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Small-scale Fabrication Process of Clay-containing Thermosetting Nanocomposites

by

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Abstract

Clay/Epoxy nanocomposites were fabricated using shear mixing to determine the increase in mechanical properties over those of pure epoxy. The effectiveness of the fabrication process was improved and explained in detail to provide composites researchers with the ability to fabricate thermosetting nanocomposites efficiently. The effects of process variables on the resulting nanocomposite materials were determined through repeated fabrication and testing. The effects of void removal and shear mixing variables were determined through alteration of the fabrication process. When the effects of the process variables had been determined, a fabrication procedure based on the results was used to fabricate nanocomposites containing 2%, 4%, and 6% nanoparticles by weight. Tensile tests were performed to determine the extensional moduli and tensile strengths of nanocomposite samples. Experimental values were compared to the developed mathematical models as well as to the values of the neat resin.

Introduction

Nanocomposites are composite materials containing a matrix material and a nanofiller. A nanofiller is a material with at least one size dimension less than 100 nanometers. The most common type of nanofillers are nanoparticles. Nanocomposites exhibit improved mechanical properties at low weight fractions of nanoparticles [1]. Nanocomposites is a new field with enormous potential for improving mechanical properties of composite materials. The Toyota Research Group first reported the improved properties of a nylon-6 nanocomposite in the early 1990s. Since then thermoplastic nanocomposites have been used extensively in the automotive industry and have also branched into other industries [2].

There are several materials that are used as nanoparticles, including metals and clays. Clay nanofillers are often called clay nanoparticles or clay nanoplatelets. Clay is the most commonly used nanoparticle, due to its availability and low cost [3]

A common type of matrix material is a polymeric material. Polymeric materials can be divided into three basics categories: thermoplastics, thermosets, and elastomers. Thermoplastics are lightweight polymeric materials. Thermosets have higher density and strength than thermoplastics due to an irreversible change that takes place at the curing temperature of the material. Elastomers are rubber-like materials with lower rigidity than other polymeric materials [4].

There are a variety of thermosetting materials. Epoxy is a thermosetting material that is commonly used in engineering applications due to its high strength and stiffness. It is also useful because the properties of the cured epoxy can be changed through manipulation of the cure process [5]. Thermosetting materials have higher strength and stiffness than thermoplastic materials. Despite this fact, far less research has been done on thermosetting nanocomposites. There are many fabrication methods used for thermoplastic nanocomposites, however many of these do not work as well on thermosetting systems [6]. Thermosetting nanocomposites are not widely available for commercial use at this time. Fabrication of thermosetting nanocomposites is important to researchers for comparison to theoretical models. Researchers must be able to effectively fabricate these nanocomposites on their own. Although several researchers have produced thermosetting nanocomposites, the published material generally focuses on the results of the fabrication rather than the details of the process used.

In this study, variables of a nanocomposite fabrication process were studied in an effort to maximize the effect of the nanoparticles on the extensional modulus and tensile strength of the resulting nanocomposite. Material testing was performed on the fabricated specimens to determine the properties of the nanocomposite. The experimentally determined properties were compared to the properties of the neat resin as well as analytical models that predict mechanical properties of the nanocomposite.

Technology and Literature Review

Nanocomposites are composite materials made up of a matrix material and nanofillers. Polymer-clay nanocomposites use a polymeric material for the matrix and clay nanoparticles for the filler [4]. It has been shown that nanoparticles increase the mechanical properties of composite materials at low weight fractions more than conventional composites of similar weight fractions [7]. The amount of increase in the extensional modulus is directly related to the weight fraction of nanoparticles. The extensional modulus usually shows a near-linear increase at low weight fractions and starts to level off as the weight fraction increases. This is due to regions of agglomeration (inadequate dispersion) of the nanoparticles [8].

The increase in properties of nanocomposites over conventional composites is related to the large interfacial region created by nanoparticles. The interfacial region is the region where the material properties are different than those of the filler or the matrix. The difference in material properties in the interfacial region is caused by the nanoparticles restricting the motion of the polymer chains. The large interfacial region and the small distance between nanoparticles due to the total number of nanoparticles allows for an increase in mechanical properties beyond what is seen in conventional composite materials [9].

Epoxy resin is a common thermosetting polymeric matrix material. Epoxy has several characteristics that make it one of the most widely used matrix materials in nanocomposites. The low viscosity of epoxy makes it ideal for pouring into molds and void removal. Since nanoparticles increase the viscosity of the material they are mixed with, the low viscosity of epoxy also allows for higher weight fractions to be fabricated using a shear mixing method. The shear mixing methods will be discussed in detail later. Compared to other thermosetting materials, epoxy has high strength and stiffness. It is also relatively easy to obtain different properties. Mixing different types of epoxies together, using different curing agents, and using special additives will all affect the properties of the resulting cured state epoxy. Curing variables, such as cure time, cure temperature, and curing agent (hardener), will also affect the properties [10].

Clay nanoparticles are one of the most commonly used nanoparticles. Several different types of clays are used as nanoparticles, such as kaolinite, illite, and smectite, and are made up of layered silicates [1]. These layers are typically less than 10 nm thick. Clay layers tend to clump together and form agglomerates due to attractive forces between the layers. To obtain a nanocomposite using layered silicates, the agglomerates must be separated into individual silicate layers. Each agglomerate can contains thousands of silicate layers. Separating these layers plays a large role in the increase in properties at low weight fractions [4]. For the nanocomposites in this study, smectite nanoclay was used. Smectite consists of a triple layer structure. The central layer consists mainly of an octahedral alumina sheet. The two outer layers are silica tetrahedral sheets. The layers are bonded by oxygen ions. Smectite clays are ideal for use in nanocomposites because the bonds between the layers are weak compared to other clays such as micas, making separation of the layers easier [1].

Mixture of clays in epoxy does not guarantee the formation of a nanocomposite material. Clays in their pristine state are hydrophilic, whereas epoxies are hydrophobic. This means that mixture with an epoxy could result in poor bonding and mechanical properties. Modification to the clay is done by exchanging interlayer cations of the clay layers with organocations. Clays modified in this manner are called organophilic clays or organoclays [4].

Clay/Epoxy nanocomposites are classified by the dispersion level of nanoparticles in the matrix. There are three main levels of dispersion: phase separated, intercalated, and exfoliated. These dispersion levels are illustrated in Figure 1. There are also intermediate levels such as ordered exfoliation. Phase separated nanocomposites form when clay nanoparticles agglomerate and form layered structures. The matrix material is unable to penetrate between the layers. The weaker bond between the layers of the agglomerate will fail earlier than the bond between the matrix and nanoparticles. This can lead to significantly lower tensile strength than that of pure epoxy. When only very few polymer chains penetrate between the nanoparticle layers, the composite is said to be intercalated. Although polymer material is present between layers, this does not mean that there is enough to ensure complete bonding of the nanoparticle surface. Because of the small amount of polymer between the layers, much of the potential interfacial region is lost. The nanoparticles are still structured at this level of dispersion. Exfoliated nanocomposites contain randomly oriented nanofillers. There is no structure between nanofillers at this level [2]. Producing an exfoliated nanocomposite is much more challenging than producing an intercalated nanocomposite [11]. Many studies have made use of transmission electron microscopes (TEM) to determine the level of nanoparticle dispersion [2, 3, 8, 11-14]. Many different processing techniques have been used, however TEM has shown that these techniques often yield intercalation or partial exfoliation only [11].

The enhancement of mechanical properties is dependent on the level of dispersion of the nanoparticles. An intercalated nanocomposite tends to show a smaller increase in the modulus than an exfoliated nanocomposite [8]. The tensile strength is more strongly related to the degree of exfoliation. Although an increase in elastic modulus can be seen in most studies [8, 11-14], an increase in tensile strength is not always found. In many cases the tensile strength decreases significantly [8, 12, 14].

There are several methods used to disperse nanoparticles into polymers. One method that has been found to be effective for thermosetting materials is shear mixing . Shear mixing uses shear forces to break down agglomerates and separate the clay layers [4]. Proper mixing of nanoparticles is essential to obtaining increased properties in the nanocomposite. Inadequate mixing of the epoxy and nanoparticles will not produce an exfoliated nanocomposite and the effect of the nanoparticles will be lessened. The order in which the materials are mixed, the shear force during mixing, and the mixing time affect the nanoparticle dispersion [1]. The shear force necessary depends on the type of epoxy as well as the type of nanoparticle used. Without proper shear force, the silicate layers will not separate. Several studies have shown that excessive shear force can decrease the mechanical properties of the resulting nanocomposites. This is due to the clay layers breaking instead of separating [3, 11]. The mixing time has an effect on the dispersion of nanoparticles as well. Mixing time generally improves the dispersion. Increasing the mixing time has been shown to promote an even distribution of nanoparticles. This is important to obtain uniform properties as well as prevent premature failure [2].

Bench casting method was chosen as the fabrication process to be used with the shear mixed nanocomposites. The bench casting is a relatively simple small-scale fabrication method currently used in nanocomposite research [4]. In bench casting, the nanocomposite mixture is poured into an open mold. The mixture is then cured. There are several drawbacks to the casting method. The viscosity can limit the weight percentage of nanoparticles that are effective in nanocomposites due to problems with void removal and pouring the mixture into the mold [7, 8]. The open mold used in bench casting also leaves the specimens susceptible to falling debris. The main problem with bench casting is producing repeatable, high quality samples. There are several steps in the casting process. The process begins after dispersing the nanoparticles into the epoxy and hardener. The mixture can then be degassed. After degassing the mixture is poured into the mold. The mold is then put in an oven and heated past the curing temperature. The casting process is complete when the composite has cured and cooled. There are several factors in the casting process that affect the properties of the nanocomposite. These include degassing, cure temperature and cure time [10].

Many epoxy resin systems suggest a degassing procedure after mixing, however the addition of nanoparticles increases the viscosity, which makes the release of air bubbles more difficult. An appropriate degassing procedure has been shown to significantly increase the tensile strength of nanocomposites. Yasmin et al. [8] reported a 45% improvement in tensile strength of nanocomposite subjected to additional vacuum time over those with less vacuum time. The amount of time the mixture spends in the vacuum chamber, the vacuum pressure, and the method by which the mixture is inserted into the mold all affect the void content of the nanocomposite.

The cure time and cure temperature used to cure a thermosetting material has a considerable effect on the properties of the cured material. The strength, tensile modulus, and ductility of the material can all be affected. It is therefore necessary to determine the mechanical properties of epoxy experimentally instead of using tabulated values [5].

Analytical Models

For the analytical evaluation of the material properties of the nanocomposites, the modified Eshelby Model [15] was used. The Eshelby Model is a micromechanical model that accounts for inhomogeneity of a material. This is used to predict the shear modulus ($\overline{G}$)and bulk modulus ($\overline{K}$) of particle composites. The modified Eshelby model for one filler is shown in Equations (1) – (4).

$$\overline{G} = G_r\left\{1-\frac{V_{filler}\left(G_{filler}-G_r\right)}{G_r+2S_{1212}\left(G_{filler}-G_r\right)}-\frac{V_{void}\left(-G_r\right)}{G_r+2S_{1212}\left(-G_r\right)}\right\}^{-1} \quad (1)$$

$$\overline{K} = K_r\left\{1-\frac{V_{filler}\left(K_{filler}-K_r\right)}{K_r+\frac{1}{3}S_{1212}\left(K_{filler}-K_r\right)}-\frac{V_{void}\left(-K_r\right)}{K_r+\frac{1}{3}S_{1212}\left(-K_r\right)}\right\}^{-1} \quad (2)$$

where

$$S_{1212}=\frac{3K_r+6G_r}{15K_r+20G_r} \quad (3)$$

and

$$S_{kkll}=\frac{9K_r}{3K_r+4G_r} \quad (4)$$

In the modified Eshelby model, 'V' is the volume fraction and 'S_{ijkl}' is Eshelby's tensor for spherical inclusions. The tensors are defined in Equations (3) and (4) in terms of the bulk modulus and shear modulus. The subscripts 'r' and 'filler' represent the resin and nanoparticles, respectively. The effect of the void volume fraction (V_{void}) is also taken into account, as can be seen in Equations (1) and (2).

Nanocomposites can be assumed isotropic due to the small size of the nanoparticles as well as the random dispersion. The isotropic relation shown in Equation 5 can then be used to determine the tensile modulus of the nanocomposite ($\overline{E}$).

$$\overline{E}=\frac{9\overline{K}}{1+3\overline{K}/G} \quad (5)$$

The tensile strength of nanocomposites ($\overline{\sigma}$) can be estimated from the properties of the constituents. The rule of mixture can be modified by using the filler strength reducing factor (F_R) [1] as shown in Equations (6) through (8).

$$\bar{\sigma} = \sigma_r V_r + F_R \sigma_f V_f \tag{6}$$

$$F_R = \left[1 - \frac{\tanh(u)}{u}\right] \Big/ \left[1 - \operatorname{sech}(u)\right] \tag{7}$$

$$u = p\sqrt{G_r V_r / \left[E_f (1 - V_f)\right]} \tag{8}$$

where p in Equation (8) is the aspect ratio, assumed to be 200, and σ is the strength.

Fabrication Process

Montmorillonite (MMT) is the most commonly used clay nanofiller. MMT is a smectite clay. The surface area to volume ratio of an individual layer is higher than many other smectite clays [9].

The nanoparticle used in this project was Nanomer I.30E, developed by Nanocor. Nanomer I.30E is a MMT clay that has been made organophilic through surface modification and is well suited to be dispersed in epoxy resins. Table 1 lists the properties of an exfoliated layer of Nanomer I.30E. Due to the difficulty in determining the actual properties of individual clay layers, the mechanical properties are approximate.

Although the majority of epoxy/clay nanocomposite research has been done using diglycidal ether of bisphenol A (DGEBA) [4] as the matrix material, diglycidal ether of bishpenol F (DGEBF) has several properties that are beneficial for the addition of nanoparticles. The viscosity of DGEBF is lower than that of DGEBA. Since fillers such as nanoparticles increase viscosity, the lower viscosity of DGEBF increases the amount of filler that can be added. DGEBF has mechanical properties comparable to those of DGEBA.

The epoxy used was Epon 862 (DGEBF), a product of the Hexion specialty chemicals company. The hardener used was Epi-cure Curing Agent W (epicholohydrin), also from Hexion specialty chemicals. The specified weight ratio of Epon 862 to Curing Agent W is 100:26.4.

A mold was designed and machined out of ground and polished cold rolled steel. It was designed to allow for more variations in the fabrication process. A nanocomposite sample made using the new mold can be seen in Figure 2. A high shear mixer, IKA RW 20 was used to mix the epoxy, hardener, and nanoparticles. A VWR Model 1430 vacuum oven hooked up to a Welch 8905A vacuum pump was used to remove voids and cure the nanocomposites.

The effects of process variables were tested through repeated fabrication and mechanical testing. After testing of a set of specimens was completed, extensional modulus and the ultimate strength were calculated for each sample. The results were then compared to values of pure epoxy as well as previous specimens. By comparing the results, the effect of the variable in the fabrication process that was changed could be determined. If a step in the fabrication or testing was not performed correctly or gave results that were unexpected, the same fabrication process was repeated to ensure the accuracy of the results. At least six specimens were made for each modification to the fabrication process. The sample data were used to determine the average mechanical properties.

The weight percentage of nanoparticles was held constant for the duration of the parameter variation testing. Void removal became a critical issue at 6% weight for one of two fabrication methods used in a study with similar materials. These problems were not experienced at 4% weight [7]. Based on this, 4% weight percentage was used for the parameter variation testing.

There are several ways that the nanoparticles can be added to an epoxy resin system. The nanoparticles can be added directly to the resin with heat applied. Heating the resin lowers the viscosity, which facilitates nanoparticle dispersion. A second method is to first mix the nanoparticles with the curing agent. This can be done at room temperature since the curing agent has much lower viscosity than the epoxy. The nanoparticles can also be added after the epoxy and hardener have been mixed [18].

The epoxy, hardener, and nanoparticle were mixed using a mechanical mixer. When the nanoparticles were added they were gently stirred for approximately one minute by hand. For the first method, the epoxy was then heated to 50°C when mixed with the nanoparticles. The hardener was then mixed in for half an hour at the same mixing speed. When the nanoparticles were mixed with the curing agent first, they were mixed in at room temperature. Two additional hours of mixing at the same speed was performed with the addition of the epoxy. Mixing of epoxy and hardener was always performed at room temperature due to the decrease in the pot life with added heat [10]. Next the mixing times and speeds were varied. The speeds used were 700, 1000, and 1500 rpm. The mixing times tried were 2 hours through 12 hours. The vacuum time was held constant at 12 hours and the mixture was drained into the mold for all cases. The draining procedure is discussed in the following section.

The increase in viscosity in the nanocomposite mixture compared to the resin prevented the complete escape of trapped air, which instead formed a foamy bubble layer at the top of the nanocomposite mixture. After degassing, the mixture could not be poured directly into the mold due to this bubble layer.

As shown in Figure 3, a small hole was made in the bottom of the pouring container (a clear plastic cup). The hole was plugged and taped over and the plastic cup was put inside another plastic cup so that it could stand upright. This also served to prevent spillage if the hole was not properly plugged. After degassing, the plug was removed and the mixture allowed to drain into the mold. The goal of this method was to leave the bubble layer undisturbed.

Degassing of the nanocomposites was accomplished using vacuum pressure. The vacuum pressure was held constant at 20 in Hg. The time was varied in an effort to determine the minimum amount of time required to obtain the maximum benefit by this method of degassing.

It was noticed during fabrication that additional voids are added during the pouring process. The amount of voids added during this procedure is significantly smaller than the number of voids added during mixing. However since the mixture was degassed before being poured into the mold, the voids added during this process contributed significantly to the overall void content of the specimen. Several vacuum procedures were tried in an effort to remove this problem. Vacuum pressure was again applied to the mixture after it was in the mold. It was expected that a top bubble layer would form and could be removed by an abrasion process later.

The cure process of epoxy greatly affects the properties of the resulting material. It is possible that different cure processes may lend themselves to a greater increase in mechanical properties with the addition of nanoparticles. For this study, the cure temperature and time were held constant. The samples were placed in the vacuum oven and heated to 120°C for 4 hours. Vacuum was not applied during the cure process.

In bench casting, there are several issues to overcome. One issue is the removal of voids, which is discussed above. Another is the quality and repeatability of the specimens. An appropriate release agent must also be chosen. Since the mold is used repeatedly, thorough cleaning between every fabrication was necessary to avoid buildup of epoxy and release agent on the mold. Since bench casting is open to the environment, it was also important that the fabrication area stay clean. Any debris that fell onto the mold after the release agents had been applied was removed using compressed air.

Mechanical Testing

After the nanocomposite samples had been removed from the mold, they were made ready for tensile testing. The apparatus used for testing was an MTS 810 controlled by the MTS Flex Test SE controller. Specimens were loaded at a rate of .002 in/min. The strain was found using an extensometer, MTS 634.25E-24. Grips designed for plastic specimens, MTS 41-842-108, were used in the MTS machine. The grip pressure was initially set at as low as possible. This was in case the specimen needed to be repositioned. After the specimen had been aligned properly in the grips, the grip pressure was set to approximately 400 psi. Vishay 2300 data acquisition system and Labview were used to collect force, strain and displacement data. The specimen was tested to failure and the maximum force recorded. The tensile test setup is shown in Figure 4. Strain gauges were the first choice in measuring the strain, and several specimens were tested with strain gauges attached. An extensometer was also used to obtain strains.

The void volume fraction is needed for the modified Eshelby model. The void volume fraction can be determined by knowing the density of the nanocomposite and the constituents. The specific gravity and density of the nanocomposites samples was tested using the method described in ASTM D 792 [19]. The specific gravity (SG) of the nanocomposite is first found using Equation (9), where ‘m’ represents the mass and the subscripts ‘air’ and ‘water’ denote the mass in air and the mass in water.

$$\mathrm{SG} = \frac{m_{air}}{m_{air} - m_{water}} \tag{9}$$

Once the specific gravity of the nanocomposite is known, the density of a nanocomposite ($\bar{\rho}$) is given by Equation (10), where ρ_{water} is the density of the water.

$$\bar{\rho} = \mathrm{SG} \cdot \rho_{water} \tag{10}$$

The density of the cured epoxy/hardener mixture can be found experimentally. The density of the nanocomposites was also determined experimentally. Equation (11) can be rearranged to solve for the void volume of the nanocomposite, shown in Equation (12). The weight fraction of filler is represented by W_{filler}.

$$\bar{\rho} = \frac{(1 - V_{void})}{\left(\frac{W_{filler}}{\rho_{filler}}\right) + \left(\frac{1 - W_{filler}}{\rho_{resin}}\right)} \tag{11}$$

$$V_{void} = 1 - \bar{\rho}\left(\frac{W_{filler}}{\rho_{filler}} + \frac{(1 - W_{filler})}{\rho_{resin}}\right) \tag{12}$$

Analysis and Discussion

Six pure epoxy samples were fabricated to be used as control samples. The value obtained for the modulus was used in the Eshelby model as well. The density of the epoxy was also determined to be used in void analysis of nanocomposite samples. The epoxy was assumed free of voids for the void volume calculations of the nanocomposites. A summary of the results of the epoxy fabrication can be found in Table 2.

It was necessary to determine the effects of certain process variables first, due to their effects on other variables. The most efficient mixing method was determined early on. Next the pouring method was determined because it affects the void content of the nanocomposite sample. Minimizing the voids added during this process was necessary to determine the vacuum time needed for adequate void removal. It was also necessary to determine the most effective release agent to use on the mold.

Three mixing methods were tested to determine which yielded the greatest improvement in extensional modulus. Mixing the nanoparticles with the hardener was the first method tried. This method yielded an 8.2% increase in the extensional modulus. At weight percentages higher than 4% however, the hardener/nanoparticle mixture turned into a paste due to the small amount of hardener used. This prohibited mixing at higher weight fractions. Next the nanoparticles were mixed with the epoxy/hardener mixture. This method yielded an 8.9% increase in the extensional modulus. Lastly, mixing the nanoparticles with epoxy showed a 10.3% increase in the extensional modulus. Based on these initial tests, epoxy/nanoparticle mixing was chosen to be used for the remainder of the testing.

The initial epoxy/nanoparticle method consisted of mixing the epoxy and nanoparticles at 1000 rpm and a temperature of 50^{o}C for 2 hours. The hardener was then added and mixed for half an hour at 1000 rpm and room temperature. It was found that low viscosity of the heated epoxy increased the nanoparticle dispersion compared to the higher viscosity of the epoxy/hardener mixture at room temperature. The hardener also has low viscosity, however the small amount of hardener that is mixed with the nanoparticles could have resulted in an uneven dispersion. The comparatively large amount of epoxy the nanoparticles were mixed with also made it promising for higher weight fractions.

The two methods of pouring the mixture into the mold were studied. The first method, removing the bubble layer and pouring, was found to be ineffective due to the difficulty in removing all bubbles. As the bubbles were scooped out of the container, the scooping motion pushed some of the bubbles into the degassed mixture. An additional degassing period of 4 hours in the mold was added to these samples. This was to determine if the extra bubbles could be efficiently removed. The second method was draining the mixture into the mold as shown in Figure 3. This method produced specimens with no visible air bubbles. The size of the sample was much easier to control using this method because the mixture drained slower than it could be poured. The average tensile strength of the specimens that were poured into the mold was 4792 psi, which was lower than the 5049 psi tensile strength found on the specimens that had been drained. This indicates a possible increase in micro or nano-sized voids in the material.

Partall High Temperature Wax and polytetrafluoroethylene (PTFE) spray were tried as the release agents to aid in removing the tensile specimens from the mold. The wax was found to make release from the mold considerably easier than the PTFE spray. On several occasions a nanocomposite sample stuck to the base plate of the mold and broke during removal from the mold when the PTFE spray was used. The wax however, left more residue on the sides of the mold that was difficult to remove and resulted in poor quality of the sample near the edges. To avoid damaging specimens during removal without sacrificing sample quality near the edges, both release agents were used. A thin layer of Partall wax was used between the base plate and form plate. This eased separation of specimens and form plate from the base plate. PTFE spray was used on the edges of the form plate that were in contact with the sides of the tensile specimens. This produced a better edge quality. The wax was removed after each fabrication, however the PTFE did not need to be removed, and was applied every fourth fabrication.

In an effort to determine the point of maximum exfoliation, the mixing time was varied at three different speeds. The epoxy and nanoparticles were mixed for 2 and 12 hours at 700, 1000, and 1500 rpm.

As seen in Figure 5, the mixing time in the range used has little effect on the modulus. A maximum difference of 4 ksi can be seen at 1500 rpm. The level of dispersion was expected to increase with mixing time up to a certain point and level off after that. Based on this assumption and the small change modulus over the ranges tested, the necessary mixing time was deemed to be at or less than two hours. An extra fabrication process was performed with 4 hours mixing at 1000 rpm to ensure that no additional increase in modulus would be obtained between 2 and 12 hours. This data point can be found in Figure 5, which shows only slight difference in the modulus.

The mixing speed had a much greater impact on the extensional modulus. The modulus decreased as the mixing speed increased. The change in modulus obtained from mixing at 700 rpm and 1000 rpm was much smaller than the change from 1000 rpm to 1500 rpm. This indicates breaking of the clay layers due to the extra shear force, lessening their effects on the composite. The data suggests that lowering the mixing speed further may increase the extensional modulus. The small change in modulus between 700 rpm and 1000 rpm could also suggest that 700 rpm is a near optimum mixing speed. Further testing is required to draw any definitive conclusions.

In this study, the effects of the vacuum time on void content and tensile strength were studied. After 4 hours in a vacuum chamber at 20 in Hg, the bubble layer was not well defined, which demonstrates the difficulty of removing voids in nanocomposites mixtures. At 8 hours, the bubble layer seemed well defined. The tensile strength and void content were studied on samples subjected to vacuum for 8, 12, and 24 hours.

As seen in Figure 6, the maximum tensile strength was obtained using a 24 hour vacuum time. The extensional modulus of these three specimen groups did not follow the same trend. Figure 6 shows a decrease in the extensional modulus after 12 hours of vacuum. An increase in the viscosity during pouring was also noticed after 12 hours. This could be due to the working life of the epoxy after the hardener has been added. A curing process will take place very slowly at room temperature for this epoxy/hardener mixture. Since the curing procedure plays a crucial role in the properties of the nanocomposites, it is likely that some degree of cross-linking had already taken place prior to pouring. This could cause changes in the properties of the cured material. Because the increase in modulus is more important in this study, a 12 hour vacuum was deemed the most appropriate of the three vacuum times tested.

Two additional vacuum procedures were studied to produce high quality samples. The nanocomposite mixture was subjected to 2 hours of vacuum after being poured but prior to being cured. The second procedure studied was applying vacuum pressure during the cure process. The two hour vacuum prior to curing was found to be the more effective method, with a 36.6% increase in the tensile strength. A 29.9% increase was found when vacuum was applied during the cure process. The vacuum during cure was most likely less effective due to the rapidly increasing viscosity of the nanocomposite mixture during the cure process.

After the effects of fabrication variables had been determined, the process was adjusted to maximize the increase in the extensional modulus and used for the final testing. The epoxy and nanoparticles were mixed first for two hours. The mixing speed was 700 rpm and the temperature of the mixture was approximately 50°C. The mixture was allowed to cool for ten minutes and the hardener was added at room temperature. The hardener was mixed at 700 rpm for 30 minutes. The mixture was poured into the draining container and degassed for 12 hours at 20 in Hg vacuum pressure. The mold was prepared using PTFE spray on the sides of the sample area and using Partall High Temperature wax on the base plate. The nanocomposite mixture was drained into the mold and placed in the vacuum oven. Vacuum was again applied at 20 in Hg for two hours. Vacuum pressure was removed and the nanocomposites were cured at 120°C for 4 hours.

The abovementioned process was used to fabricate at least six specimens at 2%, 4%, and 6% weight nanoparticles. The data were used to determine the average mechanical properties. A summary of the extensional moduli of the individual specimens can be found in Table 3.

Figure 7 shows the increment patterns of the extensional moduli with the variation of weight fractions. As expected, the modulus increased with the weight fraction. The effect of the nanoparticles on the extensional modulus can easily be seen in the figure. An increase of 5.7%, 12.4%, and 16.2% in the extensional modulus was obtained at 2%, 4%, and 6% weight nanoparticles, respectively. The rate of increase was highest between 2% and 4% weight nanoparticles. The fairly linear increase in the extensional modulus in the range of nanoparticle weight percentages used suggests that this fabrication process may be viable at higher weight percentages. Further testing is needed to determine the full useful range of this fabrication process.

After the void volume of the nanocomposites was determined, the Eshelby model predictions for the extensional moduli were calculated. Figure 8 shows the experimental findings for the extensional moduli as well as the Eshelby model calculated with the void volumes found experimentally. Table 4 shows the average void volumes based on four measured samples. The near constant void volume suggests that the vacuum process is sufficient at all weight percentages, and could possibly be sufficient for higher weight fractions.

The experimental values of the extensional modulus are higher than the values predicted by the modified Eshelby model one of the conventional micromechanical analytical models. This is an evidence that conventional methods cannot be directly used to estimate the properties of nanocomposites. This is because the interfacial area of nanocomposites are much larger that microcompsoites.

Conclusions

Based on the study on the fabrication process and resulted mechanical properties, the following conclusions were obtained:

The best mixing speed and time of those tried for the epoxy/nanoparticle mixing procedure was determined. The epoxy was first mixed with the nanoparticles at 50°C. The mixing speed was 700 rpm and the mixing time was 2 hours. The hardener was then added and mixed at 700 rpm for 2 hours at room temperature.

The extensional modulus was found to increase as the mixing speed decreased. The lowest speed used in this study was 700 rpm. The data suggests that slower speeds may result in a higher extensional modulus. The mixing time had no significant effect on the extensional modulus in the range used. This suggests that the final level of dispersion is reached in less than 2 hours of mixing.

Methods of inserting the nanocomposite mixture into the mold and vacuum procedures were investigated to limit the effects of voids on the mechanical properties of the nanocomposites. A vacuum time of 12 hours at 20 in Hg as well as 2 hours of vacuum after insertion into the mold was found to be the most beneficial. The draining method introduced in this paper was found to be very effective in reducing the amount of voids in the nanocomposites.

The shear mixing of epoxy/clay nanocomposites was found to be effective for increasing the extensional modulus in the range of 2% to 6% nanoparticles by weight. The increase in the extensional modulus is almost proportional to the weight percentage of nanoparticles.

Analytical evaluation using a conventional micromechanical model for the extensional modulus did not closely predict the actually properties. The values predicted by the modified Eshelby model were much lower than the experimental values. These large regions of altered polymer mobility affect the improvement of properties and explain the difference in the modulus values.

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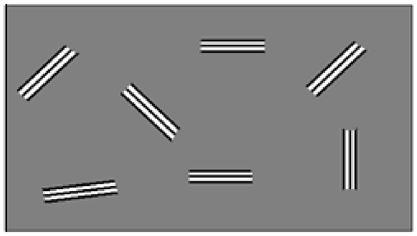
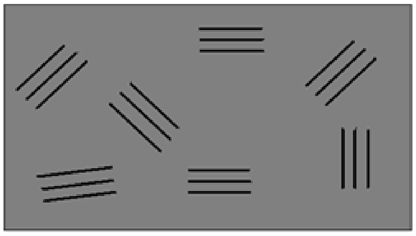
References

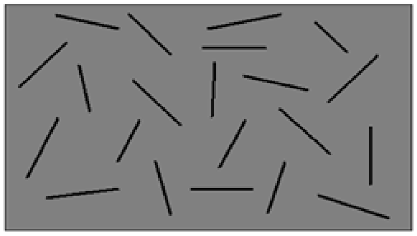
1. L. A. Utracki, Clay-Containing Polymeric Nanocomposites Volume 1, Shawbury, Rapra Technology Limited (2004).
2. T.-K. Oh, “The effect of shear force on microstructure and mechanical property of epoxy/clay nanocomposite,” M.S. thesis, University of Florida, Gainesville, FL, USA (2004)
3. C. Chen, T. B. Tolle, Journal of Polymer Science Part B: Polymer Physics, **42**, pp. 3981-3986 (2004).
4. J. H. Koo, Polymer Nanocomposites: Processing, Characterization, and Applications, McGraw-Hill (2006).
5. S. H. Goodman, Handbook of Thermoset Plastics, New Jersey: Noyes Publications (1986).
6. F. Gao, Materials Today, **11** (13), pp. 1843-1851 (2006).
7. S. C. Zunjarrao, R. Sriraman, R. P. Singh, Journal of Material Science, **41**, pp. 2219-2228 (2006).
8. A. Yasmin, J. L. Abot, I. M. Daniel, Scripta Materialia, **49** (1), pp. 81-86 (2003).
9. P. M. Ajayan, L. S. Schadler, P. V. Braun, Nanocomposite Science and Technology, Wiley-VCH (2003).
10. H. Lee, K. Neville, Handbook of Epoxy Resins, New York: McGraw Hill (1967).
11. S. Saber-Samandari, A. A. Khatibi, D. Basic, Composites Part B: Engineering, **38** (1), pp. 102-107 (2007).
12. B. Qi, Q. X. Zhang, M. Bannister, Y.-W. Mai, Composite Structures, **75** (1), pp 38-46 (2006).
13. J.-J. Luo, I. M. Daniel, Composites Science and Technology, **63** (11), pp. 1607-1616 (2003).
14. A. Yasmin, J.-J. Luo, Composite Science and Technology, **66** (14), pp. 2415-2422 (2006).
15. J. Y. Park, A.-H. Zureick, Polymer Composites, **26** (2) pp. 181-192 (2005).
16. E.T. Thostenson, C. Li, T.-W. Chou, Composite Science and Technology, **65** (3), pp. 491-516 (2005).
17. Diglycidyl Ether of Bisphenol F – Performace Properties, Technical Data Sheet, Hexion Specialty Chemicals (2005).
18. Dispersion guidelines for I.30E, http://www.nanocor.com/tech_sheets/T13%20-%20I30E.pdf, accessed February 2007.
19. ASTM Standard D 792, ASTM (2002)
20. J. Y. Park and N. Lee, Journal of Reinforced Plastics and Composites, **26** (6), pp. 601-616 (2007)
21. T. Watson, “Flexural properties of Epon 862,” http://tiims.tamu.edu/2005summerREU/papers/Watson.pdf, accessed December 2007.
22. J. H. Choi, C. K. H. Dharan, Journal of Composite Materials, **36**, pp. 2267-2285 (2002).
23. L. A. Utracki, Clay-Containing Polymeric Nanocomposites Volume 2, Rapra Technology Limited (2004).



A. Phase Seperated



B. Intercalated



C. Fully Exfoliated

▬ Polymer ☰ Clay Layers

Figure 1: Dispersion Levels of Clay Nanocomposites

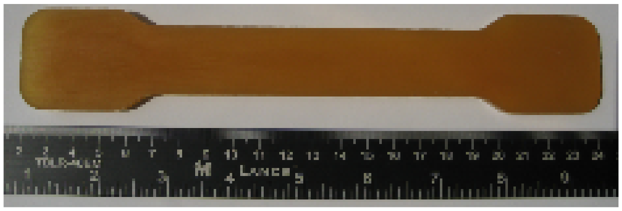


Figure 2: Nanocomposite Tensile Sample

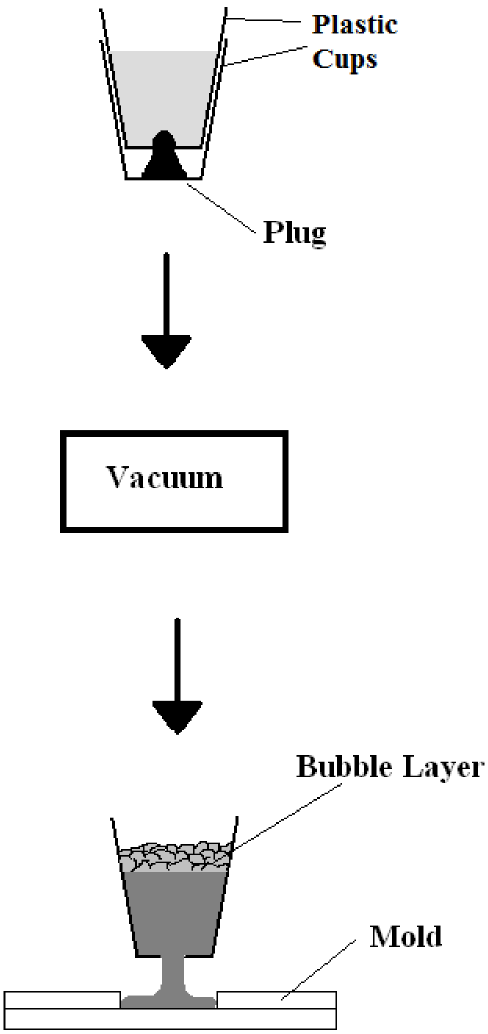


Figure 3: Illustration of Draining Method Effects of Degassing Procedure

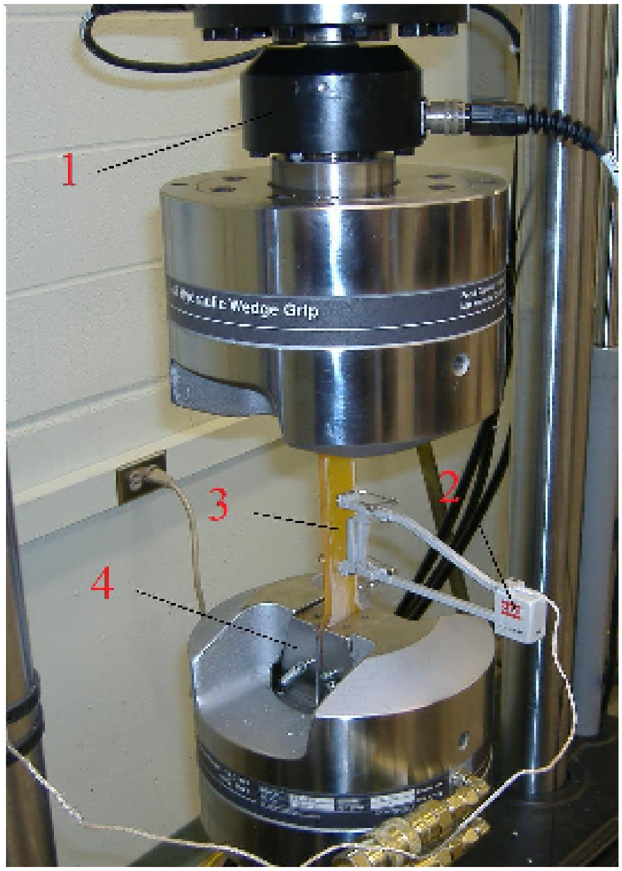


Figure 4: Tensile Test Setup, (1) 5 KIP Load Cell, (2) Extensometer, (3) Tensile Specimen, (4) Composite Grips

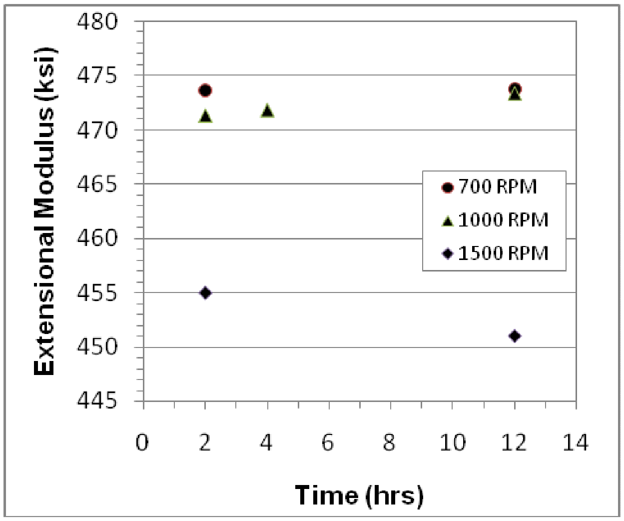


Figure 5: Effects of Mixing Speed and Mixing Time on the Extensional Modulus

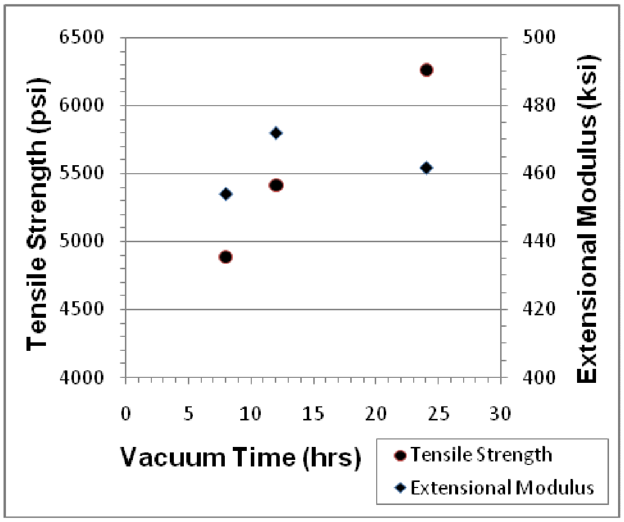


Figure 6: Effect of Vacuum Time on Extensional Modulus and Tensile Strength

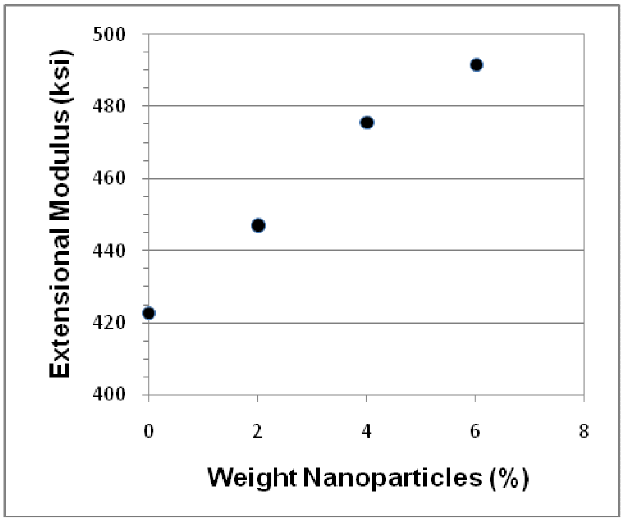


Figure 7 Effect of Weight Percentage of Nano-particles on the Extensional Modulus

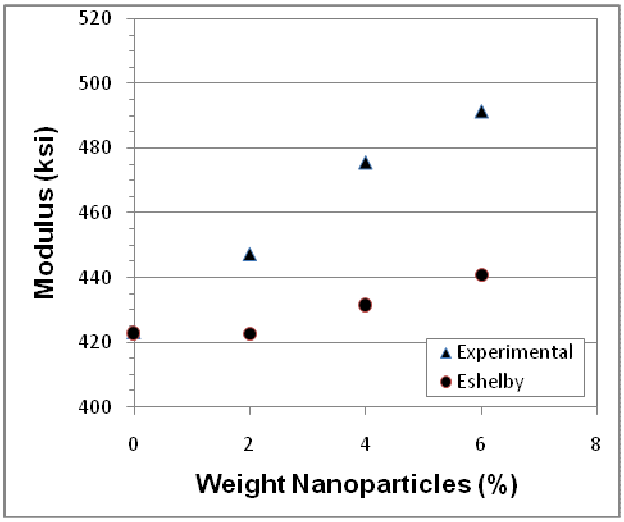


Figure 8: Experimental and Modified Eshelby Model Predictions of Extensional Modulus

Table 1: Approximate Properties of Individual Clay Layer of MMT

Property	Nanomer I.30E
Density (g/cm^3)	2.385 [16]
Tensile Modulus (GPa)	170 [6]
Tensile Strength (GPa)	1 [6]
Average Aspect Ratio	200-500 [17]

Table 2: Summary of Epoxy Fabrication

	Average Value	Standard Deviation
Modulus (ksi)	423	4.3
Tensile Strength (psi)	8326	1195
Density (g/cc)	1.198	0.003

Table 3: The Averaged Extensional Moduli of the tested specimens

	Epoxy	2%	4%	6%
Average (ksi)	**423**	**447**	**476**	**491**
St. Deviatio (ksi)	**4.3**	**11.2**	**11.0**	**11.3**
C.O.V. (%)	**1.026**	**2.512**	**2.316**	**2.292**

Table 4: Void Volume Fractions of the Samples

Weight Perentage	Sample 1	Sample 2	Sample 3	Sample 4	**Average**
2%	0.007	0.011	0.007	0.011	**0.009**
4%	0.008	0.012	0.014	0.010	**0.011**
6%	0.009	0.008	0.012	0.009	**0.010**