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Room temperature processing of epoxy-clay nanocomposites

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Polymer/Clay nanocomposites consisting of an epoxy matrix filled with nanolayered silicate clay particles have been investigated. Recent and ongoing research has shown that dramatic enhancements can be achieved in mechanical and thermal properties by adding a small volume percent of clays. In the present work nanocomposites are processed by mechanical mixing of epoxy with organoclays and unmodified clays using a high speed electric shear mixer at room temperature. The addition of different organoclay wt% [1–3, 5 and 10] indicates good enhancement in hardness, dynamic mechanical properties, and also the molecular mobility of the polymer is reduced by the presence of the silicate layers, which in turn causes large stiffness improvements. X-ray diffraction (XRD) results show the intercalation/exfoliation of clays in the epoxy matrix. The influence of organoclay restricts the weight loss at varying temperatures. Experiments show improved elastic modulus for both modified and unmodified clays. © *2004 Kluwer Academic Publishers*

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1. Introduction

Polymer/clay nanocomposites consists of polymer matrix with nanosize layered silicate clay fillers. Good improvement in properties can be achieved in such materials due to the high surface contact area of the reinforcing filler which causes high strength, modulus and thermal properties at low clay loading level (usually <5 wt%) [1–3]. As a result of this, they have wide application from the automotive to the aerospace industries owing to their low density combined with good mechanical and physical properties. The first successful material, processed by the Toyota research group was Nylon6/clay from which wide variety of nanocomposites were developed with different matrix materials consisting of thermoplastic/thermoset polymers and nanoclay fillers [4–7].

Smectic clays, particularly montmorillonite (MMT) minerals serve as good nanofillers owing to their ease dispersability in the organic matrix. MMT consist of nanosized layers of alumino/silicate sheets in which alumina sheets sandwiched between two silicate sheets cause a net negative charge. This charge is counterbalanced by exchangeable metal ions present in the surface of the layers. MMT clays are generally hydrophilic in nature, this is made organophilic by replacing exchangeable cation such as alkylamonium cations which render them organophilic favoring intercalation/exfoliation in the organic matrix [8, 9].

When processing the nanocomposites, the main mechanism in forming intercalation/exfoliation is the shear force which is applied to the polymer/clay solution that favors separation of clay layers to disperse uniformly in the matrix. Vaia *et al.*, suggested that good dispersion of clays can be obtained from conventional shear devices such as extruders, mixers, ultrasonic agitators etc. [10]. Besides this, the formation of intercalation/exfoliation structure depends on structure and cation exchange capacity (CEC), curing temperature and curing agents [11, 12].

Many authors [13–20] have processed epoxy/clay nanocomposites using amine curing agent under hot curing conditions. In the present work we processed this nanocomposite using triethyl tetra amine (TETA) curing agent at room temperature by a high speed electrical shear rotor. The intercalation/exfoliation structure was studied using X-ray diffraction (XRD) by addition of modified and unmodified montmorillonites. The thermal stability of these nanocomposites was studied by thermogravimetry analysis (TGA) and mechanical properties were studied under quasi- static tension tests.

2. Experimental procedures

2.1. Materials

The matrix used in the present study is epoxy resin system DGEBA (Araldite LY556) and the amine curing agent TETA, both obtained from CIBA Ltd. Basle (Switzerland). The reinforcing clay nanoparticle is Garamite®-1958 available from Southern Clay Products Inc., Gonzales, Texas (USA). This clay is an alkyl quaternary ammonium clay [21]. The unmodified clay (Na^+-bentonite) is obtained from Ennore Clays and

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Muds Ltd., Chennai (India). The properties of composite materials both with modified and unmodified clay conditions were studied.

2.2. Nanocomposite fabrication

In the present experiment an epoxy/clay nanocomposite is prepared by mixing the clay with 1–3, 5 and 10 wt% and processing in the electric shear mixer which rotates at ~1000 rpm. The mixer rotates horizontally in the matrix which causes the shear force to exfoliate/intercalate the clay during further mixing. The clay is introduced gently into the bath as rotation takes place in order to ensure good dispersion of clay in the epoxy matrix. Compounding is carried out at room temperature for 1 h with a rotation speed of 1000 rpm. It is observed that the solution becomes viscous and opaque as the silicate layers disperse and expand with time. The final product from the bath is then collected and is mixed with the 4 wt% TETA hardner at room temperature for few minutes, then the solution is left for degassing. After degassing, the solution is cast in the mold.

2.3. Characterization and property studies

X-ray diffraction (XRD) is performed on both clay and cured samples to evaluate the degree of intercalation/exfoliation and the d-spacing between clay platelets. It is carried out with a scanning rate of 2°/min with Cu K_α radiation ($\lambda = 1.5$ Å) operating at 30 KV and 15 mA. Thermogravimetry analysis (TGA) is carried out by using Netzsch Model STA 409 PC with a thermogravimetric analyzer (TA instrument). The sample of 5 mg each in an alumina crucible is used for the TGA test with a heating rate of 5°/min. Dynamic mechanical analysis (DMA) is carried out at the frequency rate of 20 Hz using the Netzsh model DMA 242 C under atmospheric conditions. The storage modulus and the loss factor (tanδ) are obtained in three point bending. Tensile testing is carried using Instron at 1 mm/min according to ASTM standard D638. Shore D hardness is obtained for composites series using ASTM standard D2240. The heat deflection temperature (HDT) is obtained by ASTM standard D648.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD pattern of organically modified clay and unmodified clay which shows the d-spacing. The interlayer distance is obtained from Bragg's law $2d\text{Sin}\theta = n\lambda$, where θ is the Bragg angle, λ is the wavelength used, n is the orders. The d-spacings are ~17 Å and 13.34Å respectively. This indicates that the d-spacing for organic clay is higher than unmodified clay. The d-spacing of unmodified clay is less by about 3.5 Å than that of the organoclay. Fig. 2 shows the diffraction pattern for the epoxy filled with the organic clay, since there is no diffraction peak for (001) plane, the clay's interlayer distance (d-spacing) may be more than 7 nm or it may be a fully exfoliated nanocomoposite sturucture [22], which indicates that the polymer matrix has gone in the intragallery region forming intercalate/exfoliate nanocomposite. The diffraction pattern for epoxy with unmodified clay is shown in Fig. 3, which indicates sharp diffraction peaks with little increase in the d-spacing. This in turn indicates an intercalated structure with a small increase in d-spacing. Hence it is understood that the unmodified clay acts as a filler with small or almost negligible increase in d-spacing.

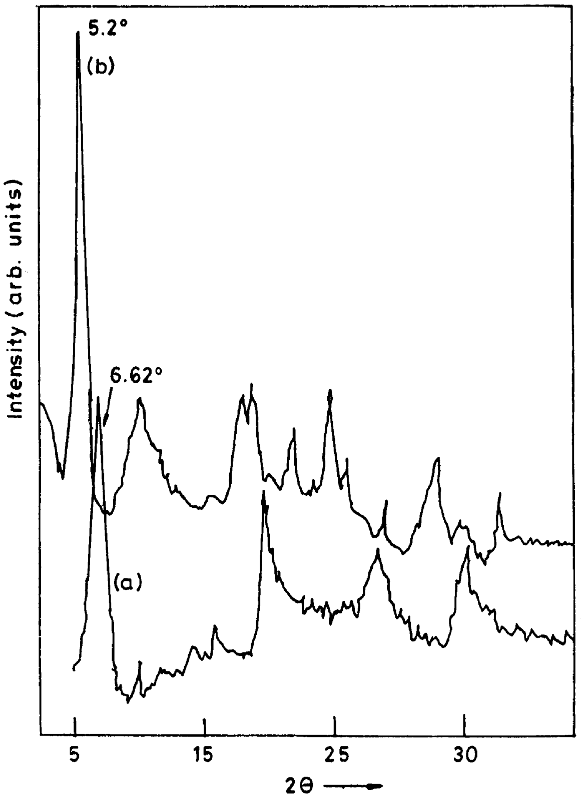

Figure 1 X-ray diffraction patterns of (a). Na^+ Bentonite (b). Organo clay.

3.2. Thermal analysis

Fig. 4 shows the TGA values for epoxy/organo clay nanocomposites. The curve shows that the decomposition of the sample takes place in single stage. For epoxy alone the weight loss starts at 280°C which gradually rises by further addition of the organoclay up to 340°C. The thermal decomposition of those nanocomposites shifts towards the higher temperature range which confirms the enhancement of thermal stability of the organoclay nanocomposites. Similar results are obtained in epoxy with unmodified clay as in Fig. 5, but there is a marginal shift in temperature of ~315°C in the decomposition range. This shows that modified clay is better weight loss arrester than unmodified clay composites. At around 600°C, all the curves merge together and became flat which indicates the presence of the inorganic residue (i.e., Al_2O_3, MgO, SiO_2) [23]. Hence, it is observed that the decomposition product is mainly due to the polymer matrix and not from the clay particles.

3.3. Tensile properties

The stress/strain curves for the epoxy with organoclays and unmodified clays under uniaxial tension are shown in Figs 6 and 7. Fig. 8 shows the variation of elastic

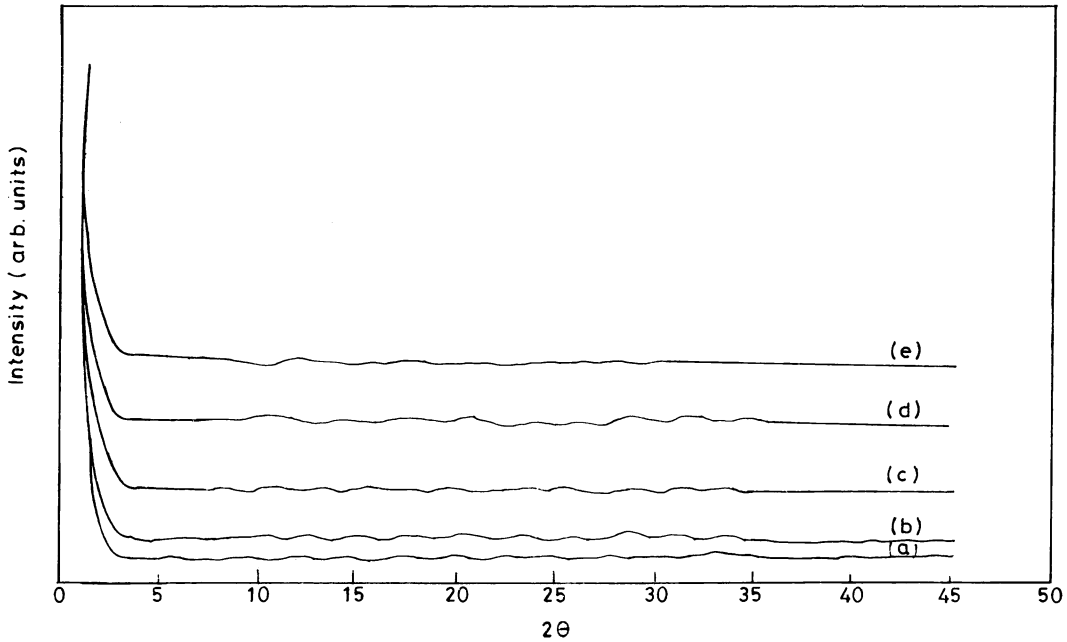

Figure 2 XRD pattern for epoxy with (a) 1% organoclay, (b) 2% organoclay, (c) 3% organoclay, (d) 5% organoclay and (e) 10% organoclay.

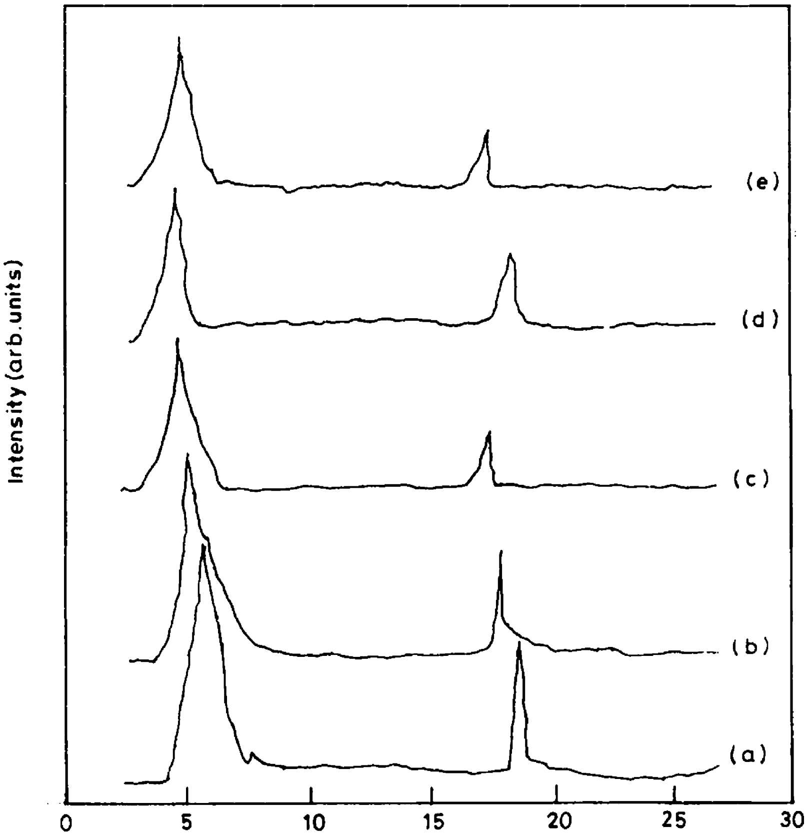

Figure 3 XRD pattern for epoxy with (a) 1% clay, (b) 2% clay, (c) 3% clay, (d) 5% clay, and (e) 10% clay.

modulus with organo clay and unmodified clay content. It is observed that the modulus of the nanocomposites increases continuously with increasing clay content. In epoxy/unmodified clay composite, there is not much improvement in the elastic modulus which indicates that the distribution of clay in the molecular level is absent and hence does not contribute to the molecular strength. An improvement in modulus of about three times is observed with an addition of 10 wt% of organoclay. There is reduction of strength at 2% and then increases gradually for the increase of organoclay up to 10 wt%. From Fig. 6, it is also observed that the epoxy with organoclay content, the improvement of elastic modulus is due to the exfoliation/intercalation of nanoscale clay particles in the matrix that restricts the mobility of polymer chains under loading. This is also due to the good interfacial adhesion between the particles and the epoxy matrix. The orientation of clay platelets and polymer chains with respect to the loading direction can also contribute

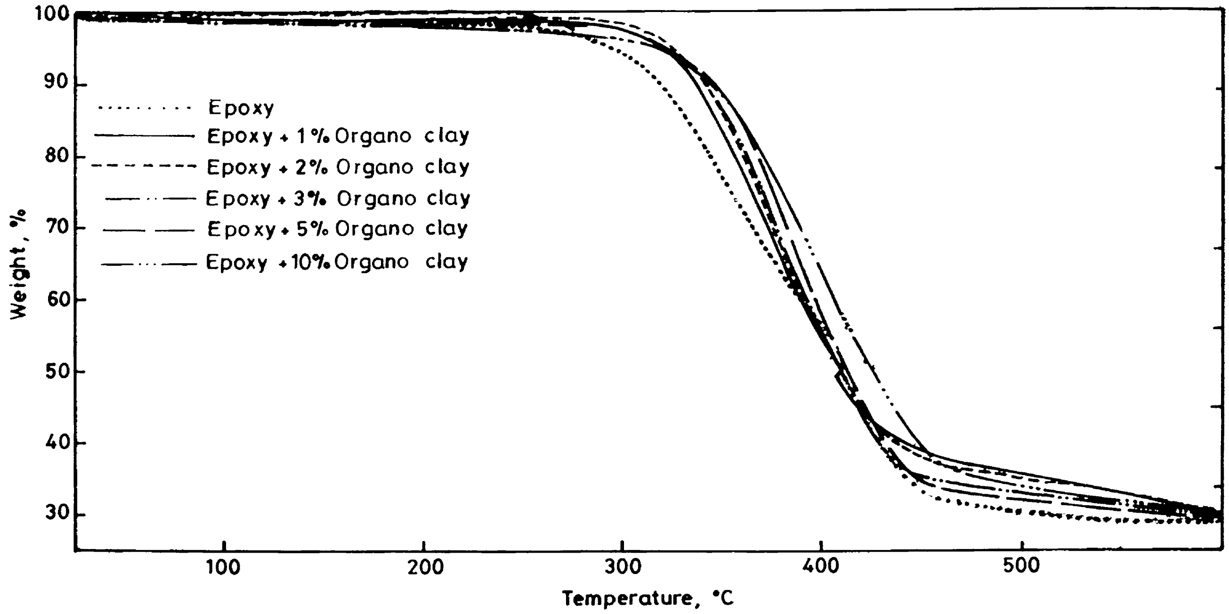

Figure 4 TGA thermograms of Epoxy/organoclay series.

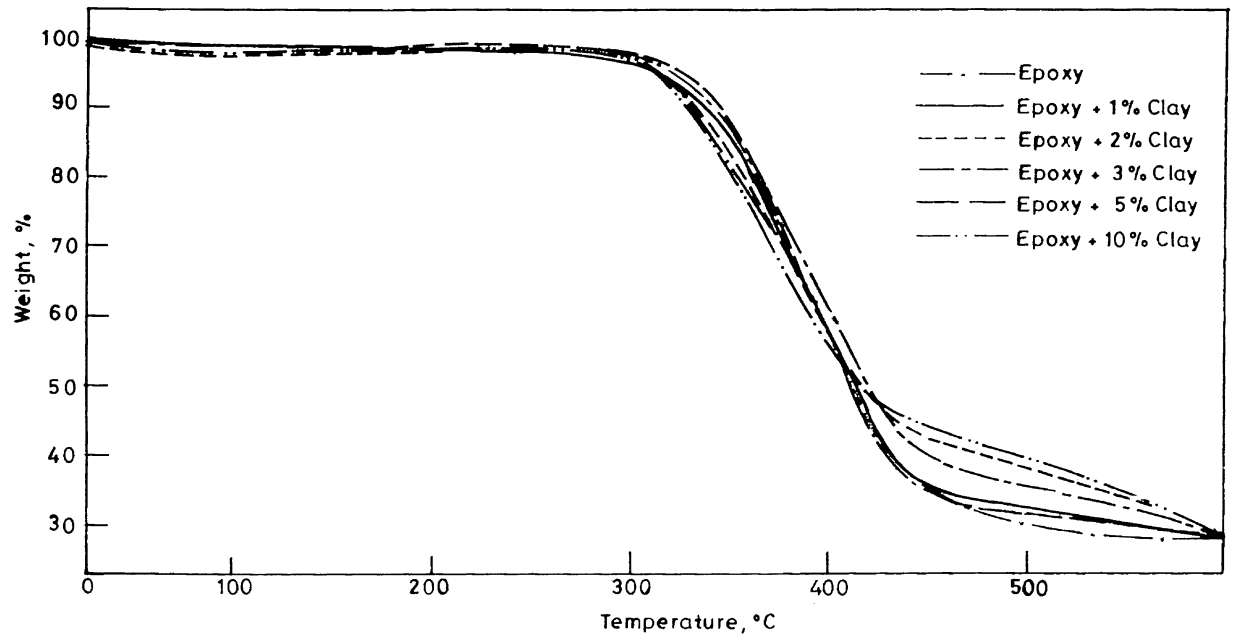

Figure 5 TGA thermograms of Epoxy/clay series.

to the reinforcement effects, however, the decreasing rate of elastic modulus improvement with higher clay content is due to the presence of excess unexfolifated aggregates.

The experimental results show that the tensile strength for all the clay contents is less than that of pure epoxy. This is similar to the results reported elsewhere [22, 24]. It requires further investigation of the processing technique to understand the reduction in strength of the nanocomposites. The compounding of nanoclay in an epoxy matrix with an electric mixer produces a highly viscous and foamy material. At higher clay content the viscosity is high. Furthermore, the ammonium ion used in this study is Garamite$^{®}$-1958 which can readily participate in the curing reaction and favors the exfoliation of the clay platelets [21]. As a result, the mixture becomes highly viscous with time and hinders the complete degassing before casting. It is also observed that for nanocomposites containing 5 or higher wt% of clay, the degassing problem becomes critical. This is due to the formation of voids which cause specimen failure at relatively low strains under tensile loading.

3.4. Dymamic mechanical properties

The effect of clay nanolayer reinforcement on the mechanical properties of the epoxy polymer was investigated by dynamic mechanical analysis (DMA). In the DMA technique an oscillatory force is applied to the sample and the response to that force is analyzed. Two different moduli are determined as a function of temperature, an elastic or storage modulus (E'), which is related to the ability of the material to return or store

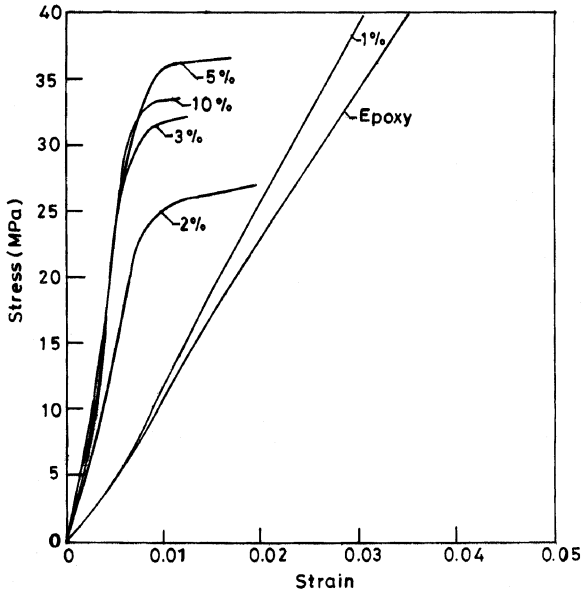

Figure 6 Stress/strain curve for Epoxy with different weight percent of organoclays.

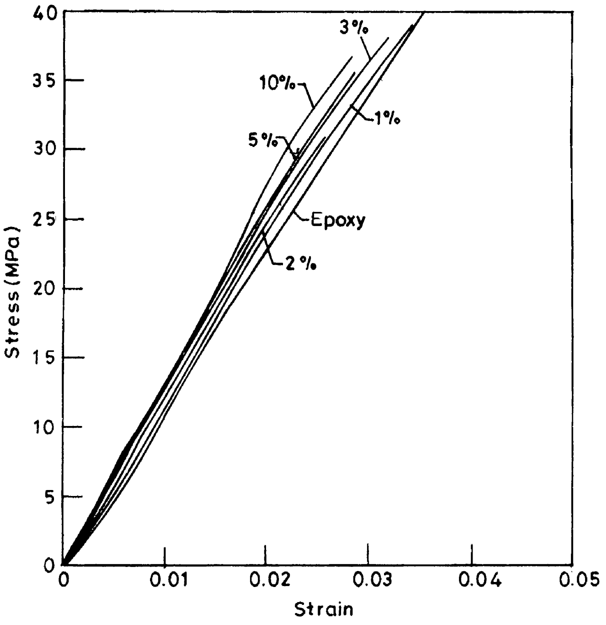

Figure 7 Stress/strain curve for Epoxy with different weight percent of clays.

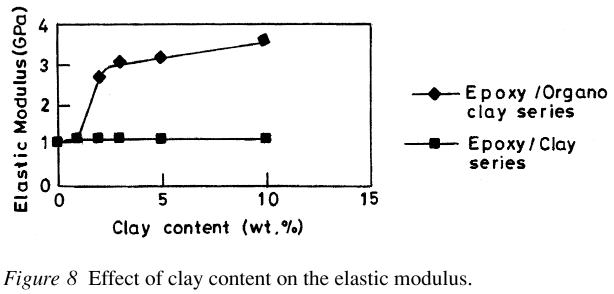

Figure 8 Effect of clay content on the elastic modulus.

energy, and an imaginary or loss modulus (E''), which relates the ability of the polymer to disperse energy. The temperature dependence of the ratio E''/E', also called tan delta (tanδ), is related to the mechanical properties of the (nano)composites. The maximum value in a tanδ vs. temperature plot is taken as an estimate of the glass transition temperature (T_g). The DMA results are to be carefully compared with previous ones as different modes such as flexure, torsional or oscillatory loads can also be applied to the sample [25]. Figs 9 and 10 show the variation of the storage modulus and tanδ with temperature, obtained by the three-point bending (flexural) DMA method for both organo and unmodified clay respectively.

Dynamic mechanical properties of epoxy/organoclay nanocomposites are shown in Fig. 9. Pure epoxy shows sharp damping peak at ~100°C and this temperature corresponds to glass transition temperature. On addition of organoclay the damping peaks splits into two segments (soft segment T_g and hard segment T_g) and also broadens the tanδ peaks as reported elsewhere [1, 26]. This is due to the arrest of the segmental motion at organic/inorganic interface with its neighborhood. The soft segment temperature for all the nanocomposites is less than the T_g of pure epoxy and that of the hard segments is higher than T_g of pure epoxy, while the broad shape of damping peaks suggest that there is partial phase mixing between soft and hard segments. The peak position temperature for the soft segment T_g increases with the addition of clay content, and the hard segment T_g is maximum for 10 wt% organoclay content. In Fig. 9, we can also see the large decrease in storage modulus, E', that occurs on heating at the T_g of soft segment, and also has constant E' value over a range up to the hard segment T_g. The improvement of E' by added clay is marginal at the temperature range below the T_g of hard segment. However, at the temperature range above the T_g of hard segment, the presence of clay evidently enhances the E' values. In general, Fig. 9 represents the increase of storage modulus E' at room temperature for epoxy/organoclay nanocomposites. Fig. 10 represents the epoxy/unmodified clay series which shows little improvement in modulus over the matrix material at room temperature.

3.5. Hardness

Fig. 11 shows the hardness of composites with modified and unmodified clays. For both composites, the Shore *D* hardness increases as clay content increases, but the rate of increase for epoxy/organoclay is higher than for unmodified clay composites. It can be further seen that for the organoclay from 1 to 5 wt% there is no increase in hardness, which shows that the resistance to indentation of (nano)composite is almost same. But for 10 wt% organoclay, the hardness reaches a maximum value of ~86. From Fig. 11, it is clear that the hardness increment is higher for organoclay nanocomposite than the unmodified clays.

3.6. Heat deflection temperature (HDT)

There is greater improvement in HDT for epoxy/organoclay than with unmodified clay as in Fig. 12. Up to 5 wt% of organoclay, the HDT continuously increases, and further addition of 10 wt% shows not much increase in HDT. Similar increase in HDT is obtained for unmodified clay contents up to 3 wt%. There is decrease in HDT on further addition of clays.

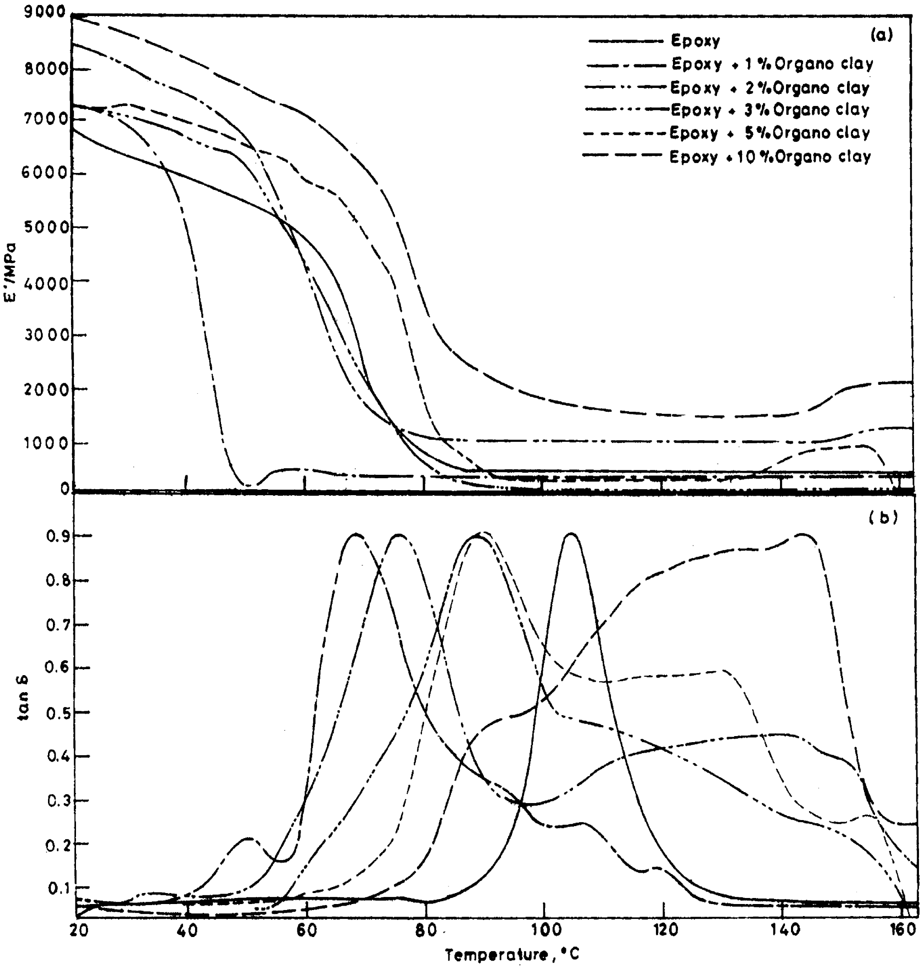

Figure 9 Temperature dependence of (a) Storage modulus (E′) and (b) tan δ for Epoxy/organoclay series.

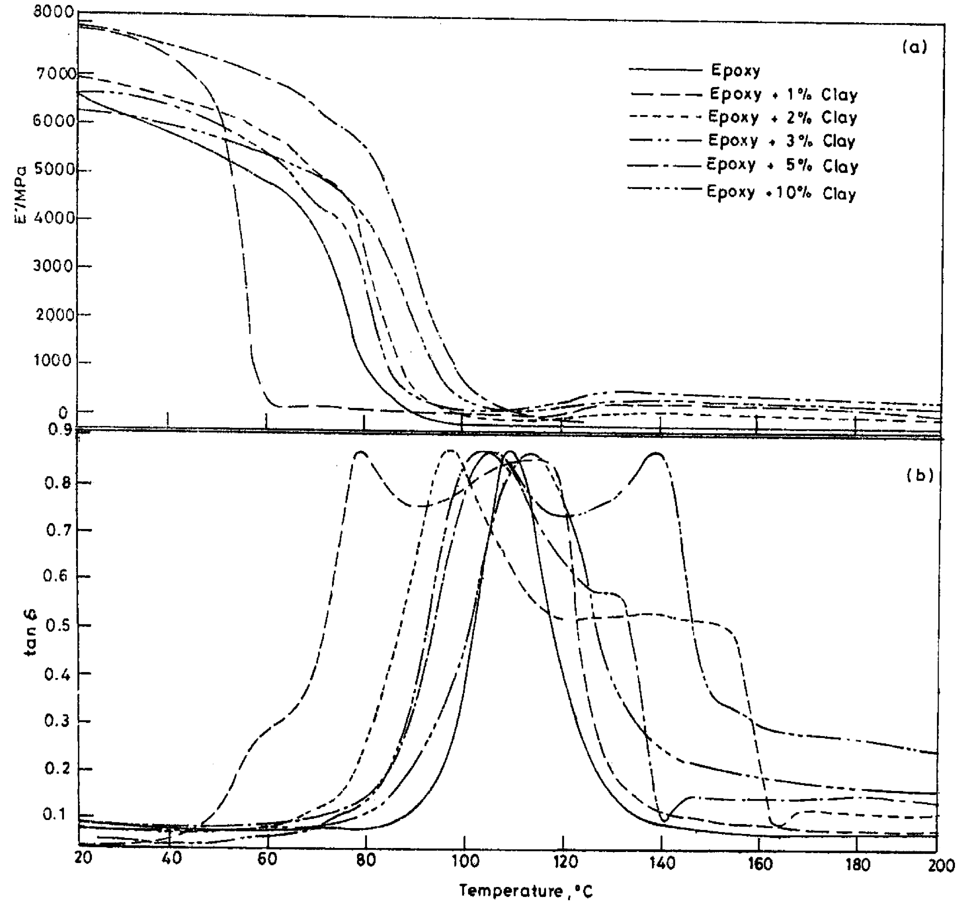

Figure 10 Temperature dependence of (a) Storage modulus (E′) and (b) tan δ for Epoxy/clay series.

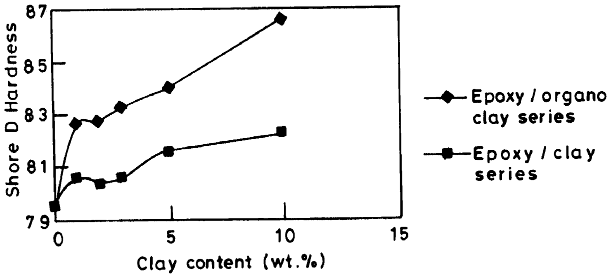

Figure 11 Hardness value for epoxy with modified and unmodified clay content.

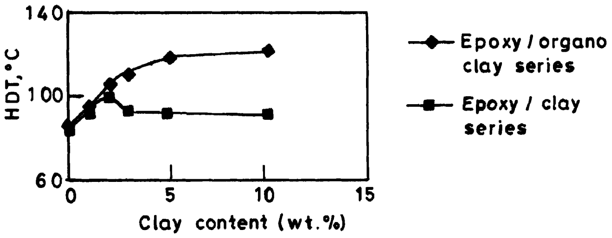

Figure 12 HDT value for epoxy with clay contents.

4. Conclusion

A series of epoxy/organoclay nanocomposites and unmodified clays has been prepared by high speed electric shear device at different clay loadings at room temperature. XRD results reveals the fully exfoliated or intercalated structure with a d-spacing of more than 70 nm in the epoxy with organoclay contents. There is very less or negligible increase in the d-spacing of the unmodified clay content in the epoxy matrix. TGA shows that the thermal stability of the nanocomposites is greater than for unmodified clay composites. DMA shows that the storage modulus for organoclay has increased about 1.8 times above that of the epoxy. With the unmodified clay loading conditions, there is very less or negligible increase in the d-spacing which suggests that the unmodified clays act as fillers in the epoxy matrix with not much improvement in properties. Initially the soft segment T_g is decreased but later it is improved with the clay loadings up to 10 wt% due to plasticizing effect from the presence of organic surfactants within the organoclay. The tensile tests indicate that the modulus in the epoxy filled with organoclay loadings is increased by 3 times over the epoxy. But in unmodified clay not much improvement is seen. In general, the degree of dispersion of nanoclay within polymer matrix plays a vital role in property improvement. The hardness and HDT shows that significant improvement can be achieved in the organoclay nanocomposites compared with the unmodified clays. The investigations on improving strength, its mechanism and the influence of nanoclay in structure-property correlations are still in progress.

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