



## **THERMAL STABILITY AND DAMPING CHARACTERS OF HIGH PERFORMANCE EPOXY LAYERED SILICATE NANOCOMPOSITES**

**T.P. Mohan, M. Ramesh Kumar and R. Velmurugan**

*Composites Technology Centre, Indian Institute of Technology Madras Chennai 600 036, India.*

### **ABSTRACT**

Well dispersed exfoliated layered silicate clay nanocomposites based on epoxy resins were synthesized by using organo modified alkyl quaternary ammonium modified and unmodified smectic clay. Thermal stability of series of each nanocomposite system with different organo clay [OC] and unmodified clay [UC] concentrations were determined by using thermogravimetric analysis (TGA). The nanocomposites show increased thermal stability than the unmodified filled epoxy polymer. The thermal stability increases with the increase in organoclay concentrations. Fourier Transform Infra-Red (FTIR) spectroscopy reveals the final char concentration consists of silicates which induces such improvement in thermal stability for nanocomposites. Vibration tests were carried for the nanocomposites by Impulse Hammer Technique (IHT) and logarithmic decrement method (LDM). The nanocomposites show improved damping factor than the unmodified clay filled polymer matrix for all the first four modes.

### **1. INTRODUCTION**

Polymer/clay nanocomposites (PCN), a new class of reinforced plastics formed by dispersing nano-sized clay particles throughout a polymer matrix have received much attention in both scientific and industrial arenas due to their enhanced mechanical and barrier properties as well as flame resistance. Generally, three methods for the formation of polymer/clay nanocomposites are mainly used: (1) Intercalation of monomers followed by in situ polymerization; (2) Direct intercalation of polymer chains from solution; (3) Polymer melt intercalation. Each of these methods has its own advantages and disadvantages. For example, the direct melt intercalation into clay layers is a preferred process for the formation of hybrid materials not only with respect to environmental issues, but also due to the ease of fabrication for its promising commercial applications. Usually, the dispersion of clay particles in a polymer matrix results in the formation of three types of composite materials. The first type is conventional phase separated composites in which the polymer and the inorganic host remain immiscible resulting in poor mechanical properties of the composite material. The second type is intercalated polymer-clay nanocomposites, which is formed by the insertion of one or more molecular chains of polymer into the interlayer or gallery space. The last type is exfoliated or delaminated polymer-clay nanocomposites, which is formed when the clay nanolayers are individually dispersed in the continuous polymer matrix. Exfoliated polymer-clay nanocomposites are especially desirable for improved properties because of the large aspect ratio and homogeneous dispersion of clay and huge interfacial area (and consequently strong interaction) between polymer chains and clay nanolayers [1,2].

Recently, PCN materials that consists of epoxy and layered materials are found to display novel properties, which can be observed from two dissimilar chemical components combining at the molecular level. We focused here on the synthesis of a new type of potentially advantageous organo smectite clays. The direct incorporation of the diamine curing agents in the galleries of montmorillonite clays in the form of alkyl quarternary ammonium ions is presented an alternative, less process intensive way of preparing epoxy-clay nanocomposites. Different degrees of clay nanolayer intercalation/exfoliation could be achieved, depending mainly on the chain length and the concentration of the diamine in the gallery. An appreciable improvement in the mechanical properties was noted in the previous studies [3], and in this paper we present the influence of the this modified amine clays in the thermal stability and damping characters were discussed.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Materials

The matrix used in this study is the DGEBA epoxy system and the curing agent is Diaminodiphenyl Methane (DDM), obtained from CIBA Ltd, Basle (Switzerland). The reinforcing clay nanoparticle is alkyl quaternary ammonium clay available under the trade name Garamite®-1958, from Southern Clay Products Inc, Gonzales, Texas (USA).

### 2.2 Nanocomposite fabrication

Initially the epoxy resin is heated at 120°C for 1 hour. The clay is gently added in to the resin bath and is mixed by using the shear mixer, until the dispersion of clay is uniform in the resin. The 25 wt.% of hardener is added at 80°C and the temperature is maintained for 4 hour. The nanocomposite specimens processed by this method are tested for characterization studies with different weight percent of clays.

### 2.3 Characterisation studies

Thin foils of about 100-200 nm thick specimens were made for transmission electron microscopy using Philip electron microscopy instrument operating at 200 KV. Thermogravimetry analysis (TGA) is carried out using Netzsch Model STA 409 PC with a thermogravimetrix analyzer (TA instrument). The samples of 5mg each are taken in an alumina crucible for the TGA test at heating rate of 10°C/min. Fourier Transform Infrared (FTIR) spectra of the char samples are collected on a Perkin Elmer FTIR instrument from 400cm<sup>-1</sup> to 4000cm<sup>-1</sup> with a resolution of 2cm<sup>-1</sup>. For each spectrum, 64 runs are collected and averaged. The specimens are made by adding ~1wt% of KBr powder and have been pressed into a disc of 13mm in diameter and 1-2mm thickness. Five specimens of cantilever beam in each nanocomposites of 250 X 25 X 3 mm were made, and one end of the beam was clamped and the other end was attached to the accelerometer to obtain the vibration mode. It was performed by Impulse Hammer Technique [IHT] and Logarithmic Decrement Method [LDM]. In the IHT, the accelerometer (Bruel and Kjaer 4374) was used to measure the displacement through the charge amplifier (Bovel and Kjaer type 2626) and the response was recorded on the Dynamic Signal Analyzer [DSA] (Agilent 35670 A). The specimens were excited by using an impulse excitation (RION PH 7117, modally tuned hammer). The signal was displayed in the fast Fourier transform [FFT]. In the LDM, the sine wave signal from the waveform generator (Hawlett Packard 33120 A) was supplied to drive the modal exciter to excite the cantilever beam

specimen. The modal exciter and accelerometer were used to excite and detect the beam tip displacements. The amplitude of the oscillation was measured by oscilloscope (Agilent 546 A).

### 3. RESULTS AND DISCUSSION

#### 3.1. Morphology of nanocomposites

TEM micrographs of epoxy-clay nanocomposites containing 10 wt.% of organo clay are shown in Fig. 1. The dark lines are the silicate layers, and the other region is the epoxy matrix. It is seen that the clay layers are well separated and dispersed uniformly in the matrix, and no segregation of micron sized clay is seen. This shows the existence of nano composites by separation of clay nano layers. The separation of MMT layers in the epoxy matrix is attributed to the strong interaction between matrix and OC fillers, as evident from the sharp increase in viscosity. It is noted that the micron size clay is reduced to the nano layers in the epoxy matrix after curing has taken place. This indicates that the nano clay is compatible with the matrix material.

#### 3.2. Thermal stability of nanocomposites

To examine the effect of clay reinforcement on the thermal stability, TGA was carried out. TGA results of organoclay, epoxy and its nanocomposites are shown in Fig. 2.a. The decomposition of the organoclay shows lower temperature weight loss at  $\sim 350^\circ\text{C}$ , due to the decomposition of the quaternary alkylammonium cations, and the decomposition of the epoxy starts at  $\sim 280^\circ\text{C}$ . On the addition of the organoclay the decomposition range of the nanocomposites is largely increased than the epoxy polymer. The nanocomposites with 10 wt.% organoclay show the decomposition at  $\sim 324^\circ\text{C}$ . This enhancement in the thermal stability is due to the presence of the clay nanolayers, which act as barrier for the volatile degradation of the material. The enhancement in the thermal stability of nanocomposite is much more pronounced even for temperature range of above  $500^\circ\text{C}$ . In such higher temperature range the presence of inorganic phases ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  etc) dominate the nanocomposites which causes such thermal stability [4]. FT-IR of the final char concentration of the 10 wt.% clay nanocomposites is shown Fig. 3.b. The Si-O absorption and OH bending bands occur in the range of  $1200\text{-}400\text{cm}^{-1}$ . The absorption band at  $3444\text{cm}^{-1}$  assigned to H-O-H stretching vibration of water molecules that are bonded to the Si-O surface. TGA of the epoxy filled with unmodified clay (UC) is shown in Fig. 3. It reveals that there is less improvement in the thermal stability at the decomposition range and at higher temperature the stability increased due to the existence of the hard silicate particles.

#### 3.3 Damping characters

Experimental results of the natural frequency of nanocomposites are shown in tables 1 and 2. In the IHT, the output signal received from the accelerometer was stored in DSA and the Fast Fourier Transform [FFT] of the time signal was obtained from DSA. 16 averages were used to plot the Frequency Response Function [FRT] of the time signal. A typical FRT obtained from the IHT is shown in Fig. 4. The series of peaks in FRT shows the natural frequency of the nanocomposite beam. The damping factor for the materials is obtained by using the half-power bandwidth method. The schematic of this is seen in Fig. 5. The expression for damping factor  $\xi$  by the half power bandwidth technique is given by [5].

$$x = \frac{Dw}{2w_n} \quad (1)$$

Where  $\Delta\omega$  is the band width at the half-power points of resonant peak for the  $n^{\text{th}}$  mode and  $\omega_n$  is the resonant frequency. The half-power points are found at 2dB below the peak value of FRT of the particular mode when the logarithmic scale is used or at  $(1/2)^{1/2}$  of this maximum peak value when the linear scale is used.

In the LDM, sine wave signal was supplied to drive the modal exciter to excite the cantilever beam specimen. During the natural frequency mode, the amplitude has increased to large extent, once the resonance was achieved. At this point, the excitation signal was disconnected freely. A typical free decay curve is shown in Fig. 6. From this decay curve, two experimental amplitude data points are collected namely  $x_1$  and  $x_{n+1}$  as seen in the figure 7. Then the damping factor  $\xi$  is calculated by using the expression [6].

$$d = \frac{1}{n+1} \ln \frac{x_1}{x_{n+1}} \quad (2)$$

$$z = \frac{d^2}{\sqrt{4p^2 + d^2}} \quad (3)$$

where  $\xi$ , the damping factor,  $n+1$  the number of cycles,  $\delta$  is the logarithmic decrement,  $x_1$  and  $x_{n+1}$  are the two displacement values at the time intervals  $t_1$  and  $t_2$  respectively.

Tables 1 and 2 show the natural frequency for the first four mode of nanocomposites. The improvement in the natural frequency is noticed for all the four modes of nanocomposites when compared with the pure epoxy polymer. The increased natural frequency is due to good dispersion of organo clay in the matrix which results in improved stiffness. The damping factor of the nanocomposites and UC filled composites tested under IHT and LDH method for the first mode is shown in Fig. 8. It is noted that the clay addition has the considerable effect in the damping behaviour of the nanocomposites. Kie et al., [7], studied the dynamic mechanical properties and argued that the damping capacity of the nanocomposites increases due to the addition of the nanoclay particles. The clay addition increases the storage modulus ( $E'$ ), and the damping loss factor ( $\tan\delta = \frac{E''}{E'}$ ), the increased  $E''$  causes such damping improvement in the nanocomposites.

#### 4. CONCLUSIONS

The nanocomposites were successfully processed under high temperature curing by mechanical shear mixing. TEM shows well dispersed clay layers in the matrix. Thermal stability of nanocomposites largely increased than the unmodified clay filled polymer composites. The damping factor for the nanocomposites shows appreciable improvement than the pure matrix and conventional micron clay filled composites.

## 5. REFERENCE

1. Kojima. Y, Usuki. A, Kawasumi. M, Okada. A, Fukushima. Y, Kurauchi. T, Kamigaito, Journal of Materials Research, 8 (1993) 1185-1189.
2. Tie Lan and Thomas J. Pinnavaia, Chemistry of Materials, 6 (1994) 2216-2219.
3. R. Velmurugan and T.P. Mohan, Journal of Materials Science, Article in Press.
4. Yuan-Hsiang Yu, Ching-Yi Lin, Jui-Ming, Polymer, 44 (2003) 3553-60.
5. S.A. Surarer, R.F. Gibson, L.R. Deobald, Experimental Technique, 4 (1984) 9-24.
6. Wren G.G, Kinra V.K, Journal of Testing and Evaluation, 16 (1988) 77-85.
7. Kie, Xu, Polymer, 44 (2004) 1009.

## 6. ACKNOWLEDGEMENT

The support provided by MHRD, Govt. of India, is greatly acknowledged.

## TABLES

Table1. Frequency dependence of epoxy filled with organoclay series

Material	Natural frequency at mode 1, Hz	Natural frequency at mode 2, Hz	Natural frequency at mode 3, Hz	Natural frequency at mode 4, Hz
Epoxy	17.87	117.50	191.35	297.00
E + 1% OC	18.87	134.00	205.75	305.00
E + 2% OC	20.25	135.00	216.75	327.00
E + 3% OC	22.50	148.10	233.00	332.00
E + 5% OC	18.50	128.25	229.00	317.00
E + 10% OC	18.50	123.75	271.25	-

Table 2. Frequency dependence of epoxy filled with unmodified clay series

Material	Natural frequency at mode 1, Hz	Natural frequency at mode 2, Hz	Natural frequency at mode 3, Hz	Natural frequency at mode 4, Hz
Epoxy	17.87	108.25	179.25	286.25
E + 1% OC	17.50	121.50	184.50	291.50
E + 2% OC	19.75	123.75	190.25	301.75
E + 3% OC	20.25	136.75	205.25	297.75
E + 5% OC	16.75	110.25	213.00	294.50
E + 10% OC	16.50	111.75	203.25	291.75

**FIGURES**

Fig. 1. TEM micrograph of epoxy filled with 10 wt.% organoclay

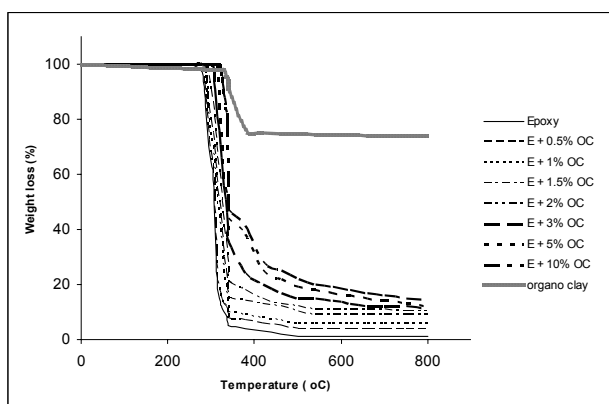


Fig. 2.a. TGA thermogram of epoxy filled with organoclay (OC) fillers

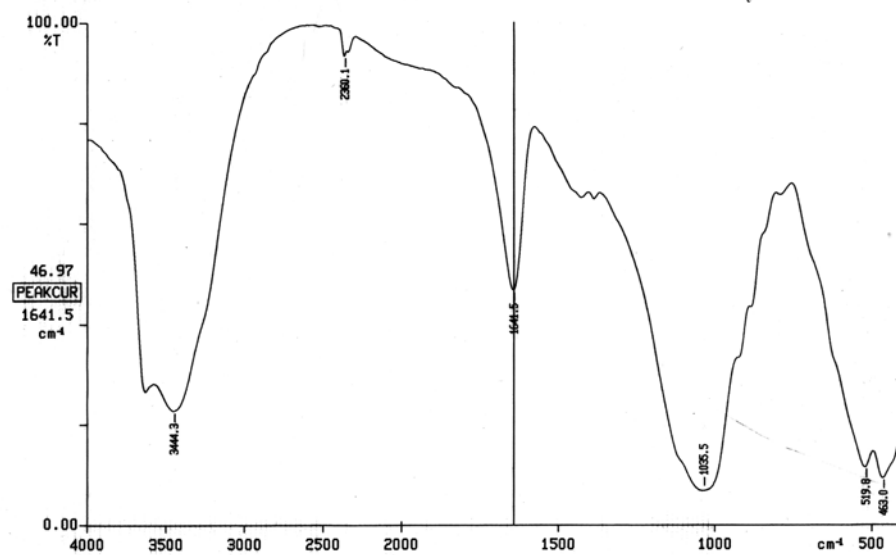


Fig. 2.b. FT-IR spectrum of nanocomposite char consisting of 10 wt.% OC fillers

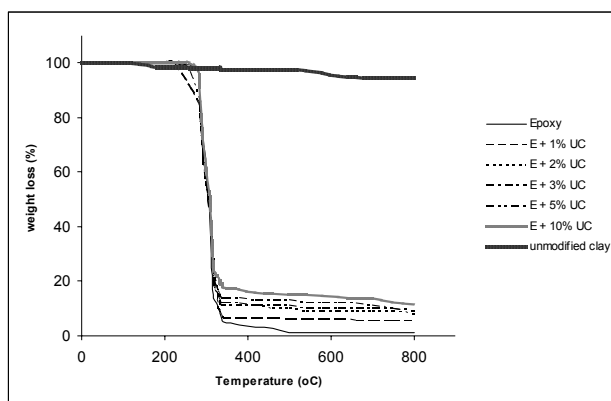


Fig. 3. TGA thermogram of epoxy filled with unmodified clay (UC) fillers



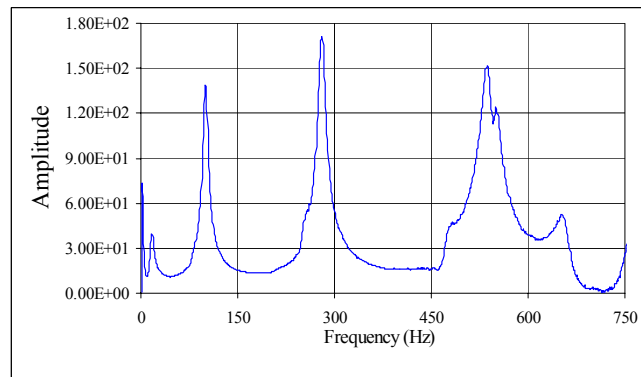


Fig 4. Typical FRF obtained for epoxy with 10 wt.% organoclay content

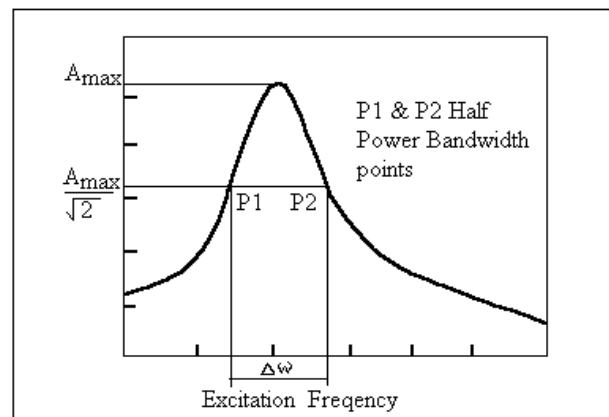


Fig 5. Free vibration test: half power bandwidth damping factor measurement

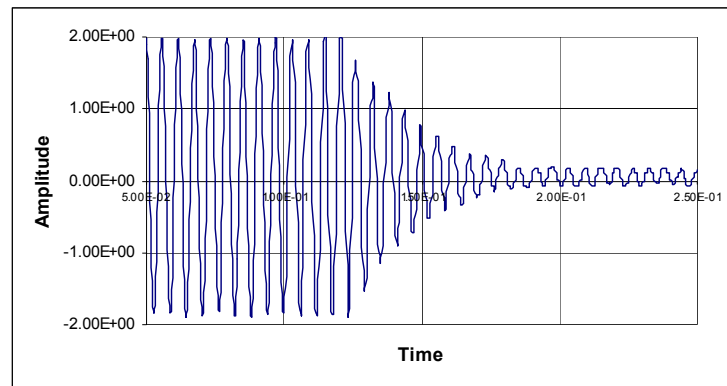


Fig 6. Typical free decay curve measured for logarithmic decrement method (LDM)

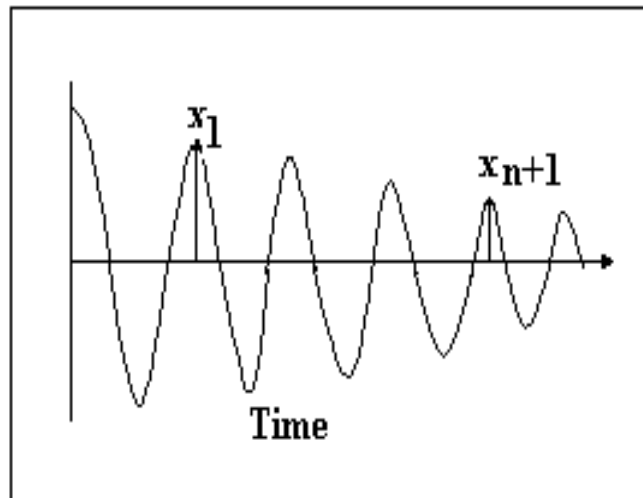


Fig 7. Free decay amplitude measurement for damping factor using LDM

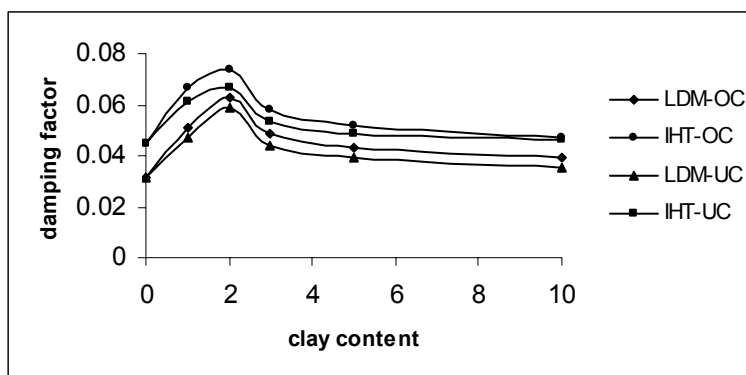


Fig. 8. damping factor of epoxy filled with UC and OC clay under IHT and LDM method of the 1<sup>st</sup> mode of natural frequency