

Influence of Organommodified Nanoclay on the Mechanical behaviour of Vinylester/Glass Nanocomposites

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Abstract: This paper reports the influence of organommodified nanoclay of three different basal spacings on the mechanical behavior of vinylester and vinylester/glass. Cloisite-15A, Cloisite-93A and Cloisite-Na were dispersed in vinylester using ultrasonication and twin screw extrusion. The improvements in microhardness and glass transition temperature were highest for Cloisite-15A. The improvements in tensile, flexural properties, interlaminar shear strength and strain to failure were highest in 4wt% Cloisite-15A/vinylester/glass specimens. The same specimens showed fatigue life of 90000 cycles at 40% peak load at 9Hz frequency showing an improvement in fatigue life over vinylester/glass. Addition of Cloisite-15A to vinylester/glass increased the stress intensity factor.

Keywords: Organommodified Nanoclay, Twin Screw Extrusion, Fatigue, Stress Intensity Factor.

1.0 INTRODUCTION

The properties of nanoclay dispersed polymer composites depend on the basal spacing of the nanoclay. Cloisite 10A, 15A, 25A, 93A, and 30B are some of the commercially available organommodified nanoclay explored as nanofillers in polymer composites. Higher basal spacing enhances the degree of exfoliation and the modifier associated with the nanoclay provides better bonding and increases the interfacial strength of the composites resulting in superior mechanical and thermal properties.

Several reports suggest the improvement of mechanical and thermal properties of polymer composites due the dispersion of nanoclay in polymers. Dispersion of Cloisite Na and Cloisite 30B in epoxy increased its glass transition temperature [1-4] due to the reduction of the mobility of polymer chains and the intercalation between silicate and polymer molecules. MMT-Na dispersed in PMMA increased T_g by 30 °C [5] and the same filler dispersed in epoxy and vinylester increased T_g by 20 °C [6]. Cloisite 30B dispersed in epoxy affects its T_g due

to the hindrance of cross linking [7] or the displacement of stoichiometry in the polymer network [8]. OMMT dispersed in epoxy increased T_g with the loading of nanoclay[8]. Thus the influence of the nanofillers on the T_g of the composites depends on the type of nanoclay, its basal spacing, filler loading, and its compatibility with the polymeric resin.

Addition of nanoclay to polymers increases the mechanical properties such as microhardness, tensile modulus, flexural modulus and interfacial shear strength. These improvements have been achieved for 4–5 wt % nanoclay addition to different polymeric resins. Microhardness increased by 11- 33 % by dispersing MMT in epoxy and SiO₂ based nanocomposites [9–11]. Young's modulus improved in the range 15 – 60 % with the dispersion of Cloisite 30B in epoxy [10 -13]. Tensile strength improved by 50 % due to the addition of MMT to epoxy [16] and decreased by 20 % [3]. Flexural strength decreased [15] by 10 % due to the addition of MMT to vinylester but it increased by 13-29 % when added to vinylester / glass and epoxy / glass [12, 14, 16]. Flexural modulus increased in the range of 4 – 40 % by the addition of MMT to glass / vinylester and glass / epoxy[12, 14 - 16]. Interlaminar shear strength increased by 18 % in MMT / vinylester / glass[12].

The influence of Cloisite 15A on the physical, mechanical and thermal properties of polymers has been reported. Its addition to epoxy increased the mechanical properties [11]. Cloisite 15A / SPEEK membrane [17] prepared via solution intercalation method confirmed intercalation and improved mechanical and thermal stability. Cloisite 15A dispersed in epoxy and vinylester improved the thermal stability and T_g [18]. Cloisite 15A showed better degree of exfoliation in the presence of peroxide and improved the mechanical properties [19]. Significant improvements in tensile, flexural and impact properties of PP [20] prepared by melt mixing in a twin screw extruder followed by injection moulding was achieved with the incorporation of organically modified nanoclay such as Cloisite Na and Cloisite 15A. Higher concentration of clay causes agglomeration and reduces the properties of nanocomposites, which was confirmed by increasing the loading of Cloisite 15 A from 3 wt % to 6wt % in the polymeric matrix [21].

Cloisite 93A is a commercially available organoclay having basal spacings of 23.6 Å which is greater than that of Cloisite Na (11.7 Å) but lower than that of Cloisite 15A (31.5 Å). M2HT is the modifier used for Cloisite 93A which is different from 2M2HT used for Cloisite 15A. Very few studies have been reported on the influence of Cloisite 93A on the properties of the polymers. Dispersion studies of nanofillers such as 5 wt % Cloisite 93A, Cloisite 25A, 30B, and Nanofil 5 and 3000 by compounding with Polyethylene (PE) have been reported [22]. Another dispersion technique using supercritical carbon dioxide (scCO₂) for dispersing Cloisite 93A and Cloisite Na in PDMS was studied and Cloisite 93A showed better dispersion than that achieved using Cloisite Na [23].

Nanofillers such as nanoclay and carbon nanotubes (CNT) which possess higher aspect ratios when compared with particulate fillers can improve the fatigue and fracture behavior of polymer composites. Arun K. Subramanian et.al [24] worked on toughening of vinylester by dispersing Nanomer 130E and CSR (Core shell rubber) and reported that addition of 5 wt% Nanomer 130E reduced the Stress Intensity Factor (SIF) by 30%. In case of 5 wt% CSR, SIF decreased by 10% compared to the neat resin. T.P. Mohan et.al [24] reported 1.75 times improvement of fracture toughness of polypropylene by the addition of 5 wt% Cloisite 15A. Fatigue life improvement by 60% for CNT / epoxy / glass nanocomposites at high fatigue cycles is reported by Cristopher et. al[26-27]. Yuanxin Zhou et.al [28] reported the fatigue life improvement of carbon nanofibre (CNF) filled epoxy resin for 2 wt% loading. Ramkumar et.al studied the effect of organically modified hectorite clay addition on the flexural fatigue response of Polyamide 6 (PA6) and significant improvement was achieved in fatigue life of 150,000 cycles[29].

Kinloch et. al. examined the influence of dispersing different modified and organomodified naoclays such as Cloisite Na, Cloisite 25A, Cloisite 30B and Nanomer 130E up to 30 wt% in epoxy and reported increase in Young's modulus in case of exfoliated structures. Fracture toughness K_{IC}, and fracture energy, G_c, initially increased as the weight fraction of the nanoclays increased and then decreased at relatively high concentrations[30]. Antonio F. A Vila et. al studied fracture stress and the laminate porosity of Nanomer 130E / epoxy. The authors reported decrease in void formation of around 77% with the dispersion of nanoclay up to 10 wt %. It was attributed to a highly exothermic chemical reaction amongst nanoclay, hardener, acetone and the resin, with consequent gel time reduction of 30% which changes the polymerization process due to the presence of nanoclay[31].

The open literature [1-31] suggested that comparative study of the influence of nanoclay of different basal spacings and organomodifiers on the thermal and mechanical properties of polymer and polymer composites is scarcely reported. The improvements depend on the compatibility of the nanoclay with the polymeric resin. The main objective of this research was to examine the influence of dispersing Cloisite Na, Cloisite 15A and Cloisite 93A in vinylester using ultrasonication and twin screw extrusion to ensure uniform dispersion based on our previous published research[32]. The nanocomposites were characterized for glass transition temperature, microhardness, tensile, flexural, ILSS, fatigue and fracture behaviour.

2.0 EXPERIMENTAL

2.1 MATERIALS

Nanoclay / vinylester specimens of one mm thickness and nanoclay / vinylester / glass specimens of 3 mm thickness were characterized. BISPHENOL based vinylester as matrix resin, Ecmalon 9911 and woven E-glass fibre (360 GSM) supplied by M/s Suntech India Pvt. Ltd, 2% Methyl Ethyl Ketone Peroxide as catalyst and Cobalt as accelerator and Di Methyl Acetamide promotor were used for the specimens. Cloisite 15A and Cloisite 93 A, which are organomodified nanoclay and Cloisite Na which is an unmodified nanoclay, supplied by M/S Sigma-Aldrich, India pvt ltd were used. The specifications of the nanoclay are presented in Table 1.

Table 1 Specifications of nanoclays

Nanoclay	d-spacing (Å)	Particle size (µm)	Modifier
Cloisite Na	11.7	2-13	Unmodified
Cloisite 15A	31.5	2-13	2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium salt
Cloisite 93A	23.6	2-13	M2HT: methyl, dehydrogenated tallow ammonium salt

2.2 PROCESSING AND CHARACTERISATION OF NANOCLAY / VINYLESTER

2.2.1 PROCESSING OF NANOCLAY / VINYLESTER

Nanoclay up to 5 wt % was dispersed in vinylester using a high speed tip ultrasonicator of frequency 37 kHz and co-rotating twin screw extruder. The twin screw parameters for the dispersion process were selected based on the previous published work on the same resin and nanofiller [32]. The dispersion was carried out at 100 rpm screw speed and room temperature using the extruder.

2.2.2 CHARACTERISATION OF NANOCLAY / VINYLESTER FOR GLASS TRANSITION TEMPERATURE AND MICROHARDNESS

Differential Scanning Calorimeter, Mettler DSC-823 was used to obtain the glass transition temperature of nanoclay / vinylester at heating rate of 10 °C / min. Microhardness of nanoclay / vinylester was determined using microhardness tester, MVH-1 fitted with automatic loading capacity, video port for photography and instrumented with 100X to 400X magnification capability.

2.3 PROCESSING AND CHARACTERISATION OF NANOCLAY / VINYLESTER / GLASS

2.3.1 FABRICATION OF NANOCLAY / VINYLESTER / GLASS

The nanoclay / vinylester gelcoat processed using ultrasonication and twin extrusion was used along with 2D mat glass fibres for fabricating nanoclay / vinylester / glass specimens of 3 mm thickness by wet hand lay-up technique, maintaining gelcoat to fibre ratio of 35: 65 by wt %. The laminates were cured for 24 hours under

room temperature conditions and not post-cured, as most of the marine composites are not post cured as per the manufacturer's recommendations.

2.3.2 CHARACTERISATION OF NANOCCLAY / VINYLESTER / GLASS FOR TENSILE, FLEXURAL AND ILSS

Nanoclay / vinylester / glass specimens of dimensions 216 x 19 x 3 mm³ were characterized for tensile behaviour as per ASTM D638 at a strain rate of 2 mm/min and a gauge length of 80 mm, using a 10-ton capacity high precision UTM, supplied by M/s Kalpak Instruments and Controls, Pune, India.

The specimens of dimensions 80 x 8 x 3 mm³ were characterized for flexural behaviour in three point bending mode, as per ASTM D790, using a span length of 50 mm and crosshead speed of 2 mm/min. Flexural strength (N/mm²) was obtained by:

$$FS = (3PL) / (2BD^2) \quad \text{-----} \quad (1)$$

FS – Flexural Strength [MPa],

P – Peak load [N],

L – Span length [mm],

B – Breadth of the specimen [mm] and

D – Depth of the specimen [mm]

Flexural Modulus was obtained by:

$$\text{Flexural Modulus} = PL^3 / 4BD^3\delta, \text{-----}(2)$$

Where,

P – Peak Load [N]

L – Length between supports [mm]

B – Breadth of the specimen [mm]

D – Depth of the specimen [mm]

δ – Deflection at load 'P'

The specimens of dimensions 45 x 6 x 3 mm³ were characterized for Interlaminar Shear Strength (ILSS) by conducting flexural test in three point bend mode at a strain rate of 2 mm/min as per ASTM 2344. ILSS was obtained by:

$$\text{ILSS} = 0.75P / BT \text{-----} \text{-----}(3)$$

Where,

P – Peak Load [N]

B – Breadth of the specimen [mm]

T – Thickness of the specimen [mm]

2.3.3 CHARACTERIZATION OF CLOISITE 15A / VINYLESTER / GLASS FOR FATIGUE AND FRACTURE

The critical stress intensity factor (K_{IC}) of the SENB specimens was determined as per ASTM -D790 for vinylester / glass and 4 wt% Cloisite15A / vinylester / glass. The specimens of dimensions 127 x 13 x 6 mm³ were tested using a span length of 65 mm in three point bend setup on a 10 ton capacity UTM used for other mechanical tests in this research. The rate of loading was maintained at 1mm / min with load resolution of 0.5 N. Figure 1 shows single edge notch bend (SENB) specimen used for determining the peak load. K_{IC} was determined using equation (4).

$$K_{IC} = \sigma \sqrt{\pi a \beta} \left(\frac{a}{W} \right) \text{-----(4)}$$

Where,

$$\sigma = 6 M / BW^2 \text{ (N/mm}^2\text{)} \text{-----(5)}$$

B = thickness, mm (13 mm)

W = depth, mm (6 mm)

M = bending moment = PS /4 (N-mm)

S = span, mm (65 mm)

P = peak load, N

a = crack length, mm (3 +/- 0.2 mm)

$$\beta \left(\frac{a}{W} \right) = 1.09 - 1.73 \left(\frac{a}{W} \right) + 8.2 \left(\frac{a}{W} \right)^2 - 14.2 \left(\frac{a}{W} \right)^3 + 14.6 \left(\frac{a}{W} \right)^4 \text{-----(6)}$$

The fatigue behaviour of the specimens in flexural mode was determined as per ASTM-D790 using specimens of dimensions 127 x 13 x 6 mm³ and span length 90 mm. A 10 ton capacity high precision computer controlled fatigue testing machine supplied by M/s Kalpak instruments and controls, Pune, INDIA. The tests were conducted for vinylester / glass and 4 wt% Cloisite 15A / vinylester / glass at frequencies 9 Hz and 6 Hz, at 40%, 60%, and 80% of the flexural peak loads and 2 to 3 mm amplitudes, in accordance with ASTM C393-62. Stress verses number of cycles were plotted.

2.4 SEM

Scanning Electron Microscope (Hitachi SU-1500 SEM instrument) was employed to study the interfacial strength and failure modes of the tensile fractured nanoclay / vinylester / glass specimens.

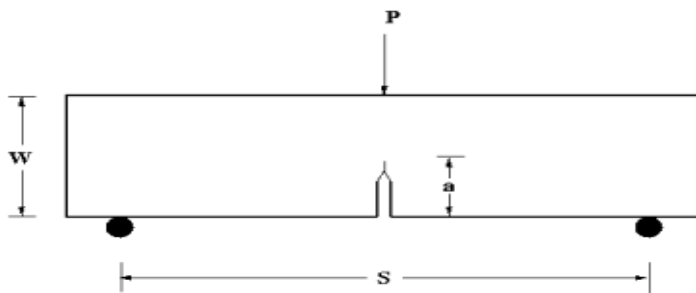


Figure 1 SENB specimen in three point bending set up

3.0 RESULTS AND DISCUSSION

3.1 GLASS TRANSITION TEMPERATURE OF NANOCCLAY / VINYLESTER

Figure 2 shows the influence of nanoclay addition to vinylester on the glass transition temperature (T_g). While marginal increase in T_g was observed with the addition of 2 wt % nanoclay to vinylester, significant improvements were observed with the addition of up to 5 wt % nanoclay, irrespective of the type of nanoclay used. The increase was greatest in case of Cloisite 15A based specimens followed by Cloisite 93A and Cloisite Na. The basal spacing and the modifier used in Cloisite 15A influenced the modification of polymer chains in vinylester and hence resulted in increase of glass transition temperature. Similar results have been reported by authors [1-4], while contradictory results are presented by authors [7-8].

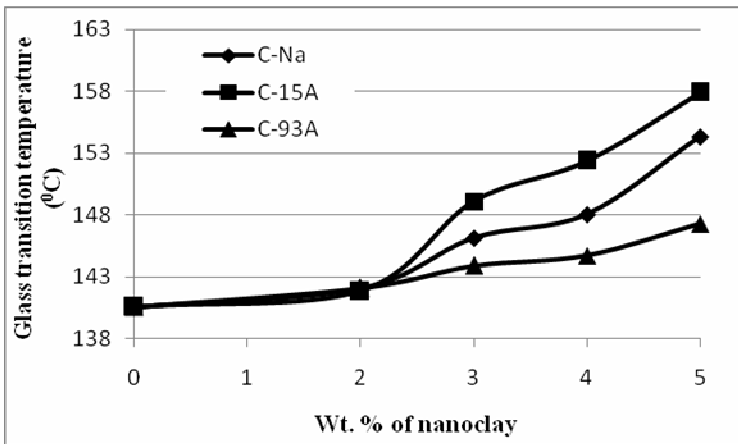


Figure 2 Glass transition temperature of nanoclay / vinylester

3.2 MICROHARDNESS

Microhardness of nanoclay / vinylester is shown in Figure 3. Addition of up to 4 wt % nanoclay to vinylester increased its microhardness. But, the same decreased for 5 wt % addition. Similar results are presented by authors [9-10]. Addition of 4 wt % Cloisite 15A to vinylester increased its microhardness by 5.5 units. The increase in microhardness due to the addition of nanoclay can be attributed to the formation of network like structure of intercalated/exfoliated MMT platelets with vinylester molecules effectively restricting the indentation [33]. The improvements in hardness due to the addition of 0 to 5 wt % Cloisite Na and Cloisite 93A to vinylester were lower than that of Cloisite 15A. This may be because of the lower basal spacings of the nanoclays and the modifier of Cloisite 93A.

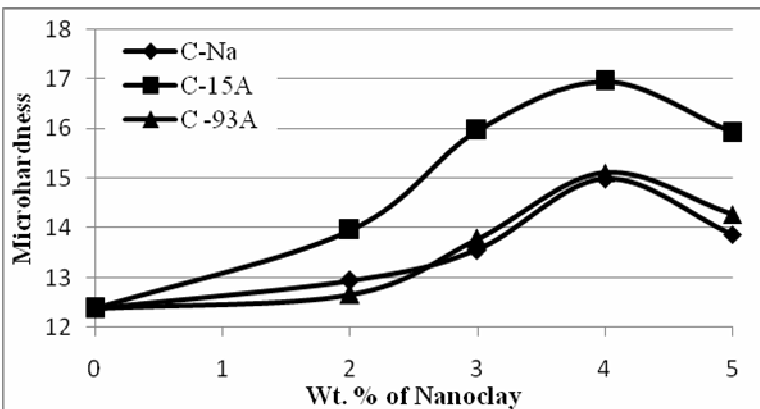


Figure 3 Microhardness of nanoclay / vinylester

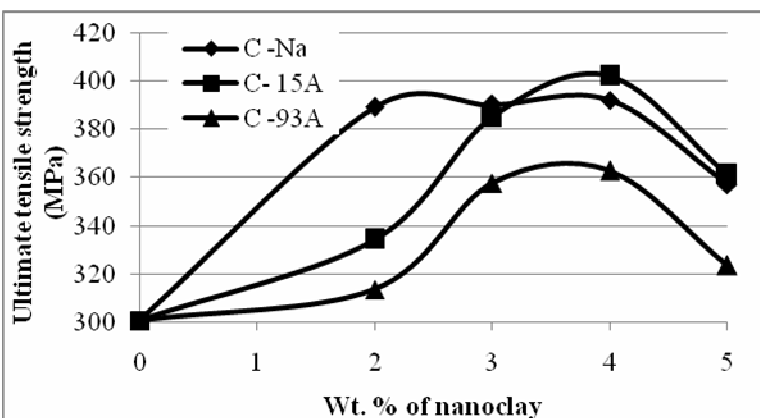


Figure 4 UTS of nanoclay / vinylester / glass

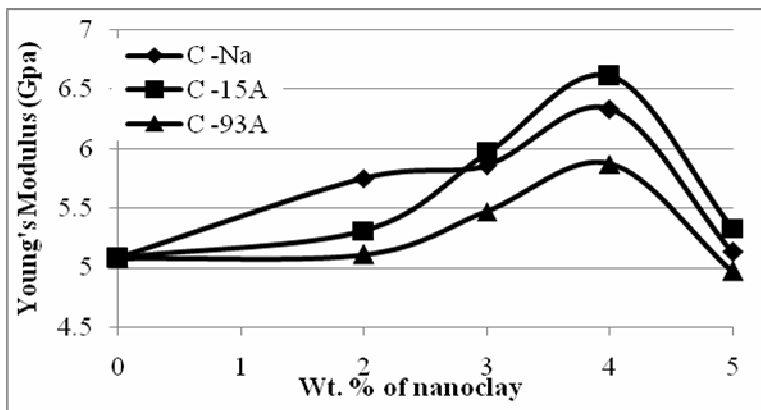


Figure 5 Young's Modulus of nanoclay / vinylester / glass

3.3 TENSILE BEHAVIOUR OF NANOCCLAY / VINYLESTER / GLASS

Figure 4 shows that UTS of nanoclay/ vinylester/ glass increased with the addition of nanoclay. The improvements were highest in case of 4 wt % Cloisite 15 A addition to vinylester followed by Cloisite Na and Cloisite 93A. While the addition of 2 wt % Cloisite Na increased the UTS of vinylester / glass significantly, its addition from 2 to 4 wt % did not show any improvement and 5 wt % addition decreased the UTS of vinylester / glass. Addition of Cloisite 15A and 93A to vinylester / glass gradually increased the UTS up to 4 % and decreased for 5 wt %. These results are in agreement with that of [14] and contradictory to that of [8]. The increase in UTS due to the addition of 4 wt % Cloisite -15A to vinylester / glass was by 102 MPa. The improvements in case of Cloisite Na and Cloisite 93 A were 100 MPa and 63 MPa respectively. The results indicate that both basal spacing and the modifier of the nanoclay influence the mechanical behaviour of the nanocomposites.

Figure 5 shows the influence of the addition of Cloisite Na, Cloisite -15A and Cloisite 93A to vinylester / glass on their Young's modulus. Gradual increase in Young's modulus was observed with the addition of nanoclay up to 4 wt % and the same decreased for 5 wt %. The improvement in Young's modulus with the addition of Cloisite 30B to vinylester is reported [10-13]. The improvements to the extent of 0.8 GPa, 1.3 GPa and 1.6 GPa were observed with the addition of 4 wt % each of Cloisite 93A, Cloisite Na and Cloisite 15A respectively to vinylester / glass.

3.4 FLEXURAL BEHAVIOUR OF NANOCCLAY / VINYLESTER / GLASS

Figure 6 show the influence of nanoclay addition on the flexural strength of vinylester / glass. The increase in flexural strength by 55 MPa was observed with the addition of 4 wt % Cloisite Na. But the same decreased for 5 wt % addition. While significant increase in flexural strength was observed with the addition of 2 wt % Cloisite 15A, the improvement was gradual from for 2 to 4 wt %, and it decreased for 5 wt % addition. Highest improvement of 80 MPa was observed with the addition of 4 wt % Cloisite 15A. Addition of Cloisite 93A resulted in marginal increase in flexural strength i.e. 30 MPa with 4 wt % addition. Also, the flexural strength with 5 wt % Cloisite 93 / vinylester / glass was lower than that of vinylester / glass. Increase [15-16] and decrease [14] of flexural strength with the addition of nanoclay to polymer have been reported.

Figure 7 shows influence of 0-5 wt% nanoclay addition to vinylester / glass on their flexural modulus. It increased gradually up to 4 wt % addition of nanoclay and decreased for 5 wt % addition. Highest improvements of 2.3 GPa, 2.5 GPa and 5 GPa in flexural modulus were observed with the addition of Cloisite 93A, Cloisite Na and Cloisite 15A respectively. This is in agreement with elsewhere reports [12, 14-16].

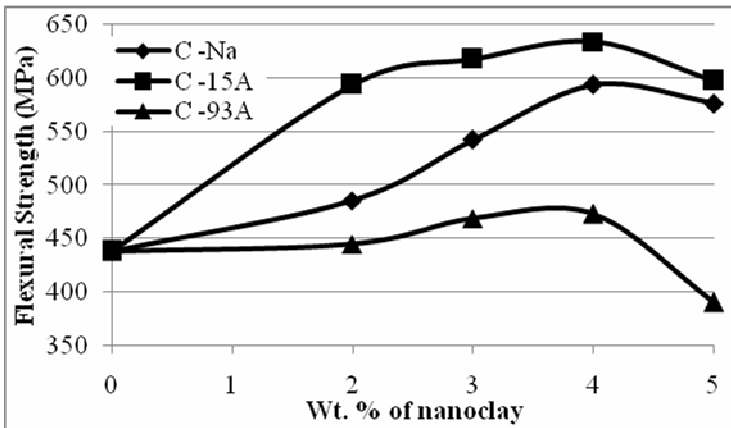


Figure 6 Flexural strength of nanoclay / vinylester / glass

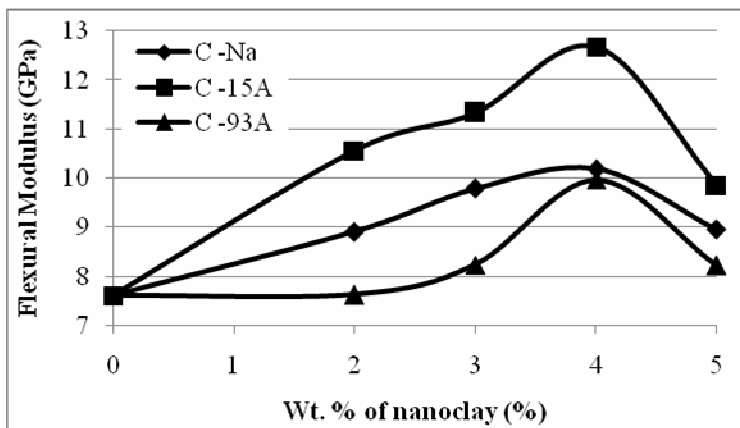


Figure 7 Flexural Modulus of nanoclay / vinylester / glass

3.5 INTERLAMINAR SHEAR STRENGTH (ILSS)

Figure 8 shows interlaminar shear strength of nanoclay / vinylester / glass composites dispersed with 0 – 5 wt % nanoclay. Addition of nanoclay increased the interlaminar shear strength gradually up to 4 wt %, but the same decreased for 5 wt %. Highest improvements of 2.7 GPa, 4.5 GPa and 7.6 GPa in interlaminar strength with the addition of Cloisite 93A, C-Na and Cloisite 15A respectively was observed. Similar results have been reported by A Haque et.al. [12].

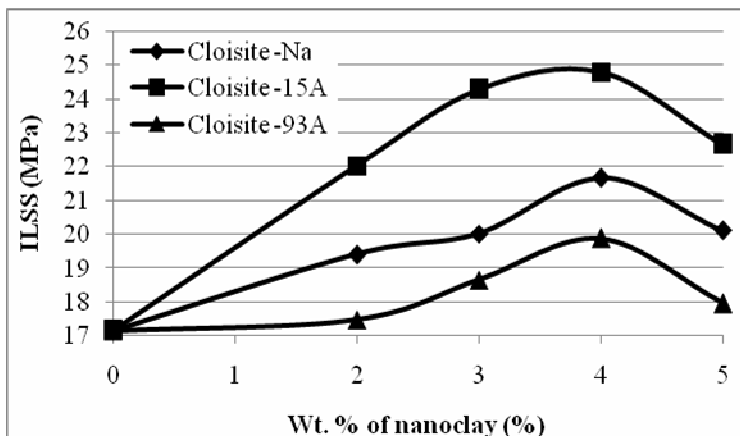


Figure 8 ILSS of nanoclay / vinylester / glass

3.6 FRACTURE TOUGHNESS

Fracture toughness results of 0 – 5 wt % Cloisite 15A / vinylester / glass are presented in Table 2. Addition of nanoclay to vinylester / glass increased the fracture toughness and the stress intensity factor. K_{IC} increased by 50 % in 5 wt% Cloisite 15A / vinylester / glass compared to that of vinylester / glass. The toughening effect of the OMMT may be attributed to the plastic deformation of the vinylester around the particles similar to the toughening of OMMT / epoxy as discussed By Kinloch et.al. [30]. The mechanism underlying the increase in K_{IC} is explained using Faber and Evans model. When a growing crack meets nanoclay, the crack gets deflected out of plane. When the crack encounters further nanoclay particles, it gets twisted and tilted. The area of the fracture surface increases, leading to increase in fracture toughness. The deflected crack experiences mixed mode loading and hence it requires higher energy than in mode I, leading to increase in K_{IC} .

Table 2 Stress intensity factor and fracture energy of C-15A / vinylester / glass

Material	$K_{IC}(N/mm^2m^{1/2})$	Gc (MPa-m)
Glass/Vinylester	24.905	0.071521
Glass/Vinylester/2% C-15A	27.185	0.06141
Glass/Vinylester/4% C-15A	29.946	0.062059
Glass/Vinylester/5% C-15A	36.186	0.116534

3.7 FATIGUE BEHAVIOUR

Figure 9 - 11 represent the flexural fatigue behaviour of nanoclay / vinylester / glass with 0 % and 4% C-15 composites at 40%, 60% and 80% peak load and 9Hz frequency. The improvement in fatigue life due to C-15 addition was observed at lower peak loads. 4 wt % C-15 A dispersed specimens survived 90000 cycles at 40% peak load 9Hz frequency. The improvements may be attributed to enhanced modulus, coupled with improved surface hardness. The nanoclay addition promoted toughening and influenced the crack propagation characteristics of vinylester / glass[29].

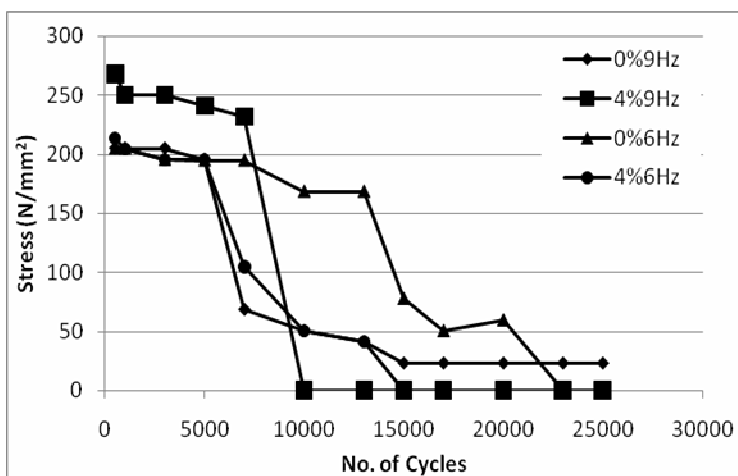


Figure 9 Stress v/s number of cycles in fatigue at 80% peak load

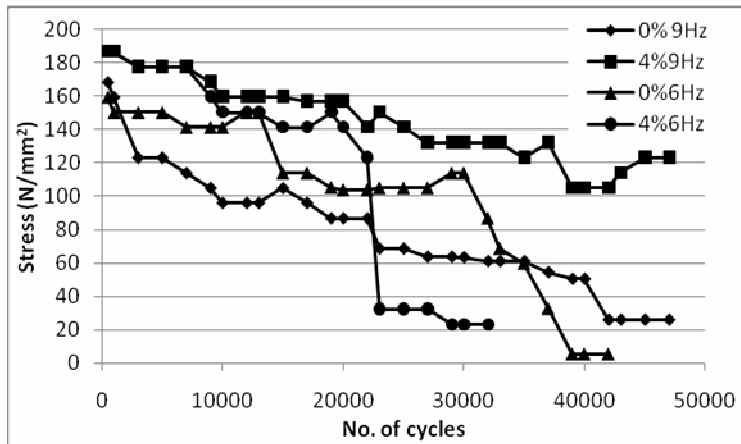


Figure 10 Stress v/s no. of cycles under fatigue at 60% peak load

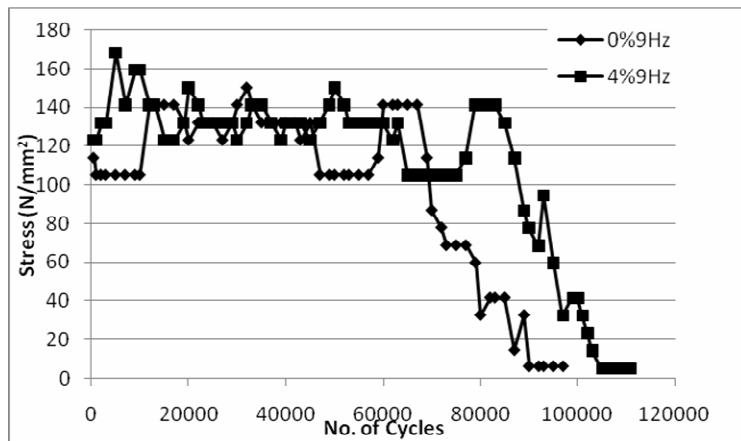


Figure 11 Stress v/s no. of cycles under fatigue at 40% peak load

3.8 SEM

Figure 12 represents the SEM micrographs of tensile fractured specimens of neat resin and 4 wt% nanoclay / vinyl ester / glass. The fractured specimens of neat resin samples in Figure 12 (a) shows clean surface of fibres without any resin adhered to it indicating weak interfacial bonding. 4 wt % Cloisite 15A samples in Figure 12 (c) showed more resin adhered to the fibre surface compared to that of 4 wt% Cloisite Na in Figure 12 (b) and Cloisite 93A in Figure 12 (d). Thus, Cloisite 15A proved superior to the other two in terms of interfacial bonding and mechanical properties.

4.0 CONCLUSIONS

Based on the experimental study of the influence of nanoclay of different basal spacings and modifiers on the mechanical and thermal properties of vinyl ester and vinyl ester / glass, the following conclusions were arrived at:

Both glass transition temperature and microhardness increased with the addition of nanoclay to vinyl ester irrespective of the nanoclay used.

Increase in glass transition temperature was monotonic with nanoclay loading up to 5 wt %. But, microhardness increased upto 4 wt % and decreased in 5 wt % nanoclay specimens.

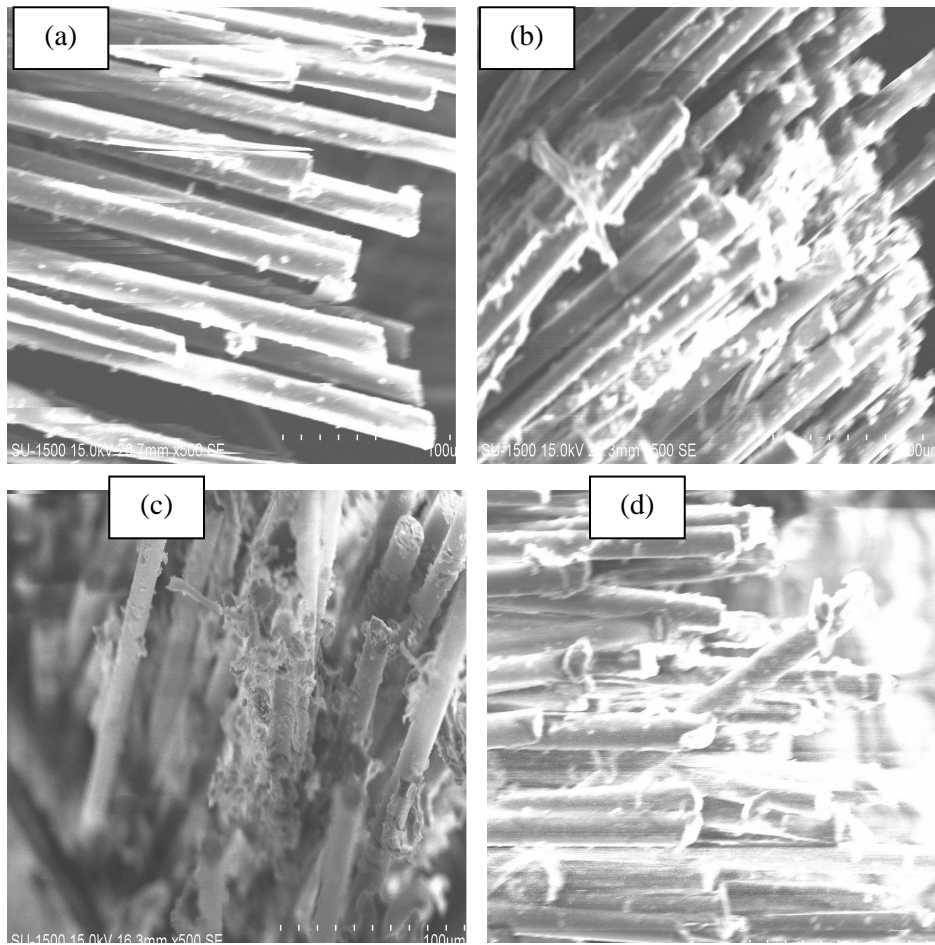


Figure 12 SEM images of tensile fractured surfaces of nanoclay / vinylester / glass composites at 500 X (a) vinylester / glass (b) 4 wt% Cloisite-Na / vinylester / glass (c) 4 wt% Cloisite-15A / vinylester / glass (d) 4 wt% Cloisite-93A / vinylester / glass

Ultimate tensile strength, flexural strength, interlaminar shear strength, Young's modulus and flexural modulus of vinylester / glass increased with the addition of up to 4 wt % nanoclay in all the specimens. The improvement was highest in case of Cloisite 15 A based specimens followed by those of Cloisite Na and Cloisite 93A, which was confirmed by SEM. The performance of different nanoclay used indicated that basal spacing alone does not contribute to the improvement in mechanical properties and the modifier also plays a major role.

Based on the performance of Cloisite 15A / vinylester / glass with respect to the tensile and flexural properties, the same specimens were characterized for fatigue and fracture behaviour. The addition of Cloisite 15A improved the critical stress intensity factor in mode I fracture and at 40 % peak load the fatigue life was greater than 90,000 cycles.

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