This is to certify that the

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Rigid Epoxy CLay Thermoset Nanocomposites

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RIGID EPOXY CLAY THERMOSET NANOCOMPOSITES

By

Mark Richard Sislo

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ABSTRACT

RIGID EPOXY-CLAY THERMOSET NANOCOMPOSITES

By

Mark Richard Sislo

Nanocomposites are formed when a compositional change occurs on a nanometer length scale. Toyota research first demonstrated an organoclay exfoliated Nylon-6 polymer matrix which, greatly improved the mechanical and thermal properties of the pristine polymer, in automotive under-the-hood applications. Compared to the conventional composite these improved thermal and mechanical properties were found to be superior due to improved phase morphology and interfacial properties. In the present work, an organic modified silicate is first prepared, then due to favorable hydrophobic interactions, the epoxy system ideally polymerizes within the gallery resulting in an exfoliated clay nanolayers thoughout the polymer matrix.

The *in-situ* intragallery polymerization greatly improves such properties as permeability, tensile strength, storage modulus and glass transition temperatures. Interestingly it was found the organic used to modify the clay was responsible for a decrease in glass transition temperature, while increasing the storage modulus.

To my family and my new family of the future, thank you for all your love support and patience.

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INTRODUCTION

1.1 Nanocomposite

1.1.1 Concept

In the late 1980's Toyota researchers introduced the first nanocomposite polymer, consisting of nylon-6 interspersed with layers of a smectic clay, montmorillionite. [1,2] The clay greatly improved the mechanical properties of the nylon polymer with a small amount of silicate loading. Subsequently Toyota found the nanocomposite polymer to have an increased resistance to heat and used it for a timing belt cover, proving its merit for under-the-hood automotive applications. Since then, research in polymer nanocomposites has received an enormous amount of attention due to its fundamental science and applications.[3-9]

Composite materials are formed when at least two distinctly different materials are combined to form a monolith. The overall properties that this monolith exhibits are not only dependent on the parent materials, but also the phase morphology and interfacial properties. [4]A nanocomposite is formed when a compositional change occurs on a nanometer length scale. This is different from the conventional composites, where phase mixing occurs on the macroscopic scale. The main difference is the nanocomposite's improved interfacial properties and unique phase morphology, which gives rise to superior mechanical properties.

1.1.2 Formation of Nanocomposite Through Traditional Clay-Modification

One approach in preparing the nanostructured hybrid organic-inorganic composites is by the sol-gel processing method. [10-12] In this method, the inorganic phase is formed by the hydrolysis and condensation of a metal oxide precursor in the presence of a preformed polymer or polymer precursors, which can simultaneously polymerize. Although this method has proven applications, it will no longer be addressed due to the fact that this method was not practiced in the following thesis. Instead, the epoxy nanocomposites of interest in the present work were formed by first exchanging cationic alkylammonium surfactants into clay galleries, this increasing the likelihood of intercalation by the prepolymer. An expanded gallery height as well as a newly rendered organic environment in the galleries, both of which favor the intercalation of the epoxy polymer, accompanies this exchange process. The onium ions also encompass acid catalyzing properties that bias intragallery polymerization. The catalytic interfacial properties and unique phase morphology, which gives rise to superior mechanical properties.

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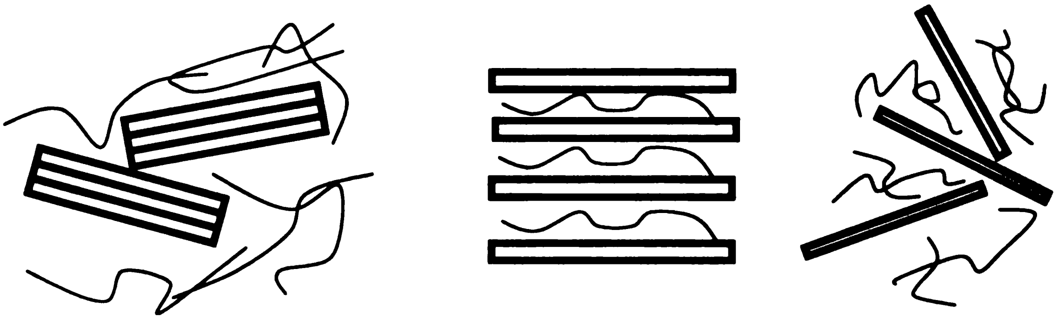


Conventional Composite

Intercalated Nanocomposite

Exfoliated Nanocomposite

Figure 1.1 Schematic of the structural differences between the conventional composite and the intercalated and exfoliated nanocomposite.[13]

1.1.3 Polymer Clay Nanocomposites

Clay as a reinforcing agent posses unique characteristics, including a large surface areas (~760 m^2/g) and a high aspect ratio (200-2000), which enhances the polymer's capability to carry an applied load and facilitates stress transfer to the reinforcement phase, improving tensile and impact properties. Other research has utilized different fillers as nanoscale reinforcement of a polymer, such as metal fibers, layered phosphates etc.[13-16] As is the case in many applications in material chemistry, some fillers may yield a gain in physical properties, but suffer in practical applications due to high cost. In this particular research we have chosen a cost-efficient montmorillonite clay as the reinforcement agent.

The most common clays used in nanocomposites stem from the smectite family. This family of clays possess the platy morphology and cation exchange capacity (CEC) capable of polymer intercalation, while remaining stable and large enough to reinforce a cured epoxy system. More specifically, montmorillonites was used as the most readily available naturally occurring smectite clay. Also, it was found that a synthetic smectite clay, fluorohectorite, possessed unique characteristics such as evenly distributed basal charge, ideal CEC and large aspect ratio, all characteristics which are beneficial for nanocomposite application.

These clays from the smectite family are two-dimensional layered silicates possessing an effective particle size of about 2 microns. The 2:1 silicates are 9.6Å-thick layers stacked face-to-face to form turbostratic tactoids. Each silicate layer (~2000Å diameter) is made of two tetrahedral sheets with an octahedral sheet sandwiched between the two tetrahedral sheets. Corner sharing of SiO4, or a less common by AlO4 tetrahedra forms the tetrahedral sheets. Clay layers have a negative charge generated from a substitution of metal ions in the octahedral and/or tetrahedral sheet by a lower valent metal ion (e.g., Si^{4+} by Al^{3+}, Al^{3+} by Mg^{2+} or Fe^{2+}/Mg^{2+} by Li^{+}). This net negative charge from the silicate layers is neutralized by gallery cations, such as Na^{+}, Li^{+}, Ca^{2+}, and K^{+}. The hydrophilic gallery cations are capable of being exchanged by other inorganic cations or hydrophobic organic cations.[17-19] A Schematic that illustrates a side-on view of a 2:1 silicate layer is provided in Figure 1.2.

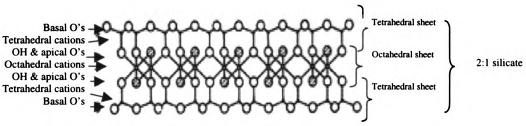
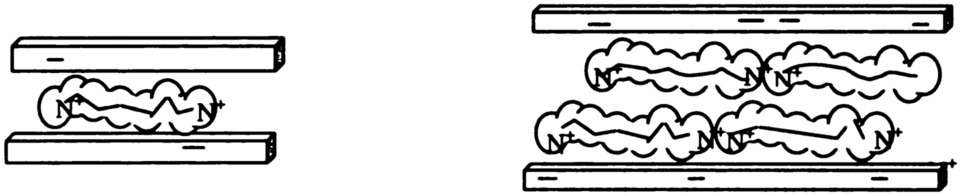


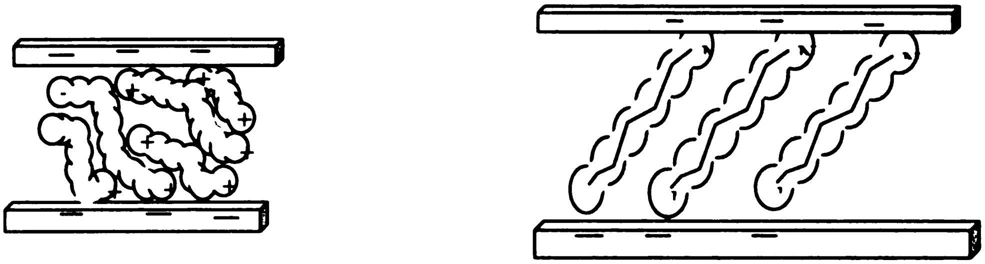
Figure 1.2 An illustration of the location of atoms in generic 2:1 smectic clay.

1.1.4 Organoclay

Organic cations as clay-modifiers ensure a spontaneous intercalation of prepolymers and monomers into the gallery. The two major contributing factors in the formation of an exfoliated or a particular type of intercalated composite is the charge density and the size of the organic species. Examples of different types of intercalated Jeffamine structures are illustrated in Figure 1.3.



A: Lateral Monolayer **B: Lateral Bi-Layer**



C: Pseudo-trilayer **D: Paraffin**

Figure 1.3 Orientations of Jeffamine surfactants in the galleries of layered silicates with different layer charge densities. [20,21]

In low charge density clays that have an intercalated long alkylammonium chain, the chains lie parallel to the siloxane basal surface in the form of a monolayer or bilayer. High-charge density clay, on the other hand, tends to configure the chains as in a paraffin structure. Moreover, high charge density clay with a shorter alkylammonium chain may transform from paraffin to a lateral monolayer, structure. Instances in which short chain organics exist in the gallery, the gallery may not be swellable by a polymer due to the strong electrostatic interactions between the layers and intergallery cations.

Organic cations may co-exist within a gallery of inorganic cations. These mixed organic/inorganic exchanged clays, known as homostructures (uniform mixtures of inorganic and organic cations in the same gallery). They result due to a competition between the inorganic and organic cations for the binding sites.[22,23]

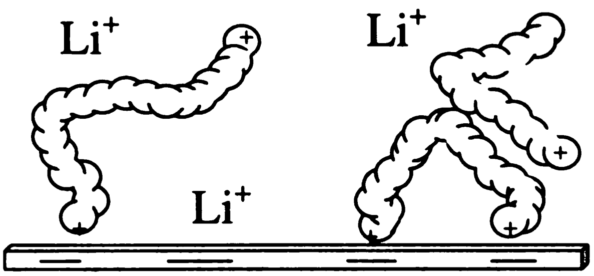


Figure 1.4 Possible distributions of inorganic cations and organic diprotonated Jeffamine cations in a mixed ion smectite.

When used for nanocomposite formation, a mixed organic-inorganic clay decreases the plasticizing effect on the composite compared to fully exchanged organic clays. Also, mixed ion clays provide a cost effective method for clay modification by reducing the use of high-cost surfactant molecules.

If a fully exchanged organic modified clay is desired, such clays can be formed through multiple exchanges or by using excess organic cations may overcome this competitive binding between the organic and undesired inorganic cations. In some polymeric systems the presence of the metal cations in the gallery may have a significant impact on the swelling of an organoclay with a prepolymer or monomer, the significance being greater as the degree of hydrophobicity of the system increases.

1.2 Composite types

Polymer-clay composites can be broken down into two major types, "conventional composites" and "nanocomposites."[13] A conventional composite consists of clay tactoids within a polymer matrix with no intercalation of the polymer into the gallery. Inorganic phases in these composites serve mainly as a filler and play no significant functional role other than economic considerations. In some cases these clay tactoids may improve the modulus of a pristine polymer or vary its optical properties, but sacrifices in other mechanical properties such as elasticity and toughness will result.

Nanocomposites can be divided into two types, intercalated and exfoliated. Intercalated nanocomposites are formed when one or more molecular layers of polymer are intercalated into the clay galleries.

In the exfoliated case, a new phase is formed between the polymer and layered silicate nanolayers. Individual clay layers are spread throughout the continuous polymer matrix. The average distance to which the clay layers are separated is dependent on the silicate loading. Microstructurally, the registry of the silicate layers is no longer apparent. The interaction between the clay layers is small compared to the interactions between the polymer chains and the clay surfaces.

In terms of X-ray diffraction patterns of nanocomposites, the interlayer spacing may be ordered or disordered. [24]

1.2.1 Intercalated Composites

Intercalated composites have been an enticing field of material science and continue to be so.[18,19,25,26] Improvements including decreased permeability, dielectric strength, non-linear optical properties and electrical conductivity are of major interest. These intercalated composites can be synthesized by direct polymer intercalation or by *in situ* polymerization of intercalated monomers. [18,19] Beginning with an intercalated oligomer, the polymer could be formed by radical ionic polymerization within the galleries. When one uses hydrophilic polymers, such as polyvinyl alcohols or polyethylene oxide, the intercalation can be performed in aqueous solutions where the clay layers exist in a highly swollen or exfoliated state. Here the spontaneous intercalation of the hydrophilic prepolymer is more likely, although the solvent still must be removed. Organic solvents can be used for the hydrophobic polymers as well. Another method can be used also, wherein the composite is be synthesized under neat conditions (no solvents). This neat method helps to avoid the problems of removing the solvents.

1.2.2 Exfoliated Nanocomposites

Exfoliated composites can display enhanced properties far superior to the pristine polymers. Toyota was the first to exfoliate clay in an engineering polymer matrix. Fukushima, demonstrated organic modified clays exfoliated in the thermoplastic nylon-6 polymer matrix.[1] They observed enhancements in the composite's mechanical, thermal, barrier and flame retardant properties of the polymer.[1,2,27] Some mechanical properties are given in Table 1.1.

Since then, many other polymeric systems have been successfully synthesized as nanocomposites. Some of the more recent polymer systems include polyimid[27], acrylnitrile rubber[28], polyester[29], epoxy[30,31]and polysiloxane[32].

Nylon-6 exfoliated nanocomposites were synthesized by exchanging the Na^+ ions in montmorillonite with hydrophobic ammonium cations of ω-amino acid. In this case the ring opening polymerization of ϵ-coprolactom occurred in the intralayer space. The formation of these composites resulted in enhanced performance properties in comparison to the pristine nylon-6 polymer[33] (see Table 1.2). The prospect of dramatic weight savings and improvements in properties set off widespread research activity for applying this technology to other types of polymers.

Table 1.1 Mechanical Properties of Toyota's Nylon-6 Clay Composites.[33]

Composite Type	**Clay wt%**	**Tensile Strength (Mpa)**	**Tensile Modulus (GPa)**	**Impact (kJ/m^2)**	**HDT (°C) @ 18.5 kg/cm^2**
"Nanoscopic" (Exfoliate)	4.2	107	2.1	2.8	145
"Micro" (Tactoids)	5.0	61	1.0	2.2	89
Pristine Polymer	0	69	1.1	2.3	65

HDT- Heat Distortion Temperature

For the synthesis of exfoliated polymer-clay nanocomposites, in situ polymerization is the method of choice in most systems. In this approach, a strong driving force, chemical and/or mechanical, (such as the shear force from blending) may be needed to achieve the exfoliated phase. The key to achieving exfoliation of a thermoset system is controlling the intra and extra-gallery rate of polymerization. Ideally, the rate of polymerization within the gallery makes use of its catalytic cations that can improve the rate of polymerization inside the gallery in comparison to that of the bulk polymer. On the other hand, if the rate of the extragallery polymerization should exceed that of the intragallery, the result will be a conventional, or at best, an intercalated composite. Figure 1.5 illustrates the polymerization of an epoxy polymer.

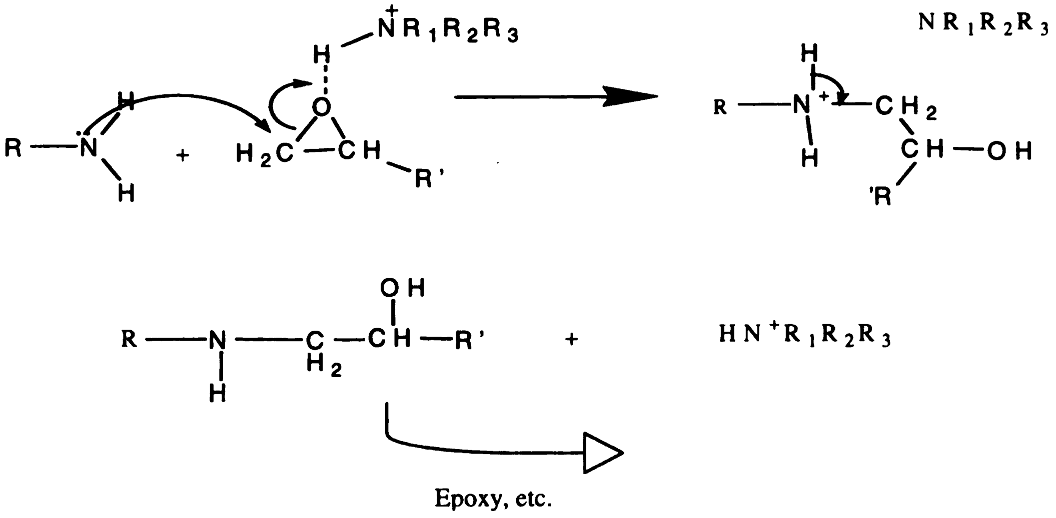


Figure 1.5 Schematic of the acid catalyzed intergallery epoxide ring opening.[29,31,34] R' contains additional epoxy groups for the formation of a network polymer.

Exfoliated composites result in many enhanced mechanical properties. The turbostratic alignment of clay particles creates a torturous pathway for gas molecules, creating a nanocomposite with low permeability and increased flame retardancy. This is illustrated in Figure 1.6.

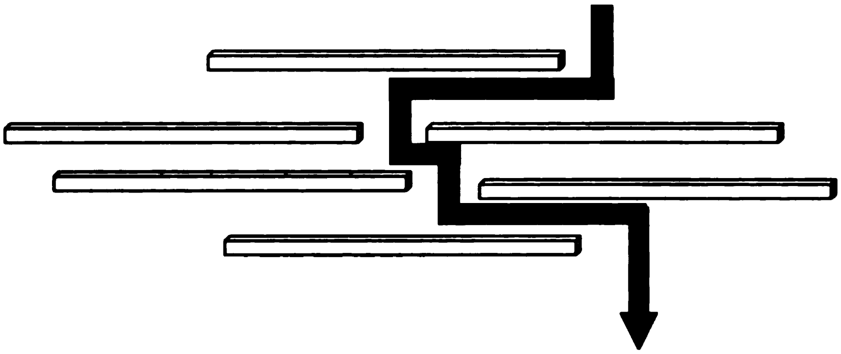


Figure 1.6 Schematic of tortuous pathway for gases to travel through the exfoliated composite.[7]

The plate alignment of an exfoliated clay also showed evidence of increased tensile strength.

1.3 Objectives

The dispersion of layered silicates in an engineering polymer matrix enhances the mechanical properties such as an increased dimensional stability, increased thermal stability, increased flame retardance and improved barrier properties. It is known that organoclays serve as good precursors to nanocomposite formation in polymer systems, such as the epoxies Epon 828 and 826 with various diamines serving as a curing agent. Mechanical properties of the nanocomposites are most greatly enhanced when the clay layers are completely dispersed (exfoliated) in the polymer matrix, as opposed to the agglomeration of clay layers forming tactoidic or intercalated systems.

The goals of my research are to prepare epoxy clay nanocomposites via *in situ* polymerization using an organic modifier to create a favorable intercalation of the prepolymer. After successfully synthesizing an intercalated or exfoliated composite, I investigated the relationship of the microstructural properties and interfacial properties that govern the mechanical behavior of the nanocomposites.

Characterization of these nanocomposites is done by using X-ray powder diffraction (XRD). This technique provided a reliable way to determine the orientation and stacking of layers by observation of reflections in the basal plane. Thermal Gravimetric Analysis (TGA) provided information on thermal stability, while Dynamic Mechanical Analysis (DMA) was used to investigate the glass transition temperature (Tg) of the nanocomposites as well as the relative stiffness.

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Chapter 2

HYBRID ORGANIC-INORGANIC NANOCOMPOSITES FORMED FROM AN EPOXY POLYMER AND AN AMINE CURING AGENT

2.1 Introduction

Composites reinforced by a nanoscale filler in which structural and compositional changes occur have attracted a great deal of attention in the past fifteen years.[1-10] These nanocomposite materials have received much of their appreciation from the overall property improvements provided by the composite phase morphology and interfacial properties.[11-13] Layered silicates dispersed as a reinforcing phase in a polymer matrix are an important form of a hybrid organic-inorganic nanocomposite. Composites reinforced on a nano-length scale are usually found to be superior to conventional composites and pristine polymers, and require lower loadings.

In the synthesis of clay-polymer nanocomposites, there have been many potential pathways reported in the investigation of thermosets and thermoplastics.[14-18] In most cases, the polymer requires an organophillic precursor in order for it to intercalate into the clay. Therefore, an exchange of an organic surfactant prior to the intercalation of the prepolymer or monomer is required. Direct intercalation of the preformed polymer into the gallery has previously been noted, and will not be mentioned any further.[19]

The organic species most commonly exchanged in the gallery prior to the prepolymer is an alkylammonium chain (R_nN^+), where the alkyl chains can be highly varied. The chain can range from single alkanes to multiple functionalized organics. In most cases long alkyl groups and catalytic functionality result in a desired exfoliated polymer-clay nanocomposite for typical hydrophobic engineering polymers. If the alkyl chains fail to facilitate intercalation it's likely due to the lack of hydrophobicity, thus not creating enough driving force for the prepolymer or monomer to intercalate. On the other hand, if the alkyl groups are too long or too large, it may cause a steric hindrance in the attempt to intercalate. Another possible mishap that may occur is if too many alkylammonium ions exist in the matrix, without being involved in the cross-linking. This results in the loss of mechanical performance due to the dangling alkyl ammonium ions acting as a plasticizer, essentially solvating a portion of the cross-linked matrix.

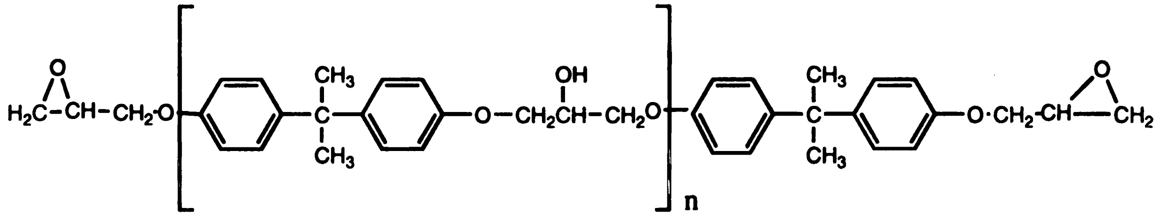
In creating an organo-clay, one would like to increase the hydrophobicity of the clay making it more susceptible for the prepolymer or monomer to intercalate. Although a fully exchanged organoclay proves beneficial for organic intercalation, it does have a down side. The increased cost it would endure on the entire composite would be a lot more than a mixed ionic organic-inorganic clay. This mixed ion clay would also benefit by reducing the amount of plastizing effect that may occur. However, inorganic cations may interfere with the interaction between the prepolymer or monomer and the organic species within the clay. Ideally, one would desire an inorganic cation that would not inhibit the intercalation of the prepolymer or monomer into a mixed cationic clay. It has been found that protons and lithium cations, in particular, are small enough to avoid any disrupted intercalation. These two inorganic cations are known to relocate in the interstitial space in the brucitic sheet of montmorillonite, as opposed to other inorganic cations, which are limited by their larger ionic radii.[20]

The relocation of the smaller cations in the clay results in an environment better suited and more susceptible for the intercalation of the prepolymer and monomer. Moving protons or lithium cations to the interstitial space exposes more of the siloxane oxygens of the clay sheet, thus increasing bonding interactions with the alkylammonium cations and prepolymers, resulting in an improved driving force for the monomers to penetrate into the gallery. This driving force may also increase the chance of forming a desired exfoliated nanocomposite. The present work explains why lithium cations may be a better choice than protons for the intercalation of epoxy prepolymers into a homostructured clay.

2.2 Experimental

2.2.1 Materials

The epoxide (also know as our prepolymer) used in the formation of the layered silicate-epoxy nanocomposites was the poly(bisphenol A-coepichlorohydrin) (shell EPON 826) with an average molecular weight of 377g/mol (see Figure 2.1).



n=0 (90%), n=1(10%)

Figure 2.1 Structure of poly(bisphenol A-coepichlorohydrin), resin EPON 826.

The curing agent was poly(oxypropyleneamine) (Huntsman Chemical, Jeffamine, D-series) shown in Figure 2.2.

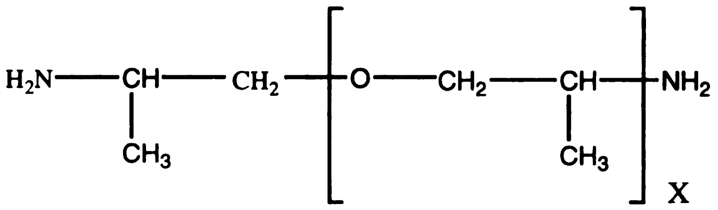


Figure 2.2 Jeffamine curing agent with the molecular weight dependent on x. Jeffamine D230, x=3.1 and Jeffamine D2000, x=33.1.

The clays used in forming our composites were natural occurring, polymer grade Nanocor montmorillonites (Wyoming and New Castle) and a Dow Corning's synthetic clay Fluorohectorite. Relevant properties are given in Table 2.1.

Table 2.1 Forms of Phylosilicates used

Material	**d_{001} Å**	**Ions Exchanged with**	**CEC (meq/100g) +/-10%***	**Aspect Ratio**
Na^+ PGN	12.3	Li^+, H^+	100	300-500
Na^+ PGW	12.6	Li^+, H^+	120	200-400
Li^+ FH	13.2	H^+	121	~2000

*Cation Exchange Capacity by Nanocor using the Methyl Blue Method. d_{001} peaks are measured from an air-dried sample.

2.2.2 Inorganic Exchange

Proton and lithium forms of layered silicates were obtained via ion exchange with hydrochloric acid and lithium chloride, respectively. Ten grams of clay was suspended in 1000mL aqueous suspension, titrated with 0.295M HCl or 0.295M LiCl for proton or lithium exchange, respectively, to achieve a 5 fold excess of cations based on the CEC. The products were centrifuged, washed and blended several times to remove the chloride ions, then air-dried. The d_{001} peak, inorganic cations and CECs are listed in Table 2.1.

2.2.3 Synthesis of Jeffamine Layered Silicate

The intercalation of Jeffamine cations within the gallery will help ensure a favorable intercalation of the prepolymer. This exchange is done by protonating the Jeffamine with .295 M HCl, then adding the protonated Jeffamine to an aqueous suspension of clay and stirring for twenty-four hours. The products were centrifuged, washed and blended several times, then air-dried. The amount of Jeffamine used for homostructure formation added was dependent on the desired percent exchange and the CEC of the clay. The basal spacings of the clay galleries were determined by XRD. The oxygens in the Jeffamine have a high affinity to be associated with the basal oxygens. The orientation of the Jeffamine cation in the clay gallery was found to be dependent on the solution, solvent type and temperature. Due to the effects of the type and amount of solvents D2000 will act like an accordion, straightening and stretching out when exposed to heat and low amounts of solvent, while when more saturated with a particular solvent, as in water, the D2000 chain coils and shrinks in length. Figure 2.2 lists the d_{001} basal spacing ranges for each percent exchanged.

Table 2.2 Range of basal spacings of Jeffamine intercalated forms of Smectite clays.

***% diprotonated D2000 Exchange**	d_{001} **Range (Å)**	**H_2O Washings**
*PGN		
33%-100%	35.5-43.7	6 @ 500mL
*PGW		
33%-100%	38-45.5	6 @ 500mL
*FH		
33%-100%	46-58.2	6 @ 500mL

*All inorganic cations are Li^+, but the values are the same if protons are used in place of lithium cations.

2.2.4 Preparation of Epoxy-layered silicate composites using mixed ion Jeffamine, and H^+ or Li^+ intercalates.

The epoxy and the free form of the Jeffamine were mixed in stoichiometric amounts at 25°C and stirred. The mixture was than added to the clay of choice and stirred until homogeneous (approximately 15 minutes). The already intercalated Jeffamine (D2000) was assumed to partake in the epoxide cross-linking and taken into account in the stoichiometric calculation of the amount of D230 to be added. The mixture of polymer and clay was then outgassed in a vacuum until evacuation of dissolved air from the mixture was complete. Then the mixture was poured into a silicone mold and cured at 75°C for three hours then 125°C for three hours. This slow ramp of curing was done to give time for the organic material to intercalate and polymerize within the gallery prior to the gel point. Each sample required approximately three grams of material.

2.3 Characterization Methods

2.3.1 Powder X-ray diffraction (XRD)

The XRD instrument was a Rigaku rotaflex 200B diffractometer. XRD patterns were recorded using a rotating anode, Cu K_α X-ray radiation (λ=1.541838Å) and curved crystal graphite monochrometer while the X-ray operated at 45KV and 100 mA. The diffraction patterns were collected from 1-8 degrees 2Θ with a scanning rate of 2 degrees 2Θ per minute. The DS and SS slit widths were 1/6. The uncured samples were prepared on a glass slide with filter paper adhered to the slide. The sample was then applied as a thin film. The cured samples were prepared by mounting a flat piece of the sample into an approximately a .75 x .25 inch aluminum mold.

2.3.2 Thermal Analysis

Thermogravimetric Analysis (TGA) was performed using a Cahn TG System 121 thermogravimetric analyzer. Samples were heated to 800°C using a heating ramp of 5°C per minute under a nitrogen atmosphere.

2.3.3 Mechanical Analyzer

The storage modulus, loss modulus and tan δ were measured using a TG instrument model 2980 Dynamic Mechanical Analyzer-V-140. Stress was applied using the DMA multi-frequency three-point bend apparatus. Oscillations were set at an amplitude of .2 μm/sec and the static force was set at .01μ. The heat ramp was increased from approximately 40°C to 90°C at 4°C per minute.

2.4 Results and Discussion

2.4.1 Proton and Lithium Exchanged Clays

The native sodium ions of montmorillonite were exchanged by lithium cations or protons in the hopes to improve the exposure of the siloxane surface to the polymer. Protons and lithium cations are the only two ions that are small enough to migrate into the interstitial space of the tetrahedral sheet of the clay or relocate to the interstitial space of the octahedral-brucitic sheet upon heating to 250°C.[20] Protons were initially thought to be the inorganic ion of choice due to the acidic nature of the cation. The acidic environment should catalyze the epoxy ring opening, resulting in a heightened polymerization rate within the gallery that promotes exfoliation of the composite. Figure 2.4 shows the X-ray diffraction of a 100% H^+ exchanged PGW (CEC=120), as well as a 50:50 homostructure containing protons and D2000 respectively. The presence of water is evident in the inorganic clays where it shows a slightly larger d-spacing of the proton-exchanged clay, compared to the sodium type shown in Figure 2.4 (14Å and 12Å respectively). This is due to the greater free energy of hydration of the proton resulting in larger hydration spheres.

The TGA of the 50:50 molar mixture of H^+: diprotonated D2000 exchange shows positive factors in that the protons showed accelerated degradation of the clay (Fig. 2.3), however, had no significant impact on degradation of the polymer (page 38, Fig. 2.6).

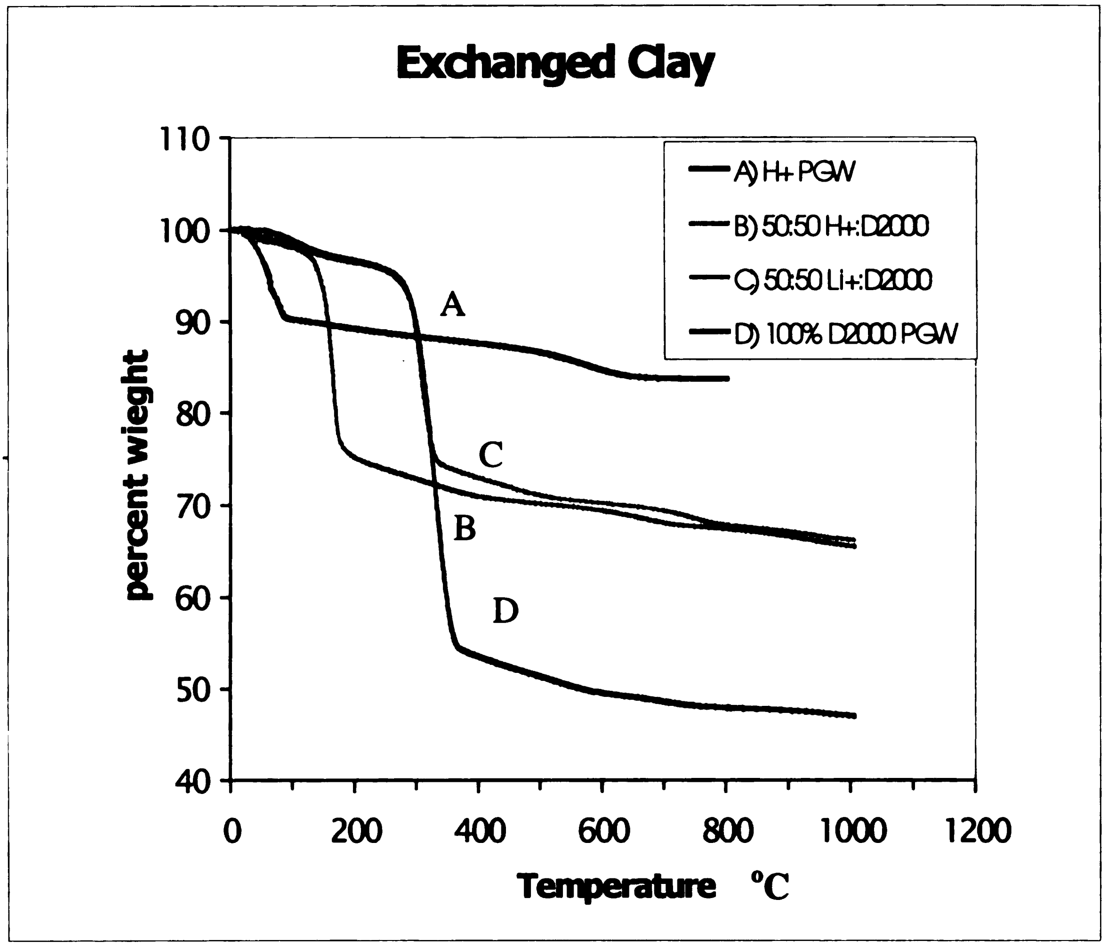


Figure 2.3 TGA curves of the exchanged forms of PGW montmorillonite. A) fully protonated clay, B) 50:50 proton: diprotonated D2000 exchanged clay, C) 50:50 lithium: diprotonated D2000 exchanged clay, D) 100% D2000 exchanged clay.

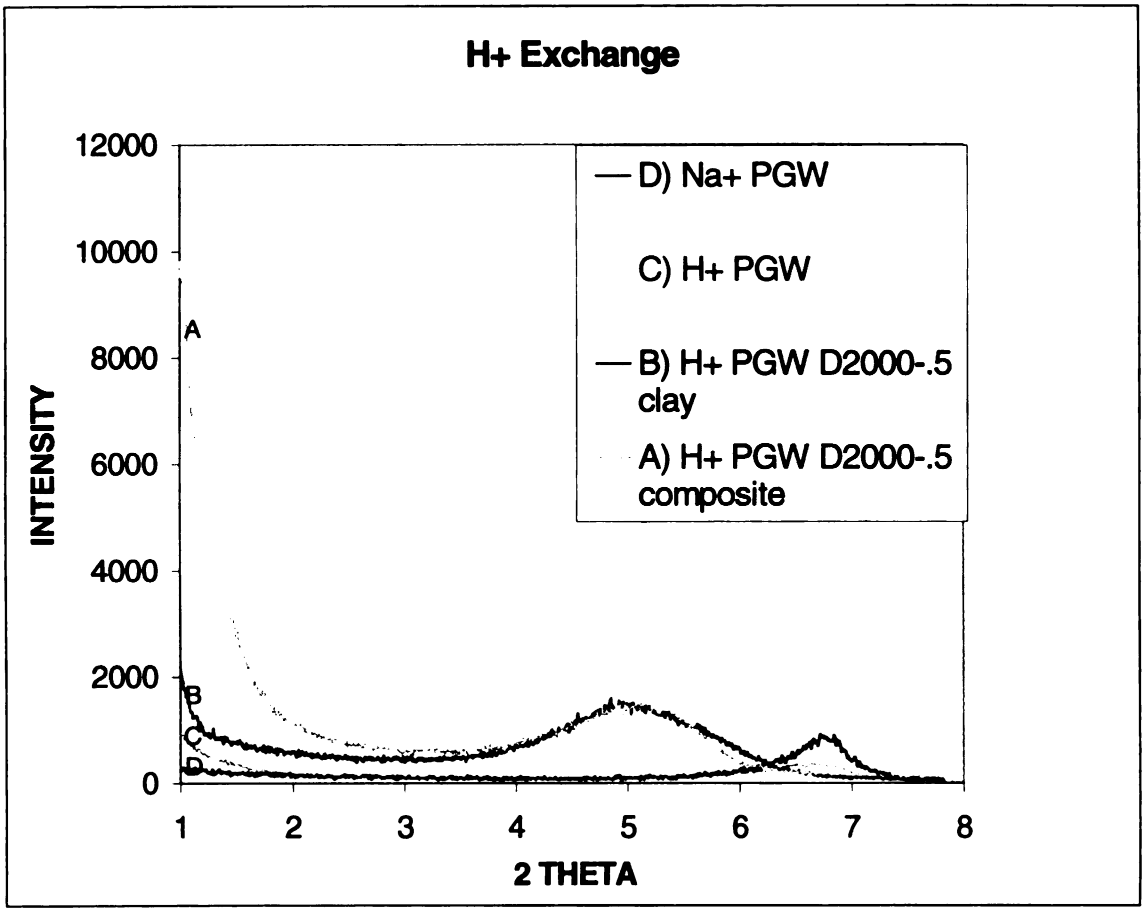


Figure 2.4 X-Ray diffraction of different stoichiometric proton and D2000 exchanged clays. A) 50:50 proton: diprotonated D2000 exchanged clay composite (6% silicate loading), B) 50:50 Proton: diprotonated D2000 exchanged clay, C) fully protonated clay, D) Na$^+$ PGW.

Our efforts to synthesize 50:50 exchanged D2000 and protons, however successful, taught us that protons would hinder our composite properties rather than benefit them. Figure 2.4 (B) shows the clay XRD pattern for an intercalation of a monolayer of D2000 with a d-spacing of 18Å. The pattern A shows the XRD of a 50% proton- diprotonated D2000 exchange clay-epoxy nanocomposite d-spacing and 18Å also. Interestingly enough, what we thought could increase our chances of achieving an exfoliated nanocomposite turned out to disrupt the initial intercalation of the polymer. The protons already exchanged in the clay galleries likely protonated the basic curing agent (D230) resulting in the intercalation of additional, shorter Jeffamines. The relatively short molecules of D230 appeared to "pin" the galleries at 18Å, preventing the exfoliation of the clay layers.

The results for proton-exchanged clays led us to explore another avenue to expose more of the siloxane oxygen sheets. The lithium cation is known also to have a sufficiently small ionic radius (0.76Å) to migrate in the interstitial space of the octahedral sheet or nestle itself in the interstitial space of the tetrahedral sheets.[20-23] Figure 2.5 (A), (B), (C) shows the three possible lithium positions for lithium-exchanged clay. Because lithium has a larger hydration sphere than sodium, the XRD pattern of a hydrated Li^+

montmorillonite shows a slightly larger d-spacing than its sodium counterpart shown in Figure 2.7, page 39. The 50:50 Li^+: diprotonated D2000 exchanged clay (Figure 2.7 (B)), shows a d-spacing similar to that of the proton clay (Figure 2.7(C)), but in Figure 2.7 (A) the 50% lithium exchanged composite shows an exfoliated composite.

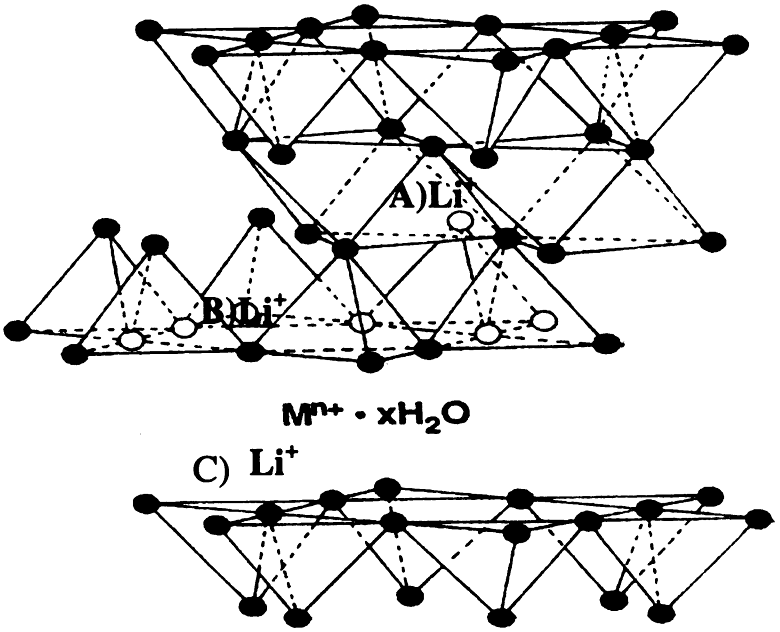


Figure 2.5 A schematic of Lithium binding sites for exchanged montmorillonite with an undetermined amount of water. **A)** shows how an anhydrous lithium cation can nestle in the interstitial space of the tetrahedral sheet and **B)** shows the lithium cation migrated to the octahedral sheet at elevated temperatures. [20-23] The hydrated Li^+ (C) will occupy the gallery interlayer.

2.4.2 Mechanical Testing

Using the pristine 826-D230 polymer as our reference material, we attempted to improve the storage modulus and glass transition temperature (Tg) using a clay modifier. Glass transition temperature occurs during a material's transition from a stiff, rigid material to a placid state. Storage modulus is a measure of how much a material can resist deflection by an applied load. In three-point-bending, an oscillating force is applied on the sample as the temperature increases. The modulus is then determined in accordance to how much the composite's position recovers from that applied load. Recording Tg of a composite is to analyze the peak max of the tan δ curve. Tan δ is defined as the storage modulus divided by loss modulus (where loss modulus is essentially the amount by which the material does not recover from the applied load oscillations).[24] The peak of Tan δ shows the greatest change from storage to loss modulus indicating the most significant change of free volume or relaxation times.[24]

On the basis of Figure 2.8 (page 40), we can compare the storage modulus and Tg of the pristine, organic and inorganic clay modified composites. The PGW-D2000 full exchanged composite (6% silicate) shows a significant improvement in storage modulus. The organic interactions between D2000 and the prepolymer results in a polymerization within the gallery thus leading to dispersed clay particles within the matrix. The storage modulus is much improved in comparison to the pristine polymer. The PGN-D2000 (full exchange) on the other hand, has a Tg that is lowered significantly. The lowering of the Tg with increasing D2000 tends to be a common trend in these 826-D230 thermoset systems. The greater ability for D2000 to reconfigure itself within the system results in a free volume change at lower temperatures. It is found that the free volume of D2000 is solvent and temperature dependent when confined in the clay, as shown by the various d-spacings shown in Table 2.2. The storage modulus is mainly silicate dependent, although the organic modified silicate may result in a larger storage modulus due to the favored organic-organic interactions, which result in the clay particles being better dispersed throughout the matrix resulting in a tougher composite. The non-exfoliated clay particles in the polymer matrix that may result in an increased storage modulus (inorganic clay in particular) are known to be brittle. The dependence of the storage modulus on temperature is indicative of how elastomeric the composite is. The D2000 shows a steeper slope of storage modulus verses temperature showing evidence of its more rubbery nature. Where the pristine and inorganic silicate composite show a smaller slope indicating a more rigid, brittle material. The brittle nature of these composites comes from the fact that the inorganic clay exists as tactoids within the matrix, thereby, increasing the number of possible places where the composite may fracture.

Comparing the same stoiciometric equivalent composites at different silicate loading reinforces the theory of storage modulus being dependent on the percent silicate loading. On page 41, Figure 2.9 A, B and C shows 100% D2000 exchanged nanocomposite with a 6%, 3% and 1% silicate loading respectively. The storage modulus of all three decreases with lower silicate loading.

In the interest in limiting cost and optimizing Tg, while still increasing the composites' storage modulus, a one-half stoichimometric Li^+-D2000 exchanged PGW clay was chosen for use in other composites. Figure 2.10 shows DMA of these composites. Analysis of these spectrums tells us that full exchanged clay is not necessary to achieve a significant improvement in storage modulus, but reinforces the need for a greater silicate loading to achieve this. The half exchanges exemplifies that there is an optimum silicate loading. Figure 2.10 shows that inorganic clay optimizes the storage modulus at approximately 3% silicate loading, but optimal silicate loading for the organic-modified clay is approximately 6%. The half exchanged silicate composite shows promise in improving Tan δ while increasing the storage modulus. Although Tg is still sacrificed slightly, it is conceivable that an optimized percent-exchanged clay may exist to improve both Tg and storage modulus.

2.5 Conclusion

In preparation of the thermoset epoxy clay nanocomposites, curing agents can be protonated and then exchanged (or vice-versa) into the galleries of a smectic clay which promotes intercalation of an epoxy resin, and ultimately an exfoliated nanocomposites. The clay modification approach may be used in many other polymeric systems, in order to remove excessive dangling chains in the nanocomposite matrix. Polymer precursors with amino, hydroxy and amide functionalities should all be good candidates.

This work may continue to progress from here. Modifying clay to ensure an exfoliated system, most likely, would yield a tough material with a high tensile modulus. These composites also may be great film candidates for high barrier applications. Due to the viscosity concerns of these composites, films may be difficult to cure at the needed thickness (approximately .0275 mm), for coating applications.

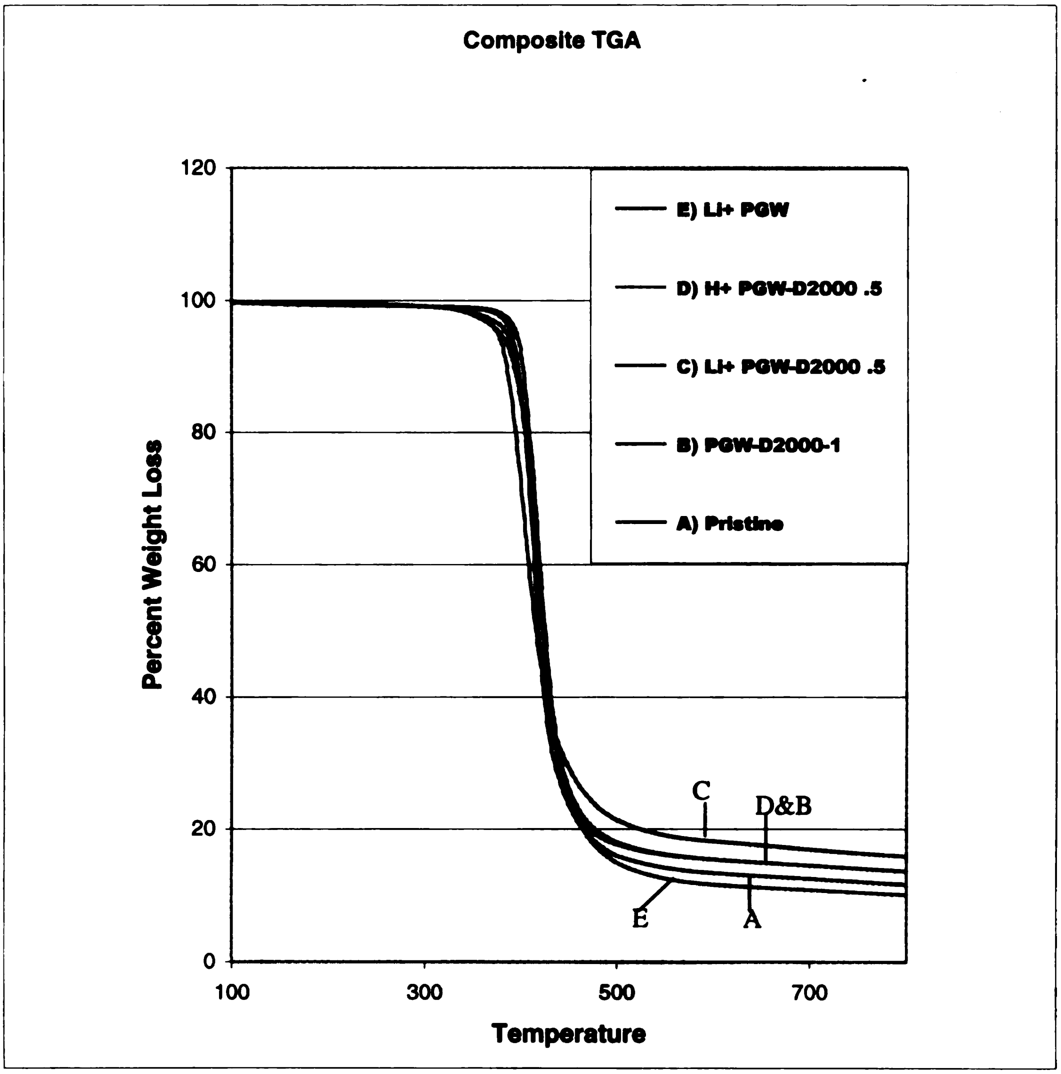


Figure 2.6 TGA curves for Epon 826/D230 epoxies at 6% silicate (PGW) loading. A) pristine polymer, B) fully exchanged D2000, C)50:50 Li^+ : diprotonated D2000, D) 50:50 H^+: diprotonated D2000 and E) fully protonated PGW.

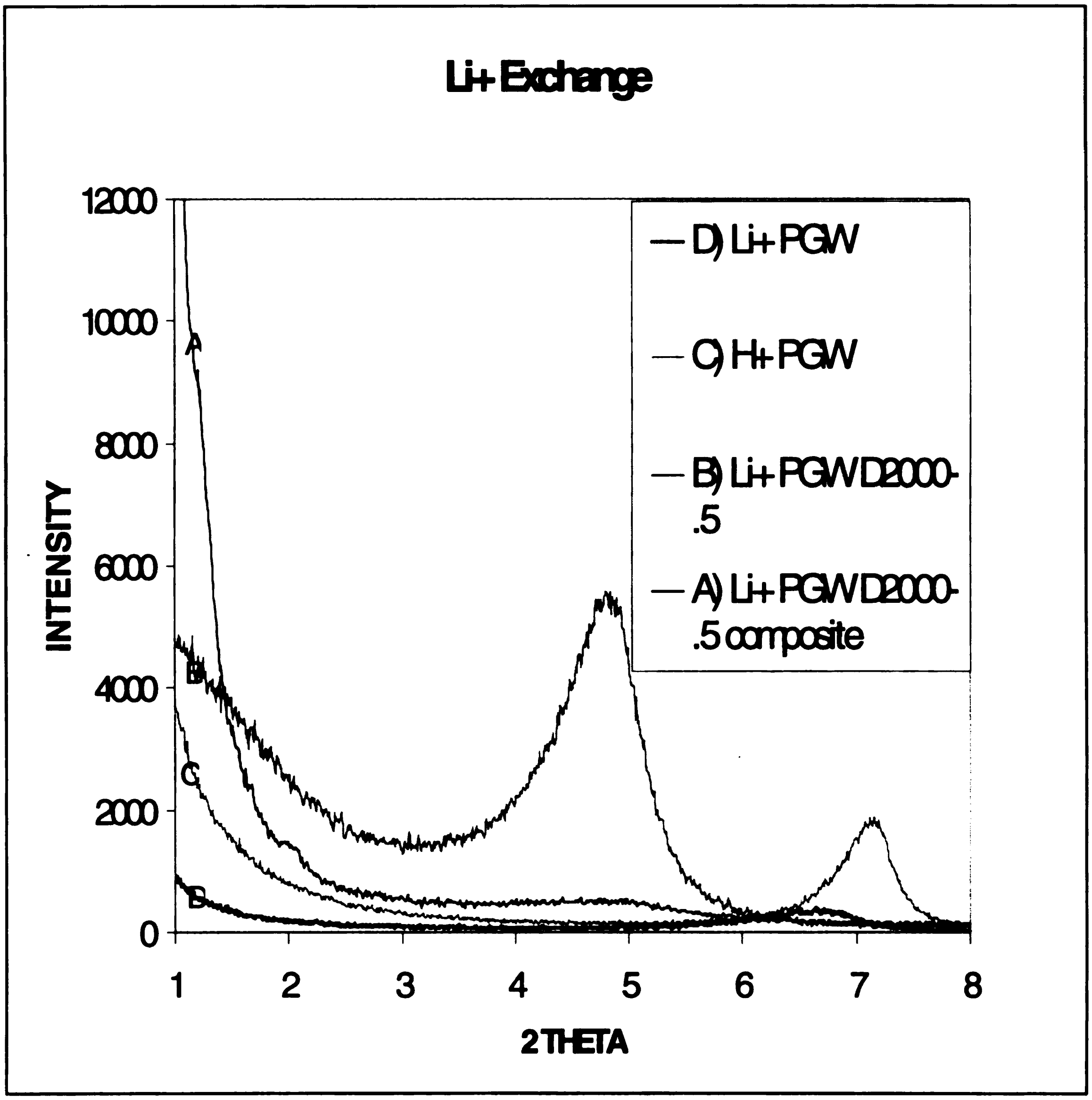


Figure 2.7 XRD patterns of proton (C) and lithium-exchanged PGW montmorillonites: A) Epon 826-D230 composite prepared from 50:50 lithium: diprotonated D2000 exchanged PGW composite, B) 50:50 lithium : diprotonated D2000 exchanged PGW clay, C)fully exchanged proton PGW, D) fully exchanged Li$^+$ PGW.

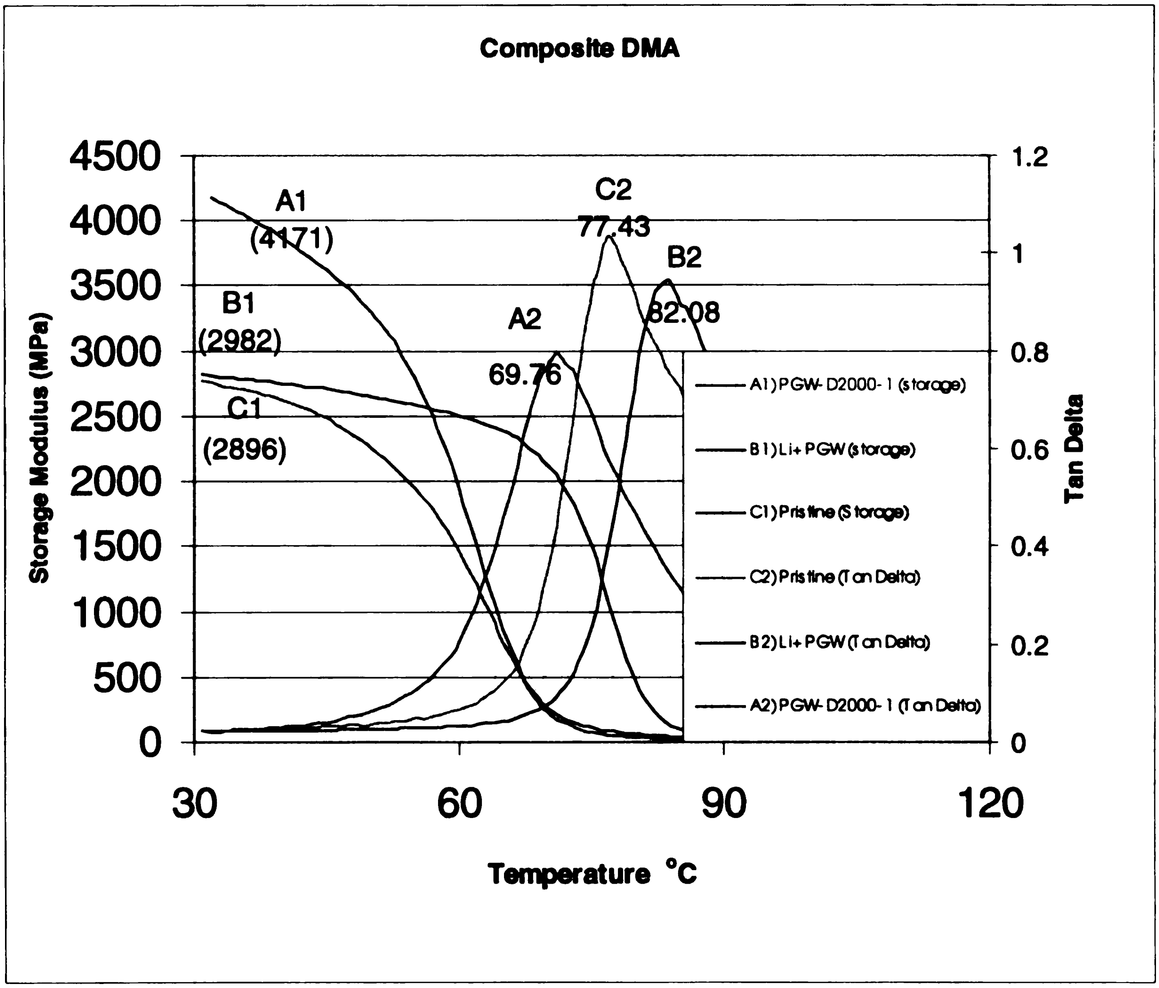


Figure 2.8 Comparison of DMA's storage modulus and tan δ for the Epon 826-D230 epoxy polymer (6% silicate loading): (A) composite containing a fully exchanged diprotonated D2000 PGW, (B) composite containing a fully exchanged Li^+ PGW, (C) pristine polymer.

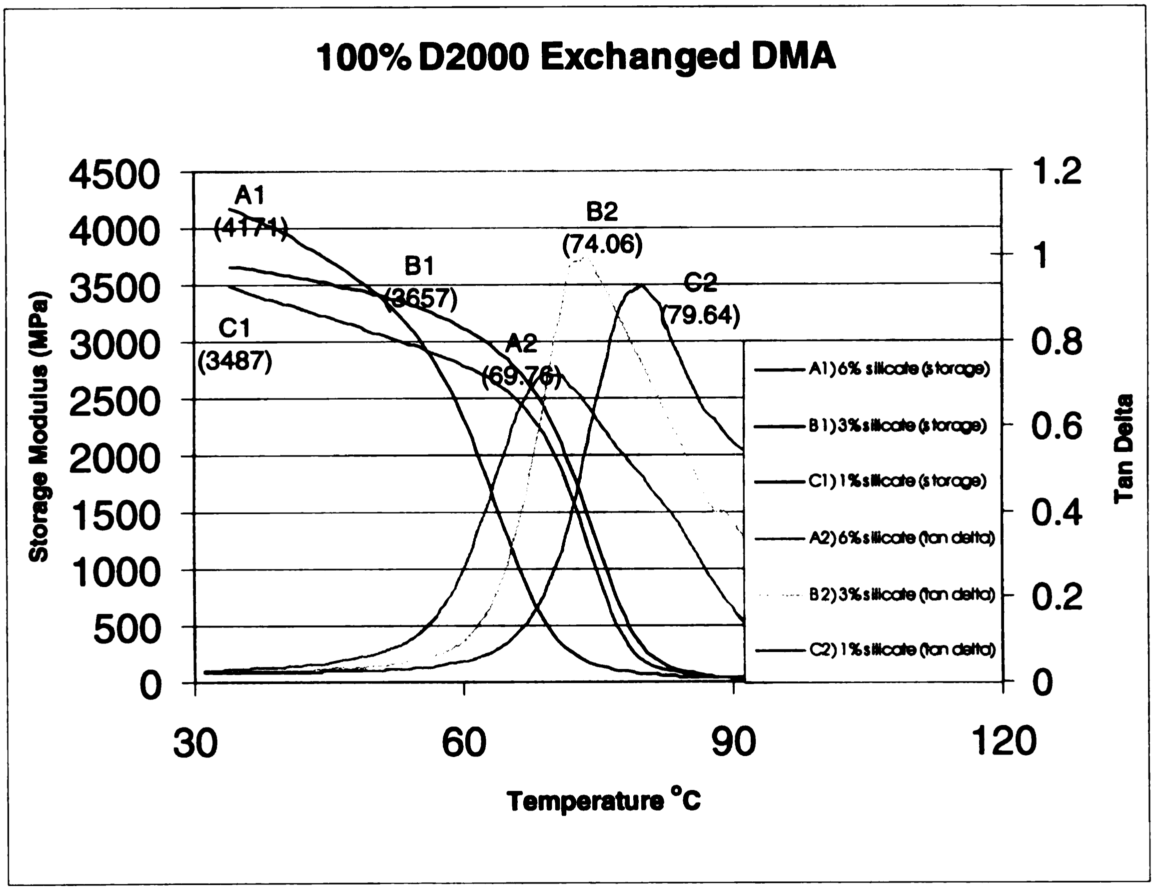


Figure 2.9 A comparison of full exchanged D2000 PGW Epon 826-D230 composites at various silicate loadings. Shown are the storage modulus and tan δ, indicating Tg, (A) 6%, (B) 3%, (C) 1%.

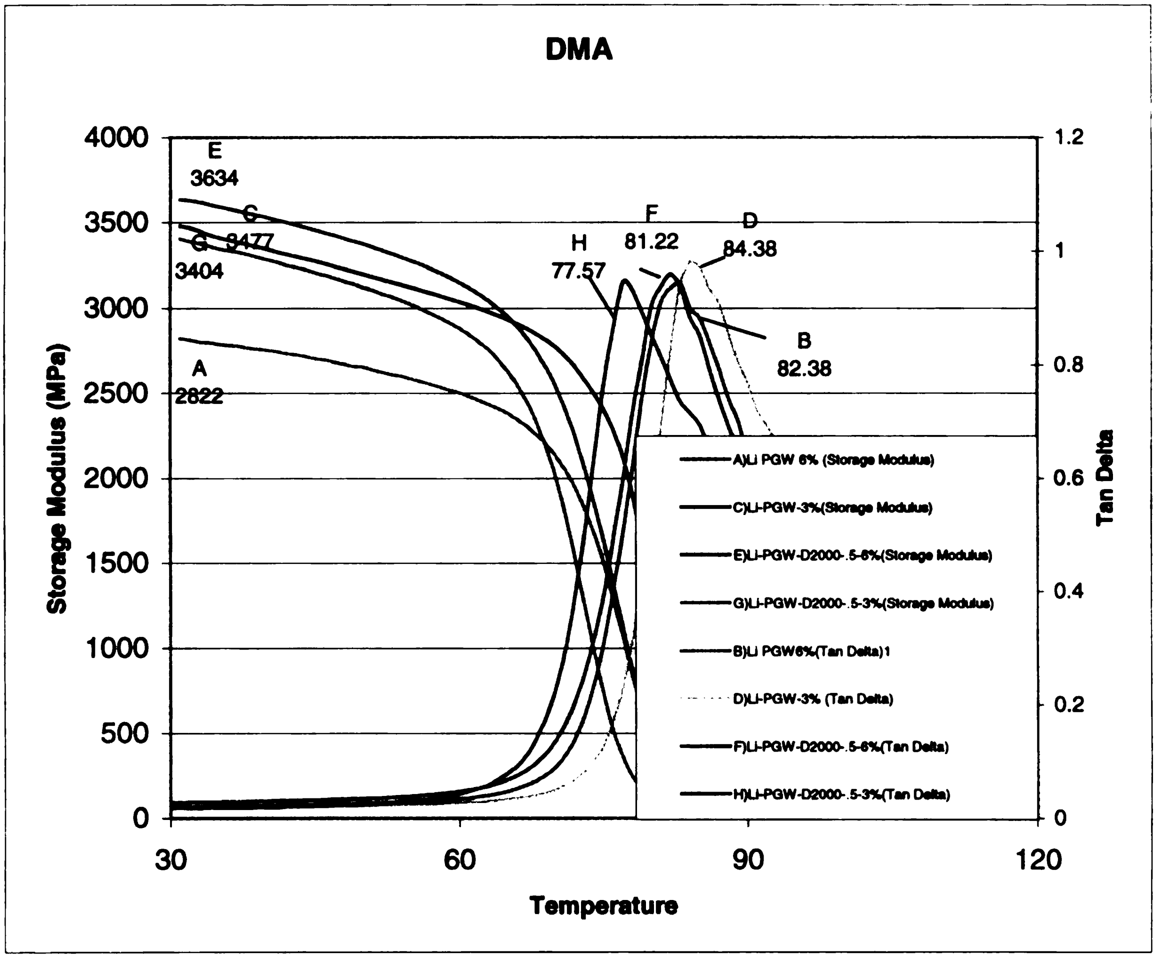


Figure 2.10 Storage modulus and Tan δ of Epon 826-D230 composites prepared from fully exchanged Li^+-PGW montmorillonite and a 50:50 Li^+ : diprotonated D2000 exchanged PGW montmorillonite. (A) 100% Li^+ PGW (6% silicate), (B) 100% Li^+ PGW (3% silicate), (C) 50:50 Li^+ : D2000 (6% silicate), (D) 50:50 Li^+ : D2000 (3% silicate).

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