INVESTIGAȚII PRIVIND INFLUENȚA NANOTUBURILOR DE HALOISIT ASUPRA CARACTERISTICILOR TERMO-MECANICE ŞI VIBRAȚIONALE ALE MATERIALELOR LAMINATE DE TIP RĂŞINĂ EPOXI RANFORSATĂ CU FIBRE DE STICLĂ

INVESTIGATIONS OF INFLUENCE OF HALLOYSITE NANOTUBES ON THE THERMO-MECHANICAL AND VIBRATION CHARACTERISTICS OF GLASS FIBER REINFORCED EPOXY LAMINATES

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This paper presents the investigations of thermo mechanical and free vibration properties by reinforcing halloysite nanotube (HNT) with various weight proportions (0,2,4,6,8, and 10wt%) in glass fiber reinforced epoxy (EP/GF/HNT) nanocomposites. Theoretical study was also carried out to study the vibration characteristics of EP/GF/HNT nanocomposites. It was found that the addition of HNT improved the thermo-mechanical and damping properties. Dynamic mechanical analysis showed an increase in the storage modulus and glass transition temperature up to 4wt% of HNT. Vibration analysis proved that the addition of HNT enhanced the internal damping and increased the natural frequency up to 4wt%.

Keywords: : *Composites, HNT, Epoxy, Vibration, Damping , DMA*

1. Introduction

The fibre reinforced polymer composites are now sentenced as the suitable materials for various applications in automobile, aerospace and building sectors, because of their numerous practical advantages like ease of processing, fast production cycling, and low processing cost over traditional materials. In practice, these composite materials are designed to perform in different static and dynamic conditions. Fiber - reinforced plastics (FRPs) uses polymer as the matrix and a fiber as the reinforcing agent. The fibers improve strength properties in the direction they are aligned in the matrix. Epoxy resins are increasingly used as matrixes in composite materials for many applications, and can be used to produce fiber reinforced composites with greater mechanical strength, chemical resistance, electronic insulating properties and having the capability of good adhesion to the embedded fiber [1, 2] E-glass fibers are the most popular, although other fibers have similar and even superior performance, the main attractive of glass fibers is that they are inexpensive. So E-glass fibers have been used widely for manufacturing advanced polymer matrix composites [3].The disadvantage of fiber reinforced plastics (FRPs) is that the polymer has weak mechanical properties, which limits the potential to improve the strength to weight ratios even further[4], It is a limiting factor when designing a structure. Also in order to improve the properties of the composite materials the adhesion between the matrix and fiber must be improved which can be achieved by two methods , one is modifying the glass fiber surface with an organic agent and another method is to modify the polymer with proper agents [5] like nano materials, thus creating a nanocomposite. The nanoparticle provides improved interfacial surface area and smaller interparticle distances, which are believed to contribute to improved mechanical properties [6]. Even though no significant conclusions have been found on how properties of nanocomposites perform based on reinforcing agents, researchers are experimenting with different nanoparticle/fiber/polymer combinations. Over the past decades, considerable progress has been made [7-11]. Polymer nanocomposites reinforced with fibers are a relatively new type of composite material, of which the possibilities are numerous but not yet fully explored.

Halloysite nanotubes (HNTs) have recently become the subject of research attention as a new type of additive for enhancing the mechanical, thermal and moisture barrier performance of polymers [12-16]. HNT's are readily obtainable, are much cheaper than other nanofillers such as carbon nanotubes and they are biocompatible [17]. The application of HNT in EP/GF composites is still

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largely unexplored. It is now accepted that nanoparticles can solve vibration damping issues [18]. The modal analysis for fiber glass/epoxy laminates has been carried out and it is found that it exhibits increased natural frequency with the addition of nanoclay. For higher frequencies, the nanoclay content of 2wt% leads to a higher energy dissipation [19].

However, there are no reports available on the thermo-mechanical vibration, and damping characteristics of epoxy laminates. In this study, the influence of HNT on the thermo-mechanical, vibration and damping behaviour of epoxy laminates is studied. Theoretical study is also carried out to study the vibration characteristics of Epoxy/Glass fiber / HNT nanocomposites

2. Experimental Details

2.1 Materials

Poxy LY 556 resin is selected as the matrix material for this research work and corresponding hardener is HY 951 which were supplied by Vantigo. The resin hardener ratio is 100:10 by weight as recommended by the supplier. Plain woven type E-glass fabrics are used as major reinforcement which was supplied by Binani, Goa. The halloysite nano tube (HNT) was procured from Natural nano, Inc. New York.

2.2 Dispersion of HNT into epoxy

For the preparation of nanocomposites, a certain amount of HNT is agitated in acetone for 30 min with the help of high intensity probe type ultrasonicator to de-agglomerate the HNTs. Epoxy LY556 grade resin was preheated to lower the viscosity and to enable better wetting of the particles. Pre-calculated amount of pristine HNTs and epoxy resin was mixed together by mechanical stirrer for 1 hour and the temperature of the resin was maintained at 70°C then the mixture was sonicated for one hour by using the ultrasonicator. To reduce the chances of voids, the HNT dispersed resin is kept under vacuum for 60 min. Once bubbles are trapped, proportionate amount of hardener HY951 was added and manually mixed for 5 min.

2.3 Fabrication of Composite laminates

The filled composite laminates are manufactured by stacking the glass fabric one above another with the HNT filled resin mix well spreaded between the fabrics. To ensure uniform thickness of the sample a spacer of size 3mm is used. The mould plates are sprayed with release agent. The whole assembly is kept in a hydraulic press and a temperature of 100^{o}C is applied for 2 hours along with pressure. At the end of the process, the complete setup is cooled slowly to room temperature and allowed to cure for a day in order to minimize the thermal residual stress. The obtained laminate thickness is approximately 3mm. The fiber volume fraction of this composite laminate is approximately 36%. The unfilled epoxy/glass-fiber composite is also fabricated in the same manner except that there are no HNT fillers. The HNT contents varied as 0, 2,4,6,8 and 10 wt% based on the weight of the matrix , to study the effect of HNT weight fraction on performance of composite.

3. Characterisation

In the present study, Dynamic Mechanical Analysis (DMA) and Vibration analysis tests were done to characterize the properties of the synthesized EP/GF/HNT nanocomposites. The properties of nanocomposites were compared with those of unfilled EP/GF composites.

3.1. Dynamic Mechanical Analysis (DMA)

Dynamic analysis method is widely used to determine relative stiffness and damping characteristics of polymeric and composite materials. It is an effective technique to analyse the interaction between a nanofiller and polymer in a composite by measuring the viscoelastic response of the composite. Dynamic mechanical analysis (DMA) thermograms of the samples were obtained at a frequency of 1 Hz in a nitrogen atmosphere, with a range of temperatures starting from 35^{0}C up to 275^{0}C with a scan rate of 5^{0}C per minute.

3.2. Vibration Analysis

The Figure 1 shows the experimental setup used for carrying out the vibration analysis of EP/GF/HNT nanocomposite. This test is carried

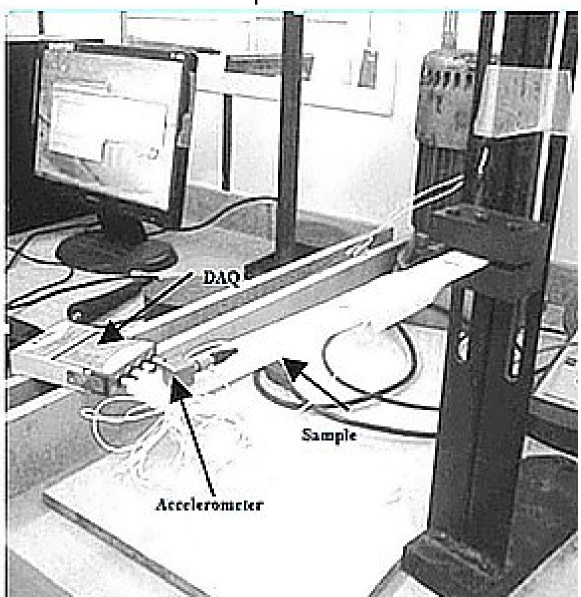

Fig. 1 - Experimental setup for modal analysis.

out to find the damping factor and natural frequency of the samples. The free vibration test (FVT) is used to compute the natural frequency and damping factors of various weight proportions of EP/GF/HNT nanocomposites. Each composite test specimen was fixed in the form of cantilever beam; the accelerometer which is used to detect the dynamic characteristics of the composite samples, was glued using wax at the free –end side of each cantilever laminate and then the beam was stimulated for the free vibration. The vibration acceleration time histories were recorded by the data acquisition software with a computer.

3.2.1. Damping Factor

Numbers of methods are available to set up damping experiment for vibration. A simple and frequent method is to get the experimental data concerning dynamic material behaviour by studying the free transverse vibration of cantilever beam. The information on the beam behaviour is gathered from experiments and by comparing it with the behaviour of a uniform, homogeneous Bernouli-Euler cantilever beam. The logarithmic decrement is used for calculating the damping ratio (ε) of the cantilever laminate from the recorded acceleration time histories based on the following equation

$$\varepsilon = \frac{1}{2\pi y} \ln \frac{g_x}{g_{x+y}} \tag{1}$$

Where g_x is the peak acceleration of x th peak, g_{x+y} is the peak acceleration of the peak y cycles after x th peak and tx is the time instant at x cycle in peak acceleration, as shown in the Figure 2.From the fast Fourier transformation (FFT), the vibration frequency spectrum was obtained from the measured time histories. The main peak corresponds to the natural frequency of the composite.

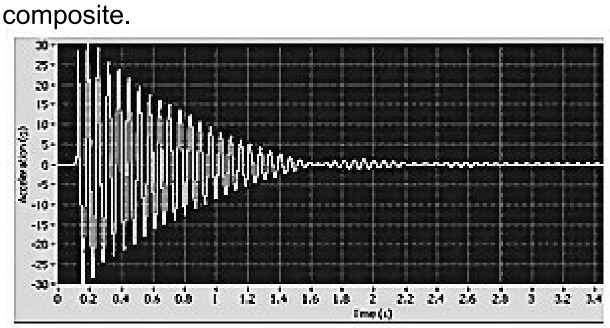

Fig. 2 - Vibration – time history response of the EP/GF/HNT nanocomposite sample.

3.2.2. Natural frequency

The following Euler-Bernoulli equation of motion is used to find out the natural frequency for the samples. It is given by

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

Assuming steady-state vibration in harmonic form, we have

$$w(x,t) = W(x)\sin(wt - \phi) \tag{3}$$

Substituting Equation (3) in (2) :

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

$$\beta^4 = \frac{w^2 m}{EI} \tag{5}$$

When 0 < x < l. The solution of equation (5) is:

$$W(x) = A_1 Sin\beta x + A_2 Cos\beta x + A_3 Sinh\beta l + {} + A_4 Cos\beta l \tag{6}$$

The constants of equation (6) are obtained by applying boundary conditions. The expressions for natural frequency (ω) of the first mode we have

$$\omega = \frac{3.515}{l^2}\sqrt{\frac{EI}{\rho A}} \tag{7}$$

4. Result and Discussion

The data related to the mechanical properties of EP/GF/HNT composite systems have been presented and discussed in the following sections.

4.1. Dynamic Mechanical Analysis (DMA)

The effect of HNT reinforcement on thermo-mechanical properties of EP/GF/HNT nanocomposites is investigated by dynamic mechanical analysis (DMA). An elastic or storage modulus (E^1) and tan delta (tanδ) were measured.

4.1.1. Storage Modulus (E^1)

Figure 3 shows the temperature dependence of the storage modulus of EP/GF/HNT composites. The storage moduli of the EP/GF/HNT nano composites with various HNT loadings were higher than that of unfilled EP/GF composites.

It is interpreted that the storage modulus (E^1) of unfilled EP/GF composite as 9998MPa (at 35°C) It increases continuously upto 4wt% HNT addition. Composite with 4wt% HNT shows a maximum value of 14449MPa which is 44.5% higher than unfilled composite this could be probably due to better interfacial bonding between fiber and matrix which results restrictions in chain mobility at 4wt% HNT loading. On further addition of HNT, storage modulus decreases. For epoxy

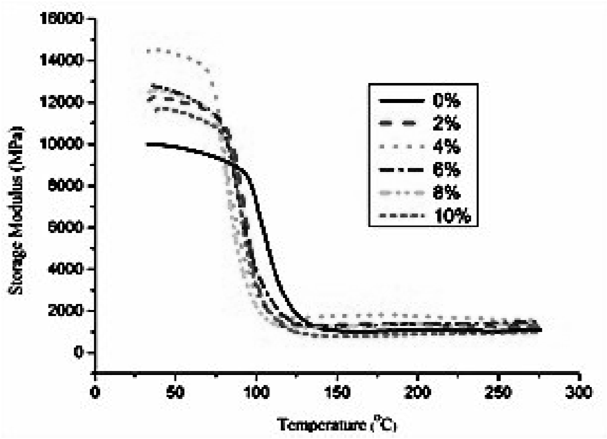

Fig. 3 - Effect of HNT wt% on Storage modulus of EP/GF/HNT nanocomposite.

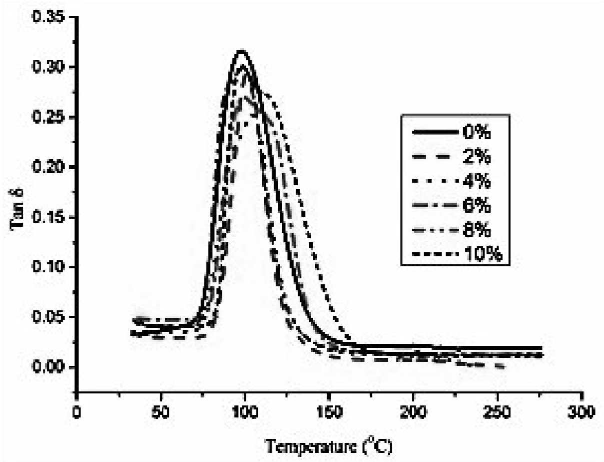

Fig. 4 - Effect of HNT wt% on Tanδ of EP/GF/HNT nanocomposite.

with 10wt% HNT, storage modulus is 11700MPa. The decrease in storage modulus at higher HNT weight proportions(>4wt%) may be due to agglomeration, segregation of nanoparticles in the matrix etc., that act as a weak zone due to weak interface bonding between matrix and particle which contributes to less storage modulus. The results further shows that the decrease in storage modulus with the increase of temperature owing to the dilute nature of the polymer in all weight proportions. This is supported by the results reported by Zhang and Zhang [20] that storage modulus is higher while the molecular movement is limited, thus causing the storage of mechanical energy to increase. As the temperature of the composite samples was increased, the storage modulus decreased regularly [21]

4.1.2. Damping Co-efficient (tan δ)

The Figure 4 shows the variation of damping coefficient tan δ, with the temperature for unfilled and HNT filled composite. The temperature at which damping coefficient reaches maximum is interpreted as the glass transition temperature (T_g) of the material [22]. It was expected that T_g will be higher for EP/GF/HNT nanocomposites compared to unfilled EP/GF composite due to filler effect, that would reduce the mobility of polymeric chain in the inter-phase region. On addition of HNT the tan δ peak shifts to a higher temperature which suggests that there is an increase in T_g. The increase in T_g is due to the arrest of segmental motion of organic /inorganic interface with its neighbourhood [23] also the chemical bonding at the interface lead to hindered relaxational mobility in the polymer segments near the interface. Maximum increase in T_g of 105°C is observed for 4wt% HNT. On further addition of HNT (>4wt%), there is no appreciable change in T_g. The reduction in T_g after 4wt% is because of factors such as, lacking of surrounding entanglements and reduced crosslink density.

4.2. Vibrational Analysis

The effect of HNT weight proportion on the free vibration properties have investigated and the results are listed as follows.

4.2.1. Natural Frequency

The average natural frequency of all the composites is given in Table 1.

Table 1

Effect of HNT wt% on natural frequency and Damping ratio of EP/GF/HNT nanocomposite samples

HNT Wt%	Natural Frequency (Hz)		Damping Ratio (ε)
	Experimental	Theoretical	
0	13.98	16.06	0.01641
2	16	17.31	0.01911
4	16.66	18.24	0.01959
6	16.36	18.04	0.01867
8	15.74	17.62	0.01751
10	14.46	16.87	0.01668

The theoretical values obtained by the Euler-Bernoulli beam theory are also given in the Table 1. The natural frequencies computed by theory have good agreement with the experimental values. The natural frequency of the composite increases with the addition of HNT and maximum increase in the natural frequency was observed at 4wt% of HNT. This behaviour is attributed due to increase in stiffness upto 4wt% of HNT addition. At high content of HNT (>4wt%), the stiffness decreases due to agglomeration of HNT, weak fiber-matrix interface, etc. and hence there is decrease in the natural frequency, but it is still higher than the unfilled EP/GF composites.

4.2.2. Damping ratio

The average damping ratios of all the composites are given in Table 1. It is observed that there is an improvement in damping up to 4wt% addition of HNT and then it decreases with further addition of HNT. Large stiffness variation in the fiber matrix interface because of addition of uniformly dispersed HNT has caused high internal damping, resulting improvement in damping [24]. But for further addition of HNT (>4wt %) due to the agglomeration the damping ability reduces. Similar tendency was observed by Mohan et.al [25].

5. Conclusion

Glass fiber reinforced epoxy composites crammed with various weight proportions of HNT (EP/GF/HNT) has been successfully fabricated using combination of hand layup and compression moulding methods. A marked improvement in thermo-mechanical and vibrational properties has been observed in the EP/GF/HNT nanocomposites.

The EP/GF/HNT nanocomposites shows higher storage modulus than the unfilled EP/GF composites for all the weight percentages of HNT addition and composite with 4wt% HNT exhibits the highest storage modulus. The unfilled EP/GF composite has the highest tanδ value indicating that there is a large degree of mobility. Reinforcement of HNT decreased the damping behaviour of composites as HNT acted as a barrier to the free movement of molecular chain.

Addition of HNT significantly influences the free vibration characteristics of the nanocomposites investigated. The enhanced natural frequency and damping ratio are observed on addition of HNT up to 4 wt%. Experimentally estimated natural frequencies are in good agreement with theoretical method results.

We anticipated that these studies will optimized the use of HNT and its utilization in development of unique cost effective advanced hybrid composites possessing appropriate damping behaviour and thermal stability. Thus from the results of present study, the EP/GF/HNT nanocomposites can be used for engineering and aerospace applications.

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