

## Clay/Epoxy Nanocomposites: Processing and Mechanical Properties

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### ABSTRACT

The present work is focused on evaluating the effect of the processing method and nanoclay (montmorillonite) content on the tensile, compressive and impact properties of clay-epoxy nanocomposites. Nanocomposites are synthesized by two methods: mechanical mixing and shear mixing. Both these methods are capable of producing bulk quantities of clay-epoxy nanocomposites. The x-ray diffraction (XRD) analysis indicates that the nanoclay has exfoliated in the mechanically mixed specimens. Results show that as nanoclay content increases the tensile modulus increases for both mechanically and shear mixed specimens, while the compressive modulus remained largely unchanged. The total energy absorption under impact loading is found to be higher in mechanically mixed specimens.

### INTRODUCTION

The interest in clay-polymer nanocomposites has been increasing ever since Toyota demonstrated commercial applications of nylon 6/clay nanocomposites [1]. Other types of nanoparticles are also being incorporated into polymeric resins in order to fabricate materials with increased performance. Some common examples of the nanoparticulate reinforcements include carbon based nanoparticles such as nanotubes, metals such as copper and aluminum, and ceramics such as alumina and silica. These nanoparticles are loaded into epoxies, PMMA, nylon, and polystyrene, as well as types of polymers. The nano-scale particles possess enormous surface area. Hence, the interfacial area between the two intermixed phases in a nanocomposite is substantially larger than traditional composites. This results in increased bonding between the particles and the matrix. Therefore, several mechanical, thermal and electrical properties of nanocomposites are observed in order to be better than those of conventional micro-composites or the neat matrix resin [2-9]. In some cases the nanoparticle reinforced resins have been used as matrix materials to fabricate conventional micro-composites [10, 11].

The main applications of nanocomposites are in the automotive, energy and packaging sectors. The current global nanocomposite market size is around US\$300 million and is expected to exceed US\$ 1b within the next five years [12, 13]. Currently, nanoclay filled composites account for almost 25% by volume of total nanocomposites usage and their market share is rapidly increasing. The relatively low cost of nanoclay, and rising energy and polymer prices are contributing to the increased use of clays as fillers to achieve saving of matrix polymers.

Clay-epoxy nanocomposites have attracted considerable technological and scientific attention because these materials offer a wide array of property improvements at very low filler content. Montmorillonite clay has a layered structure in which individual layers of typically 1 nm thickness and 0.1-2  $\mu\text{m}$  length and width have interlayer spacing of 2-3 nm [14]. These layers are bonded together by Van der Waal's forces. The enhancement of mechanical properties in nanocomposites depends on the intercalated or exfoliated content (Figure 1) of nanoclay in the polymer matrix [15, 16]. In the exfoliated condition their surface area can be as high as 750  $\text{m}^2/\text{g}$ . However, the complete exfoliation of nanoclay still remains a significant challenge in various types of polymers. The development of simple and cost effective processing methods that lead to the complete exfoliation of nanoclay particles will result in the widespread applications of these composite materials.

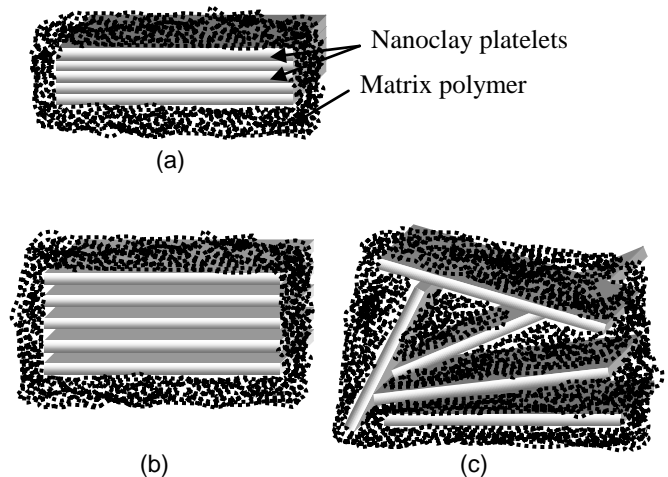


Figure 1. Schematic representation of the microstructure of clay-polymer nanocomposites (a) conventional clay particle (b) intercalated structure and (c) exfoliated structure.

In the present work two processing methods have been used to synthesize bulk quantities of clay-epoxy nanocomposites. XRD analysis is carried out to determine the dispersion of nanoclay in the composite material. The effect of processing method and nanoclay content on the tensile, compressive, and impact properties of nanocomposites is evaluated. These properties are compared with those of the neat epoxy resin to observe the difference caused by nanoparticles.

## EXPERIMENTAL

### Materials

The nanoclay selected for the study is Cloisite® 30B, supplied by Southern Clay Products. This clay is a natural montmorillonite mineral modified with a quaternary ammonium salt. The nanoclay particles were surface modified in order to facilitate their dispersion and exfoliation within the epoxy matrix. Epoxy resin D.E.R. 332, manufactured by DOW Chemical Company, was used as the matrix material. Amine based hardener D.E.H. 24 is used with the selected epoxy resin. A diluent C<sub>12</sub>-C<sub>14</sub> aliphaticglycidylether is mixed with the epoxy resin to reduce its viscosity. The ratio of epoxy, diluent and hardener is taken as 83.5:4.4:12.1 in all specimens.

### Nanocomposite Fabrication

Five compositions of nanocomposites were synthesized in the present study, containing nanoclay in 0.125, 0.25, 0.50, 1 and 2 vol.%. These composites were synthesized by mechanical and shear mixing methods providing total ten types of nanocomposite specimens.

Obtaining the complete exfoliation of nanoclay in the synthesized composites is a significant challenge. This process was first optimized for mechanical mixing. The viscosity of the resin plays an important role in determining the shear forces exerted on nanoclay particles during the mixing process. Therefore, resin and diluent were mixed to reduce the viscosity of the mixture. Then, the desired quantity of nanoclay was added to the resin and hand stirred until all the clay was immersed. The mixture was stirred at 650 rpm for 2 hr using a variable speed drill press (JDP-17FSE) fitted with a high shear impeller. The mixing speed and time were selected based on preliminary investigations. It was found that the best exfoliation results were obtained when the mixing was carried out at 50°C. The mixture was then degassed at 45°C. First a small quantity of the material was cured for XRD analysis. If the exfoliation was not complete then it was stirred for additional 30 min and then the hardener was mixed. The composite slabs were cast in aluminum molds, cured for 24 hr at room temperature and then post cured at 100°C for 3 hr. The processing was carried out with 4 liter of resin in each batch.

The fabrication of shear mixed nanocomposites was carried out using a three step process. First, the desired volume fraction of nanoclay was added to the epoxy-diluent mixture and hand stirred until all the nanoclay was immersed. Then, the mixture was placed under the drill machine and mixed at 650 RPM for 30 min to obtain homogeneous distribution of nanoclay within the resin. The mixture was then shear mixed using a three roll mill (EXAKT 50) at 180 rpm. The shear mixing was carried out twice on each batch. Following the mixing process degassing and curing was done in a manner similar to that described previously.

### XRD Analysis

The nanocomposites were characterized by Rigaku Miniflex x-ray diffractometer using Cu K $\alpha$  radiation, measured at 30 kV/15mA. The data was recorded in the range of  $2\theta = 2-$

10° [6, 7], at the step size of 0.01° and the counting speed of 0.5°/min. These parameters were selected based on preliminary studies to give sufficient resolution in the acquired XRD data.

### Mechanical Testing

The dimensions of mechanical test specimens are presented in Figure 2. Tensile and compression tests were performed on an Instron 4467 mechanical test system at a deformation rate of 0.5 mm/min. ASTM D638-02 [17] and D695-02 [18] were adopted to determine the test parameters for these tests, respectively. The tensile test specimen had straight sides as shown in Figure 2 and had dimensions suggested for the type IV specimens in the selected standard. An extensometer with gauge length of 25.4 mm was used to obtain the strain data in tensile tests. The displacement was measured for calculating strain in compression tests.

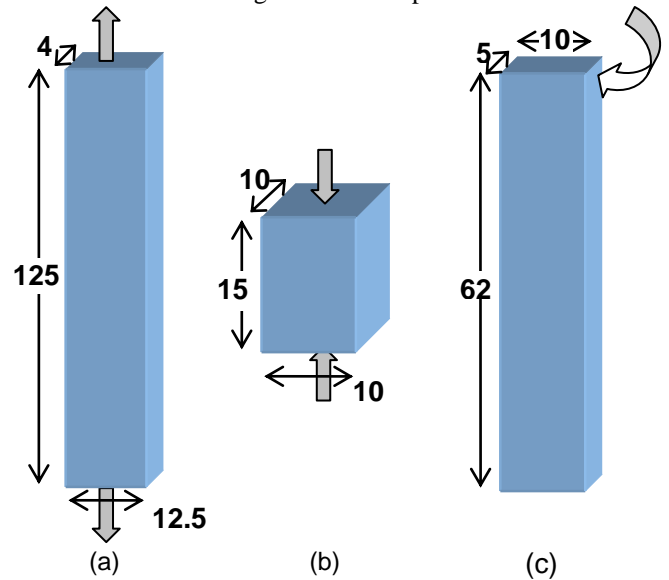


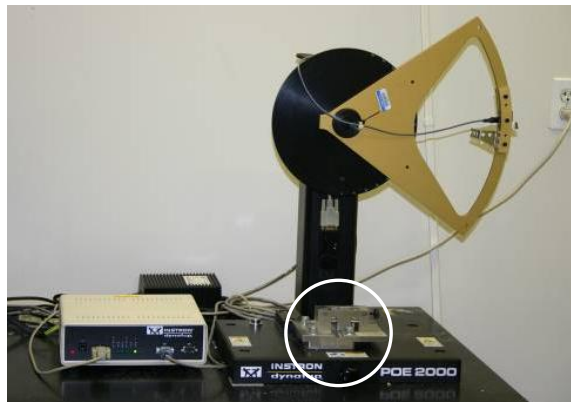
Figure 2. Dimensions and test orientations for (a) tensile (b) compressive and (c) impact test specimens. All dimensions are indicated in mm (figures not to scale).

Izod impact testing was performed using a Dynatup POE 2000 instrumented impact tester, shown in Figure 3, which specializes in testing polymers and composites. The unnotched test specimens were prepared in accordance with the ASTM standard D4812-05 [19]. Load, displacement and energy data was obtained for impact testing. At least five specimens of each type were tested and the average values are reported.

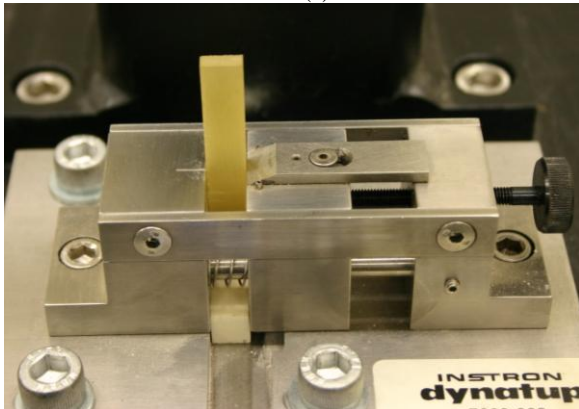
## RESULTS AND DISCUSSION

### XRD Observations

Among the methods of determining the dispersion characteristics of nanoclay in polymers, XRD and transmission electron microscopy (TEM) are widely used. In the present study XRD is given preference over TEM because the composite material is processed in bulk quantities of 4 liter in each batch.



(a)

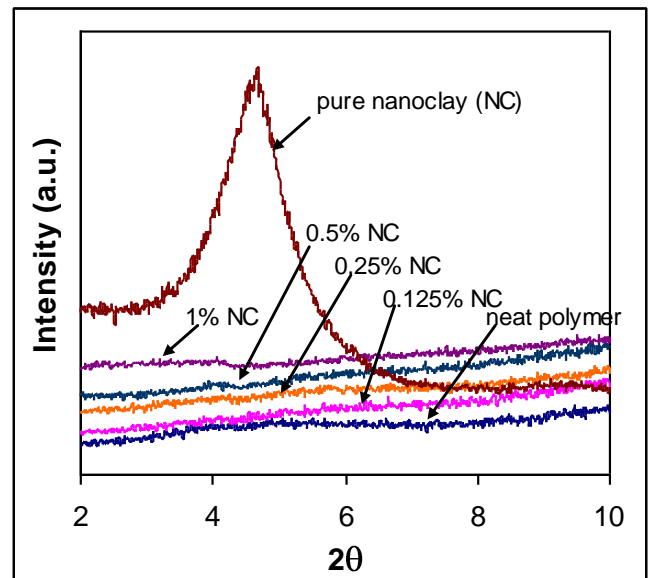


(b)

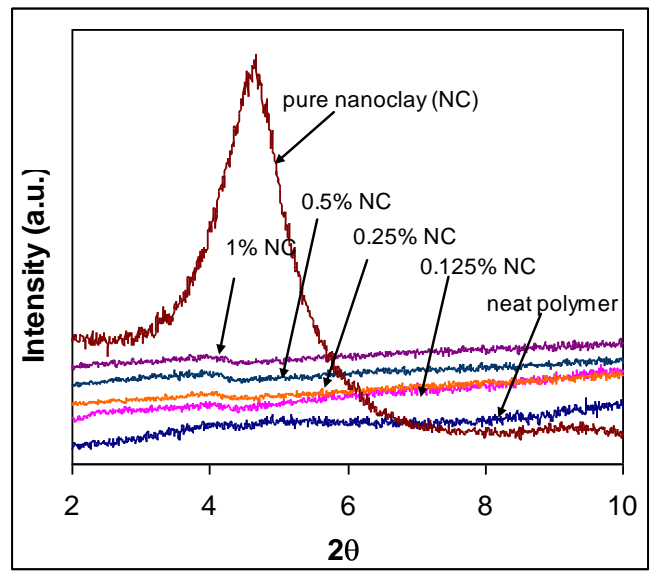
Figure 3. (a) Impact test setup and (b) Izod specimen and the holding fixture (circled part in (a)).

TEM observes the structure of the material in a very small area, which is less than  $0.2 \mu\text{m}$  in length and width at  $10^6$  magnification. The structure observed in such a small area may not be representative of the large batches. Therefore, XRD is used as the characterization technique because it uses relatively large specimen size and sample selection will have much smaller effect on the results.

The XRD spectra for the synthesized nanocomposites are shown in Figure 4, which are arbitrarily separated on the y-axis for various nanoclay contents. The spectra for pure nanoclay and neat epoxy resin are also included in the same figure for comparison. The neat epoxy resin specimens contain resin, diluent and hardener. It can be observed that the nanocomposites synthesized using mechanical mixing (Figure 4a) do not exhibit any peak in their spectra, which indicates that the nanoclay has exfoliated. Most of the specimens synthesized using shear mixing show a small bump in the spectra in the  $2\theta$  range of  $4.1\text{--}4.2^\circ$  as shown in Figure 4b, which is a shift from the  $2\theta$  value of  $4.6$  for the pure nanoclay. Hence, the nanoclay has intercalated in these composites but not exfoliated. The specimens tested in the present study contain up to 2 vol.% (approximately 4 wt.%) of nanoclay, which can result in low intensity of peaks in the XRD data. A comparison of Figures 4a and 4b shows that peaks can be clearly identified in the shear mixed specimens, which also contain nanoclay in the same volume fractions. Hence, absence of peaks in mechanically mixed specimens is a result of exfoliation.



(a)

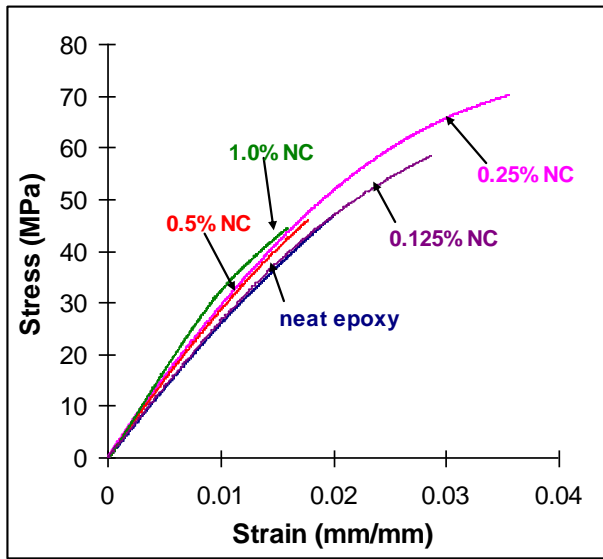


(b)

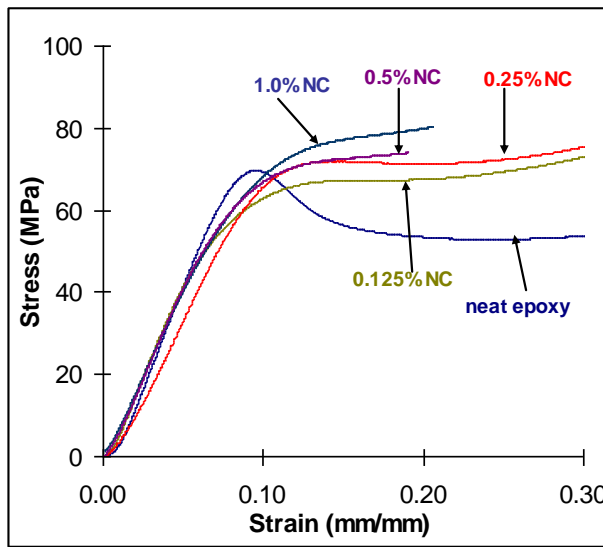
Figure 4. XRD spectra of various nanocomposites prepared by (a) mechanical mixing and (b) shear mixing. All nanoclay (NC) figures are in volume %.

### Tensile and Compression Tests

The stress-strain curves obtained from the tensile and compressive testing of the neat matrix resin and mechanically mixed nanocomposites are presented in Figure 5. Similar trends were observed for specimens prepared by shear mixing. The calculated tensile and compressive moduli and strengths are presented in Figures 6a and 6b, respectively. The tangent modulus is presented as the tensile modulus because the tensile stress-strain curves did not show a significantly large linear elastic region. The fracture strength is presented as the tensile strength because the curvature in the graphs is small.



(a)

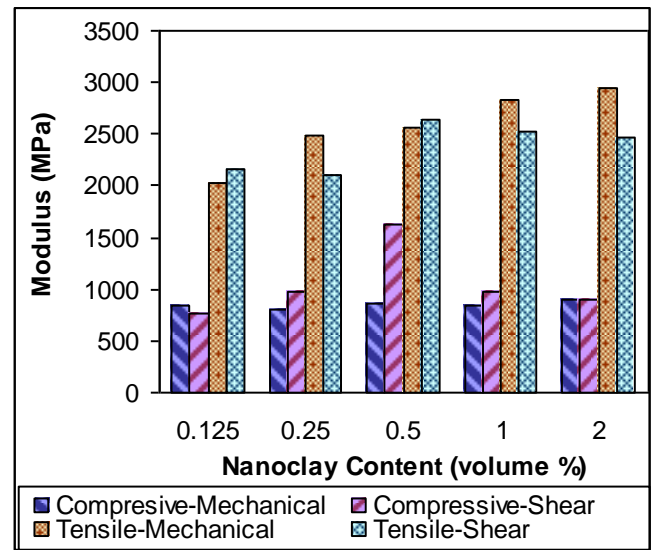


(b)

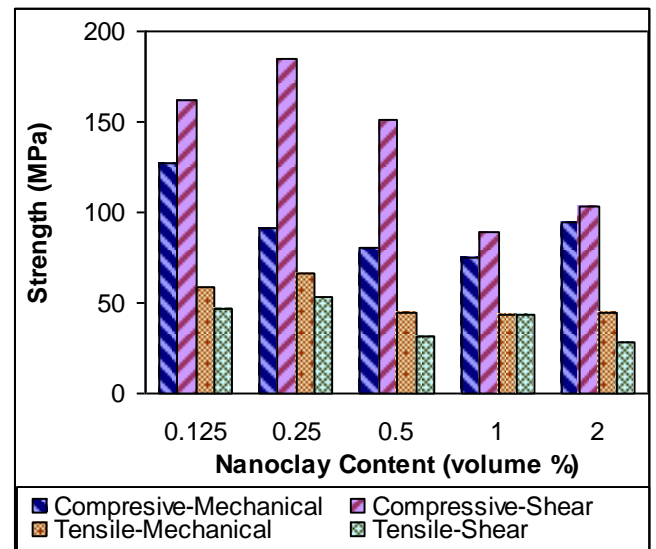
Figure 5. (a) Tensile and (b) compressive stress-strain curves for neat epoxy and mechanically mixed nanocomposites. The values for nanoclay (NC) content are given in vol. %.

The compressive modulus is calculated as the slope of the linear elastic regions of the stress-strain curves. The 0.2% yield strength is presented as the compressive strength.

It can be observed from Figure 6 that the tensile modulus increases with increasing nanoclay content. The mechanically mixed specimens with exfoliated nanoclay exhibit a higher modulus than the shear mixed specimens, which contain intercalated nanoclay. The modulus shows an increase of about 50% with the addition of only 2 vol.% nanoclay. Similar observations have been reported by other researchers [20]. The added stiffness achieved through the incorporation of nanoclay particles, results in no discernable optimum value for the elastic modulus. However, the maximum strength was exhibited by the 0.25 vol.% nanoclay specimens. The tensile strength decreased with further increase in the nanoclay content. Increase in tensile modulus and decrease in strength have also been observed in other published studies [21].



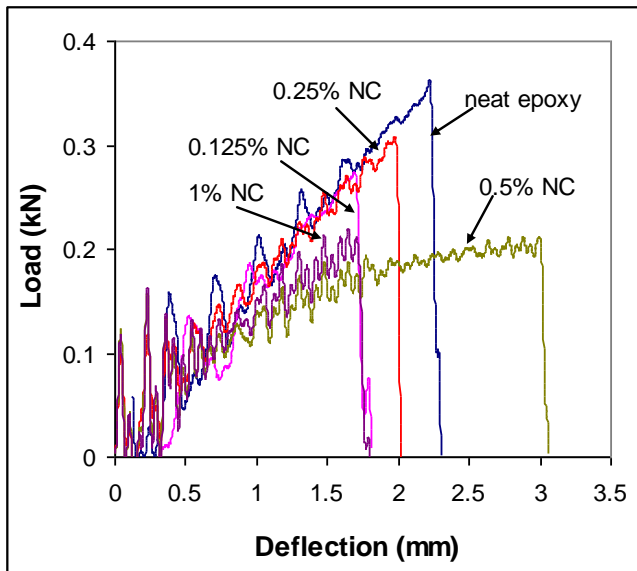
(a)



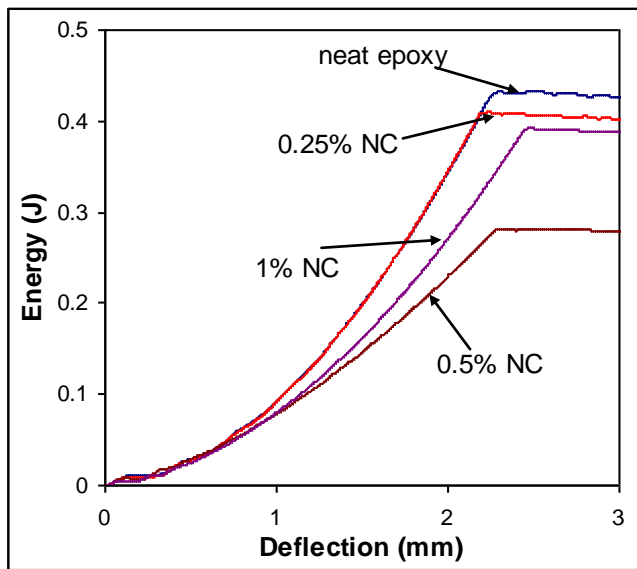
(b)

Figure 6. Tensile and compressive (a) modulus and (b) strength of clay-epoxy nanocomposites.

The effect of nanoclay on the compressive properties of nanocomposites is similar. The compressive modulus increased by about 30% and the maximum strength was observed for 0.25 vol.% of exfoliated nanoclay composites. However, in this case the shear mixed specimens showed higher strength and modulus as opposed to the mechanically mixed compositions. A better understanding of the compressive properties of composites can be obtained by observing the stress-strain curves in Figure 5b. The curve for the neat resin shows an approximate 20% decrease in strength past the yield strength. However, the nanocomposites do not show a similar decrease. The main compressive failure mode in epoxies is the initiation of cracks in the direction of compression due to the lateral expansion under the Poisson's ratio effect. In the case of nanocomposites the increased modulus leads to smaller lateral expansion, leading to delayed crack initiation.



(a)



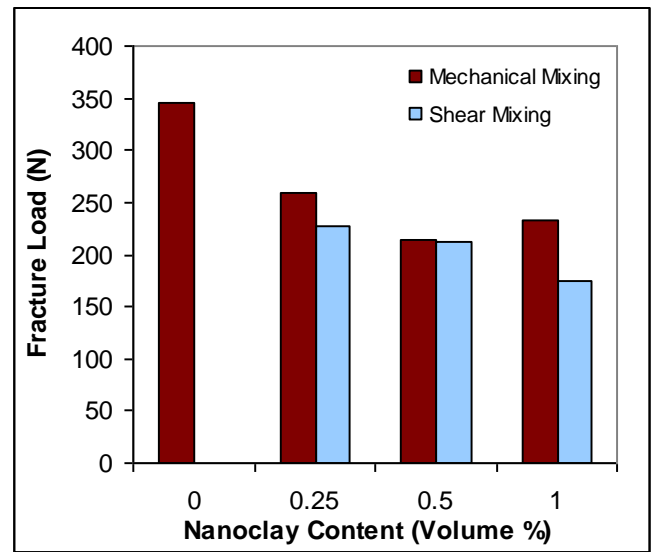
(b)

Figure 7. (a) Load-deflection and (b) energy-deflection curves for nanocomposite specimens prepared by mechanical mixing. All nanoclay (NC) values are in volume %.

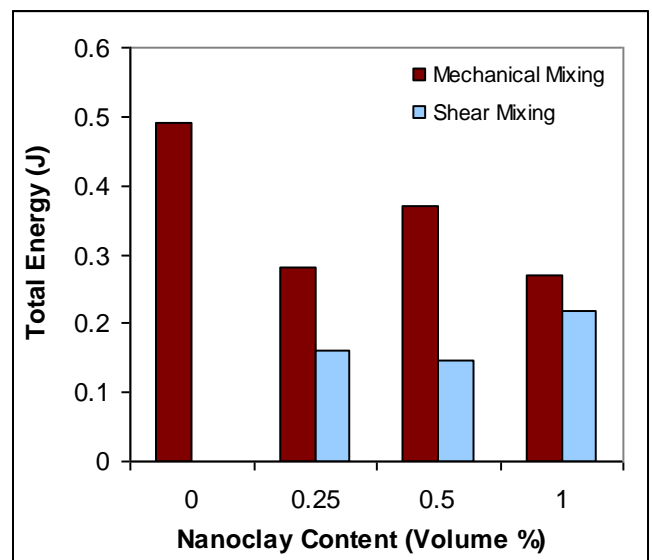
Hence, the decrease in strength after the yield point is not observed. Increase in the nanoclay content leads to higher compressive modulus resulting in the final failure at lower strain values.

### Impact Tests

The load-deflection and energy-deflection curves for mechanically mixed specimens are presented in Figure 7. Curves for shear mixed specimens also showed similar trends. The total fracture process takes less than 1.5 ms for most nanocomposites. Figures 7a and 7b show that most specimens attain the peak energy absorption in the range of 2-2.5 mm deflection. The presence of second phase particles leads to the deflection and branching of the crack tip in composite materials and slows down the fracture process, leading to lower slope in the energy-deflection curves.



(a)



(b)

Figure 8. Variation in (a) fracture load and (b) impact energy for nanocomposites

The results presented in Figure 8 show that the energy absorption in the neat epoxy resin is higher than that of nanocomposites. Reduced tensile and compressive failure strains lead to fraction of nanocomposites at lower deflection leading to lower total energy absorption compared to the neat epoxy resin. It is observed that the specimens with exfoliated nanoclay show higher fracture load and total energy absorption than specimens containing intercalated nanoclay. The dominant effect of crack initiation and propagation on the properties of clay-epoxy nanocomposites had been established previously through fracture toughness studies [22]. For specimens with a notch or a blunt crack the Mode I stress intensity factors ( $K_{IF}$ ) were observed to be lower than the neat epoxy in previously published studies. The  $K_{IF}$  was found to be higher only in the nanocomposites which used a sharp starter crack.

## REMARKS

Scattered results can be found published on other mechanical and physical properties of a number of nanoclay-polymer systems. The Vickers hardness was found to increase by 16% in clay-epoxy nanocomposites compared to the neat resin [23]. In dynamic mechanical analysis the storage modulus was found to increase by 31% due to the addition of about 1.6 vol.% nanoclay [24]. In this study the glass transition temperature was observed to be the maximum at 0.5 vol.% nanoclay. The tensile modulus showed a trend similar to that observed in the present study, but the strength increased up to the addition of 1 vol.% nanoclay and decreased after that. Wear rate of bentonite clay-polyester nanocomposites were found to improve whereas for organoclays-polyester these properties were found to deteriorate with increase in the clay content [25]. Similar trend was exhibited by the nylon 6/clay nanocomposites [26]. Water uptake was found to be lower in some clay-epoxy nanocomposites than the neat resin [27]. The data on mechanical properties of a large number of clay reinforced nylon, polyester and polypropylene based nanocomposites is available in a recent review article [28].

## CONCLUSIONS

In the present study epoxy matrix composites containing 0.25-2 vol.% nanoclay were synthesized using bulk processing methods. The composites processed by mechanical and shear mixing processes provided exfoliated and intercalated structure, respectively. The effects of nanoclay content and dispersion on the tensile, compressive, and impact properties were studied and compared. The tensile and compressive modulus showed improvements with increased nanoclay content. However, the tensile and compressive strengths decreased as nanoclay content increased. The impact strength and energy absorption for nanocomposites were higher for mechanically mixed specimens, but lower than the neat epoxy resin. Various mechanical properties exhibited mixed trends with increased nanoclay content in the composite. In most cases, exfoliated specimens showed better properties than intercalated specimens. Hence, applications of these materials should be selected in such a way that enhanced performance can be obtained by using the improved properties.

## ACKNOWLEDGMENTS

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## Processing Techniques

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### CLAY - EPOXY NANOCOMPOSITE SYNTHESIS

The advantage of using a low cost filler can only be realized if the synthesis process does not add significantly to the cost of the raw materials. It is desired that the existing composites synthesis methods be used to obtain high quality nanocomposites so that the infrastructure establishment cost can be minimized. Numerous techniques, based on chemical or mechanical processing methods, are available for dispersing nanoparticles in polymers. Some of the mechanical processing methods used for clay-thermoset nanocomposites are described below.

#### Mechanical Mixing

Mechanical or stir mixing is a widely used technique for dispersing microparticles in polymers. Use of this technique for synthesis of nanocomposites is highly desired because it can save the cost of establishing new infrastructure. The parameters affecting the mixing process are temperature, mixing speed, and impeller design. The processing temperature affects viscosity and plays an important role in achieving exfoliation. The vortices formed by the impeller generate shear forces that can break Van der Waal's bonds between nanoclay platelets and lead to exfoliation. Hence, the design of impeller is also an important parameter in this process.



A variable speed drill press modified as mechanical mixer

#### Shear Mixing

Shear mixing is commonly used as a method for dispersing nanoclay in thermosets. Three-roll mills are widely used for the purpose of mixing. The material is fed between the feed roll and the center roll and is collected from the apron roll. The exfoliation of nanoclay depends on the shear force applied by the rolls on the material, which is controlled by the

separation between rolls and the viscosity of the resin. Two shear mechanisms are applicable in such processing systems, which include the direct shear forces applied by the rolls and the shear caused in the vortices formed in the material coming out of the rolls. The reagglomeration of dispersed particles can be a problem in this method if the processing parameters are not optimized.



A three roll mill used for shear mixing.

#### Ultrasonic Mixing

In several recent studies ultrasonic mixing has been used as a means to exfoliate nanoclay in polymers. This technique is based on imparting high energy vibrations in a localized region causing separation of nanoclay platelets. However, such vibrations lead to significant localized heating. Polymeric resins such as epoxies are thermal insulator. Hence, the heat generated in the mixing process is not dissipated effectively and can initiate the self polymerization reaction in the mixing region. Recent process modifications include using ultrasonic mixing in conjunction with mechanical mixing and the use of an external cooling bath. Ultrasonic frequency, power and mixing time are the variables in this process.



A sonotrode used in ultrasonic mixing.