

# Mechanical Assisted Modification of Halloysite Nano Clay: Characterization and Its Effect on Mechanical Properties of Halloysite-Epoxy Nano Composites

M. Rudresh<sup>1</sup>, B. H. Maruthi<sup>2</sup>, H. P. Nagaswarupa<sup>3</sup>, B. S. Surendra<sup>4</sup>,  
M. R. Anil Kumar<sup>5</sup> and N. Raghavendra<sup>6</sup>

<sup>1&2</sup>Department of Mechanical Engineering, <sup>3,4,5&6</sup>Research Center, Department of Chemistry  
East West Institute of Technology, Bangalore, Karnataka, India  
E-Mail: rudresh.m1987@gmail.com

**Abstract-** Modification of Halloysite nano clay has been done using 3-aminopropyltriethoxysilane in the presence of distilled water as solvent media. Untreated and modified nano clay was characterized by Powder X-ray diffractometer (PXRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR). Functionalization of Halloysite nano clay is also strongly affected the morphological parameters and enabling the application in epoxy nano composite. However, the influence of modified clay concentration on the mechanical properties of epoxy/nanoclay composites, with different concentrations (2%, 3%, 4% and 5%) of nano clay in the epoxy resin was investigated. Experimental results showed that the mechanical properties of epoxy were improved upto 4 wt% of HNP's, evidently because of the loading of modified clay. The tensile strength, tensile Modulus, flexural strength, flexural modulus and fracture toughness of the nanocomposites increased by 13%, 17%, 9%, 14% and 27% respectively this demonstrated that the composites were strengthened.

**Keywords:** Modified Halloysite Clay, Epoxy Nano Composites, Mechanical Properties, Ultrasonication, Clay Concentration

## I. INTRODUCTION

Nowadays, Halloysite nano-particles (HNP's) become a hot topic for researchers to enhance the mechanical properties of polymer for strengthening and toughening of epoxy based nanocomposites [1-4]. HNP's are having two-layered aluminosilicate with a hollow nanotubular structure. Artificially, the external surface of the HNP's had comparable properties to SiO<sub>2</sub> and the inner cylinder core was identified with Al<sub>2</sub>O<sub>3</sub>. HNP's has a 1:1 Al: Si ratio and stoichiometry Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (OH)<sub>4</sub>·2H<sub>2</sub>O, which resemble to multi-walled carbon nanotubes (CNTs) [5-8].

These HNP's are a less expensive than other nano-particles, for example, CNTs owing to expensive of their cylindrical structure, aspect ratio in nano-scale and furthermore because of their resemblance to layered clay minerals, for example, montmorillonites (MMTs), having the likelihood to be additionally intercalated chemically or physically in polymer [9-10].

Advantages of HNP are utilized as filler for polymer composites are separate nano-particles with lower surface charge. Such particles may wipe out the requirement for

intercalation and exfoliation to blend with the polymers to create homogeneous molecule scattering. Then again, certain surface alterations to HNP's may furnish intercalations of HNP's layers with organic and inorganic mixtures, prompting their layer extension opposite to the base layers, which may give the chance of exfoliation of individual layers, like those of modified MMTs. Initial results have shown that mixing epoxies with a specific measure of HNP's can increase their fracture durability, strength and modulus, without giving up their thermal and mechanical properties, for example, Tg [11,12].

To achieve homogeneous mixing of HNP's in epoxies remains a test because of agglomeration of huge molecule bunches [13]. It is trusted that the agglomeration of HNP's is caused primarily because of their moderately high surface energy on their particle size results in a large surface area (specific area = 60 m<sup>2</sup>/g) [14] and agglomerate affected by the vander Waals constrain. The moderate shear stresses given by the regular mechanical mixing strategy, for example, ultrasonic vibration and utilizing stirrer for shear blending or magnetic bar are neglected to eliminate particle agglomeration [15].

Notwithstanding, the utilization of severe shear stresses, for example, utilization of ultrasonication, may separation the agglomerates and accomplish a homogeneous scattering of HNP's in the polymer network. In the meantime, as with organically modified MMTs, surface modification to HNP's may deliver the chance to extend the basal spacing of HNP's by the intercalation of inorganic and organic compounds in their interlayers, which may make it simple to create a homogeneous blend of HNP's with polymers amid blending. Moreover, surface adjustment may likewise give superior wetting and bonding of HNP's with polymers network [16].

In present work, Modification of HNP's was done by using 3-aminopropyltriethoxysilane in presence of distilled water as solvent media and used ultrasonication to obtain homogeneous blending of Halloysite/epoxy nano-composites with improved homogeneity of HNP's in the epoxy matrix with different weight percent of nanoclay loading which showed improvement in mechanical performance.

## II. MATERIALS AND METHODS

For fabrication of epoxy based composites Halloysite nanoclay (kaolin clay) (HNP's) was used as a reinforcement. It was procured from Sigma Aldrich, India. (3-Aminopropyl)trimethoxysilane liquid was procured from Sigma Aldrich, India as modifier for clay. Epoxy resin (LAPOX L-12) of medium viscosity is selected as the matrix. Its chemical name is Bisphenol-A-Diglycidyl-Ether (DGEBA). Hardner diamino-diphenyl-methane (DDM) with commercial designation K-6 is selected for the present work. The LAPOX L-12 epoxy resin and the corresponding curing agent K6 are of commercial grade which makes ease for industrial application are procured from Atul Ltd. Gujarat, India as shown in Table I.

TABLE I PHYSICAL PROPERTIES OF HNP'S NANO CLAY

Properties	Typical Values	Unit
Molecular weight	294.19	g/mol
Average diameter	30-70	Nm
Average length	1-3	$\mu\text{m}$
Surface Area	64	$\text{m}^2/\text{g}$
Density	2.53	(true specific gravity)
Refractive Index	n20/D 1.54	
Pore Size	1.26-1.34	mL/g pore volume

### A. Surface Modification of HNP's Nano Clay Using 3-Aminopropyltriethoxysilane

HNP's nanoclay of 3 gm was added to 300ml distilled water which is used as solvent and the dispersion was done by using mechanical stirrer for 10 minutes at room temperature. At the same time 3 gm of 3-aminopropyltriethoxysilane was mixed with 300 ml distilled water. This solution was added by constant stirring to the clay dispersion and stirred continuously for half an hour. It was then filtered off by using vacuum pump; Buchner flask and Buchner funnel with filter paper. The filtered clay is then dried at 60°C in an autoclave for 3 hr. The clays were ground to fine with a pestle and mortar.

### B. Sample Fabrication

Polymer nano-composites samples were prepared by blending epoxy resin with modified HNP's nano-clay with different weight percentages (2%, 3%, 4 %, 5% and 6%) of by mechanical mixing for 30 min at 1200rpm. Consequently, the mixture was placed in ultrasonicator for about 20 min to avoid air bubbles formed during blending and hardener was added with constant speed. The blend was then poured into preheated molds afterwards placed in an autoclave at 85 °C for 8 hrs for curing.

### C. Characterization

The modified and un-modified HNP's nano clay was characterized by PXRD using Philips X'pert-PRO X-ray diffractometer with graphite monochromatized  $\text{CuK}_\alpha$  ( $\lambda =$

1.5418 Å) radiation at the scan rate of 2° min<sup>-1</sup> and 2 $\theta$  ranging from 10° to 80°. The fractured surfaces of the samples were examined using field emission scanning electron microscopy (VEGA3 TESCAN) and all specimens were coated with a thin layer of sputtered gold before analysis by using Quoram Sputter coating equipment. Fourier Transform Infrared Spectrophotometer (FT-IR) of SHIMADZU (Model: IRAffinity-1S) is used to take FT-IR spectra in the range from 400 to 4000 cm<sup>-1</sup> in transmission measurement mode. The instrument resolution is set for 4 cm<sup>-1</sup> and with 45 numbers of scans.

### D. Mechanical Properties

Tensile test specimens are tested as per ASTM D638 standards with the standard dimension of specimen 50mmX13mmX5mm at a constant rate of traverse of the moving grip of 1 mm/min. Three point bending test specimens are tested according to ASTM D790 standard having the standard dimension of 125mmX12.7mmX3.2 mm at a constant rate of traverse of the moving grip of 5.2 mm/min and support span of 100mm. Fracture toughness specimens are tested according to ASTM E399 standards having the standard dimension of 48mmX10mmX5mm at a rated speed of 2mm/min, with distance between supports is 40mm. Five specimens of each composition for the above three properties are tested using a Universal Testing Machine AUTOGRAPH AG-IS 10 KN.

## III. RESULTS AND DISCUSSION

### A. PXRD of Halloysite Nano Clay

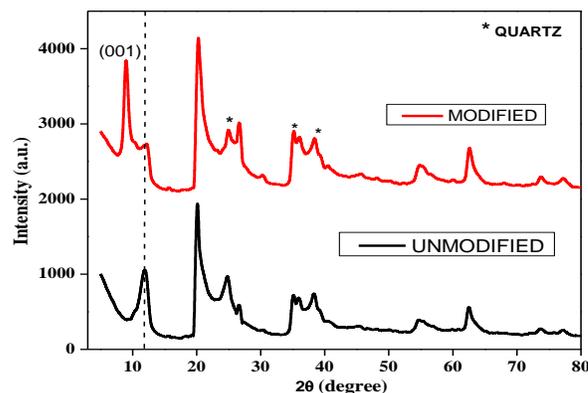


Fig. 1 PXRD pattern of Modified and unmodified HNP's

Fig.1 shows the powder X-ray diffraction patterns of the modified and unmodified HNP's [17]. The basal spacing of unmodified HNP's is approximately 7.2 Å, based on the diffraction angle for the peak at  $2\theta = 11.8$  [18]. The 7.2 Å reflections belong to the intact portion of HNP's, which represents dehydrated HNP's. However, using 3-aminopropyltriethoxysilane shifts the peak to the lower  $2\theta$  value along with a new peak at around 8.0, due to the expansion of layers in the direction perpendicular to the base plane with a final basal spacing of 15.1 Å [19]. Clearly, a peak at  $2\theta = 11.9$  can be seen for the untreated HNP's/epoxy composite while the peak at  $2\theta = 8$  is invisible.

### B. Morphological study of HNP's Nano Clay

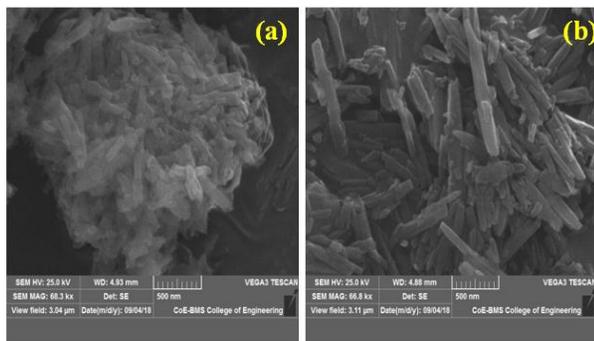


Fig.2 SEM images of (a) Unmodified (b) Modified Halloysite nanoclay.

Micromorphology of unmodified and modified HNP's nanoclay was observed by SEM as shown in fig. 2a & 2b. Fig. 2a shows unmodified HNP's nano clay which reveals nanotube structures with immense block impurities stacked together. Fig. 2b shows the morphological changes of nano clay modified by 3-aminopropyltriethoxysilane and it is showed that the tubular structure of modified nanoclay become thicker than that of the unmodified HNP's. Therefore the dispersibility is improved and agglomeration is reduced, indicating that 3-aminopropyltriethoxysilane is well anchored on the HNP's surfaces [20].

### C. FTIR HNP's Nano Clay

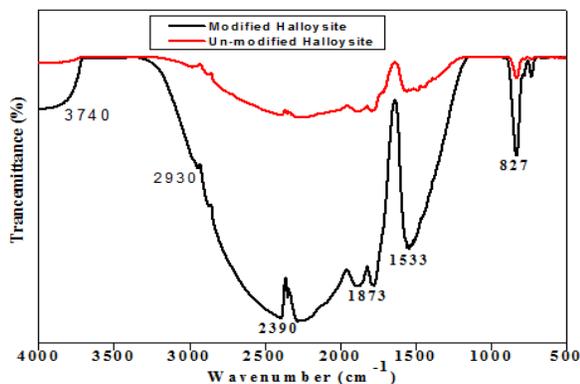


Fig.3 FT-IR spectra of Unmodified and modified HNP's nanoclay

Fig.3 shows FT-IR spectrum of unmodified HNP's nano clay and 3-aminopropyltriethoxysilane treated HNP's nano clay. Modified nano clay exhibit new FTIR peaks, such as the stretching CH<sub>2</sub> vibration band around 2930 cm<sup>-1</sup>, the peak around 1533 cm<sup>-1</sup> belongs to deformation of NH<sub>2</sub> vibration. This is further supported by the increase in peak intensity as well as the shift to lower frequency for the water-bending vibration at 1873 cm<sup>-1</sup>. The O-H deformation of inner hydroxyl groups is observed at 827 cm<sup>-1</sup>. Additionally, the broad peak of water OH stretching of hydroxyl groups, centered at 3740 cm<sup>-1</sup>, was further widened in the spectra of modified nano clay it shows the presence of the 3-aminopropyltriethoxysilane in the modified clays [21].

### D. PXRD of Epoxy/HNP's Nanocomposite

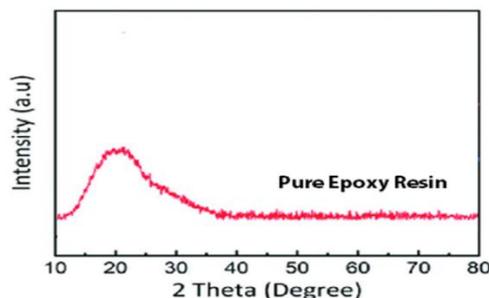


Fig.4 PXRD patterns of pure epoxy resin specimen

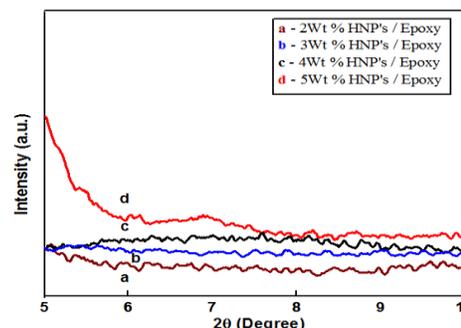


Fig.5 Comparison of XRD patterns of HNP's specimens a) 2 wt % HNP's / epoxy b) 3 wt % HNP's / epoxy c) 4 wt % HNP's / epoxy and d) 5 wt % HNP's / epoxy

XRD patterns of the neat Epoxy resin and HNP's/Epoxy nanocomposites are shown in Fig.4 and Fig.5. Nanocomposites are of two kinds from the structural point of view one is intercalated and another exfoliated. In intercalated nanoclay, the polymer molecules are embedded inside the silicate layers of the clay framing multi layers; in exfoliated nanoclay, the silicate layers breakdown into single platelets and situate themselves in an irregular way [23].

So as to check whether the polymer resin entered between the clay layers, the diffractograms of the pristine Epoxy and HNP's/Epoxy were reported. Pristine HNP's exhibit d-spacing of 12.98 Å at 2θ = 7°. Samples of HNP's/Epoxy with 2 wt% - 5 wt% were analysed in that 4 wt% exhibit good exfoliation and superior dispersion compared to other samples as shown in Fig. 5.

### E. Microstructural Analysis of Nano Composite

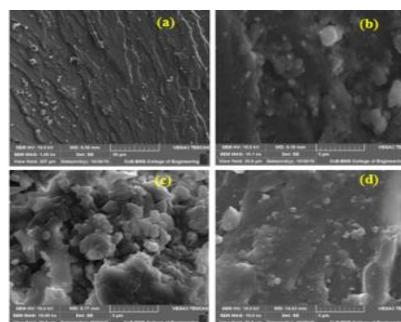


Fig.6 SEM micrograph of fractured surfaces of (a) Neat epoxy (b) 2 wt% HNP's/Epoxy (c) 4 wt% HNP's/Epoxy (d) 5 wt% HNP's/Epoxy

SEM micrographs of tensile fractured epoxy (Fig.6a) exhibits a relatively smooth fracture surface with single crack propagation and epoxy/HNP's composites exhibit strong interfacial bonding (Fig.6b and Fig.6c) and moistening of the HNP's with polymermatrix.

The 4 wt% HNP's/epoxy based samples (Fig.6c) revealed good interfacial bonding and absence of agglomerations prominent the superior mechanical properties[24]. Above 4 wt% HNP's/epoxy samplesexhibit agglomerations reduction in the mechanical properties (Fig. 6d).

F. FT-IR of Nano Composite

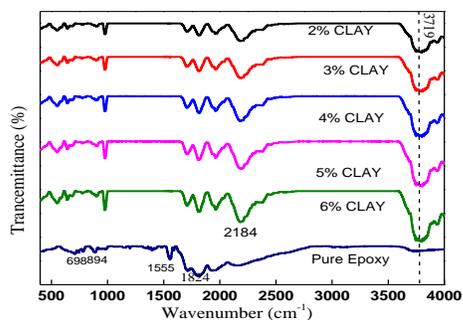


Fig. 7 FT-IR of neat epoxy and HNP's/epoxy nano composites

The interaction of HNP's with epoxy plays vital role in final properties of polymer nanocomposites. In Fig. 7 FT-IR spectrum of neat epoxy and HNP's/epoxy nanocomposites were showed. A characteristic peakat 3719 cm<sup>-1</sup> is assigned to the hydroxyl groups, which suggested the interactionbetween modified HNP's and epoxy.It can be notedas the amount of HNP's was increased, the % transmittance of the hydroxyl groups increased [25].

G. Mechanical Properties of HNP's/Epoxy Nano Composites

A few researchers studied that the mechanical properties are rely on the exfoliation of HNP's in the polymer matrix [26-31]. Exfoliation of HNP's in polymer relies on the procedure adopted for blending of HNP's/Epoxy.Epoxy based nanocomposites formed by reinforcing HNP's nanoclay in epoxy are tested for mechanical properties. Tensile Strength, tensile modulus, Flexural strength, flexural modulus and fracture toughness increased in epoxy nano composite with increase in HNP's up to 4 wt% as shown in Fig.8 to fig. 12.

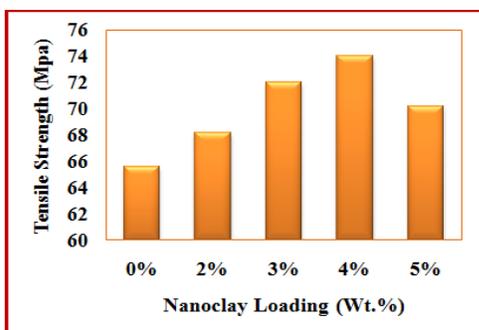


Fig. 8 Tensile strength of neat epoxy and HNP's/epoxy nano composites

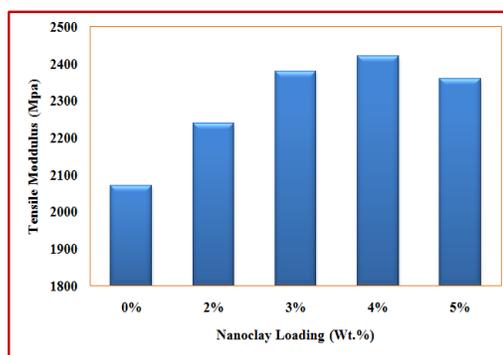


Fig. 9 Tensile Modulus of neat epoxy and HNP's/epoxy nano Composites

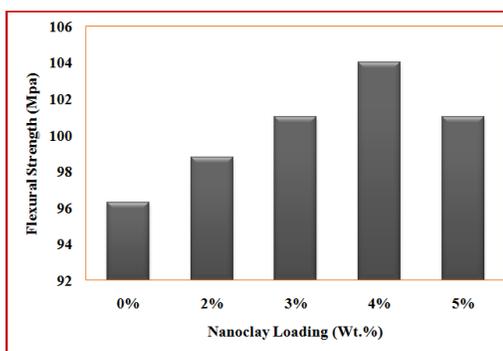


Fig. 10 Flexural strength of neat epoxy and HNP's/epoxy nano composites

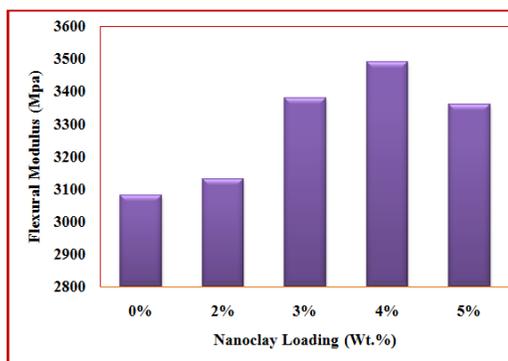


Fig. 11 Flexural modulus of neat epoxy and HNP's/epoxy nano composites.

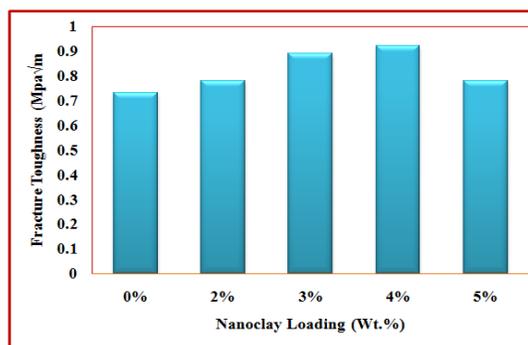


Fig. 12 Fracture toughness of neat epoxy and HNP's/epoxy nano composites

4 wt % HNP's/epoxy based specimens showed increase in tensile strength, tensile modulus, flexural strength, flexural modulus and fracture toughness by 13 %, 17 %, 9%, 14% and 27 % respectively compared to neat epoxy specimens. These enhancements are credited to the blending of among epoxy and HNP's so the mobility of chain network is limited under clay loading. The solid interfacial connection that exists in the hybrid composites may likewise limit the mobility of the polymer matrix in the interface between the HNP's and matrix permitting better put stress within the composite beyond 4 wt % HNP's blending in epoxy become difficult because of viscosity of the matrix bringing about the arrangement of agglomerates, which acted as the sites for stress concentration and crack initiation. High percentage of HNP's added to polymers can break the chain network of the nanocomposites during the mechanical stirring, shear mixing and ultrasonic techniques due to this low level of HNP's loading utilizing these current strategies has delivered superior results.

#### IV. CONCLUSION

The experimental studies of the influence of HNP's on the mechanical properties of Epoxy based nanocomposites lead to the following conclusions: The HNP's concentration was varied from 1wt% to 5 wt% and tensile strength, tensile modulus, flexural strength, flexural modulus and fracture toughness was determined as a function of HNP's concentration. The investigation revealed the following conclusion. First, the HNP's modification using 3-aminopropyltriethoxysilane produces better dispersion of HNP's in the epoxy resin and increases intercalation effect. From SEM, it can be seen that clay particles have a tendency to form agglomerates before modification and forms thick tubular structure after modification. Second, mechanical properties are increased up to 4 wt% of HNP's. Specifically, tensile strength, tensile modulus, flexural strength, flexural modulus and fracture toughness increased by 13 %, 17 %, 9%, 14% and 27 % respectively compared to neat epoxy specimens.

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