

Mechanical and Morphological Properties of Organic–Inorganic, Hybrid, Clay-Filled, and Cyanate Ester/Siloxane Toughened Epoxy Nanocomposites

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ABSTRACT: Organic–inorganic hybrids involving cyanate ester and hydroxyl-terminated polydimethylsiloxane (HTPDMS) modified diglycidyl ether of bisphenol A (DGEBA; epoxy resin) filled with organomodified clay [montmorillonite (MMT)] nanocomposites were prepared via *in situ* polymerization and compared with unfilled-clay macrocomposites. The epoxy-organomodified MMT clay nanocomposites were prepared by the homogeneous dispersion of various percentages (1–5%), and the resulting homogeneous epoxy/clay hybrids were modified with 10% HTPDMS and γ -aminopropyltriethoxysilane as a coupling agent in the presence of a tin catalyst. The silicized epoxy/clay prepolymer was further modified separately with 10% of three different types of cyanate esters, namely, 4,4'-dicyanato-2,2'-diphenylpropane, 1,1'-bis(3-methyl-4-cyanatophenyl) cyclohexane, and 1,3-dicyanato benzene, and cured with diaminodiphenylmethane as a curing agent. The reactions during the curing process between the epoxy, siloxane, and cyanate were confirmed by Fourier transform

infrared analysis. The results of dynamic mechanical analysis showed that the glass-transition temperatures of the clay-filled hybrid epoxy systems were lower than that of neat epoxy. The data obtained from mechanical studies implied that there was a significant improvement in the strength and modulus by the nanoscale reinforcement of organomodified MMT clay with the matrix resin. The morphologies of the siloxane-containing, hybrid epoxy/clay systems showed heterogeneous character due to the partial incompatibility of HTPDMS. The exfoliation of the organoclay was ascertained from X-ray diffraction patterns. The increase in the percentage of organomodified MMT clay up to 5 wt % led to a significant improvement in the mechanical properties and an insignificant decrease in the glass-transition temperature versus the unfilled-clay systems. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1263–1273, 2007

Key words: clay; mechanical properties; morphology; nanocomposites; polysiloxanes

INTRODUCTION

Nanostructured, hybrid, organic–inorganic composites have attracted considerable attention recently, both with respect to fundamental research and from an application point of view.^{1–3} The inclusion of metal oxide particles in organic polymer matrices via a sol-gel process is an effective approach toward enhancing the mechanical properties of matrices.^{4,5} Inorganic materials that can be broken down into nanoscale building blocks, such as montmorillonite (MMT) clays, can be superior alternatives to the sol-gel process for the preparation of nanostructured, hybrid, organic–inorganic composites.⁶ Polymer/clay nanocomposites are organic–inorganic nanocomposites that possess dramatically improved properties because of nanometer-sized dispersions of organically modified

clay in the polymer matrix.^{6–8} For example, the incorporation of a few percent of clay into polymer matrices brings appreciable increases in the modulus, strength, gas-barrier properties, thermal stability, flame retardancy, and heat distortion temperature in comparison with pristine polymers.⁹

Toyota researchers demonstrated that an exfoliated, organoclay-filled nylon 6 matrix possesses greatly improved thermal, mechanical, barrier, and even flame-retardant properties.^{10,11} This approach has since been extended to other polymers such as polyimide, polyamide, unsaturated polyester, polyoxyethylene, polystyrene, polystyrene maleic anhydride, amine-terminated butadiene acrylonitrile, poly(methyl methacrylate), polypropylene, poly[oligo(oxyethylene)] methacrylates, polyurethane, and poly(butylene terephthalate).¹² There has been intense interest in epoxy/clay nanocomposites because such materials have been demonstrated to possess significantly improved physical properties over pristine polymers and epoxy crosslinked polymers, which have excellent chemical resistance, good electrical insulation properties, and good adhesion to glass and

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metals and can be easily fabricated.^{13–15} Epoxies are widely used in the aerospace and automobile industries in the areas of structural composites and adhesives and in the electronic industries for encapsulating electrical circuit components and electronics packaging.^{16,17} However, the important problems in engineering applications of epoxy thermosets include low stiffness and strength and also the exothermic heat generated by the curing of epoxy resins, which causes serious processing difficulties.¹⁸ Messersmith and Giannelis¹⁹ reported that exfoliated epoxy/clay nanocomposites were obtained when anhydride was used as a curing agent. Wang and Pinnavaia²⁰ and Lan and coworkers^{21,22} conducted more intensive investigations of epoxy/clay nanocomposites and found that the exfoliation behavior of clay was determined mainly by the structure of the organoclay and the curing temperature adopted. Ashok Kumar et al.²³ studied hydroxyl-terminated polydimethylsiloxane (HTPDMS) as a toughening agent for the epoxy resin and found that HTPDMS is the most suitable polymer for epoxy modification because of its versatile behavior, such as flexibility due to —Si—O—Si— linkages, high thermal and thermooxidative stability, high moisture resistance, good dielectric properties, and excellent UV and chemical resistance. They also found that 10 wt % HTPDMS is optimum. Dinakaran and Alagar²⁴ investigated the modification of an epoxy resin with cyanate esters as coreactive components (4–12 wt %) and the formation of flexible oxazolidinone aliphatic cyclic rings. Cyanate esters chemically react with epoxy and form hybrid polymers, which exhibit low dielectric constants (2.5–3.1), thermal and mechanical characteristics, and water absorption (0.6–2.5%), excellent heat and chemical resistance, and low volume shrinkage; this makes them materials of choice in high-performance applications.^{25,26}

Although the incorporation of siloxane and cyanate ester into epoxy systems improves the impact strength and thermal stability,^{23–27} it reduces the stress–strain properties and glass-transition temperature (T_g). To prevent the loss of stress–strain properties, organically modified MMT clay (0–5%) is incorporated with a siliconized cyanate ester/epoxy matrix via a cation-exchange process because of the formation of an exfoliated nanostructure with improved thermomechanical properties, such as high crosslinking ability and high strength.^{16,28}

Therefore, in this study, an attempt was made to improve both the toughness and strength of an epoxy resin without an appreciable loss in the glass–rubber transition temperature through the formation of an exfoliated network of cyanate ester-siliconized epoxy and organically modified MMT clay via the *in situ* polymerization method with HTPDMS and three different cyanate esters as chemical modifiers. The mechanical and morphological properties of the hybrid epoxy

nanocomposites were also studied and compared with various concentration of the clay and three different types of cyanate esters.

EXPERIMENTAL

Materials

A commercially available epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] called LY 556, having an epoxy equivalent of about 180–190, and diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy, Ltd. (India). Cyanogen bromide, cyclohexanone, bisphenol A, resorcinol, and *O*-cresol (SRL, India) were used as received. MMT K10 and HTPDMS, (molecular weight of 17,000–18,000 g/mol and a viscosity of 800–900 cP), were purchased from Aldrich Chemicals. Cetyl ammonium bromide, cross-linking agent γ -aminopropyltriethoxysilane (γ -APS), and catalyst dibutyl tin dilaurate were obtained from Lancaster and E-Merck (India).

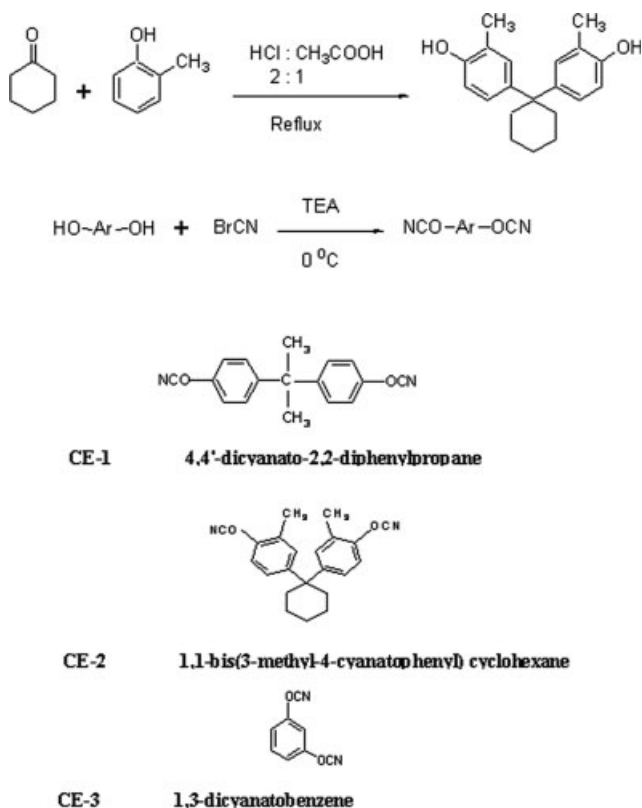
Synthesis of 1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane

Cyclohexanone (0.05 mol), *o*-cresol (0.1 mol), and a mixture of hydrochloric acid and acetic acid (2 : 1 v/v) were reacted at 50°C. The pink product was isolated, washed with water to remove acid, dissolved in a 2M NaOH solution, kept overnight and filtered to remove resinous material, acidified with dilute hydrochloric acid, filtered, washed with distilled water, and dried at 90–100°C (Scheme 1).

Yield: 81%. mp: 186°C. IR (KBr, cm^{-1}): 3536, 3407 (O—H), 2926, 1600, 1506, 1450, 1268, 1174, 1119, 1032, 895. ¹H-NMR (ppm): δ 1.24–2.03 (m, 4H), 2.31 (s, 6H), 3.24–3.45 (m, 6H), 6.67 (d, $J = 8.3$ Hz, 2H), 6.86 (d, $J = 8.3$ Hz, 2H), 8.54 (s, 2H). ¹³C-NMR (ppm, CDCl_3-d_6): δ 154, 139.6, 129.4, 125.0, 123.6, 114.3 (C aromatic); 44.3, 37.0, 26.3, 22.8, 16.5 (C aliphatic).

Synthesis of the cyanate esters

To a 1-L, three-necked flask fitted with a paddle stirrer and nitrogen inlet was added 1 mol of diol in 600 mL of acetone; CNBr (2 mol) in acetone (100 mL) was added dropwise and was followed by triethylamine (2.2 mol), which was also added dropwise. The reaction was continued for 1 h at –15°C; the contents became pale yellow and were filtered under a vacuum to separate triethylammonium bromide. The product in acetone was precipitated by the addition of ice-cold water. The white solid obtained was filtered and recrystallized from water/methanol (1 : 1) under ice-cold conditions. The yield and melting point of 4,4'-dicyanato-2,2'-diphenylpropane were 64% and 78°C,



Scheme 1 (a) Synthesis of 1,1-bis(3-methyl-4-hydroxy phenyl) cyclohexane and cyanate esters and (b) Synthetic route of cyanate esters.

respectively; the yield and melting point of 1,1'-bis(3-methyl-4-cyanatophenyl) cyclohexane were 76% and 82.9°C, respectively; and the yield and melting point of 1,3-dicyanobenzene were 68% and 101°C, respectively. The structures of all the cyanate esters are shown in Scheme 1.

Preparation of the siliconized epoxy prepolymer

A fixed amount of the epoxy resin, 10% HTPDMS, a stoichiometric amount of γ -APS (with respect to the hydroxyl groups of HTPDMS), and the catalyst dibutyl tin dilaurate were thoroughly mixed at 90°C for 30 min with constant stirring. The product was then degassed to remove ethanol that formed during the condensation reaction between γ -APS and HTPDMS, as shown in Scheme 2.

Preparation of the cyanate ester modified, siliconized epoxy blends

A fixed amount of the siliconized epoxy resin, 10 wt % cyanate ester, and a stoichiometric amount of DDM (with respect to the epoxy) were thoroughly blended at 100°C for 10 min with constant stirring. The product was then degassed to remove entrapped air, poured

into a preheated mold, kept at 140°C for 3 h, and post-cured at 200°C for 2 h.

Preparation of the organically modified clay

Crude MMT clay (25 g) was treated with 5 L of a 0.1N solution of NaCl with 24 h of continuous stirring at 70°C. Upon the centrifugation of the solution at a high speed, an opaque, whitish layer accumulated in the bottom of the centrifuge tubes beneath a translucent gel. The gel was isolated and washed several times with deionized water until no chloride was detected. Then, purified Na-MMT clay was dried at 70°C and stored in a desiccator.

Then, 15 g of the purified MMT clay was dispersed into 1200 mL of distilled water at 80°C. Cetyl ammonium bromide (5.7 g) in 300 mL of distilled water was poured into the hot MMT/water solution and stirred vigorously for 1 h at 80°C. A white precipitate was formed, isolated by filtration, and washed several times with a hot water/ethanol (1 : 1) mixture until no bromide was detected in the filtrate by one drop of a 0.1N AgNO₃ solution. The cetyl ammonium ion exchanged MMT was then dried for several days at 75°C and ground with a mortar and pestle, and then the less than 50- μ m fraction was collected. The organophilic clay was stored in a desiccator.

Preparation of the epoxy/clay nanocomposites

Before curing, the epoxy resin was blended with the desired amount of the organophilic clay via mechanical stirring at 70°C for 24 h. A stoichiometric amount of the curing agent corresponding to epoxy equivalents was added. The product was subjected to a vacuum to remove trapped air and then was cast and cured at 140°C for 3 h. The castings were then post-cured at 200°C for 2 h and were finally removed from the mold and characterized.

Characterization

Fourier transform infrared (FTIR) spectra were recorded with a PerkinElmer 781 infrared spectrometer with KBr pellets for solid samples. The viscous samples were directly applied by being dabbed onto a KBr pellet. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400-MHz NMR spectrometer with CDCl₃ as the solvent.

The tensile properties were determined with an Instron model 6025 UK per ASTM D 3039. The sample dimensions were 25 × 10 × 3 mm³. The flexural strength was measured with an Instron model 4031 per ASTM D 790, and the Izod impact strength was studied per ASTM D 256.

Dynamic mechanical analysis (DMA) of the samples was determined with a Netzsch DMA 242 between

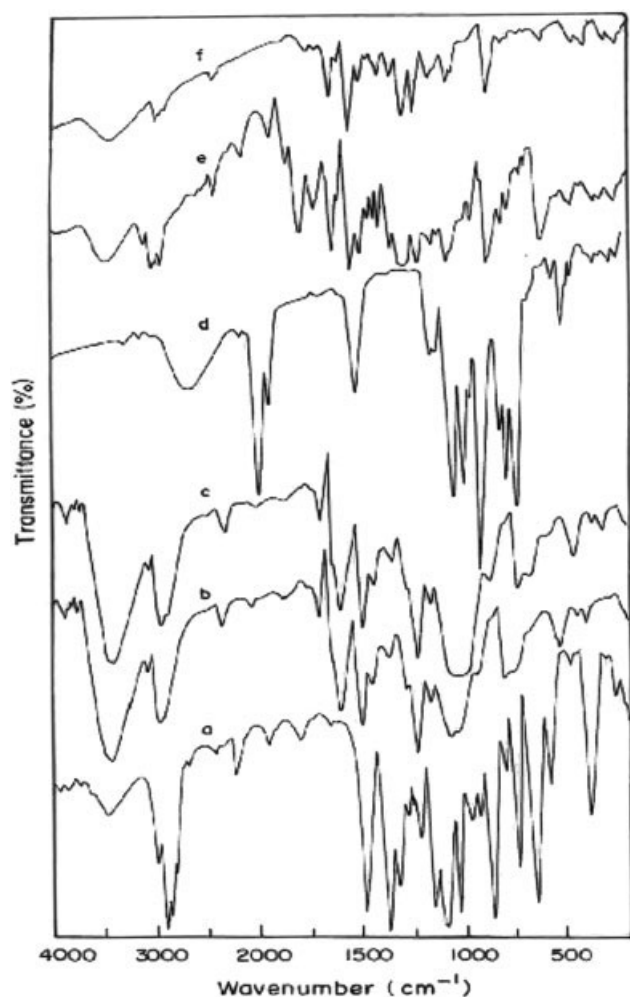


Figure 1 FTIR spectra of (a) neat epoxy, (b) γ -APS-cured epoxy, (c) siloxane-modified epoxy, (d) pure cyanate ester (CE-2), (e) cyanate ester (CE-2) silicized epoxy after heating at 140°C for 3 h, and (f) cyanate ester (CE-2) silicized epoxy cured with DDM at 140°C for 3 h and postcured at 200°C.

peak at 2253 cm^{-1} in Figure 1(d), which has vanished for the epoxy-cured cyanate ester systems. The cyclotrimerization of cyanate groups, followed by the reaction with epoxy groups, results in the formation of several intermediates, including isocyanurate, oxazoline, and oxazolidinone.^{24–27}

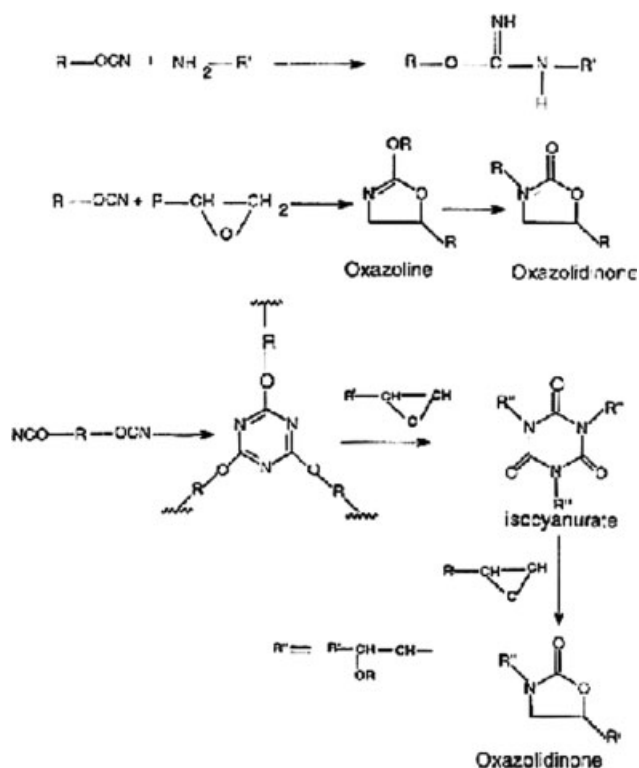
The appearance of new absorption bands at 1750 cm^{-1} in Figure 1(e) due to the formation of oxazolidinone and other absorptions bands at 1650, 1690, and 1750 cm^{-1} is due to the formation of products such as oxazoline, isocyanurate, and cyanurate, respectively. Furthermore, it is also evidenced that the reaction of epoxy and isocyanurate causes a considerable decrease in the intensity of the epoxy band at 914 cm^{-1} .

FTIR spectra of the DDM-cured, cyanate ester silicized epoxy [Fig. 1(f)] system shows absorption peaks at 1750 and 1690 cm^{-1} , which confirm the for-

mation of oxazolidinone and isocyanurate. There is no absorption for the triazine vibration at 1565 cm^{-1} , and this further confirms the conversion of cyanurate into oxazolidinone and isocyanurate by the reaction with the epoxy resin.

DMA

Shown later in Figure 4(a,b) are the dynamic mechanical spectra of the unfilled and filled MMT clays in cyanate ester/siloxane toughened epoxy matrices, respectively. The dynamic mechanical spectrum of the DDM-cured epoxy resin exhibits a well-defined relaxation peak centered at 164.8°C, which is ascribed to the glass–rubber transition of the polymer. The dynamic mechanical spectra of all the systems clearly display single α transitions on the internal friction ($\tan \delta$)/temperature curves. The α transition slightly shifted to a lower temperature upon the addition of the cyanate ester and HTPDMS into the DGEBA epoxy systems. Figure 2 clearly displays single α transitions for the silicized epoxy system and (CE-1) cyanate ester silicized epoxy at 163.6 and 163.0°C, respectively, which could be related to the glass–rubber transition. The loss tangent is a sensitive indicator of crosslinking, and T_g , the $\tan \delta$ relaxation, is inversely proportional to the crosslink density. The siloxane and cyanate ester introduced epoxy systems have lower crosslink densities, and subsequently, the glass–



Scheme 3 Reactions during the curing process between cyanate ester and epoxy-functional groups.

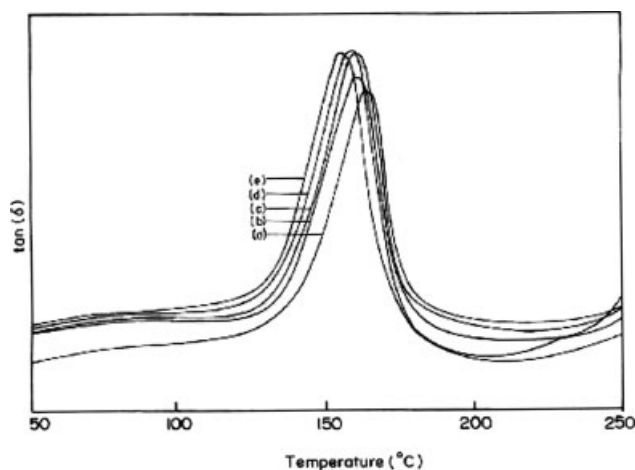


Figure 2 Variation of $\tan \delta$ as a function of the temperature of (a) neat epoxy and (b) 10% HTPDMS, (c) 10% HTPDMS and 10% CE-1, (d) 10% HTPDMS and 10% CE-2, and (e) 10% HTPDMS and 10% CE-3 modified epoxy systems.

rubber transition shifted to a lower temperature.^{23,24,27} The lower crosslink density is confirmed by the greatest height of the $\tan \delta$ relaxation observed in Figure 2, which is indicative of greater relaxation strength in comparison with neat epoxy. The reasons for the lower crosslink density and reduced T_g may be the presence of freely rotating $-\text{Si}-\text{O}-\text{Si}-$ linkages and the formation of aliphatic oxazolidinone rings by the reaction of cyanate ester with an epoxy ring (as shown in Scheme 1) through the incorporation of HTPDMS and cyanate ester, respectively.

For the MMT clay filled hybrid epoxy systems, the α transition (as shown in Fig. 3 and Table I) further shifted to a lower temperature than those of unfilled-clay/epoxy systems when the contents of siloxane and cyanate ester were the same. The effect on T_g by the addition of an organoclay into epoxy has been widely studied, with many investigators reporting an increase in T_g values,²⁹ whereas others have found a slight decrease^{30,31} or no change. Dinakaran et al.,²⁴ Becker et al.,³² and Kornmann et al.³³ observed a reduced T_g with clay addition and theorized that this may have been the result of a number of factors, such as changes in the reaction chemistry (catalyzed epoxy homopolymerization of epoxy during a swelling period by cetyl ammonium cation), a thermal degradation of the surface modifier, a plasticizing effect of unreacted resin or hardener monomers, or an increase in the free volume of the hybrid systems. Nonetheless, FTIR spectroscopy shows that the curing reactions occurred to completion for the composite for this composite system. In this case, the presence of aliphatic surfactant chains (cetyl ammonium ion) in the organo-modified MMT clay could have been responsible for the insignificant depression in the glass–rubber transition temperature for the clay-filled nanocomposites,

which is comparable to the internal plasticization effect. The lower relaxation strength present in the organoclay-filled epoxy systems versus the unfilled-clay system can be observed in Figure 3. The lower relaxation strength or higher crosslinking may be due to the exfoliation of the polymer molecules between the clay layers, which greatly reduces their molecular mobility; this is confirmed by XRD and mechanical studies because the relaxation strength is associated with molecular mobility.²⁴

Figure 4 shows that with the inclusion of MMT clay in the matrix, the systems displayed increased storage moduli of glassy and rubbery states in comparison with the unfilled-clay systems. In the glassy state, the dynamic storage moduli of all the clay-filled hybrid systems are significantly higher than those of the neat epoxy, and the moduli increase with an increasing concentration of the MMT clay in the epoxy matrices.³⁴ In the clay-filled hybrid systems, the organo-modified MMT clay dispersed homogeneously in the epoxy matrices at the nanometer level, and thus the increased modulus could be attributed to the nano-reinforcement effect of the organo-modified MMT clay on the epoxy matrix. A higher rubbery-state modulus at $T > T_g$ was observed in the organo-modified MMT clay filled hybrid epoxy systems than in the neat epoxy systems. The moduli of the rubber plateau for polymer networks are generally related to the crosslinking density of the materials. The storage moduli of the clay-filled nanocomposites are significantly higher than those of the neat epoxy, implying the significant nanoreinforcement of the organo-modified MMT clay, which induces the formation of the crosslinking networks of the epoxy resin.³⁵ In this work, the nanoreinforcement of organo-modified MMT clay could be the dominant factor affecting the moduli of the nanocomposites.

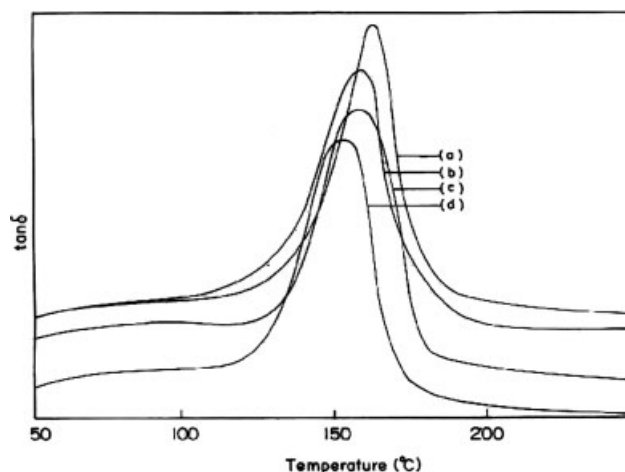


Figure 3 Variation of $\tan \delta$ as a function of the temperature of (a) 0, (b) 1, (c) 3, and (d) 5% clay filled, cyanate ester/siloxane modified epoxy systems.

TABLE I
Data on the Thermal and Morphological Properties

System ^a	T_g from DMA (°C)	Storage modulus (MPa)	SEM morphology observations	Exfoliation observed after 24 h of swelling at 70°C
A	164.8	2911.2	Homogeneous	—
BC ₅	160.2	4117.6	Heterogeneous	Yes
D ₁ C ₅	152.8	3965.1	Heterogeneous	Yes
D ₂ C ₅	151.4	4007.6	Heterogeneous	Yes
D ₃ C ₅	149.7	3891.2	Heterogeneous	Yes

^a A = neat epoxy; BC_x = organoclay-reinforced siliconized epoxy; D_yC_x = organoclay-reinforced, cyanate ester siliconized epoxy; x = weight percentage of the organoclay (0–5); y = type of cyanate ester (CE-1, CE-2, and CE-3) used in the hybrid system.

Mechanical properties

The introduction of HTPDMS into the epoxy resin decreased the tensile strength and modulus as well as the flexural strength, and this may be explained by the presence of flexible siloxane linkages, weak interfacial attractive forces of pendant methyl groups present in the HTPDMS, and a weak interface boundary between the siloxane and epoxy matrix.²³ In Figures 5–9, the matrices involving cyanate esters in the siliconized epoxy prepolymer show an increasing trend for the flexural strength and modulus and a decreasing trend for the tensile properties. This may be due to the formation of an aliphatic oxazolidinone ring between the cyanate ester and epoxy matrix, which exhibits a more thermoplastic character and imparts resistance to bending stress and improved toughness.^{24,36} The improvement in the impact strength is observed with the incorporation of both siloxane and cyanate ester, and this may be due to high-energy absorption, chain entanglement between the epoxy and cyanate ester resin, and resilient behavior of the flexible siloxane molecule.

The tensile properties of nanocomposites formed from organomodified MMT clay were measured to determine the effect of interfacial properties on rein-

forcement. Figures 5 and 6 compare the tensile strengths and moduli as functions of the clay loading. XRD and IR results indicated that all the clay nanolayers were fully exfoliated and that the matrix was fully cured. Clay-filled hybrid nanocomposite systems behave similarly, with the tensile strength and modulus increasing with the clay loading. A clay loading up to 5 wt % improves the tensile strength by 2.5 and 55% in comparison with neat epoxy and cyanate ester/siloxane toughened epoxy systems, respectively.

In addition, the clay loading in the completely exfoliated hybrid nanocomposites increases the values of the flexural strength and modulus as well as the impact strength in comparison with unfilled-clay/resin systems, as shown in Figures 7 and 8. Normally, reinforced composites exhibit a decrease in the elasticity with respect to the neat resin systems. Wang and Pinnavaia³⁷ attributed the improvement of both the toughness and strength in the case of the exfoliated nanocomposites in part to the plasticizing effect of the dangling (surfactant) chains in the polymer matrix and the reinforcement effect of the nanolayers. This may be attributed by nanolevel reinforcement of organomodified MMT clay and the ability to hinder the molecular motions and network junctions. When

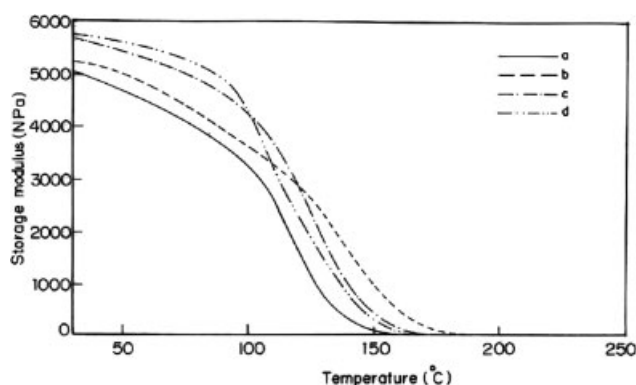


Figure 4 Effect of clay on the storage modulus for (a) neat epoxy and (b) 1, (c) 3, and (d) 5% clay filled, cyanate ester/siloxane epoxy nanocomposites.

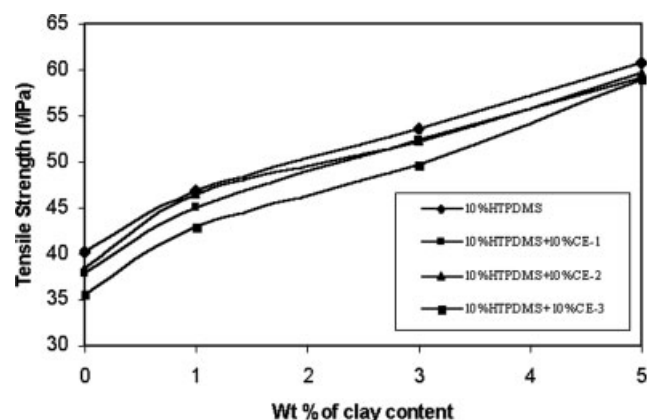


Figure 5 Effect of clay on the tensile strength in cyanate ester/siloxane epoxy nanocomposites.

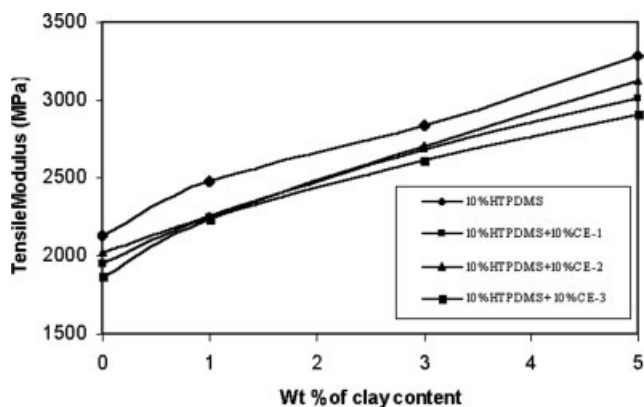


Figure 6 Effect of clay on the tensile modulus in cyanate ester/siloxane epoxy nanocomposites.

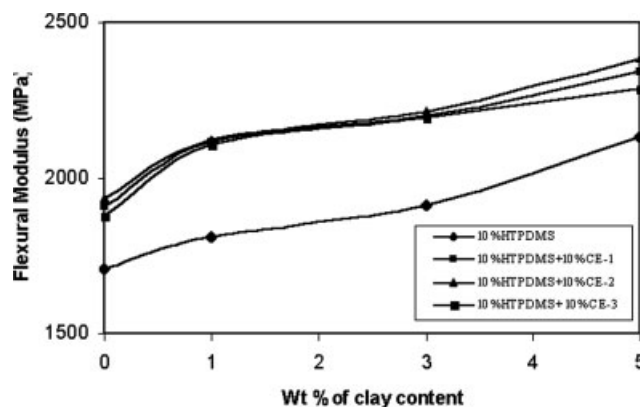


Figure 8 Effect of clay on the flexural modulus in cyanate ester/siloxane epoxy nanocomposites.

the clay content was 5 wt %, the impact strength of the hybrid systems was improved by 66% in comparison with the neat epoxy, and it was improved by 35% in comparison with the cyanate ester siliconized epoxy, as shown in Figure 9. The flexural strength in the hybrid systems was enhanced by 12 and 40% in comparison with the neat epoxy and cyanate ester siliconized epoxy systems, respectively.

Scanning electron microscopy (SEM) investigation

The morphology of the organic–inorganic hybrid systems was investigated by means of SEM and is shown in Figure 10. The SEM photograph in Figure 10(b) clearly proves that the organoclay-filled epoxy is homogeneous with no phase separation between the silicate layers and epoxy matrix and with excellent adhesion between the MMT layers and the epoxy matrix.^{12,24} The excellent adhesion could be due to the formation of intermolecular specific interactions between cetyl ammonium ion modified clay and DGEBA and hence the formed exfoliated structure.

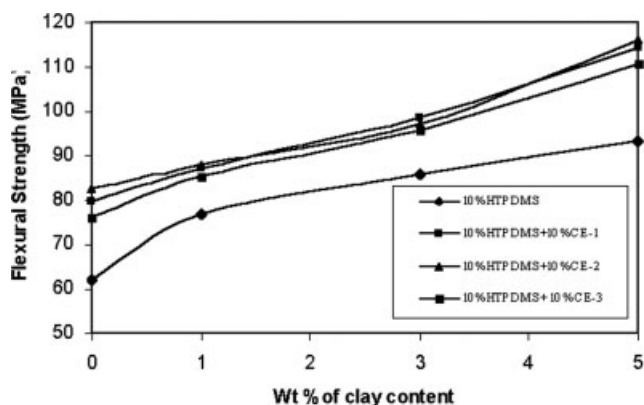


Figure 7 Effect of clay on the flexural strength in cyanate ester/siloxane epoxy nanocomposites.

The homogeneous dispersion of epoxy/clay hybrid systems gradually became highly translucent with the polymerization process through the introduction of HTPDMS into the system and showed a heterogeneous morphology. The occurrence of possible phase separation is induced by the polymerization of siloxane and the partial incompatibility of HTPDMS with epoxy. The discrete, spherical, siloxane-rich particles were uniformly dispersed in the continuous epoxy matrix, as shown in Figure 10(c), which further confirms the visual observation of translucence. This may be due to the fact that HTPDMS is chemically bonded with the epoxy resin through γ -APS. The two-phase morphology with a uniformly dispersed domain is one of the familiar characteristics of phase separation.

Dinakaran et al.²⁴ reported a homogeneous morphology for both cyanate ester and organoclay modified epoxy systems. In this work, the fractured surface of the organoclay-filled, cyanate ester siliconized epoxy systems revealed a heterogeneous morphology due to the partial incompatibility of HTPDMS and a uniform dispersion of the siloxane moiety through the crosslinking agent in the heterogeneous morphology,

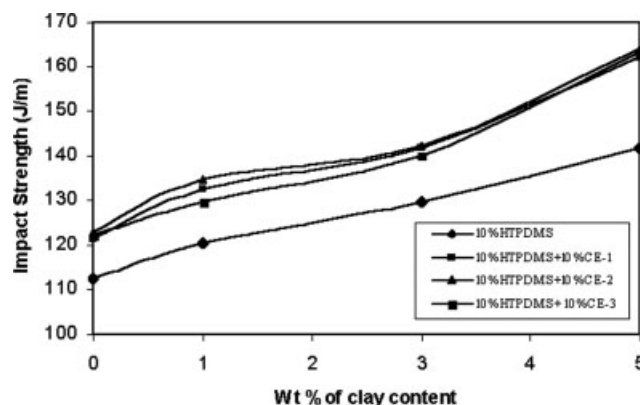


Figure 9 Effect of clay on the impact strength in cyanate ester/siloxane epoxy nanocomposites.

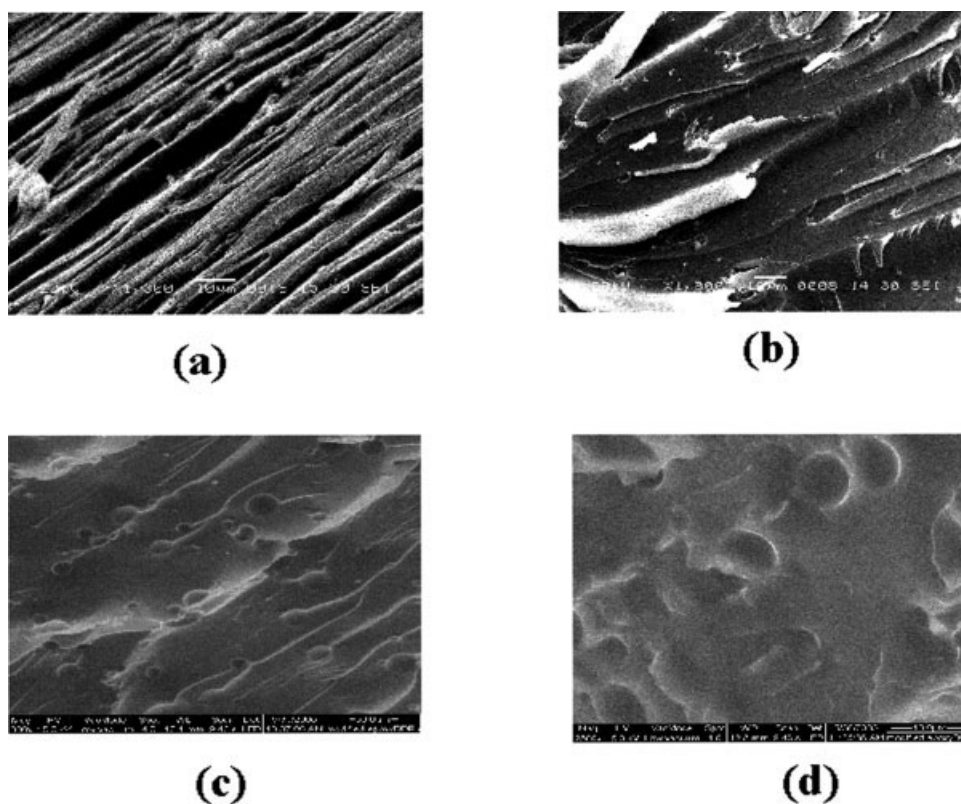


Figure 10 SEM micrographs of (a) neat epoxy, (b) 5 wt % clay reinforced epoxy, (c) 5 wt % clay reinforced and 10 wt % HTPDMS modified epoxy, and (d) 5 wt % clay reinforced and 10 wt % cyanate ester (CE-2) and 10% HTPDMS modified epoxy.

as shown in Figure 10(d). The uniform dispersion of the siloxane moiety in the hybrid systems has given additional support for the chemical reaction between HTPDMS, γ -APS, and epoxy resin.

XRD analysis

The XRD profiles of hybrid epoxy/clay nanocomposites are shown in Figure 11. The organoclay-modified epoxy system shows diffraction peaks that are identical to the observation reported earlier for a similar system^{24,30} In Figure 11, XRD patterns reveal the changes in the basal spacing during the preparation process of the epoxy/clay composites. The characteristic diffraction peaks are at $2\theta = 26^\circ$ ($d_{001} = 3.42 \text{ \AA}$) for the organic clay [Fig. 11(a)]. The diffraction peaks at $2\theta = 18.5^\circ$ ($d_{001} = 4.97 \text{ \AA}$) for the organoclay-modified epoxy after a swelling period of 8 h at 70°C are compared with those of the original clay; the peaks appeared slightly toward lower 2θ values (large d spacings) and produced a pattern consistent with intercalation, as shown in Figure 11(b). The increased d -spacing suggests that the organic molecule of the cetyl ammonium ion diffused into the gallery between the organo-MMT clay and epoxy. Remarkably, on continued heating at the same temperature, the peaks broadened and nearly disappeared after 24 h of swel-

ling, as shown in Figure 11(c–e), even when the clay loading was increased to 5 wt %. The absence of a diffraction peak confirmed the formation of an exfoliated structure. The exfoliation of the clay layers is caused by the diffusion of epoxy molecules into clay galleries; the d -spacing between all pairs of clay layers should increase and assume a Gaussian distribution. Moreover, the d -spacing should increase continuously during the curing process until gelation occurs. However, the d -spacing increased from an intercalated state to an exfoliated state only after curing was continued for a specified period of time, indicating that the transition might have taken place at a specified period of time. The increase in the d -spacing from the intercalated state to the exfoliated state suggests the formation of a high degree of adsorption between the epoxy and cetyl ammonium ion held by van der Waals forces. Because the interlayer surface is organophilic and has a greater tendency to adsorb organic molecules, an exfoliated nanocomposite is achieved. This is in good agreement with observations made by Park and Jana³⁸ and Becker et al.³²

The introduction of a siloxane moiety into the clay-filled hybrid epoxy systems shows the insignificant effect on the exfoliated structure in hybrid systems, and this may be due to the increase in the viscosity and the formation of a heterogeneous morphology.

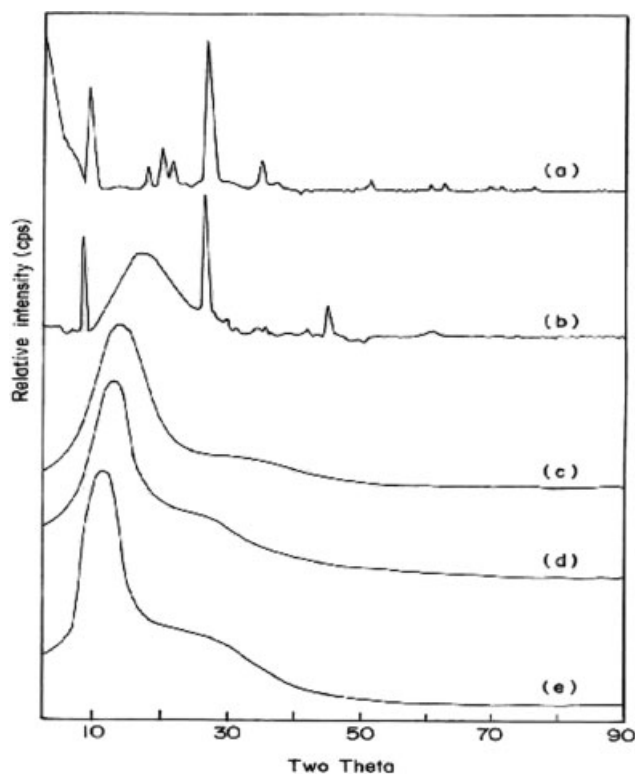


Figure 11 XRD patterns of (a) MMT clay, (b) epoxy/clay (5%) cured after swelling at 70°C for 8 h, (c) epoxy/clay (5%) cured after swelling at 70°C for 24 h, (d) siliconized epoxy/clay (5%) cured after swelling at 70°C for 24 h, and (e) cyanate ester siliconized epoxy/clay (5%) cured after swelling at 70°C for 24 h.

Hussain et al.³⁰ reported that the presence of an inorganic moiety such as phosphorus in epoxy decreases the exfoliation into intercalation, and this is possibly attributable to the increase in the viscosity of the epoxy resin by the addition of a phosphorous compound into the epoxy system, which prevents easy swelling of epoxy resins into the clay galleries. To avoid this problem, in this study an attempt has been made to retain the exfoliated structure in the siloxane-modified hybrid systems by the introduction of HTPDMS into the clay-filled hybrid systems after an exfoliated structure was achieved with organically modified MMT clay. The absence of a diffraction peak can be observed in Figure 11(d,e), corresponding to an exfoliated structure in the cured samples, even with the incorporation of HTPDMS and both HTPDMS and cyanate ester modified epoxy/clay hybrid systems. This confirms that the incorporation of a siloxane moiety could not have any significant effect on the exfoliation pattern in clay-filled hybrid systems.

CONCLUSIONS

Hybrid clay/epoxy nanocomposites were prepared by the initiation of the *in situ* polymerization of DGEBA and DDM with organically modified MMT

clay as the delaminated structure even up to a 5 wt % clay loading. The delaminated hybrid clay/epoxy system was toughened by the addition of 10 wt % HTPDMS and 10 wt % cyanate esters (CE-1, CE-2, and CE-3). The chemical reactions between HTPDMS and γ -APS as well as HTPDMS-modified epoxy and cyanate ester have been ascertained from FTIR analysis. The glass-transition behavior of the hybrid epoxy nanocomposites was investigated by means of DMA and compared with neat epoxy, and the clay-filled and cyanate ester/siloxane toughened hybrid epoxy systems displayed insignificantly decreased T_g values. It may be proposed that the decreased T_g could be responsible for the presence of aliphatic surfactant chains (cetyl ammonium ions) in the organomodified clay and the combined effect of the formation of an alicyclic oxazolidinone ring by the reaction of cyanate ester with epoxy and the free rotation of $-\text{Si}-\text{O}-\text{Si}-$ linkages in the presence of HTPDMS. Furthermore, the lower α transition and relaxation strength observed from DMA studies for hybrid clay/epoxy systems in comparison with the neat epoxy support the effect of the reinforcement of the nanoclay. The nanoreinforcement of organomodified MMT clay improved the mechanical properties. The morphologies of DGEBA, DDM, and organically modified MMT clay were homogeneous, suggesting an interfacial interaction between cetyl ammonium ion treated MMT clay and DGEBA. Because of the presence of the siloxane moiety in the clay-modified epoxy hybrids, phase separation was induced by partially incompatible HTPDMS in the hybrid systems, and the spherical siloxane particles were uniformly dispersed in the continuous epoxy matrix by the reaction of siloxane with epoxy through a crosslinking agent, as evidenced by SEM. The results of the XRD analysis suggest that exfoliated forms of MMT clay would be good reinforcements for epoxy matrices with specified swelling periods. The formed exfoliated structure was retained in the multicomponent hybrid systems, as also ascertained from XRD analysis.

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