TECHNICAL NOTE

THE REINFORCEMENT EFFECT OF NANOCLAY ON THE DAMPING CHARACTERISTICS OF HYBRID LAMINATED COMPOSITES

R. Velmurugan* and K. Karthikeyan*

Abstract

The Hybrid Nanocomposite (HNC) laminates are processed by reinforcing the chopped strand mat glass fiber and organically modified montmorillonite clay (OMT) in the polyester matrix. The different percentage by weight (1, 2, 3, and 5%) of OMT are mixed by high speed shear mixer into the polyester matrix and then the HNC laminates are fabricated by introducing pre-mixed polyester-clay into the CSM by hand lay-up technique. A tensile test result reveals that nanoclay in polyester matrix significantly improves the tensile modulus and strength of HNC. The results also indicate that increasing the amount of nanoclay beyond 2% by weight reduces the mechanical properties but surpassing the basic glass fiber filled system. The reinforcing effect of clay enhances the flexural modulus and strength. Considerable improvement in impact energy absorption is seen from the impact test. Dynamic mechanical analysis shows that incorporation of nanoclay improves the storage modulus and Loss tangent of HNC. Free vibration tests and logarithmic decrement methods are used to predict the dynamic characteristics such as natural frequency, and damping factor for the first four modes of different clay concentrations. Dynamic results show that second phase nanoscale dispersion between the matrix and E-glass fiber significantly enhances the internal damping of hybrid composites.

Keywords: *organically modified montmorillonite clay (OMT), mechanical properties, storage modulus, loss tangent, natural frequency and damping factor.*

Introduction

High performance polymer reinforced composite materials are increasingly used in aerospace applications under static and dynamic conditions. These materials provide unique mechanical properties such as stiffness, strength and impact energy with good damping capacity. These materials also have low specific weight and high resistance to environmental degradations in order to ensure safety and economic efficiency. To withstand high mechanical loading, it is usually reinforced with fibers (glass, carbon and aramid) or particles such as ceramic powders. Particles usually have the dimension in the range of 1-l0μm or even higher. They stiffen the material and may increase the strength under certain load conditions.

Montmorillonite is a crystalline material consisting of number of 1nm thick layers (or sheets) which are made of an octahedral sheet of alumina fused into two tetrahedral sheets of silica. Layers with high aspect ratio and high strength play an important role in forming intercalation/exfoliation polymer nanocomposites [1].

The new approach demonstrates the potential to change the characteristics of thermosetting and thermoplastic polymers fundamentally and aiming to improve their performance to great extent. It has been proved in recent years that reinforcement of lesser amount of nanoscale clay particles (<5%) can significantly improve the mechanical, thermal, and barrier properties of the pure polymer matrix [2-3] and are light in weight. Recent studies reveal that nanoclay composites dispersed in polymer matrix exhibit dramatic improvement in stiffness, strength, dimensional stability, improved flame retardancy, improved solvent and UV resistance. These materials also provide reduction in permeability to gases [4], improve thermal stability [5], and good ablative properties [6]. These property improvements occur at extremely low concentrations of the aluminosilicates (1- 5 Vol. %) compared to conventional filler material in a polymer (20-30%).

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* Department of Aerospace Engineering and Composite Technology Centre, Indian Institute of Technology Madras
Chennai-600 036, India, Email : rvel@aero.iitm.ernet.in

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It has been verified by several researchers experimentally that nanoparticles of metallic or organic type improve the reinforcing ability on the thermoset and thermoplastic polymer matrices. Kornmann, et. al. [7] have reported the dispersion of Montmorillonite in unsaturated polyester resin and found that the fracture toughness is doubled by dispersing 1.5% (by volume) of aluminosilicates. Suh, et. al. [8] have demonstrated that the resulting properties of polyester clay nanocomposites mainly depend upon mixing of the clay with polyester resin promoters as well as the curing conditions. R. K.Bharadwaj, et. al. [9] have shown that the tensile modulus and oxygen permeability rate are decreasing with increase of clay content. Recently A. Baran Inceoglu , et. al. [10] have synthesised the un-saturated polyester based nanocomposites with organically treated Na-Montmorillonite (Closite 30B) and non-treated Na-Montmorillonite (Closite Na^+). The tensile, flexural, and impact strength of composites with modified Montmorillonite are higher than the unmodified Montmorillonite. It is concluded that exfoliation is well formed in the modified Montmorillonite content.

Gadakaree [11] has studied that the mechanical properties of fiber reinforced composites are improved by increasing the toughness of the composites with micro-scaled fillers. Soanoudakis [12] and Wang, et.al. [13] have also studied the effect of filler particles in reinforced resin composites system and observed toughness improvement from the addition of filler particles. S.A. Meguid, et.al. [14] have demonstrated that the tensile strength and shear strength of the carbon fiber reinforced composites are improved by dispersing the carbon nanotude and alumina nanopowders. John F. Timmerman, et.al. [15] have modified the matrices of the carbon fiber/epoxy composites by dispersing the layered inorganic unmodified and modified clays and alumina nanopowders. They have shown that the incorporation of nanoclay reinforcement in the proper concentration improves the mechanical properties and lowers the micro-crack density.

However from the literature it is seen that not much work is done in the area of dynamic characteristics of HNC Laminates. In the present study we focus on the processing, study of mechanical properties, dynamic mechanical analysis and modal analysis of the HNC laminates which are considered to be novel materials for dynamic loadings. Dynamic characteristics of HNC laminates are studied for different modes and several percentages by weight of OMT.

Experimental Details

Materials

The E-glass fiber obtained from Sakthi fibers, India Ltd. in the form of the Chopped Strand Mat (CSM) 300 is used for the present study. The organically modified Montmorillonite clay from southern clay products, Texas, is used as the reinforcing fillers. High styrene content lsophthalic general-purpose polyester resin from Sakthi fibers, India, is used as matrix in order to have better diffusion into the galleries of Montmorillonite. Methyl Ethyl Ketone Peroxide (MEKP) is used as the catalyst and Cobalt nophanate as accelerator. The quantity of accelerator and catalyst are 1.5 % by volume of the resin.

Preparation of Hybrid Nanocomposites

The HNC are fabricated in two steps: in first step OMT clay is mixed with polyester matrix and the second step involves the Hand-lay process of making composites of 4 plies using Chopped Strand Mat (CSM). The 4 layers of CSM E-glass fiber mats are cut in the size of 35cm x 35cm. These are weighed to take the corresponding 1:2 amount of polyester resin. The OMT clay dry particles with several percentages by weight of clay (1, 2, 3 and 5 % by weight) are mixed with the low viscosity polyester resin at room temperature. Appropriate amount of the MMT clay is added to the resin and mechanically stirred by "high shear" mechanical laboratory shear mixer at 2000 rpm for ten hours. During mixing, clay particle are separated from the stacking of the clay layers and allows the polymers to enter between the clay interlayer. The degassing of the mixer is done for 1hr. This resin-clay premixed solution results in well-dispersed, stable suspension of the clay in the polyester resin. Approximately 1.5 % by volume of MEKP catalyst is added to the pre-mixed clay in polyester resin at room temperature to initiate the cross-linking process. This cross-linked resin-clay mixer is used to fabricate the 4 layers of CSM in the hand-lay up technique. Samples are allowed to cure for 24hrs at room temperature.

Characterization and Property Evaluation

Tensile tests are performed on the Instron machine with cross head speed of 1mm/min according to the ASTM D638. The Izod impact test is conducted to study the impact energy according to the ASTM D256. Inter Laminar Shear and Flexural tests are conducted on the cured HNC laminates according to ASTM 2344-84, ASTM 790-98 respectively.

The Dynamic Mechanical Analysis (DMA) results are obtained using NETZSCH DMA242 C thermal analyzer/Dynamic Mechanical Analyzer (DMA) system at frequency rate of 10Hz. This system measures the storage modulus and damping loss factor of the material.

Modal Testing

Modal testing is carried out to study the vibrational characteristics of the composite specimens. This study is used for the comparison of modal properties and calculation of damping factor.

HNC laminate beams are prepared for different concentration of organically modified OMT clay. The size of the specimen is 200mm x 50mm x 3mm. The first four modes of natural frequencies are obtained by considering the specimens as cantilever beam by using Impulse Technique. Impulse Technique and logarithmic decrement are used to compute the damping factor for all the specimens.

Analysis

By considering the HNC laminates as quasi-isotropy the natural frequency of the cantilever beams is obtained as follows. The equation of motion of Euler-Bernoulli for beam is,

$$m(x)\left(\frac{\partial^2 w}{\partial t^2}\right) + c\left(\frac{\partial w}{\partial t}\right) + EI\left(\frac{\partial^4 w}{\partial x^4}\right) = f(x,t) \qquad (1)$$

Where, m is mass per unit length of the beam defined as $m = \rho A$, E is Young's Modulus and A is of cross-section of beam. If no damping and external force are considered then c = 0 and $f(x,t) = 0$. By assuming $EI(x)$ and $m(x)$ as constant, the equation (1) can be rewritten as,

$$\left(\frac{\partial^2 w}{\partial t^2}\right) + \frac{EI}{m}\left(\frac{\partial^4 w}{\partial x^4}\right) = 0 \qquad (2)$$

Assuming steady state vibration in harmonic form, we have

$$w(x,t) = W(x) * \sin(\omega t - \phi) \qquad (3)$$

Introducing equation (3) in (2),

$$\left(\frac{\partial^2 W(x)}{\partial x^4}\right) - \beta^4 W(x) = 0 \qquad (4)$$

Where, $\beta^4 = \dfrac{\omega^2 m}{EI}$ $\quad 0 < x < l$

The Solution of the equation (4) is

$$W(x) = c_1 \sin\beta x + c_2 \cos\beta x + c_3 \sinh\beta l + c_4 \cos\beta l \qquad (5)$$

The constant of equation (5) are obtained by applying boundary conditions and the expressions for natural frequency of the first four modes are obtained as,

$$\omega_1 = 1.875^2 \sqrt{\frac{EI}{\rho A L^4}} \ rad/sec$$

$$\omega_2 = 4.694^2 \sqrt{\frac{EI}{\rho A L^4}} \ rad/sec$$

$$\omega_3 = 7.854^2 \sqrt{\frac{EI}{\rho A L^4}} \ rad/sec$$

$$\omega_4 = 10.995^2 \sqrt{\frac{EI}{\rho A L^4}} \ rad/sec \qquad (6)$$

Free Vibration Test (FVT)

In this method the cantilever beam is excited with impulse hammer. The time versus amplitude information recorded by accelerometer is used to calculate the damping factor by half-power bandwidth method.

The accelerometer [Bruel and Kjaer 4374] is used to measure the displacement through the charge amplifier [Bruel and Kjaer Type 2626] and the response is recorded on the Dynamic Signal Analyzer [Agilent 35670A]. The specimens are excited using the impulse excitation, modally tuned hammer [RION PH 7117]. This hammer is supplied with impact tip of varying hardness. It is observed that for the higher frequencies the harder tip is required to ensure a reproducible tip displacement vibration. Dynamic Signal Analyzer (DSA) is used to store the output from the accelerometer and force hammer. Fast Fourier Transform (FFT) of the time signal is obtained form DSA. 16 averages are used to plot the Frequency Response Function [FRF] of the time signal.

Typical FRF measured from the Hammer Impact test is shown in Fig.1. The series of the peaks in the FRF shows the natural frequencies of the HNC beam. The damping factor for the materials is obtained using the half-power bandwidth method. The expression for damping factor ζ by half-power band width technique is given by [16],

$$\zeta = \frac{\Delta\omega}{2\omega_x} \qquad (7)$$

Where,

$\Delta\omega$ = Band width at the half-power points of resonant peak for n^{th} mode

ω_n = Resonant frequency

The half-power points are found at 3dB below the peak value of the FRF for a particular mode when the logarithmic scale is used or at $\frac{1}{\sqrt{2}}$ of this peak value when linear scale is used.

Logarithmic Decrement Method (LDM)

This technique is used to measure the rate at which the vibration amplitude decays. This is used to compute the structural damping factor. The Modal exciter [National Aerospace Laboratories, Bangalore] and Accelerometer [Bruel and Kjaer 4374] accomplishes the vibration excitation and detection of the tip displacement of the beam respectively. The sine wave signal from the waveform generator [Hewlett Packard 33120A] is supplied to drive the modal exciter to excite the cantilever beam specimen in the flexural mode. Resonance is obtained by monitoring the amplitude of the oscillation on the oscilloscope and is determined when this value reaches maximum. Once the resonance is achieved, excitation signal to the modal exciter is disconnected freely.

The decay amplitude recorded with higher sampling rate in the oscilloscope is shown in Fig.2. It gives the two experimental amplitude data points which are used to calculate the damping factor of the specimen. The determination of damping factor using the Logarithmic decrement method is obtained by the experiments [17],

$$\zeta = \frac{\delta^2}{\sqrt{4\pi^2 + \delta^2}} \quad \text{and} \quad \delta = \frac{1}{n}\ln\left(\frac{x_1}{x_{n+1}}\right) \qquad (8)$$

Where,

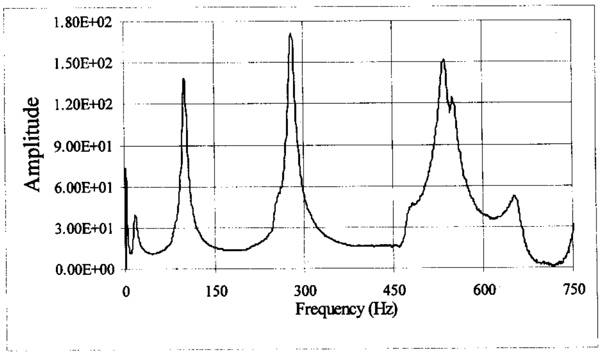

Fig. 1 Typical FRF obtained from free vibration test

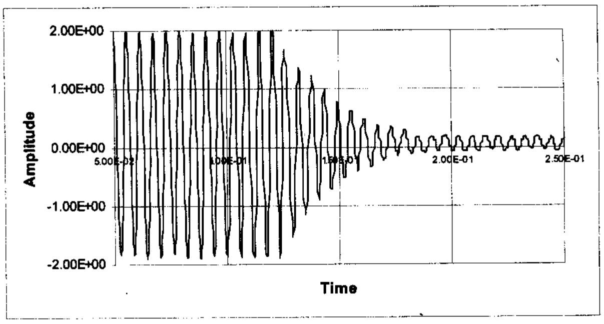

Fig. 2 Typical free decay curve measured from Logarithmic decrement method of HNC laminate beam specimen

ζ = Damping factor,

n = Number of cycles

δ = Logarithmic decrement, and

X_1, X_{n+1} are the two displacement values at time intervals t_1 and t_n

In this method we need two experimental data values from the amplitude decay curve for calculation of damping factor. Therefore by increasing the data points between the two values the random error of the resultant-damping factor is reduced.

Results and Discussions

Mechanical Properties

Tensile Test : The stress-strain behaviors of the HNC laminates for different nanoclay concentrations are shown in Fig.3. Micro filler commonly increases the stiffness and it may have detrimental effect on the strength of the composites. The rigid particulate nanoclay present in the fiber filled system increases both stiffness and strength of the HNC laminates. It is seen that the young' modulus and strength are high for 2% by weight of clay and further increase of clay reduces the strength and modulus value.

Figure 4 shows the young's modulus as a function of the different clay concentrations. It is observed that the young's modulus of the composites increases with increase (up to the 2% by weight) of clay concentrations. Further increase of clay concentrations decrease the modulus of HNC laminates but the value is above the fiber filled system. The improvement of the modulus in the HNC laminates is mainly because of the improvement of matrix modulus by filler dispersion. For practical applications where high stiffness of FRP composites is desired, the only way to improve young's modulus of the FRP is to improve the modulus property of the matrix by incorporation of rigid nano-filler into the matrix, especially nanoclay.

Figure 5 shows the tensile strength of the HNC laminates for different percentage by weight of the clay. It is observed that the tensile strength of the composites increases with increase (upto the 2% by weight) of nanoclay concentrations. However, at higher clay concentrations, gradual decrease is observed with increase of clay content. But the value is above the fiber filled composites. The improvement of the tensile strength by addition of nanoclay into the matrix is observed due to the following reasons.

a) Young's modulus of the second phase dispersed particles is higher than that of the matrix and thus the stress transfer from the matrix to the particles takes place.

b) Strong interfacial bonding between the fiber and matrix also contributes for higher strength

c) Dispersed filler particle acts as mechanical interlocking between the fiber and polyester matrix which creates high friction [18].

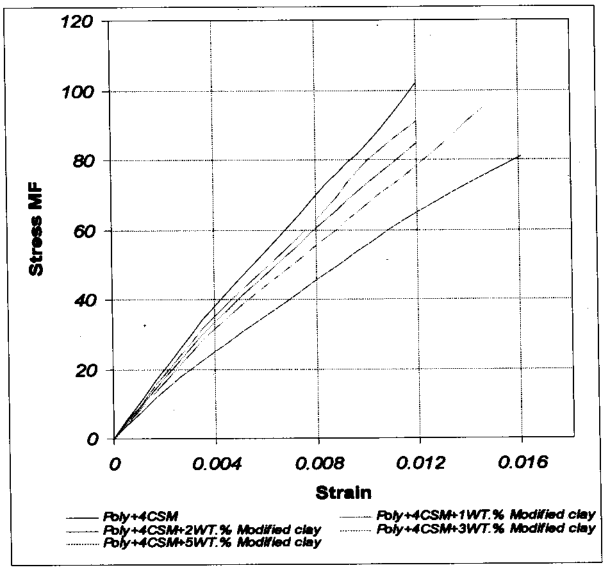

Fig. 3 Stress-strain behaviors of hybrid nanocomposites

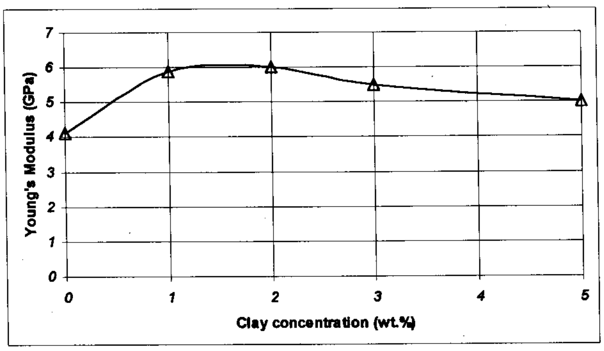

Fig. 4 Influence of OMT clay on tensile modulus of HNC

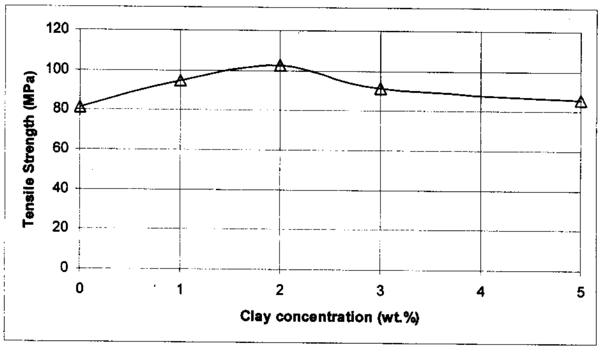

Fig. 5 Influence of OMT clay on tensile strength of HNC

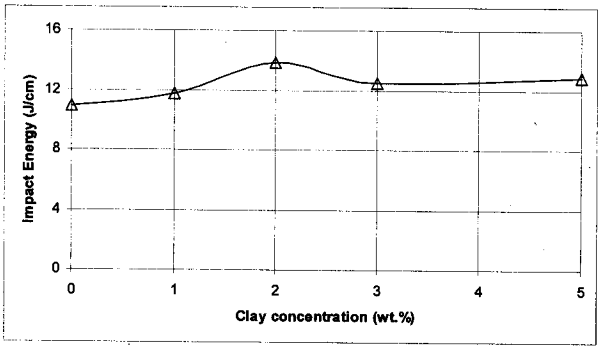

Fig. 6 Influence of OMT clay on impact energy of HNC

Impact Energy : Fig.6 shows the variation of the Impact Energy of HNC laminates for different clay concentrations. The reinforcing ability of OMT, good interface bonding characteristics between the matrix, nanofillers and glass fibers increase the impact energy of the HNC laminates with increase of clay at lower concentrations of

OMT clay. After reaching the maximum value at 2% by weight, the impact energy decreases with increase of clay concentrations. At higher clay concentration the particles tend to agglomerate between the interfaces, leading to crack initiation. This will reduce the Impact energy of the HNC.

Flexural Modulus : Fig.7 shows the variation of the flexural modulus for different clay concentration. The flexural modulus shows improvement with increasing the nanoclay content. Slight decrease is observed in higher value of clay content. The modification of matrix by incorporation of nanoparticle increases the stiffness of the HNC laminates.

Flexural Strength : Fig.8 shows that the variation of transverse flexural strength for different clay concentrations. The presence of nanoparticles in the matrix increases the strength of the HNC laminates. Gradual improvement is noticed up to 2% by weight of OMT clay concentration and then there is slight decrease with increase of weight percentage of nanoclay. But it is well above the flexural strength of the fibrous composites.

Inter Laminar Shear Strength : Fig.9 shows the variation of the ILSS of the HNC laminates for different Wt. % of OMT clay. It is seen that there is increase in ILSS at lower clay concentrations. The enhancement in the ILSS is noticed up to 2% by weight and then decreases with further increase of clay concentration. The increase in the clay concentration may act as flaw or crack initiator instead of reinforcement when the clay content is higher, since the clay particles tend to agglomerate at high clay concentrations in the matrix. These agglomerations present in the matrix-fiber interface produce the high stress concentration around the particle and lead to failure.

Dynamic Mechanical Analyses (DMA)

Figures 10 to 11 show the results of dynamic mechanical analysis performed on the cured HNC laminates over the temperature range from 30 to 180°C. Fig.10 illustrates that the storage modulus depends on the concentration of OMT clay. The fiber filler system yields a storage modulus of 12.8GPa and increases with increasing clay content up to 2% by weight. The maximum storage modulus (17.8GPa) is obtained for 2% by weight of OMT clay. In high clay concentration the storage modulus tends to decrease with increase of clay content but remains above the fiber filled composites. The variation of loss tangent over the temperature range of 30°C to 180°C, for different

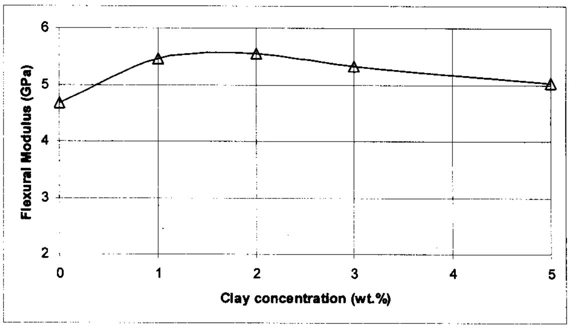

Fig. 7 Influence of OMT clay on flexural modulus of HNC

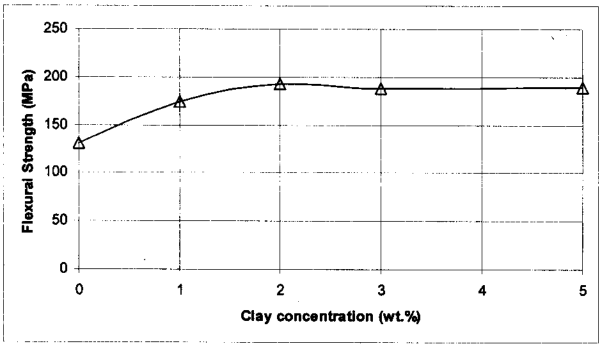

Fig. 8 Influence of OMT clay on flexural strength of HNC

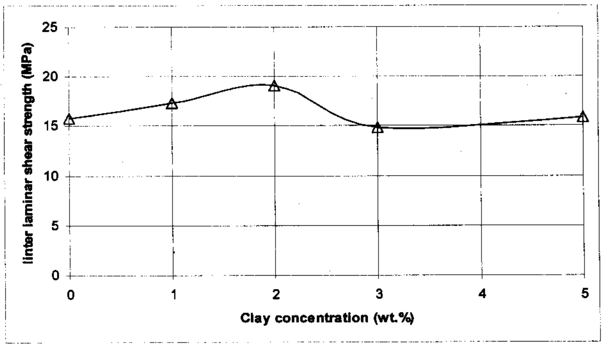

Fig. 9 Influence of OMT clay on inter-laminar shear strength (ILLS) of HNC

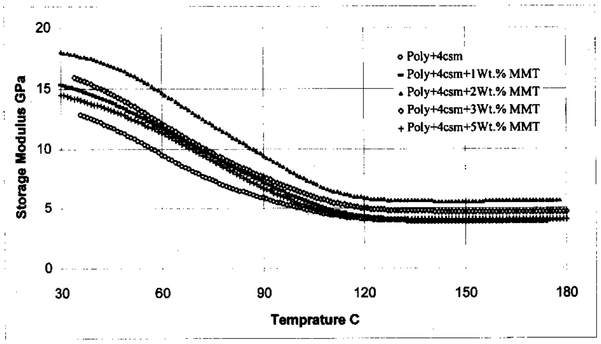

Fig. 10 Influence of MMT clay on storage modulus of HNC

clay concentration is shown in Fig.11. The peaks seen in loss tangent curve is known as the glass transition temperature (T_g) of the HNC laminates. The T_g for fiber filled matrix is about 100°C. The increase in clay concentration does not show much variation in the glass transition temperature of the laminates.

Natural Frequency

The first four modes of natural frequencies are obtained from the free vibration tests and are given in Tables-1 and 2. The natural frequencies gradually increase with increase of OMT clay concentrations up to 2% by weight because the nanoclays increase the stiffness of the material, which is seen from the tensile test results. Same trends are observed for third and fourth modes. The theoretically predicted natural frequencies matches well with experimental results at lower clay content.

Damping Factor

The damping factor of first four modes computed by free vibration and logarithmic decrement method are shown in Figs.12 to 15. The enhancement in damping factor of HNC laminates is observed up to 2% by weight of OMT clay. Polymers are high soft materials and have

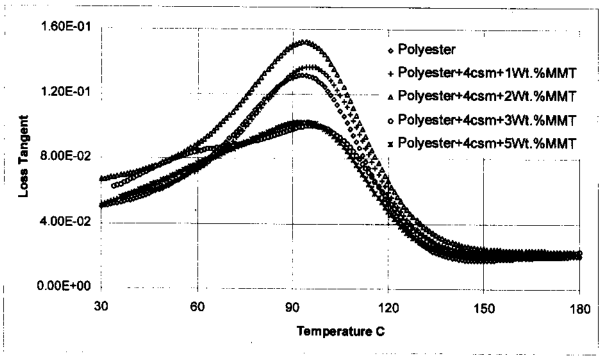

Fig. 11 Influence of OMT clay on loss tangent of HNC

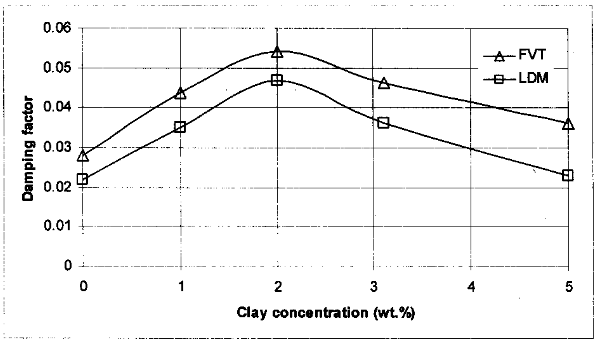

Fig. 12 Influence of OMT clay on first mode damping factor of HNC

Table-1 : Influence of OMT clay on first and second mode natural frequencies of HNC

Specimen Name	Percentage by Weight of OMT Clay	Mode I Natural Frequency (Hz)		Mode II Natural Frequency (Hz)	
		Experi	Theory	Experi	Theory
POH00	0	21	22.18	97.50	139.07
POH01	1	24	24.43	130.25	153.11
POH02	2	27	25.25	140.50	158.27
POH03	3	19	20.23	91.25	126.82
POH05	5	17	17.16	106.00	107.56

Table-2 : Influence of OMT clay on third and fourth mode natural frequencies of HNC

Specimen Name	Percentage by Weight of OMT Clay	Mode III Natural Frequency (Hz)		Mode IV Natural Frequency (Hz)	
		Experi	Theory	Experi	Theory
POH00	0	161.50	389.54	417.50	1763.03
POH01	1	196.00	428.87	456.25	840.08
POH02	2	255.00	443.32	391.25	695.83
POH03	3	320.00	355.23	415.00	695.83
POH05	5	297.00	301.30	592.50	590.18

more energy absorption capability. The reinforcement of fibers brings down the damping factor. But the presence of nanoclay improves the damping characteristics of HNC than the matrix. This is observed in HNC laminates at lower OMT clay content. The dispersion state of the nanoclay layers between the fiber and matrix interfaces exhibits high friction and mechanical interlock between them, resulting high damping improvements in the HNC laminates. The effective stress transfer between the matrix-fiber interfaces by means of the nanofiller dispersion is having the tendency to improve the dynamic loadings characteristics. It is also seen that the nanoclays having platelet arrangements offer high surface area. This imparts higher energy consumption at molecular level resulting the improvement of damping.

The increase in inter laminar shear strength improvements also support the damping factor improvements. Interlaminar stresses arise at the lamina interfaces near the edges in composites laminates. The existences of theses stresses means that part of total energy dissipation in a laminate will be due to interlaminar damping [19]. The stiffness mismatch between the matrix, discontinuous fiber and second phase nanofiller reinforcements will lead to the improvement of internal damping in HNC laminates by increasing the shear deformation near the fiber end [20].

Conclusions

The HNC laminates are processed by reinforcing the short fibre chopped strand mat for different percentage by weight of OMT nanoclays in the polyester matrix by hand lay-up technique. The incorporation of LAN in the polyester matrix filled fibers increases the tensile modulus and strength, Flexural modulus and strength, impact energy and ILSS of HNC at 2% by weight of MMT clay concentration.

Dynamic mechanical analysis shows that the presence of nanoclay improves the storage modulus and Loss tangent of HNC. Free vibration test and logarithmic decrement method are used to predict the dynamic characteristics such as natural frequency, and damping factor for first four modes by changing OMT clay content. Dynamic results show that the second phase nanoscale dispersion at 2% by weight between the matrix and E-glass fiber significantly enhances the internal damping characteristics. of hybrid composites.

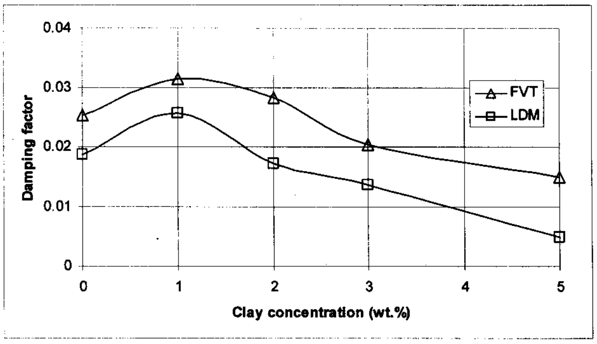

Fig. 13 Influence of OMT clay on second mode damping factor of HNC

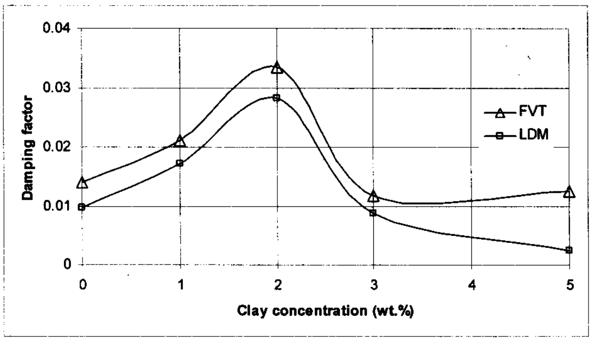

Fig. 14 Influence of MMT clay on third mode damping factor of HNC

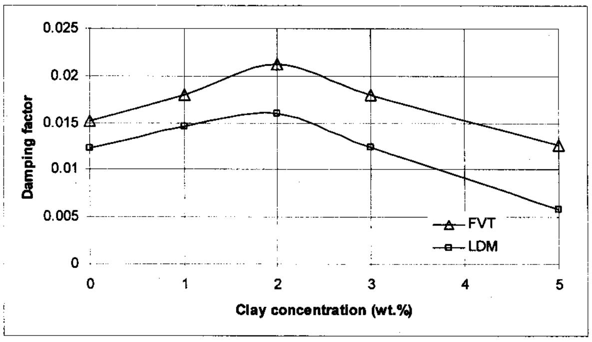

Fig. 15 Influence of MMT clay on fourth mode damping factor of HNC

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