

Synthesis and characterization of layered silicate/epoxy nanocomposite

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ABSTRACT

Layered silicate/polymer nanocomposites are materials that display rather unique properties, even at low silicate content, by comparison with more conventional particulate-filled polymers. These nanocomposites exhibit improved mechanical, thermal, optical, gas permeability resistance and fire retardancy properties when compared with the pure polymer. In this study, layered silicate/polymer nanocomposites were prepared using Na⁺ cation containing montmorillonite (MMT) and epoxy resins. Silicate particles were treated with hexadecyltrimethylammonium chloride (HTAC) to obtain the complete homogenous dispersion of the nano plaques within the polymer matrix which forms the exfoliated microstructure. In this way, organophilic silicates (OMMT) were obtained. Modification of the silicate expands the silicate galleries (from 14 Å to 18 Å) that promote the formation of exfoliated composite structure. SEM results showed that nanocomposites with organically modified MMT exhibited better dispersion than those with MMT. It was found that the tensile and flexural modulus values are increased, whereas the fracture toughness is decreased with increasing silicate content. Thermal analysis results revealed that the glass transition temperature (T_g) of the neat epoxy resin (63.6°C) increases to 68.9 °C for the nanocomposites with 3 wt. % of OMMT. By incorporation of silicate particles, the dynamic mechanical properties of epoxy; including the storage and loss modulus and T_g are increased. Optical transmission values of the epoxy were affected by MMT and OMMT silicate incorporation. It was found that flame resistance at the polymer improved by the incorporation of MMT particles to the neat epoxy .

Keywords: MMT, DSC, Tensile, Layer silicate/Epoxy, XRD , Nanocomposite.

INTRODUCTION

Silicate particles were treated with hexadecyltrimethylammonium chloride (HTAC) to obtain exfoliated microstructure in which homogenous dispersion of the nano plaques within the polymer matrix forms. The interlayer spacing of the silicates with and without modification was measured by X-Ray Diffraction (XRD) techniques.

A great number of polymers have been already used to synthesize layered silicate/polymer nanocomposites. Epoxy resins have been one of the best matrix materials for many fiber composites due to their high dimensional stability and good mechanical properties. The reactants of epoxy systems have a suitable polarity in order to diffuse between the silicate layers and form exfoliated nanocomposites after polymerization [1-5] . A diglycidyl ether of bisphenol A type epoxy system was used as the matrix in this study.

Silicate/polymer nanocomposites were processed through in-situ polymerization by blending 0-10 wt. % of the silicate particulates with the epoxy resin after ultrasonication.

Microstructure-property relation within the developed nanosystems was investigated at a fundamental level based on X-ray diffraction (XRD), scanning electron microscopy (SEM) and mechanical testing techniques. XRD was used to evaluate the exfoliation of the silicate particles within the matrix. The distribution of layered silicates was

also evaluated based on the fracture surface SEM images of the sample after tensile test. Optical microscopy coupled with image analyzer software was used to determine the void content of the nanocomposites.[7] The tensile, flexural, and fracture toughness tests were performed to characterize the mechanical properties of the nanocomposites in terms of strength, modulus, failure strength, elongation at break, and fracture toughness values. Spherical and non-spherical semi-empirical models developed for layered filler incorporated structures were also used to compare the predicted values with the experimentally measured tensile modulus values of the nanocomposites. [6-9] Optical transparency of the materials was analyzed by UV and IR transmittance spectroscopy. As a thermal property, glass transition temperature (T_g) of the nanocomposites was determined by differential scanning calorimeter (DSC).[10-12] Burning rate of materials was measured using the UL-94 horizontal burning method. The effect of particle addition on the optical, thermal, and flame retardant properties of the composite was also investigated.[13-16]

In the present research program, attempt has been made to synthesize and characterize the Synthesis and Characterization of Layered Silicate/Epoxy Nanocomposite. The nanocomposites were characterized by a number of techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), and DSC, Tensile.

MATERIALS AND METHODS

Nanocomposite materials were prepared using an epoxy resin (Diglycidyl ether of bisphenol A (DGEBA)) as a polymer matrix and sodium montmorillonite (MMT, K10- Aldrich) as a filler with a cation exchange capacity of 120 meq/100g. Typical properties of montmorillonite based on the literature are shown in Table 2.1. An amine curing agent was blended to epoxy as a hardener agent. For the modification of MMT, hexadecyltrimethylammonium chloride (HTAC, Aldrich) with 25 wt. % sol. in water and Hydrochloric acid were used.

MODIFICATION OF MONTMORILLONITE

The schematic illustration of surface modification stages of montmorillonite (MMT) silicate particles. 20 grams of the MMT was dispersed into 400 mL distilled water and stirred at a temperature of 80 °C. 0.05 moles of HTAC was mixed with 4.8 ml HCl in 100 mL distilled water. This solution was poured into the hot silicate water mixture and stirred at a temperature of 80 °C for 1 hour. The mixture was then filtered and washed with water until no chloride was detected. Chloride residue was determined using AgNO_3 as described elsewhere [3]. The organosilicate (OMMT) was then obtained after drying the filtered material at 75 °C for 2-3 days in a vacuum oven.

SYNTHESIS OF LAYERED SILICATE/EPOXY-MONTMORILLONITE NANOCOMPOSITES

Layered silicate/epoxy nanocomposite samples were prepared with 1, 3, 6, and 10 wt. % of OMMT and MMT particles. The illustrates the processing stages for insitu polymerization process. The epoxy resin was blended with the desired amount (1, 3, 6, 10 wt. %) of OMMT and MMT at room temperature for 1 hour using a mechanical stirrer. The blend was further hold in an ultrasonic bath for 20 minutes to further disperse the silicate layers in the resin. Then, a stoichiometric amount (35 parts curing agent: 100 parts epoxy by weight) of the amine curing agent was added and the mixture was outgassed by vacuuming to remove bubbles. The blend was casted into silicon molds and the nanocomposites were cured at room temperature and post cured for 1 hour at 80 °C and 2 hours at 150 °C.

CHARACTERIZATION OF NANOCOMPOSITES

X-RAY DIFFRACTION

X-ray diffraction (Rigaku, D/Max, 2500V, Cu-K α radiation: 1.54056Å) experiments were carried out on both the plain PmClAn and the composite samples. Wide-angle X-ray diffractograms were recorded at temperature of 300 °C after isothermal crystallization at this temperature for 1 h in the range of 0-70(2 θ).

SCANNING ELECTRON MICROSCOPY (SEM)

Phillips™ Scanning Electron Microscopy (SEM) was used to study the fracture surface of tensile specimens and also used to determine the silicate agglomeration morphology. Gold vapor deposition onto the fracture surface permitted for the observation of the microstructure.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimetry (DSC) is a thermal technique in which differences in heat flow into a substance and a reference are measured as a function of sample temperature while the two are subjected to a controlled temperature program. DSC was operated under nitrogen atmosphere at a flow rate of 50 mL/min. For this test, the samples of 5–6 mg of epoxy samples were placed into the aluminium crucible, respectively. Indium was used to calibrate the thermal response due to heat flow as well as the temperature prior to analysis. The dynamic measurements were made at a constant heat rate of 10°C/minute from 25 to 200°C to determine the effects of the

montmorillonite silicate addition on the glass transition temperature (T_g) of epoxy. T_g was determined by the midpoint method.

TENSILE TEST

Tensile tests were conducted using a Shimadzu AG universal test machine and samples were stressed at a constant strain rate of 2.00 mm/min until failure. The test method and sample preparation was in accordance with ASTM D638M-91a. The tensile dogbone test coupons with 10 mm in wide and 6.0 mm in thickness were prepared. The gauge length of the specimen was approximately 50 mm. The overall length of the specimen was 200 mm. Figure 2.3 is the photo showing the tensile test specimen under load. At least five specimens from nanocomposites were used for the experiments.

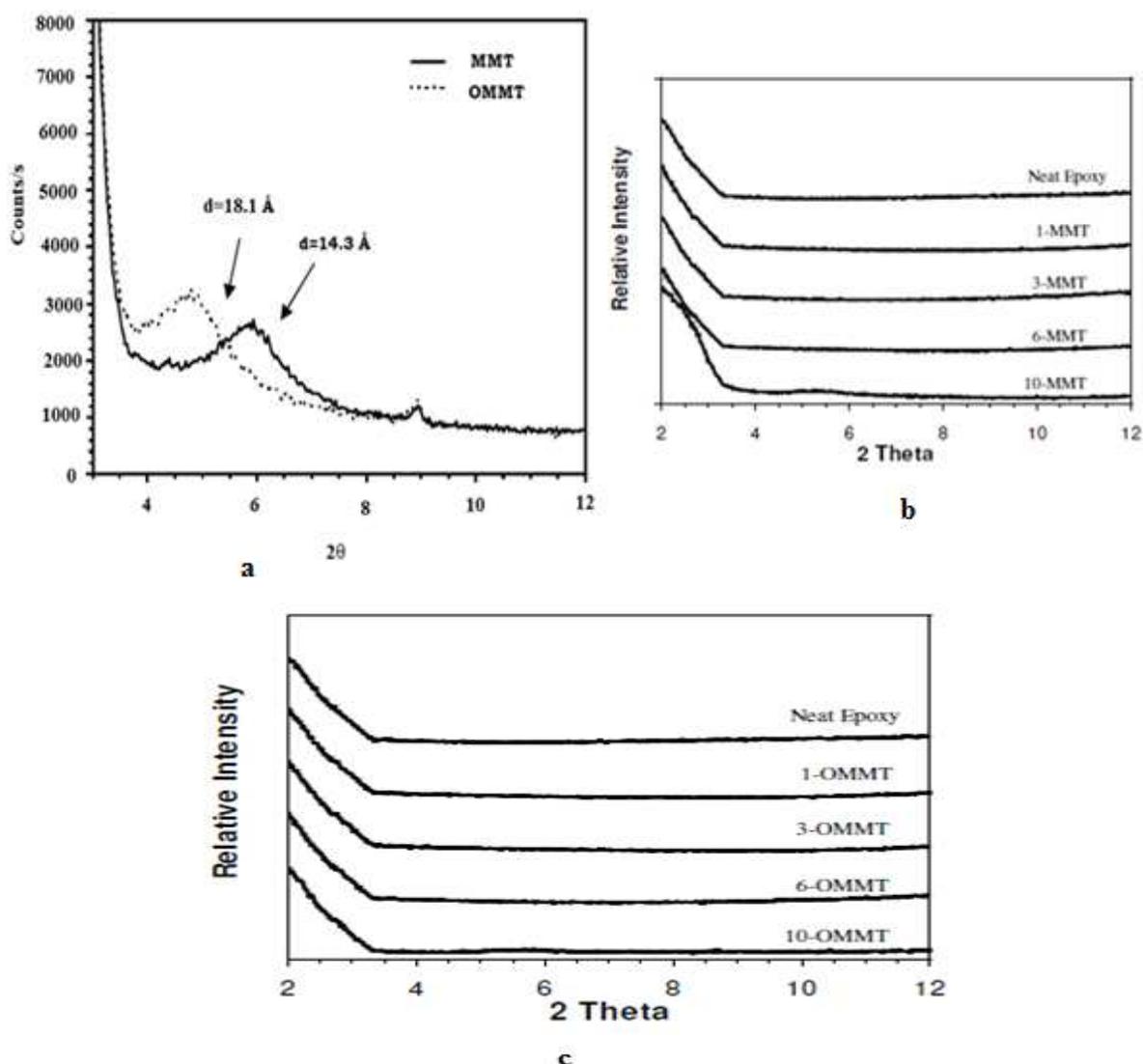


Figure -1 (a) XRD patterns of MMT and OMMT (b)XRD patterns of neat epoxy and nanocomposites prepared with OMMT loading from 1 to 10 wt%(c)Figure 2.8. XRD patterns of neat epoxy and nanocomposites prepared with MMT loading of 1 to 10 wt%.

RESULTS AND DISCUSSION

XRD :

In this study, X-Ray diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis were performed to examine the microstructural properties of the neat epoxy and layered silicate/epoxy nanocomposites and the extend of silicate layer dispersion within the nanocomposites. Figure -1 illustrates the X-ray diffractograms of natural silicate (MMT) and organically modified silicate (OMMT). MMT and OMMT exhibits characteristic XRD patterns corresponding to the d-spacing of 14.3 Å at $2\theta = 6.170$ and 18.1 Å at $2\theta = 4.870$, respectively. A greater d-spacing of OMMT implies intercalation (expansion) of the silicate galleries. The increase of the d-spacing is due to the penetration of the surfactant molecules within the galleries and exchange of Na^+ cations by the onium cation with a

long alkyl chain of the surfactant during the surface modification process. Figure 1 (b, c) exhibit the XRD patterns of the nanocomposites made of MMT and OMMT silicates with various loadings. In general, the characteristic peak of the silicates observed in Fig. 1 (a) are not detectable for the nanocomposites samples. This indicates the further intercalation of the silicate layers within the polymer matrix due to penetration of epoxy molecules into the intercalated galleries and dispersion of the silicate plaques within the polymer matrix. For nanocomposites prepared at high loadings (10 wt. %), the broad peak at about 5.5 θ implies a slight agglomeration of the silicate particles.

SEM:

Fracture surfaces of neat epoxy and nanocomposites, after tensile testing, were examined by SEM to evaluate the extent of silicate dispersion within the matrix. Backscattered SEM images of the fracture surfaces of neat epoxy and nanocomposites prepared with various MMT and OMMT concentrations are shown in Figures 2. (a) to (g).

As seen in Fig 2. (a), relatively smooth fractured surface observed on neat epoxy indicate more brittle fracture as compared to those for nanocomposites. Figures 2.(b) to (e) illustrate the fracture surfaces of the nanocomposites prepared with MMT and OMMT (3 and 10 wt. %). The bright features on the backscattered images correspond to silicate particulates. At higher magnifications (Figure 2. (f) and (g)), the silicate layers incorporated into nanocomposites are more visible.

At high silicate concentrations, relatively higher fractions of silicate agglomerations are observed from SEM images. These agglomerations results in weaker silicate/epoxy interfacial interactions and higher stress concentration regions. As the dispersed particle size becomes smaller and the particle dispersion is more uniform, the mechanical properties are improved more significantly. Smaller sizes of the particles also imply better exfoliation of the silicate layers that result in improved mechanical properties.

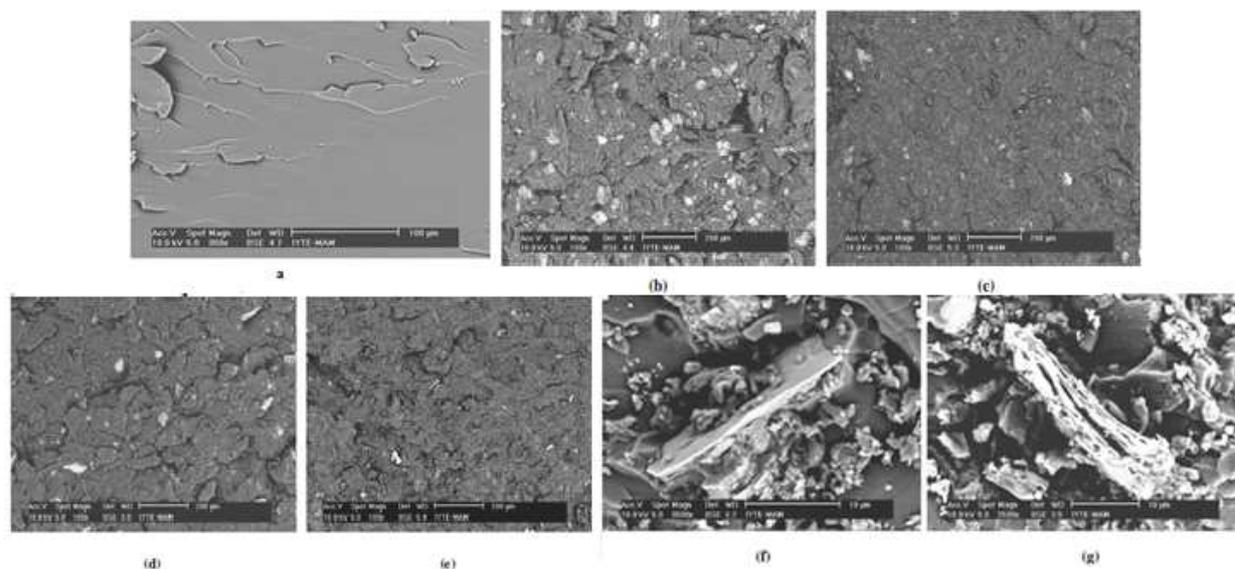


Figure 2. SEM fracture surface micrographs after tensile testing of (a) neat epoxy (350X) (b) 3 wt. % MMT /Epoxy (100X) (c) 3 wt.% OMMT/Epoxy (100X) (d) 10 wt. % MMT /Epoxy (100X) (e) 10 wt. % OMMT/Epoxy (100X) (f) 10 wt. % MMT /Epoxy (3500X) (g) 10 wt. % OMMT /Epoxy (3500X)

Fracture surface images (Figures 2. (c) and (e)) observed from the nanocomposites that in made of OMMT/epoxy indicate that organosilicate platelets are better dispersed in the epoxy matrix as compared to those for MMT/epoxy nanocomposites. This implies the surface modification and thus intercalation of silicate layers results in better dispersion of the particles within the matrix. It is obvious that larger agglomerates are formed in the structure of the material with 10 wt. % MMT.

It is obvious that the fracture modes are affected by the incorporation of silicates into the epoxy structure. It is obvious that different fracture mechanisms are active during the fracture of the nanocomposites as compared to more brittle fracture of neat epoxy.

TENSILE :

Figures 3 exhibit the tensile modulus values of neat epoxy and nanocomposites made with various amount of MMT and OMMT, respectively. The tensile modulus values tend to increase with the increasing fraction of MMT and

OMMT silicate particles up to 6 wt. % and approaches to a constant value at high loadings. The tensile modulus value is improved by 16% with 10 wt. % OMMT silicates loading as compared to neat epoxy. At high silicate loadings, OMMT exhibits slightly higher elastic modulus values as compared to those with MMT. Also, a dramatically increase in tensile modulus with increased silicate loading was also observed in exfoliated nanostructures such as MMT based thermoset amine-cured epoxy nanocomposite [6] Similarly, it was found by Isik *et al.*[7] for silicate/epoxy systems that tensile modulus of nanocomposites increases by incorporation of silicate. It was reported that the increase in modulus is directly related to the high aspect ratio of silicate layers. Nigam *et al.* examined the nanocomposites of epoxy resin with montmorillonite K-10 silicate and it was observed that addition of the 6 wt. % organosilicate to the epoxy matrix leads to 100% increase in the tensile modulus. This results were obtained by using montmorillonite K-10 silicates in a diglycidyl ether of bisphenol A and polymerized by in situ polymerization using an aromatic diamine as a curing agent.

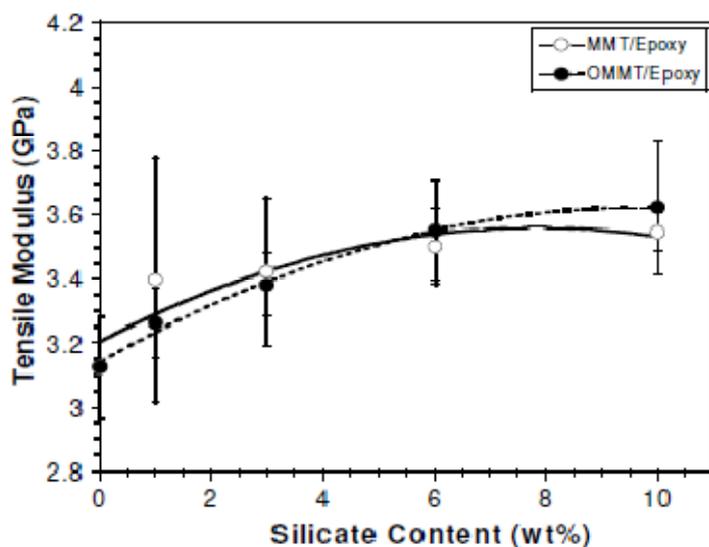


Figure 3 Tensile modulus of the neat epoxy and silicate/epoxy nanocomposites

DSC:

Figures 4 show the DSC thermograms of neat epoxy and the nanocomposites prepared with MMT and OMMT, respectively. The T_g value of neat epoxy is 63.6 °C. The T_g values of epoxy remains almost constant with the addition of MMT. For OMMT/epoxy nanocomposites, at low concentration of silicate addition, T_g increases up to 68.9 °C with 3 wt. % addition of OMMT. However, further addition of OMMT reduces the T_g up to T_g of neat epoxy. This observation suggests that organically modified silicates at relatively low contents better disperse in the polymer system and it restricts the motion of the epoxy network in the silicate/epoxy system.

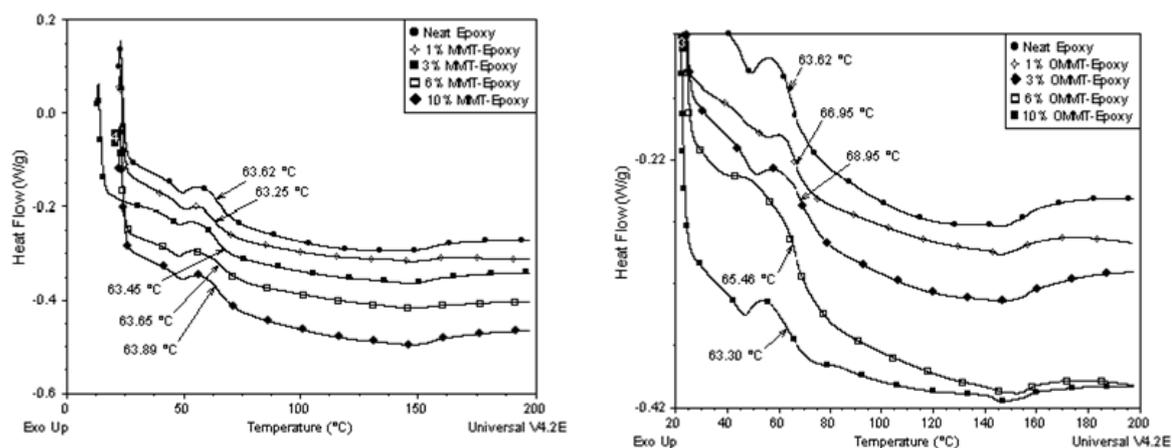


Figure 4 (a) DSC thermograms for neat epoxy and MMT/epoxy nanocomposites for various MMT content (b) DSC thermograms for neat epoxy and OMMT/epoxy nanocomposites for various OMMT content

CONCLUSION

In this study, layered silicate/polymer nanocomposites were developed based on epoxy resins and Na⁺ containing montmorillonite as the nano platelet reinforcement. Silicate particles were treated with hexadecyltrimethylammonium chloride (HTCA) through an ion exchange reaction. In this way, Na⁺ interlayer cations of the silicate is exchanged with onium cation of the surfactant that turns the hydrophilic silicates to organophilic characteristics. Silicate/epoxy nanocomposites were processed through insitu polymerization technique by blending of 0-10 wt. % of the silicate particulates with the polymer matrix using ultrasonication. Following blending, composite preparation was completed by polymerization of the cast samples.

Microstructure-property relation within the developed nanosystems was investigated at a fundamental level based on (XRD), scanning electron microscopy (SEM) techniques. Stress-strain behavior of the nanocomposites was measured using mechanical testing and thermal behavior was monitored with differential scanning calorimeter (DSC). In general, the mechanical, thermal, optical, and flame retardancy properties of the nanocomposites with OMMT were found to be better than those of nanocomposites with MMT. This is associated with the higher d-spacing of OMMT due to surface modification.

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