N, 67.5 mL). The mixture was stirred at ~70°C. When the solution was clear, 67.5 g of SNA were added to the above solution, and the suspension was continuously stirred for four hours at ~70°C. The resultant mixture was filtered. The solid was washed with a mixture of warm ethanol and water and dried.

The preparation of reactive organosilicates with covalent bonding between montmorillonite backbone was as follows: 5.0 g of sodium montmorillonite were added to 3-amino-propylmethyldiethoxysilane (10 g) in water and ethanol mixed solvent (4:1). The suspension was refluxed for four hours. The mixture was filtered and the solid was washed with hexane, acetone and water, and dried in a vacuum oven.

2.3 PROCESSING

Aerospace epoxy-organoclay nanocomposites were processed using a similar processing procedure as described in *[16]*. The desired amount of Epon 862 and the corresponding amount of organoclay were mixed and stirred at ~70°C. The mixture was degassed in a vacuum oven. Then the corresponding amount of curing agent W was added to the mixture while stirring. The resultant mixture was cast between glass plates spaced 0.25 cm apart and cured in a programmable Blue M oven using the following curing cycle: heat the casting in the oven to 121°C over 30 minutes, hold at 121°C for two hours, then heat to 177°C over 30 minutes and hold for another two hours at 177°C, and finally cool the casting in the oven to ambient temperature.

2.4 CHARACTERIZATION

DSC was performed on a TA Instruments differential scanning calorimeter 2920 modulated DSC at 2°C/min with air sweep gas. WAXD was performed in a Rigaku D/MAX x-ray powder diffractometer. The generator power was 40 kV and 150 mA, the scan mode was continuous with a scan rate of 0.6°/min, and the scan 2θ range was from 2° to 10°. Some of the SAXS testing was performed at the National Synchrotron Light Source at the Brookhaven National Laboratory (Beamline X27C with a one-dimensional detector). Some other SAXS data were taken using a flat-film statton camera on a Rigaku RU-200 with Cu K_α as its radiation source with a wavelength of 1.5418 Å. The power was 50 kV and 150 mA, and the exposure time was around 20 hours. 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 epoxy and curing agent was mounted on the holder, and the sample was heated up at 2°C/min. The data were recorded every minute.

The sample for TEM was microtomed in a Reichert-Jung ultracut microtome and mounted on 200-mesh copper grids. TEM was performed using a Philips CM200 transmission electron microscope with a LaB_6 filament operating at 200 kV.

Dynamic mechanical analysis (DMA) was performed using a Rheometrics ARES dynamic spectrometer using torsion bar geometry at a frequency of 100 rad/sec, a strain of 0.1 percent, and a heating rate of 2°C/min. The viscosity test was carried out on a Rheometrics ARES dynamic spectrometer using 25-mm-diameter parallel plate geometry at a frequency of 10 rad/sec, a strain of three percent and a heating rate of 2°C/min.

Oxygen plasma was generated in a GSC-200 plasma generator. The concentration in oxygen plasma was around 10^{18} radicals (or ions) per liter. Oxygen plasma erosion rates were determined by measuring the weight loss after treatment.

The effect of the addition of clay on the solvent uptake properties of Epon resin 862/Epicure curing agent W was examined. Seven Epon 862/W panels were made with zero percent layer silicate, one percent SC16, three percent SC16, six percent SC16, one percent I.30E, three percent I.30E and six percent I.30E. From these panels, 1.3 x 2.5 x 0.3-cm coupons were cut, labeled and thoroughly dried in a vacuum oven at 100°C. The coupons were then weighed, and three coupons from each sample were placed in one of two solvents at room temperature: methanol or acetone. At various times the coupons were removed from the solvent containers, dried, weighed and replaced into the solvent containers. The degree of solvent uptake was evident due to the increased mass of the coupons over time.

A TOS test was performed on three samples of Epon resin 862/Epi-cure curing agent W loaded with zero percent I.30E, two percent I.30E, and four percent I.30E. Five specimens of each sample, with dimensions of 1.3 x 2.5 x 0.3 cm, were initially dried and weighed. They were then placed in a convection oven at 200°C and subsequently weighed at various times. From the mass-time data, the mass fluxes were calculated as a means of determining the degree of oxidation.

3. RESULTS AND DISCUSSION

3.1 ORGANOCLAYS AND NANOCOMPOSITES

SC12, SC16 and SC18 are the organoclays prepared from Closite Na exchanged with primary onium ions in the laboratory. They are very similar in structure with a different length alkyl chain (12C, 16C and 18C). These three organoclays are very compatible with aerospace epoxy resins. Many epoxy-organoclay nanocomposites with different weight percentages (one percent to 10 percent) of these organoclays were made. The WAXD shows that there is no peak at 2θ scan ranging from 2° to 10°, which generally indicates that the interplanar spacing is larger than 44 Å, and the nanocomposites are considered to have an exfoliated structure.

To confirm the morphology of the nanocomposite, small-angle x-ray diffractions were taken at the National Synchrotron Light Source at the Brookhaven National Laboratory and Rigaku RU-200 (Table 1). SAXS data show that interplanar spacing is larger than 100 Å with an organoclay loading of less than eight percent. The weak peak in the SAXS data shows that there is some disordered structure, while there is some short-range ordered structure. For example, SAXS data show that the interplanar spacings for Epon 862/curing agent W nanocomposites with three percent loading of SC12, SC16, SC18 and I.30E are 146 Å, 151 Å, 135 Å, and 126 Å, respectively.

The carbon length of the ammonium cation appears to have no direct effect on the dispersion and exfoliation of nanoclay in the epoxy resin. However, the nanocomposites with quaternary onium ions, such as S30B and S10A, as reported before, are intercalated *[15]*. It appears that the acidic alkyl ammonium ions play a key role for the exfoliation of epoxy resin *[12]*. Even with an organoclay loading of 10 percent for SC18, the nanosheets in the nanoclay are expanded with interplanar spacing of 90 Å. I.30E, commercially available from Nanocor,

Table 1
SAXS Data, Storage Moduli and Glass Transition Temperatures (Tg) of the Nanocomposites and their Pristine Polymer

Clay	d-Spacing (Å)		Tg (°C)	G’ (dyne/cm^2)	
	NSLS	Rigaku	Tan d	Glassy (30°C)	Rubber (180°C)
NA			154	1.03E10	1.00E8
1.0% SC18	249				
3.0% SC18	135	135	145	1.23E10	1.39E8
6.0% SC18	129		154	1.30E10	2.14E8
8.0% SC18	114				
10.0% SC18	90	89/44	144	1.56E10	2.82E8
3.0% SC12	146				
1.0% SC16		238	155	1.20E10	1.16E8
3.0% SC16	156	151	154	1.18E10	1.63E8
6.0% SC16	150	141	155	1.24E10	2.45E8
1.0% I.30E	172		153	1.20E10	1.24E8
3.0% I.30E	126	125			
6.0% I.30E	100/49	100/48			
9.0% I.30E		88/44	144	1.61E10	2.31E8
12.0% I.30E		68			

was also treated with *n*-octadecylammonium hydrogen chloride, the only difference being the CEC of the original sodium montmorillonite (CEC: ~92 meq/100 g for Closite Na and CEC: ~145 meq/100 g for I.30E).

WAXD shows that the interplanar spacing of SC18 was increased to 18.0 Å from the original 10.5 Å of Closite Na, while the interplanar spacing of I.30E is 22.6 Å. This is consistent with the CECs of their original sodium montmorillonite (92 meq versus 145 meq). I.30 E is also very compatible with the aerospace epoxy resin, and an exfoliated nanostructure was obtained. We found that the morphology of the nanocomposite is directly related to the structure of surfactant (primary ammonium ion). In addition, the interplanar spacings of the nanocomposites from the synthetic organoclays (129 Å for six-percent SC18 nanocomposite and 141 Å for six-percent SC16 nanocomposite) are generally larger than those from commercial organoclay (100 Å, six-percent I.30E nanocomposite). However, the original interplanar spacing of the synthetic clay (~18 Å) is even smaller than that of commercial organoclay (I.30E, 22.6 Å). The higher

CEC means that more organic groups can be introduced into the gallery, and interplanar spacing is also larger (22.6 Å). However, when the organoclay was mixed with epoxy resin, the organoclay with high CEC has more organic groups inside which perhaps slows the epoxy resin migrating into the gallery *[17]*. Thus it makes the gallery of the nanocomposite from montmorillonite (I.30E) with high CEC smaller than that with lower CEC (SC18).

Several images of TEM of these nanocomposites were taken and the images were found to be similar. The TEM of six-percent I.30E/Epon 862/W is shown in Figure 1. The dark lines are cross sections of the silicate sheets of nanometer thickness. The original aggregates of the silicate sheets are disrupted, and each individual sheet of nanometer thickness was well dispersed in the epoxy resin. Some individual sheets are completely disordered, while some still preserve the parallel alignment of layers with ~10 nm separation. This is consistent with the SAXS results (~100 Å).

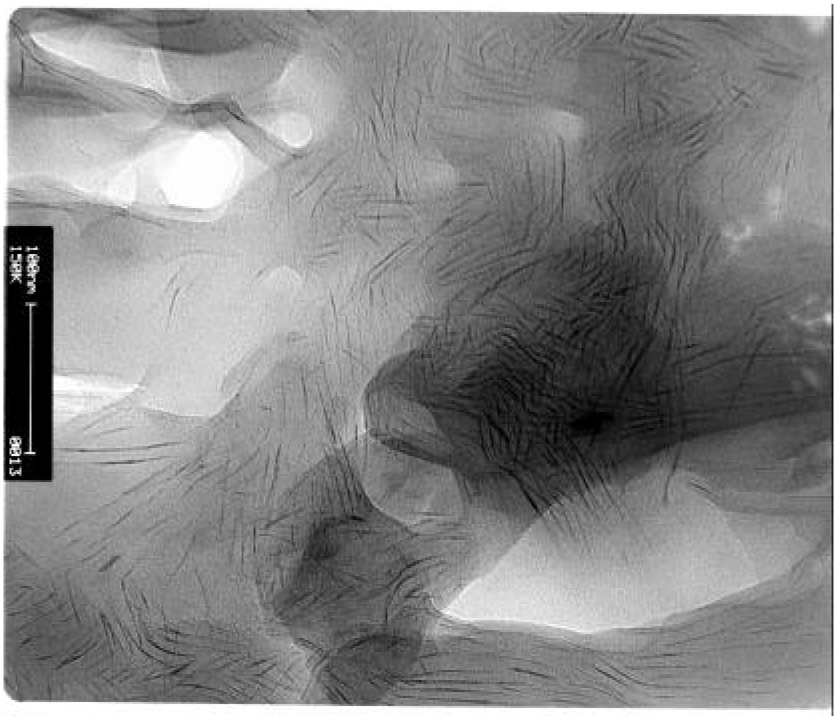

Figure 1. TEM Image of the Epoxy-Nanocomposite of 6% I.30E/Epon 862/W.

Organoclay with $HOOCC_{10}H_{20}NH_3^+$ as the pendent group was prepared by the treatment of the sodium clay with $HOOCC_{10}H_{20}NH_2$ and HCl. This organoclay had the -COOH group in the pendent group, which has the potential for forming chemical bonds with the epoxy matrix (NH_2 and OH groups in the epoxy resin). This organoclay has difficulty in dispersing well in the epoxy resin via the general stirring procedure. However, this organoclay can form a well-dispersed large panel without flocculation after 24-hour mechanical stirring and sonication with an acetone-assisting method. This nanocomposite was intercalated based on x-ray diffraction. The interplanar d-spacings of the original sodium clay, organoclay, and nanocomposite are 12.1, 16.6, and 18.9 Å, respectively. The flexural modulus, flexural strength and failure strain based on a three-point flex test were 0.428 Msi, 14.2 ksi, and 0.042. The toughness based on compact tension is 495 psi*in$^{0.5}$. The flexural modulus was improved, while the toughness and strength were decreased. More work is needed to get fully exfoliated nanocomposites with improved mechanical properties.

Sodium montmorillonite was treated with $ClCH_2CH(OH)CH_2N(CH_3)_3^+Cl^-$ (Quat188) to achieve covalent bonding between the organoclay's pendent group and the epoxy matrix. Although this organoclay has difficulty in dispersing well in the epoxy resin by general stirring, it can form a well-dispersed large panel without apparent flocculation by mechanical stirring in the sonication bath with the acetone-assisting method. X-ray characterization shows a small increase of interplanar spacing, which means that there was little penetration of epoxy resin into the gallery of the clay. The mechanical testing shows decreased mechanical properties.

Because the organoclay treated with diamines [Jeffamine D400/HCl or $H_2N(CH_2)_{12}NH_2$/HCl (C12N2)] cannot form good exfoliated nanocomposites, sodium montmorillonite was treated with mixtures of $CH_3(CH_2)_{17}NH_2$ (C18) and D400, or C18 and

C12N2. One of the pendent groups, C18, renders the organoclay compatible with the epoxy resin forming a homogeneous nanocomposite, while another pendent group, C12N2, forms covalent bonds with the epoxy resin matrix reinforcing the interfacial interaction. The initial studies showed that the organoclays with mixture pendent groups (SC18-SD400 and SC18-C12N2) could form good transparent nanocomposites with epoxy resin at the three-percent organoclay loading. However WAXD showed that the nanocomposites are intercalated nanocomposites, which are only partially exfoliated or not exfoliated at all. The interplanar spacings for SC18-SD400 and its nanocomposites are 15.2 Å and 18.0 Å, while the interplanar spacings for SC18-C12N2 and its nanocomposites are 14.4 Å and 13.5 Å. More effort should be devoted to making exfoliated nanocomposites.

Research on the introduction of covalent chemical bonding between the sheet backbone of silicate and pendent group and pendent group and matrix polymer was tried, and some progress has been achieved. Sodium clay was treated with 3-aminopropylmethyldiethoxysilane in ethanol and water solution at refluxing temperature. WAXD of the product demonstrates that the interplanar spacing of the product was 17.9 Å compared with the original sodium clay interplanar spacing of ~12 Å. This shows that the aminopropyl was grafted on the backbone of clay. This organoclay was used to make nanocomposites with Epon 862 and curing agent W. Both direct mixing of this organoclay and epoxy resin by stir-bar stirring and acetone-assisted mixing under sonication and mechanical stirring at elevated temperatures have been attempted. Although the appearance of the small molding sample appears to be uniform with three-percent loadings of organoclay, WAXD showed that the samples are not homogeneous. The x-ray diffraction of the sample bottom surface shows a clear peak corresponding to the interplanar spacing of ~18.2 Å, which is very close to the original organoclay's interplanar spacing (17.9 Å), while there is no peak at all in the sample upper surface. The situations are the same for both processing methods. Further effort is needed to open the organoclay gallery in order to let the polymer penetrate into the gallery. The reason for the difficulty of the epoxy resin penetration into the gallery of this organoclay is not very clear. Perhaps this is caused by the strong hydrogen bonding interaction between the free amine (NH_2 of the pendent organic group) and OH groups of silicate backbone. So, for this special epoxy system, another possibility of introducing the reactive group is a cyclic oxygen group, which should have much weaker interaction with the silicate backbone. It appears that much more effort is needed for these special nanocomposites with strong bonding between matrix and clay.

3.2 KINETICS STUDIES

3.2.1 Rheology

A rheological study related to 7.5-percent I.30E/Epon 862, six-percent I.30E/ Epon 862/W, and Epon 862/W was performed by DMA (Figure 2). At room temperature the viscosity of the I.30E/Epon 862/W is a little higher than that of Epon 862/W, as expected. However the increase is limited and the resin maintains its processability. As the temperature increases, the crosslinking polymerization takes place. After the polymer is formed, with the temperature continually increased, the solid polymer will begin to soften into a rubber state. The shape of the viscosity versus time and temperature is similar for all the samples. The gelling takes place more quickly for the epoxy resin with organoclay. The time and temperature of the turning point of softening for I.30E/Epon 862/W are also similar to that of Epon 862/W, but are clearly shorter (seven minutes shorter) and lower (180 versus 196°C). This demonstrates that the organoclay has some catalytic effect on the polymerization of Epon 862/W. The viscosity of 7.5-percent I.30E/Epon 862 was the highest, as expected. As the temperature increases, the

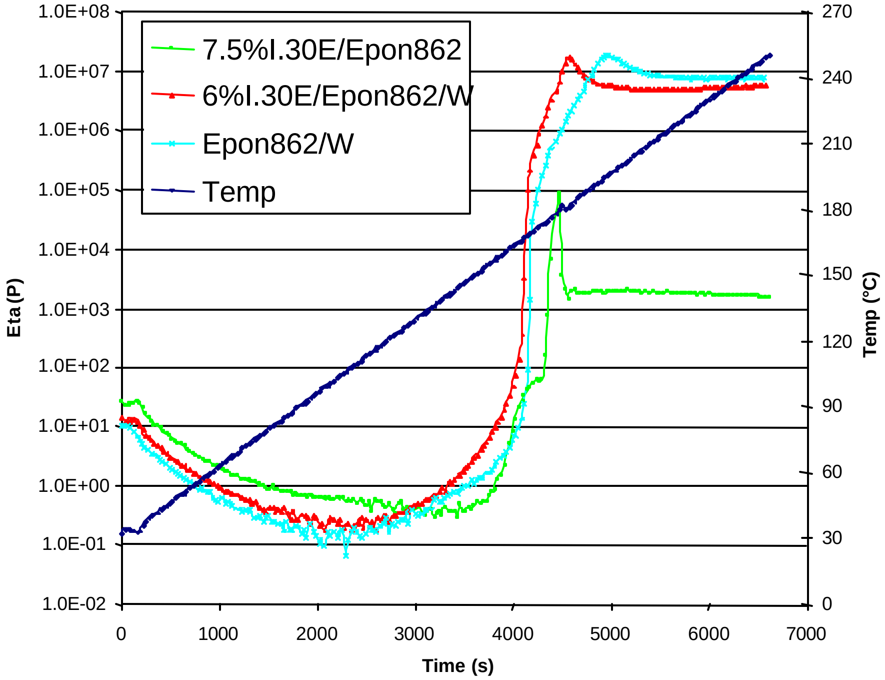

Figure 2. **The Viscosity and Temperature Change of 7.5% I.30E/Epon 862, 6% I.30E/Epon 862/W and Epon 862/W with Time.**

gelling process is also slowed. However, at ~175°C, the viscosity increases suddenly and the materials are rapidly solidified. At the same time the volume of the materials between the plates is expanded, and some material was pressed out of the parallel plates at ~180°C.

3.2.2 DSC

DSC experiments using I.30E/Epon 862/curing agent W, I.30E/Epon 862, and Epon 862/curing agent W were performed (Figure 3). With the addition of the organoclay (I.30E) to the original Epon 862/W resin, the nanocomposite system produces more exothermal heat (206.0 versus 191.4 J/g) at lower curing onset temperature (102.5 versus 122.5°C). This demonstrates that the organoclay has some catalytic effect on the crosslinking polymerization of Epon 862 with curing agent W *[12]*. While for the system I/30E/Epon 862 without curing agent W, DSC shows that self-polymerization of Epon 862 can take place. This is contrasted with the fact that there is no polymerization for Epon 862 itself at this temperature, and the monomer will

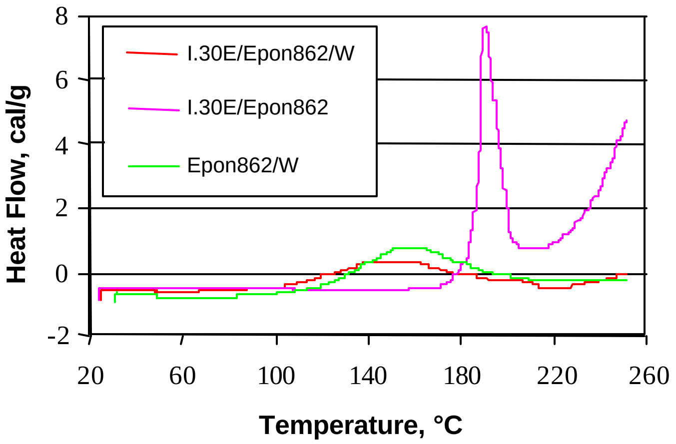

Figure 3. DSC of Epon 862/W, 6% I.30E/Epon 862/W and 7.5% I.30E/Epon 862 at 2°C/min.

decompose at a higher temperature. So the organoclay is the catalyst for this self-polymerization into polyether.

3.2.3 *In Situ* SAXS

The gallery structure will change during processing. The *in situ* SAXS at the National Synchrotron Light Source at the Brookhaven National Laboratory provides a wonderful means of monitoring the structural evolution. When Epon 862 is mixed with I.30E, some of the Epon 862 monomer will enter into the gallery of the organoclay. The interplanar spacing was increased to ~35 Å from the original 22.6 Å. For clarity purposes, some key data were selected (Figure 4). When the mixture was heated up at 2°C/min, for the I.30E/Epon 862/W, the peak gradually shifted and became a little weaker but not significantly.

Amazingly, at ~102°C, suddenly the ordered structure collapsed and exfoliation took place. Eventually, a new clear peak appears, and the intensity and interplanar spacing increased gradually. The temperature for the collapse of the ordered structure is the same as the curing onset temperature from DSC. This is perhaps because the exothermal heat from curing at

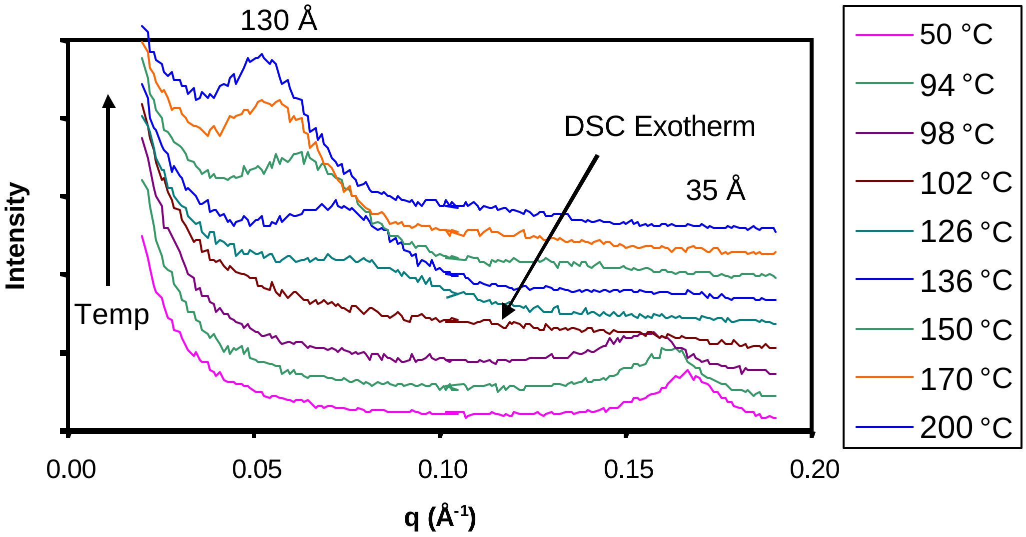

Figure 4. ***In Situ*** **SAXS of 6% I.30E/Epon 862/W at 2°C/min.**

~102°C provides enough energy to make the nanoclay sheets expand quickly and exfoliation takes place.

On the other hand, for the I.30E/Epon 862 without curing agent W (Figure 5), there is almost no change until 150°C for interplanar spacing and a small decrease for the intensity of the peak. From 150°C to 160°C, the intergallery was expanded from 40.0 to 44.5 Å, and intensity was also reduced to some extent. However after 160°C, the intergallery was expanded rapidly, and the intensity of the peaks also increased. Up to 180°C the intergallery spacing is 140 Å, and the intensity is almost four times that at 160°C or 50°C. After 184°C the expansion between sheets is large, so large that it occurs at an angle too small to be detected. DSC (Figure 3) shows that the exothermic reaction takes place at ~160°C for the system I.30E/Epon 862 without curing agent W. So the expansion of the nanosheets takes place after ~160°C for this system. This exothermal process is so rapid and intense that the expansion of the intergallery is also very fast. The exothermal peak is so intense (344.9 J/g, almost double that of Epon 862/W) that it makes the SAXS at ~190°C occur at too low an angle to be detected.

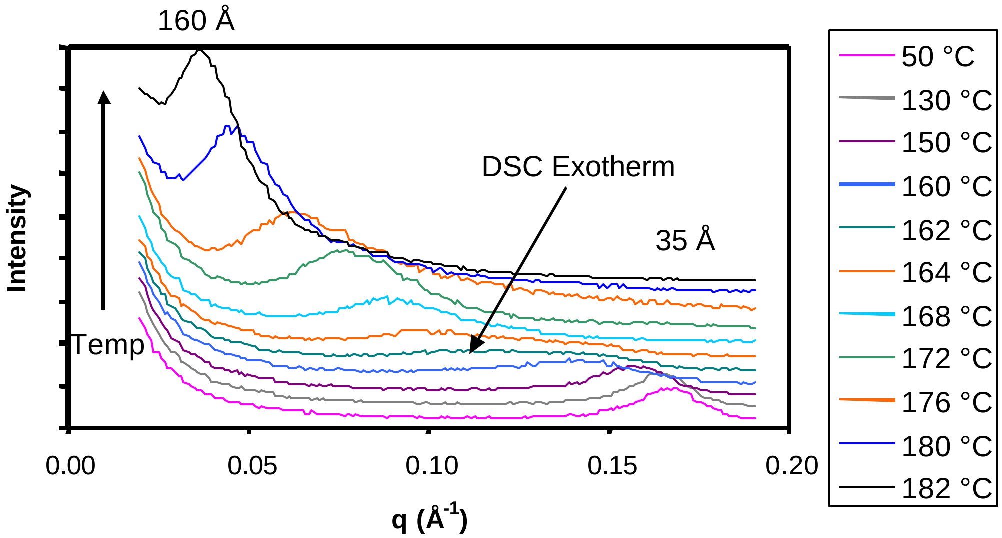

Figure 5. ***In Situ*** **SAXS of 7.5% I.30E/Epon 862 at 2°C/min.**

So, the energy is one of the requirements for the exfoliation of nanosheets. This also can explain one of the most common means of making nanocomposites – melt processing – which also requires high temperatures. The expansion of the nanosheets of the layered silicate in I.30E/Epon 862 without curing agent is much larger than that with curing agent. This is perhaps caused by the fact that the gelling and crosslinking of the matrix epoxy with the curing agent slows the expansion of the nanosheets of organoclay. The results of the kinetics studies from *in situ* SAXS, DSC and rheological testing are well related.

3.3 PROPERTIES

3.3.1 DMA

The DMA (Figure 6 and Table 1) shows that the storage modulus of the nanocomposites is higher than that of the pristine epoxy resin. Moduli increase with increased organoclay loading. Generally, the nanocomposites show more significant improvement of storage modulus in the rubbery state than in the glassy state. The dynamic storage modulus can

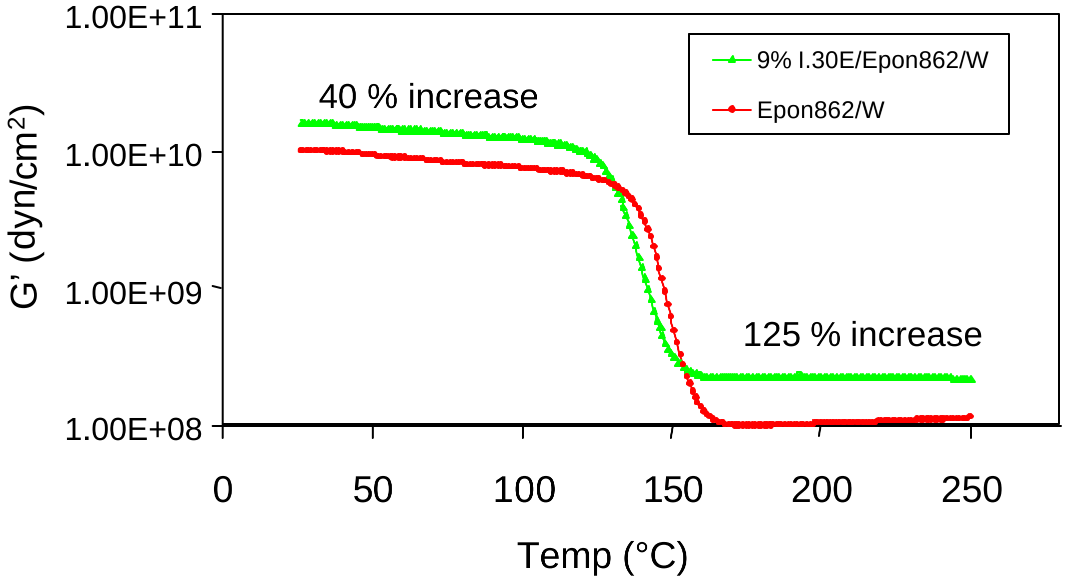

Figure 6. Dynamic Storage Modulus of 9% I.30E/Epon 862/W and Epon 862/W.

be increased up to more than 40 percent in the glassy state and 125 percent in the rubbery state. This is due to the high aspect ratio and high stiffness of the organoclay filler. The extra reinforcement from further nanosheet alignment in the rubbery state perhaps is the reason for larger increases in the rubbery state *[18]*.

3.3.2 Barrier Properties

3.3.2.1 *Survivability in Oxygen Plasma*

To test the survivability of the nanocomposites in aggressive environments, several nanocomposites (three-percent I.30E/Epon 862/W, six-percent I.30E/Epon 862/W, and six-percent SC16/Epon 862/W) and pure epoxy resin (Epon 862/W) were exposed in the oxygen plasma. Oxygen plasma contains many species such as atomic oxygen, radicals, ozone molecules, cations, anions, electrons, etc., which are extremely strong oxidants. Up to now, polymers were one of the most vulnerable materials under oxygen plasma. The surface erosion rate is shown in Figure 7. The surface erosion rates for epoxy nanocomposites are significantly retarded compared with pure epoxy resin. The retardation effect of six-percent clay

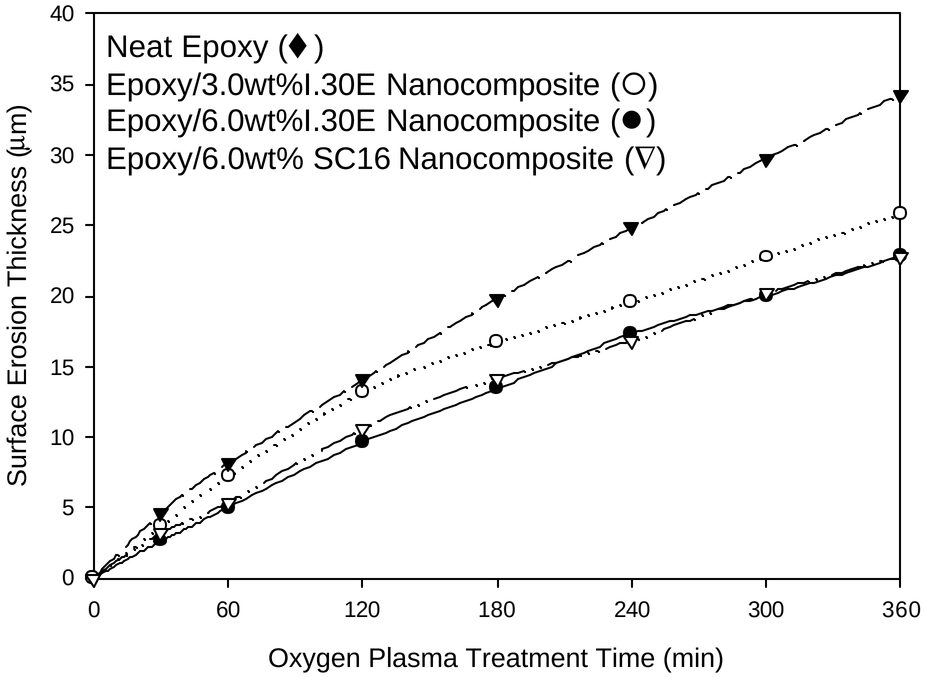

Figure 7. Oxygen Plasma Surface Erosion Rate of Epon 862/W, 3% I.30E/Epon 862/W, 6% I.30E/ Epon 862 and 6% SC16/Epon 862/W.

nanocomposite is greater than that of three-percent clay nanocomposites, while there is almost no difference in the retardation between the two different organoclays (I.30E and SC16). The SAXS showed that the interplanar spacing of nanocomposites after exposure to the oxygen plasma was reduced, indicating some epoxy resin inside the gallery was eroded. The possible mechanism for the retardation is that the nanocomposite materials can form inorganic layers when they are exposed to the oxygen plasma. The preferential oxidation of polymers and corresponding enrichment of the nanoscale-layered silicate on the surface cause the formation of the ceramic-like inorganic layer. This inorganic layer retards the penetration of the oxygen plasma and thus prevents further degradation. The nanocomposite may enhance the survivability of the polymeric materials in aggressive environments such as low-earth orbit (LEO) against atomic oxygen. Similar materials have been submitted for exposure in LEO under the Materials on International Space Station Experiment (MISSE).

3.3.2.2 *Solvent Uptake*

The solvent uptake was examined in acetone and methanol. The percentages of the sample mass gain versus square root of immersion time of Epon 862/W; one-percent, three-percent, and six-percent SC16/Epon 862/W; and one-percent, three-percent, and six-percent I.30E/Epon 862/W in methanol are shown in Figure 8. The data show that the methanol uptake for the nanocomposite is significantly lower compared with the pristine polymer. This is ascribed to the barrier effect of nanosheets of the nanoclay in the epoxy resin. High loading of organoclay is more effective for the solvent resistance, and SC16 appears more effective than I.30E. This is perhaps related to the better dispersion of organoclay in the epoxy matrix for SC16/Epon 862/W, as small-angle x-ray diffraction indicates.

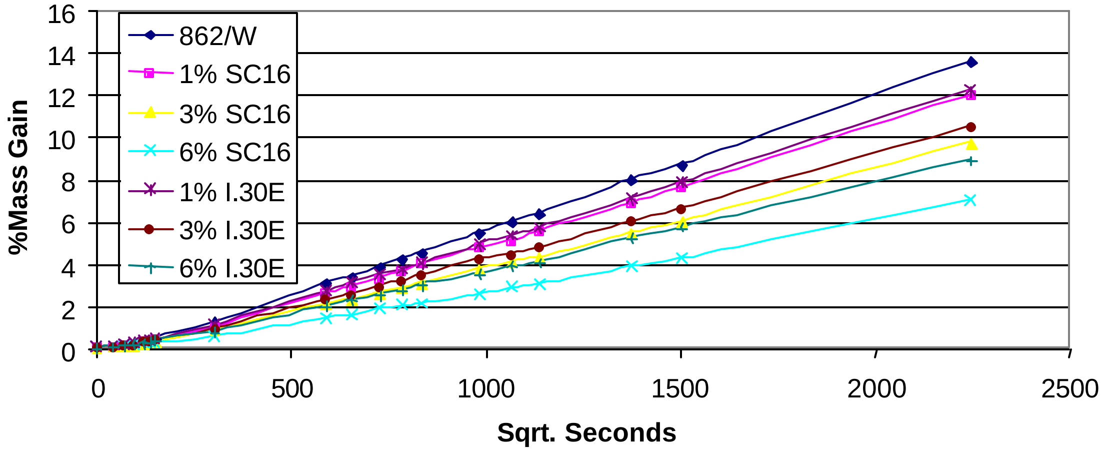

Figure 8. Methanol Uptake of Epon 862/W; 1%, 3%, and 6% SC16/Epon 862/W; and 1%, 3%, and 6% I.30E/Epon 862/W Nanocomposites.

The solvent uptake data for the samples placed in acetone and methanol are plotted in Figures 9 and 10 as evidence of a typical percent mass gain versus square root of immersion time curve. From the percent mass gain-time data of the nanocomposite coupons, the one-dimensional binary diffusion coefficient was found using the following relationship *[19]*:

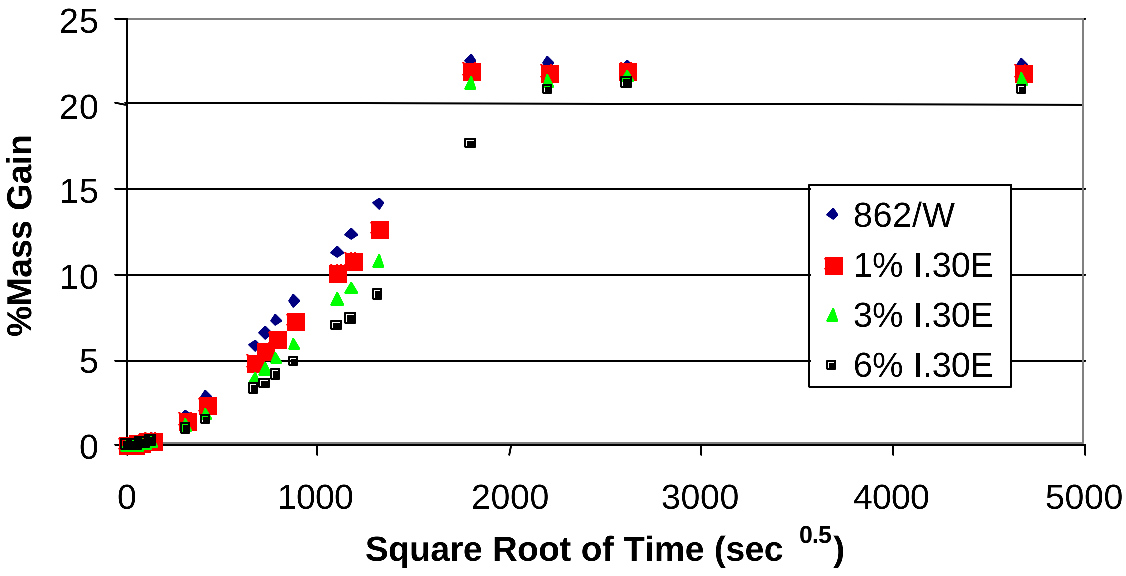

Figure 9. **Diffusion of Acetone into Epon 862/W Loaded with I.30E.**

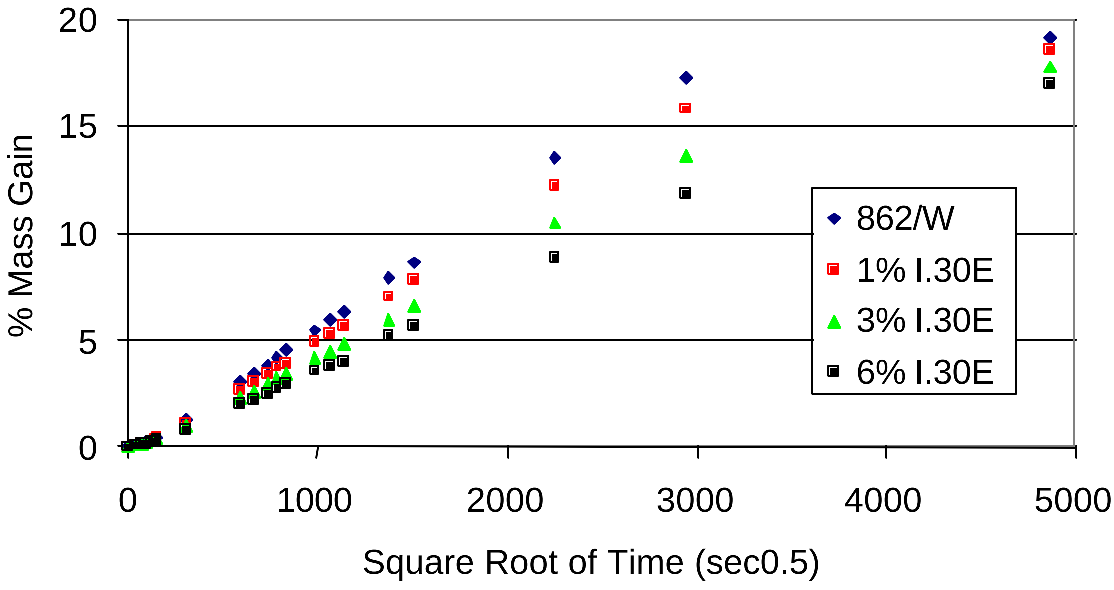

Figure 10. **Diffusion of Methanol into Epon 862/W Loaded with I.30E.**

$$D = \pi \cdot [[\, 2h / (4Mmax)]^{2} \cdot (\Delta M / \Delta t^{0.5})^{2}],$$

where D is one-dimensional binary diffusion coefficient, h is half-thickness, Mmax is maximum percent mass gain, and ($\Delta M/\Delta t^{0.5}$) is initial slope of the percent mass gain versus square root time plot. The derivation of this relationship was based on the assumption of one-dimensional diffusion, which was not completely justified in this research as all coupons had an aspect ratio of approximately four in one dimension and eight in the other. An aspect ratio of 10 or greater would be more desirable to ensure the validity of the assumption, although the one-dimensional binary diffusion coefficients calculated may be used for a semiquantitative analysis. The initial slopes of the percent mass gain versus the square root of time plots were calculated using linear regression. Values for the average one-dimensional binary diffusion coefficient of methanol and acetone in Epon 862/W with different I.30E loadings are listed as follows: for acetone, 11.3×10^{-11} cm^2 /sec (pure Epon 862/W resin), 9.10×10^{-11} cm^2 /sec (one-percent I.30E/Epon 862/W nanocomposite), 6.69×10^{-11} cm^2 /sec (three-percent I.30E/Epon 862/W nanocomposite), and 4.63×10^{-11} cm^2/sec (six-percent I.30E/Epon 862/W nanocomposite); for methanol, 4.25×10^{-11} cm^2 /sec (pure Epon/W resin), 3.54×10^{-11} cm^2 /sec (one-percent I.30E/Epon 862/W nanocomposite), 2.79×10^{-11} cm^2 /sec (three-percent I.30E/Epon 862/W nanocomposite), and 2.27×10^{-11} cm^2 /sec (six-percent I.30E/Epon 862/W nanocomposite).

The addition of I.30E had a dramatic effect on the ability of various solvents to diffuse into Epon 862/curing agent W. For acetone and methanol, a one-percent loading of I.30E decreased the diffusion coefficient by 19 percent and 17 percent. For a three-percent loading, the diffusion coefficient decreased by 41 percent and 34 percent for acetone and methanol, respectively. For a six-percent loading, the diffusion coefficient loading decreased by 59 percent and 47 percent. In all cases the SC16 caused a more significant decrease in the diffusion coefficient than did I.30E. In fact, the diffusion coefficients of the samples loaded with three-percent SC16 were close to the diffusion coefficients calculated for the samples loaded with six-percent I.30E. The diffusion coefficients calculated for the samples loaded with six-percent SC16 were typically 20 percent lower than the diffusion coefficients calculated for the samples loaded with six-percent I.30E. Again, this is perhaps related to the better dispersion of nanosheets in SC16/Epon 862/W nanocomposites.

3.3.3 Thermal Oxidative Stability Test

From the mass loss data and the measured samples' dimensions, the mass fluxes were calculated and are shown in Table 2. The mass flux, at all times, was lowest for the Epon 862/Epi-cure curing agent W samples followed by the samples loaded with two-percent I.30E and those loaded with four-percent I.30E. The data seem to indicate that the addition of layered silicate into an epoxy matrix does not enhance the thermal oxidative stability. However, the increased mass flux in the epoxy samples loaded with I.30E may have been due to the decomposition of the organic surfactants. Thermal analysis in nitrogen showed that I.30E experienced a significant degree of mass loss at 200°C. This mass loss was due to the decomposition of the *n*-octadecylamine surfactant on the surface of the inorganic silicate. In fact, 36 percent of the weight was lost before an inorganic residue remained at 800°C. Thus, the addition of layered silicates to the epoxy composite matrix may indeed enhance the thermal oxidative stability. The organoclay may continue to experience decomposition of its organic surfactants while decreasing the degree of matrix decomposition, although longer studies are needed to substantiate this hypothesis. The TOS testing of nanocomposites is still continuing. More data will be collected on four samples of Epon 862/W loaded with zero-percent silicate, two-percent A-CM_2, two-percent I.30E, and four-percent I.30E.

Table 2
Effects of Silicate Addition on Thermal Oxidative Stability
(Cumulative Mass Flux at Various Times [g/(cm^2·sec)])

Sample	After 93 hr	After 189 hr	After 353 hr	After 689 hr	After 979 hr
862/W	2.50E-09	1.89E-09	1.59E-09	1.81E-09	1.96E-09
2% I.30E	3.02E-09	2.26E-09	2.06E-09	2.29E-09	2.23E-09
4% I.30E	3.50E-09	2.65E-09	2.46E-09	2.63E-09	2.38E-09

4. CONCLUSIONS AND RECOMMENDATIONS

Exfoliated aerospace epoxy organoclay nanocomposites with organoclays (SC12, SC16, SC18 and I.30E) were successfully made. The characterization from WAXD, SAXS and TEM confirms the exfoliated nanostructure. The carbon chain length of the ammonium cation has no direct effect on the dispersion and exfoliation of nanoclay in the epoxy resin, but the acidic alkyl ammonium ions play an important role in the exfoliation of epoxy resin. The morphology of the nanocomposites is also closely related to the CEC of the montmorillonite. The clay with lower CEC is more favorable for the polymer penetration. Rheological characteristics showed that the addition of clay to the resin did not significantly alter the viscosity or cure kinetics, and that the modified resin would still be suitable for resin transfer molding. *In situ* SAXS clearly shows the morphological development of the nanocomposite during cure. DSC and *in situ* SAXS studies show that the organoclay has some catalytic effect for polymerization, and that the exothermal heat at onset curing temperature is a key factor for nanosheets exfoliation. The dynamic storage modulus of the nanocomposites was increased. Aerospace epoxy-organoclay nanocomposite can also form a passivating inorganic layer, which will enhance the polymeric survivability under oxygen plasma. The solvent uptake for the nanocomposites is significantly lower compared with the pristine polymer, and one-dimensional binary diffusion coefficients of methanol and acetone in nanocomposites are much reduced. The addition of layered silicate into an epoxy matrix did not enhance the TOS. This is perhaps caused by the low TOS of the surfactants in the organoclays. Research on the introduction of covalent chemical bonding between the sheet backbone of silicate and pendent group and pendent group and matrix polymer was attempted. An organoclay with 3-aminopropylmethyldiethoxysiloxy group was successfully prepared.

5. PUBLICATIONS

The following publications were generated during this reporting period.

Chen, Chenggang, & David Curliss. (2001). Resin Matrix Composites: Organoclay-Aerospace Epoxy Nanocomposites, Part II. *SAMPE Journal 37*(5) (11-18).

Rice, Brian P., Chenggang Chen, Larry Cloos, & David Curliss. (2001). Carbon Fiber Composite: Organoclay-Aerospace Epoxy Nanocomposites, Part I. *SAMPE Journal 37*(5) (7-9).

Fong, Hao, Richard A. Vaia, Jeffrey H. Sanders, Derek Lincoln, A. J. Vreugdenhil, Weidong Liu, John Bultman, & Chenggang Chen. (2001). Self-Passivation of Polymer-Layered Silicate Nanocomposites. *Chemistry of Materials* (4123-4129).

Chen, Chenggang, & David Curliss. (2001). Processing, Dynamic Studies and Properties of Exfoliated Aerospace Epoxy-Organoclay Nanocomposites. *Nanophase and Nanocomposite Materials IV, Proceedings of the Materials Research Society Symposium 701*.

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LIST OF ACRONYMS

CEC	cation exchange capacity
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
LEO	low-earth orbit
MISSE	Materials on International Space Station Experiment
SAXS	small-angle x-ray scattering
TEM	transmission electron microscopy
TOS	thermal oxidative stability
WAXD	wide-angle x-ray diffraction