Thermomechanical Behavior of Vinyl Ester Oligomer-Toughened Epoxy-Clay Hybrid Nanocomposites

Chinnakkannu Karikal Chozhan[a]; Rajangam Rajasekaran[a]; Muthukaruppan Alagar[a]; Periyannan Gnanasundaram[a]

[a] Department of Chemical Engineering, Anna University, Chennai, India

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Chinnakkannu Karikal Chozhan
Rajangam Rajasekaran
Muthukaruppan Alagar
Periyannan Gnanasundaram
Department of Chemical Engineering, Anna University,
Chennai, India

Interpenetrating networks of varying percentages of vinyl ester oligomer (VEO) toughened epoxy-clay hybrid nanocomposites were developed. VEO was prepared by reacting commercially available epoxy resin LY556 and acrylic acid and was used as a toughening agent for DGEBA epoxy resin. DGEBA was toughened with 5, 10 and 15% (by wt) of VEO using 4, 4'-diaminodiphenylmethane (DDM) as a curative. The formation of VEO (nucleophilic addition) and its chemical reaction with epoxy resin (via Michael addition) was confirmed by FT-IR spectra. Epoxy and VEO toughened epoxy systems were further modified with 1, 3 and 5% (by wt) of organophilic montmorillonite (MMT) clay. Organoclay-filled hybrid VEO epoxy matrices, developed in the form of castings, were characterized for their thermal and mechanical properties. Thermal behavior of the matrices was characterized by DSC, TGA and DMA analysis. Mechanical properties were studied as per ASTM standards. Data from mechanical and thermal studies indicate that the introduction of VEO into epoxy resin improved the thermal stability and impact strength to an appreciable extent. The introduction of 10% VEO into 5% organoclay-filled epoxy resin improves the impact strength (from 103.3 MPa to 141.3 MPa) by 36.7% compared to that of unmodified epoxy resin system. XRD analysis confirmed the exfoliated nanocomposites, which exhibit higher dynamic modulus (from 3012 MPa to 3710 MPa) than unmodified epoxy resin. Further SEM analysis ascertained the homogeneous morphologies of the hybrid nanocomposites.

INTRODUCTION

Epoxy resins have been noted for their unique properties, like outstanding adhesion to various surfaces, light weight, high strength, extreme durability and stability under UV exposure and chemical resistance. They are used in aerospace, automobiles, land and marine transportation, chemical process industries and electrical and electronic industries, because of their light weight and good mechanical properties and excellent processability. However, the brittle behavior of epoxy resin restricts its utility for a number of high performance applications. Therefore, numerous attempts have been made to improve their toughness. The introduction of flexible polymers and elastomers is the general approach to increase the fracture toughness. However, modification of epoxy resin with these materials is invariably accompanied by a significant drop in the dynamic modulus and the glass transition temperature [1–6]. In our earlier work, it was found that toughness of the epoxy matrices was improved by the incorporation of hydroxyl terminated polydimethylsiloxane, diglycidyl ether terminated polydimethylsiloxane and unsaturated polyester into epoxy resin [7–10].

Hence, suitable polymeric material is needed to improve the impact resistance and enhanced strain, to fracture with retaining stiffness and thermal stability of epoxy system. To achieve this, development of an interpenetrating polymer network (IPN) having flexible and rigid molecular segments can be considered as an attractive method. Since the IPN mechanism provides matrix materials with a single glass transition temperature, IPNs of thermoset-thermoset blends have been extensively studied because of their enhanced mechanical properties.

Among the different materials used for the modification of epoxy resins, vinyl ester oligomer is expected to be a suitable material to impart better toughness to epoxy resin because of its versatile behavior such as flexibility, high thermal and thermo-oxidative stability, high moisture resistance, and good dielectric properties. Vinyl ester oligomer possesses similar properties as exhibited by polyester resins, however, the reactive sites are positioned only at the end of the molecular chain, therefore crosslinking can take place only at the chain ends. The whole length of the molecular chain is available to absorb shock loading, making the vinyl ester oligomer tougher and more

resilient than polyesters. Epoxy-based vinyl ester resins have exceptionally high physical properties and chemical resistance. Additional attributes include low water absorption rates, high heat distortion temperatures, abrasion resistance combined with light weight and good flexural strength, making vinyl ester resin products ideal for marine applications as well as applications in extremely challenging environments. Karger-Kocsis et al. [11] and Cook et al. [12] studied the fracture energy, toughness and curing kinetics of the interpenetrating network structure of methacryloxy derivative of vinyl ester resin toughened with aliphatic and cycloaliphatic epoxy resin thermosets cured by aliphatic diamines.

Though the incorporation of VEO into epoxy resin systems improves its impact strength and thermal stability, it reduces the stress-strain properties and glass transition temperature. To prevent the loss of stress-strain properties and glass transition temperature, modification of VEO-toughened epoxy system, with rigid materials like bismaleimides (BMIs) is essential, owing to their excellent thermomechanical properties like high Tg, high char yield and low water absorption. However, the incorporation of BMI into VEO-toughened epoxy system reduces the impact strength. In order to compensate the loss of impact strength caused by BMI, use of MMT clay is needed. The introduction of BMI into epoxy [13–16], siliconized epoxy [17], unsaturated polyester-modified epoxy [18], VEO-modified unsaturated polyester [19–22] resin-enhanced Tg and thermal stability with loss of impact strength.

Hence, in the present study, an attempt has been made to improve the impact strength without any loss in the values of other mechanical properties as well as to achieve high thermal stability with better char yield of epoxy resin, using VEO and organophilic MMT clay as a good toughener and nanoreinforcing material for epoxy resin. The formation of VEO-toughened organoclay-filled hybrid epoxy nanocomposites is expected to have an enhanced storage modulus, barrier properties, solvent resistance, low flammability and improved mechanical properties.

EXPERIMENTAL

Materials

Epoxy resin (diglycidylether of bisphenol A, DGEBA) LY556 having an epoxy equivalent of about 180–190, with viscosity of about 10,000 cP and 4,4′-diaminodiphenylmethane (DDM), epoxy curing agent, was used as obtained from Ciba-Geigy Ltd., India. Acrylic acid (Merck, Darmstadt, Germany), and cetyltrimethylammonium bromide (SRL, India) were

used as received. Montmorillonite clay was purchased from Aldrich Chemicals, USA. VEO was prepared in the laboratory.

Synthesis of Organophilic Nanoclay

15 g of the purified Na-montmorillonite clay were dispersed into 1200 ml of distilled water at 80°C. Cetyltrimethylammonium bromide, 5.7 g, in 300 ml distilled water were poured in the hot montmorillonite/ water solution and stirred vigorously for 1 h at 80°C. A white precipitate was formed, then isolated by filtration and washed several times with a hot water/ethanol (1:1) mixture until no chloride was detected in the filtrate by adding one drop of 0.1 N AgNO$_3$ solution. The cetyltrimethylammonium ion exchanged montmorillonite was then dried for about two weeks at 75°C, ground with a mortar and pestle, and then the <50 μm fraction was collected. The organophilic nanoclay was stored in a desiccator [23] for further use.

Preparation of Organophilic Clay-Filled Epoxy Resin Nanocomposites

Prior to curing, the epoxy resin was mixed with the desired amount of organophilic nanoclay at 70°C for 24 h. An amount of the curing agent 4,4′-diaminodiphenylmethane corresponding to epoxy equivalents was also added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 h. The castings were then post-cured at 180°C for 2 h and finally removed from the mold and characterized.

Preparation of Vinyl Ester Oligomer

Vinyl ester oligomer was prepared using DGEBA epoxy resin (LY556) and acrylic acid. 1 mole of DGEBA epoxy resin and 2 moles of acrylic acid were mixed in a round-bottom flask at 70°C for 4 h with constant stirring to obtain vinyl ester oligomer [24, 25]. The reaction for the preparation of vinyl ester oligomer is given in Scheme 1.

Preparation of Hybrid Vinyl Ester Oligomer Toughened Epoxy Resin

A fixed amount of epoxy resin (100 g), varying amounts of vinyl ester oligomer resin (5, 10 and 15 g), and a stoichiometric amount of 4,4′-diaminodiphenylmethane (27.2 g), with respect to epoxy resin were mixed at 90°C for 10 min with constant stirring. The hybrid product
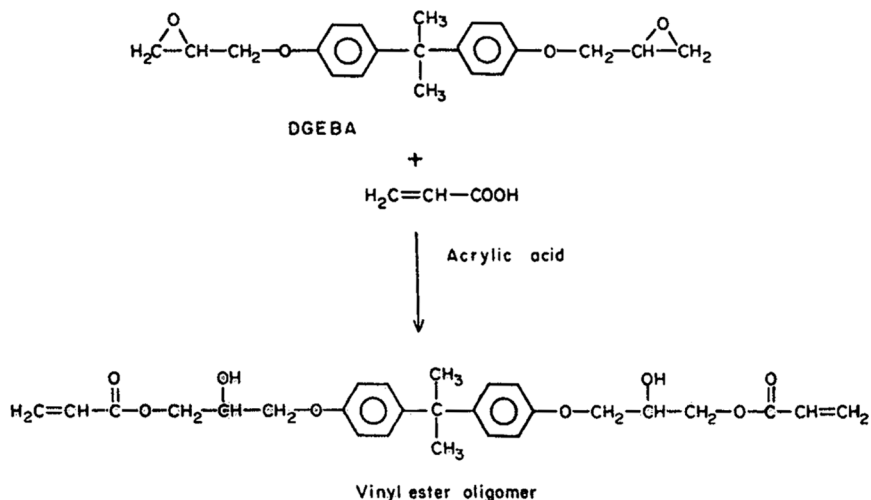
SCHEME 1 Preparation of vinyl ester oligomer.

was then degassed to remove the entrapped air and transferred into a preheated mold kept at 120°C for 3 h and post-cured at 180°C for 2 h (Scheme 2).

Preparation of Organophilic Clay-Filled Hybrid Vinyl Ester Oligomer Toughened Epoxy Resin Nanocomposites

The epoxy resin was mixed with the desired amount of organophilic clay (1, 3 and 5%) at 70°C for 24 h. To the organophilic clay-filled epoxy resin, varying amounts of vinyl ester oligomer (5, 10 and 15 g) were added at 90°C for 10 min with constant stirring. A stoichiometric amount of curative 4, 4'-diaminodiphenylmethane (27.2 g) corresponding to epoxy equivalents was also added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 h. The castings were then post-cured at 180°C for 2 h and finally removed from the mold and characterized.

Test Methods

FT-IR Spectroscopy

The IR spectra were recorded on a Perkin-Elmer (Model RX1) FTIR spectrometer, with KBr pellets, for solid samples. For viscous liquid samples, the spectra were obtained by placing the sample between two KBr pellets.
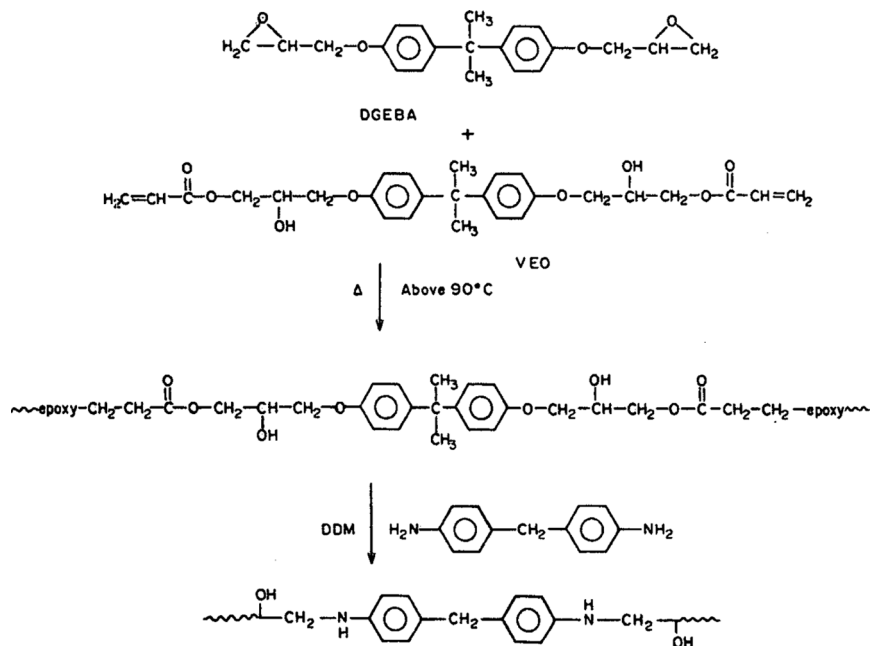
SCHEME 2 Formation of vinyl ester oligomer-toughened epoxy IPN network.

Thermal Properties

Glass transition temperature (Tg) of the samples was determined using a DSC Netzsch (TA Instruments, USA) in the temperature range between 50 and 250°C at a heating rate of 10°C per minute in nitrogen atmosphere. Thermo-gravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA Instruments, USA) at a heating rate of 10°C per min in nitrogen atmosphere. Dynamic mechanical behavior of the samples was measured using a DMA Netzsch 242 at a heating rate of 10°C per min from 30 to 300°C. The heat deflection temperature (HDT) of the samples was tested as per ASTM D 648-72.

Mechanical Properties

The tensile (stress-strain) properties were determined using INSTRON (Model 6025 UK) as per ASTM D 3039 at 10 mm/min cross-head speed using specimens with a width of 25 mm, length of 200 mm and thickness of 3 mm. The flexural (strength and modulus)

properties were measured (INSTRON, Model 6025 UK) as per ASTM D 790 using specimens with dimensions 3 mm in depth, 10 mm in width and 90 mm in length at 10 mm/min cross-head speed. The unnotched Izod impact strength of each sample was studied as per ASTM D 256. Five specimens were tested for each sample.

Hardness was measured using Durometer-Type D as per ASTM D 2240, specimens with 3 mm thickness. Hardness was determined at five different positions on the specimen at least 6 mm apart and arithmetic mean was taken.

Water Absorption

The water absorption behavior of the samples was tested as per ASTM D 570. The cured specimens (dimensions: 60 mm square, 3 mm thickness) were immersed in distilled water for 48 h. Specimens were removed and the surface water was removed using tissue paper and weighed to an accuracy of 0.001 g.

Morphology

Surface morphology of the fractured surface of the samples was observed using a scanning electron microscope (SEM; JEOL JSM Model 6360). The fractured surface of the samples was coated with platinum before scanning.

X-ray Diffraction Studies

X-ray diffraction patterns were recorded at room temperature by monitoring the diffraction angle 2θ from 10 to $70°$ as standard and 0.5 to $10°$ as low angle on a Rich Seifert (Model 3000) X-ray powder diffractometer. The diffractometer was equipped with a copper target ($\lambda = 1.5405$ Å) radiation using a Guinier-type camera employed as a focusing geometry and a solid-state detector. Curved nickel crystal was used as a monochromator. The step width (scanning speed) used was $2\theta = 0.04$ deg/min.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

The characteristic IR absorption spectra observed for acrylic acid, VEO resin, epoxy-VEO resin on heating at $120°C$, epoxy-VEO resin cured by DDM and unmodified epoxy resin are shown in Figure 1a–e. The IR absorption peaks observed for acrylic acid appear at $1729\,\text{cm}^{-1}$ ($-C=O$ stretching), $3272\,\text{cm}^{-1}$ (O$-$H stretching free bond–very broad) and $1410\,\text{cm}^{-1}$ (CH_2 in plane def – R$-$CH=CH$_2$) (Figure 1a).
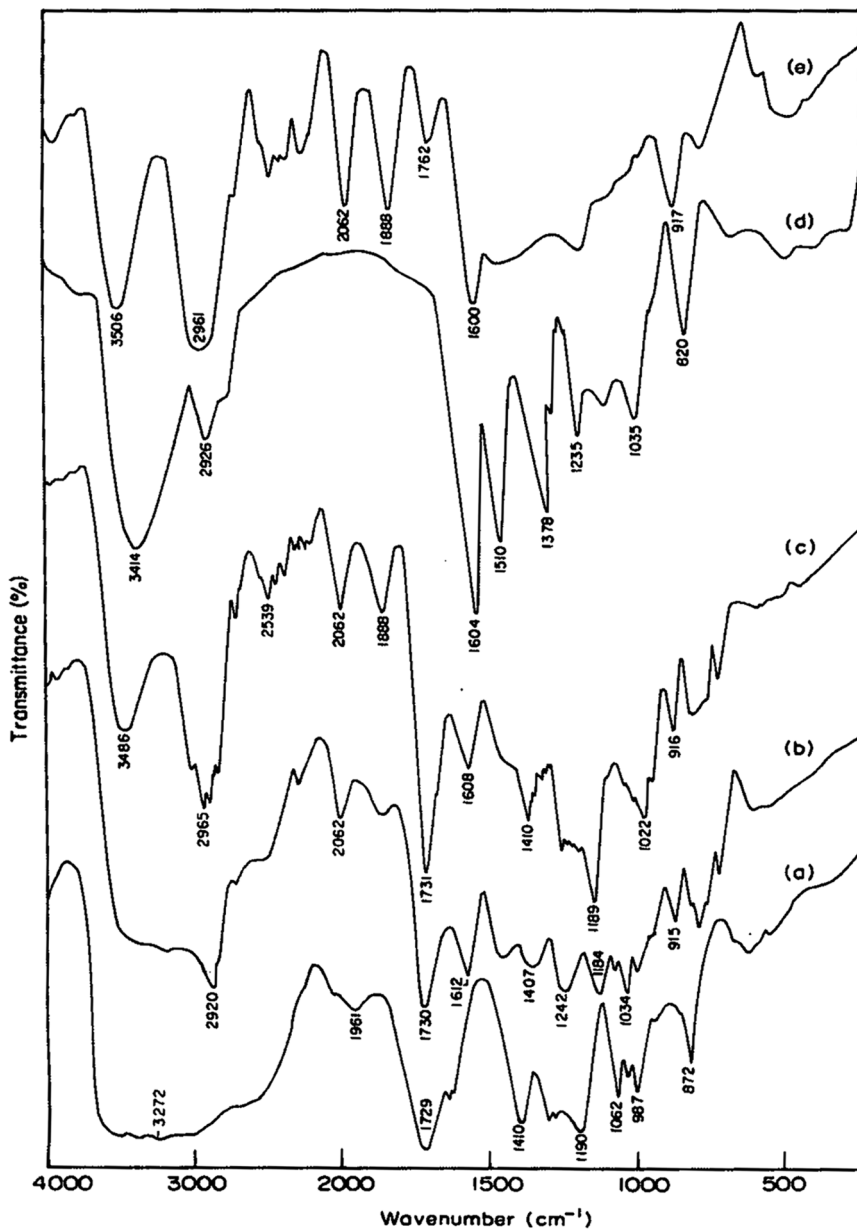
FIGURE 1 FTIR spectra of a) acrylic acid, b) vinyl ester oligomer resin, c) uncured epoxy-VEO blend with the composition of (100:10) taken after heating at 90°C for 15 min, d) VEO-toughened epoxy resin cured by DDM with the composition of (100:10) and e) uncured unmodified epoxy resin.

The characteristic absorption peaks for VEO resin appear at $1730\,cm^{-1}$, $1612\,cm^{-1}$ and $2920\,cm^{-1}$ (Figure 1b). The characteristic absorption peaks for terminal methylene group in vinyl group, the unsaturated =C−H stretching vibration and C=C stretching for the vinyl group are absent at $3095–3075\,cm^{-1}$, $3040–3010\,cm^{-1}$ and $1630\,cm^{-1}$, which confirm that the reaction between epoxy resin and VEO resin was a Michael addition. The resulting α, β-unsaturated carbonyl group is confirmed by its absorption at $1730\,cm^{-1}$ (Figure 1c). The absorption peak for the epoxide ring of epoxy resin is absent at $917\,cm^{-1}$ in the cured product of hybrid VEO-toughened epoxy resin (Figure 1d). Figure 1e shows the absorption peak for the epoxide ring of unmodified epoxy resin appearing at $917\,cm^{-1}$. Thus the data from IR spectra confirm the formation of VEO epoxy network structure.

Thermal Properties

The glass transition temperature (Tg) of unmodified epoxy and VEO-toughened epoxy systems are presented in Table 1. The glass transition temperature of the epoxy system is lowered, with increasing concentrations of VEO. This is explained by the chain lengthening and flexibility behavior of vinyl ester oligomer resin, which in turn decreases the effective crosslink density and accelerates the reaction rate and reduces the curing temperature. This creates excess free volume and reduced chain entanglement in the matrix system and leads to reduction in the values of Tg, since Tg is associated with mobility of the molecule (Table 1). The incorporation of organophilic nanoclay into both unmodified epoxy and VEO-toughened epoxy systems reduces the

TABLE 1 Thermal and Water Absorption Behavior of Hybrid VEO-Epoxy Nanocomposites

Epoxy/VEO/Clay composition	Heat distortion temperature (°C)	Glass transition temperature (°C)	Water absorption (%)
100/00/00	155	165	0.1232
100/05/00	149	158	0.1194
100/10/00	142	153	0.1139
100/15/00	137	149	0.1068
100/00/01	151	159	0.1127
100/00/03	147	156	0.1023
100/00/05	143	152	0.0562
100/10/01	139	151	0.1103
100/10/03	137	147	0.1005
100/10/05	134	143	0.0539

VEO: Vinyl ester oligomer resin.

values of *Tg*. The decrease in the values of *Tg* is due to the catalyzed homopolymerization of epoxy and plasticization of organoclay-modified epoxy systems during the swelling by cetyltrimethylammonium ions [23,26–28]. The homopolymerization of epoxy results in the reduction of crosslink density and *Tg*.

The values of HDT obtained for epoxy, VEO-toughened epoxy, organophilic nanoclay-incorporated epoxy and organophilic nanoclay-incorporated VEO-toughened epoxy systems are presented in Table 1. From the table, it is evident that the values of HDT decrease with increasing VEO concentration, due to the presence of flexible $-O-$ group formed in the α, β-unsaturated carbonyl ring structure during the reaction (Michael addition) between the vinyl group of vinyl ester oligomer resin (having lengthy and flexible behavior) and the oxirane ring of DGEBA resin. Also with increasing VEO concentration, a decrease in the crosslink density of the epoxy system would result, leading to a decrease in HDT. Besides, the IPN structures of crosslinked epoxy and crosslinked VEO, the crosslink density of the epoxy system would also be decreased (due to the interaction with crosslinked VEO) during the cure reaction which also causes a decrease in HDT. However, a decreasing trend in HDT values is observed for organophilic nanoclay-filled epoxy and organoclay-filled VEO-toughened epoxy systems. This is due to the plasticization effect of catalytic effect of the clay modifier, cetyltrimethylammonium ions, which increase the reaction rate and reduce the curing temperature.

Thermogravimetric Analysis

The incorporation of VEO into epoxy resin improves thermal stability and elevates the degradation temperature according to the increase in percentage concentration (Table 2). The presence of VEO molecular segments in the epoxy system delays the degradation process and

TABLE 2 TGA Data of Hybrid VEO-Epoxy Nanocomposites

Epoxy/VEO/clay composition	Initial decomposition temperature (°C)	Temp. at characteristic weight loss (°C)			Residue (%) 798°C
		20%	40%	60%	
100/00/00	358	376	394	419	21.3
100/10/00	365	390	411	440	28.8
100/00/03	368	395	415	448	30.4
100/10/03	373	402	420	466	32.3

VEO: Vinyl ester oligomer resin.

higher thermal energy is required to attain the same percentage weight loss than that required for an unmodified epoxy system. The delay in degradation caused by the VEO moiety is attributed to its crosslinked network and IPN structure of VEO-epoxy system. The degradation temperature of organophilic nanoclay-incorporated epoxy systems and organophilic nanoclay-incorporated VEO-toughened epoxy systems do increase with increasing the concentration of nano-clay. From Table 2, it is evident that the degradation temperature increases with increasing nanoclay concentrations, as observed in the case of VEO-toughened epoxy systems. This is due to the plastici-zation of crosslinked epoxy networks formed between clay layers by hydrocarbon chains of cetyltrimethylammonium ions present in the organophilic nanoclay [28]. Further, this enhancement of thermal stability is due to the presence of hard clay layers in nano scale, which act as barriers to minimize the permeability of volatile degradation products from the VEO-epoxy clay nanocomposites.

Mechanical Properties

The observed values for tensile and flexural properties of unmodified epoxy, VEO-toughened epoxy, organophilic nanoclay-filled epoxy and VEO-toughened epoxy are presented in Table 3. The introduction of 5, 10 and 15% VEO (by wt) into epoxy resin increases the tensile strength (4.7, 10.4 and 12.9%) and flexural strength (5.3, 11.7 and 14.9%) when compared with unmodified epoxy. This is due to the formation of crosslinked and IPN network structure between epoxy

TABLE 3 Mechanical Properties of Hybrid VEO-Epoxy Nanocomposites

Epoxy/VEO/clay composition	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
100/00/00	61.3	2645.7	106.2	1763.1	103.3
100/05/00	64.2	2769.2	111.9	1847.3	113.2
100/10/00	67.7	2896.3	118.7	1979.4	122.4
100/15/00	69.2	2985.6	122.1	2027.2	126.6
100/00/01	68.5	2965.4	119.4	2007.3	115.9
100/00/03	74.6	3213.5	129.5	2187.9	127.3
100/00/05	79.4	3443.7	138.3	2343.4	133.2
100/10/01	70.7	3036.4	121.4	2060.3	125.2
100/10/03	79.5	3452.1	136.7	2283.2	136.6
100/10/05	83.1	3592.5	144.2	2370.5	141.3

VEO: Vinyl ester oligomer resin.

and VEO, which causes the chain entanglement in the VEO-epoxy matrix system. The incorporation of 1, 3 and 5% (by wt) organophilic nanoclay into the epoxy resin increases the tensile strength (11.7, 21.7 and 29.5%) and flexural strength (12.4, 22.0 and 30.2%) (Table 3), with increasing concentrations due to the formation of nanocomposites [29–33]. Similarly, the introduction of both nanoclay and VEO into epoxy resin improves the tensile strength and flexural strength according to their percentage content. The introduction of 1, 3 and 5% (by wt) organoclay into 10% VEO-toughened epoxy resin increases the tensile strength (15.3, 29.7 and 35.5%) and flexural strength (14.3, 28.7 and 35.7) with increasing clay content. A similar trend is also observed in the values of tensile and flexural modulus (Table 3).

Incorporation of 5, 10 and 15% VEO into epoxy resin enhances the impact strength (9.6, 18.5 and 22.5) according to the percentage content of VEO. This is due to the formation of VEO-epoxy IPN and crosslinked network afforded by the lengthy and flexible VEO resin (Table 3). The incorporation of nanoclay into both epoxy and VEO-epoxy also increases the impact strength, due to the flexibility imparted by the plasticization effect of organophilic nanoclay (Table 3). The introduction of 1, 3 and 5% organoclay into 10% VEO-toughened epoxy resin increases the impact strength by 21.2, 32.2 and 36.7%, respectively. Data obtained from mechanical studies indicated that the introduction of vinyl ester oligomer into epoxy resin improves the impact strength (from 103.3 MPa to 126.6 MPa). The impact strength of 3% clay-filled epoxy system is increased by 23.2% compared to unmodified epoxy resin. The impact strength of 3% clay-filled 10% VEO-toughened epoxy system is increased by 32.2% over an unmodified epoxy system. While comparing the overall improvement attained in the mechanical properties, it was found that improvement in tensile strength/modulus and flexural strength/modulus of VEO-toughened epoxy systems is smaller than the comparable improvement of VEO-toughened epoxy-clay nanocomposites.

Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) of unmodified epoxy, VEO-toughened epoxy, clay-filled epoxy and VEO-toughened epoxy clay nanocomposites are presented in Figures 2 and 3. The loss tangent is a sensitive indicator for crosslinking. The observation from Figure 2 reveals that the tan δ peak corresponding to the values of Tg shifted towards the lower temperature by the addition of 3% clay (from 165 to 147°C). Since the relaxation peak height is associated with molecular mobility, it is observed that the exfoliation of the polymer molecules
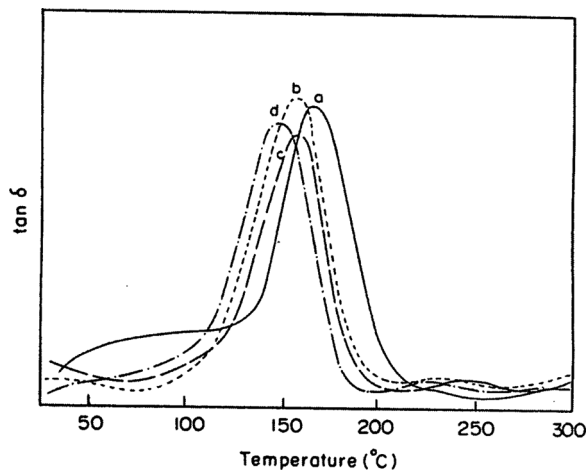
FIGURE 2 Variation of tan δ as a function of temperature a) unmodified epoxy, b) epoxy with 10% VEO, c) epoxy with 3% clay and d) epoxy/10% VEO/3% clay nanocomposites systems.

between the clay layers has greatly reduced their molecular mobility [23,26] and decreased the intensity of tan δ. The clay addition has a considerable effect in the stiffness behavior of the nanocomposites, which affects the dynamic mechanical properties of the nanocomposites. The clay addition increases the storage modulus [34,35] (ε') (Figure 3). Compared to unmodified epoxy system, when the
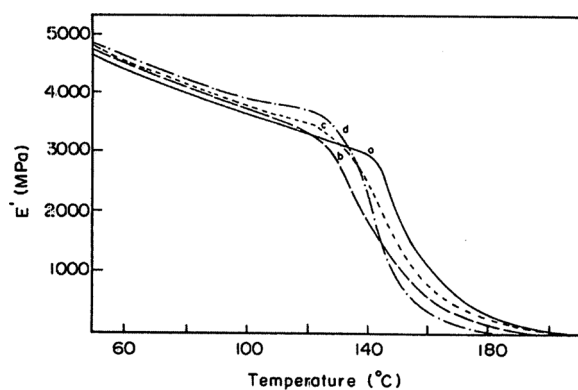

FIGURE 3 Variation of storage modulus as a function of temperature a) unmodified epoxy, b) epoxy with 10% VEO, c) epoxy with 3% clay and d) epoxy/10% VEO/3% clay nanocomposites systems.

temperature was lower than Tg, the storage modulus of the nanocomposites was increased by 18.8% (from 3012 to 3710 MPa). When the temperature was higher than Tg, the storage modulus of the nanocomposites was increased by 35.7% (from 106.2 to 144.2 MPa).

Hardness

The value of hardness of an unmodified epoxy system was found to be 86. The value of hardness for an epoxy system decreased with the incorporation of an increased concentration of VEO. The values of hardness for 5, 10 and 15% VEO-toughened epoxy systems decreased to 83, 79 and 74, respectively, due to the presence of flexible vinyl ester moiety in the oligomer resin, whereas a significant improvement was observed in the values of hardness when 10% VEO-toughened epoxy system was reinforced with 1, 3 and 5% organophilic nanoclay, and their corresponding values were 90, 94 and 97.

Water Absorption

The incorporation of vinyl ester oligomer into epoxy resin decreased the percentage water uptake, according to the percentage concentration (Table 1) due to its inherent hydrophobic nature. Further, the incorporation of organophilic clay into both epoxy and vinyl ester oligomer-toughened epoxy systems also reduced the percentage water uptake due to the fact that the permeability behavior is influenced by the nanocomposites structure.

Morphology

The SEM micrographs of fractured surfaces of the unmodified epoxy, vinyl ester oligomer-toughened epoxy resin systems revealed smooth and homogeneous microstructures (Figures 4a–d). The presence of homogeneous morphology is due to the efficient interaction between vinyl ester oligomer and epoxy resin. This indicates that there is no phase separation between the two components which confirms the compatibility of VEO with epoxy resin system. Figures 4c and 4d show the SEM micrographs of the nanocomposites prepared using organoclay in which uniform distribution of clay particles occurred in the VEO-epoxy matrix system. The cetyltrimethylammonium ions render the clay organophilic and make a better dispersion of the clay into epoxy resin, which makes for excellent compatibility between the silicate layers of clay and the epoxy resin [36]. In addition, clay-filled systems showed considerable surface roughness, prevent the crack
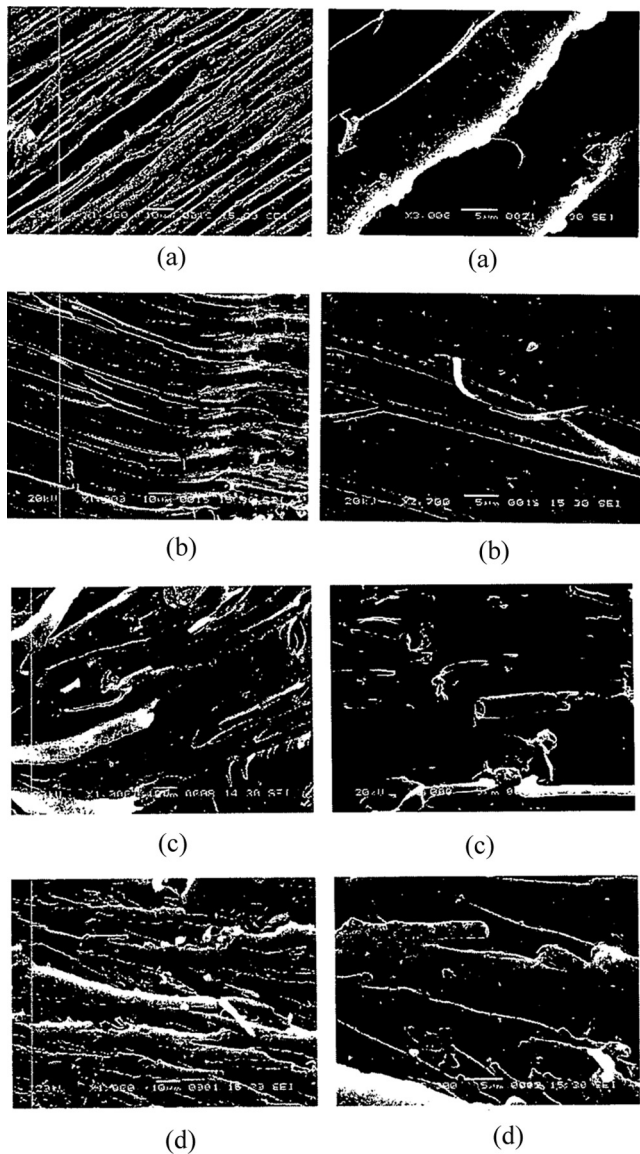
FIGURE 4 SEM photographs of vinyl ester oligomer-toughened epoxy-clay nanocomposites a) unmodified epoxy, b) 10% VEO toughened epoxy, c) 3% organoclay filled epoxy and d) 10% VEO-toughened and 3% organoclay-filled epoxy.

along the matrix, and enhances the toughness of the epoxy resin. The efficient adhesion could be due to the influence of intermolecular specific interactions between cetyltrimethylammonium ion-modified clay and VEO-epoxy matrix systems. Hence, the formed exfoliated structures [37–39] confirm the formation of nanocomposites.

X-ray Diffraction Studies

XRD measurements were made to evaluate the spacing between the silicate layers in the organoclay-filled hybrid VEO-epoxy nanocomposites (Figures 5 and 6). Bragg's Law ($n\lambda = 2d\sin\theta$) was used to
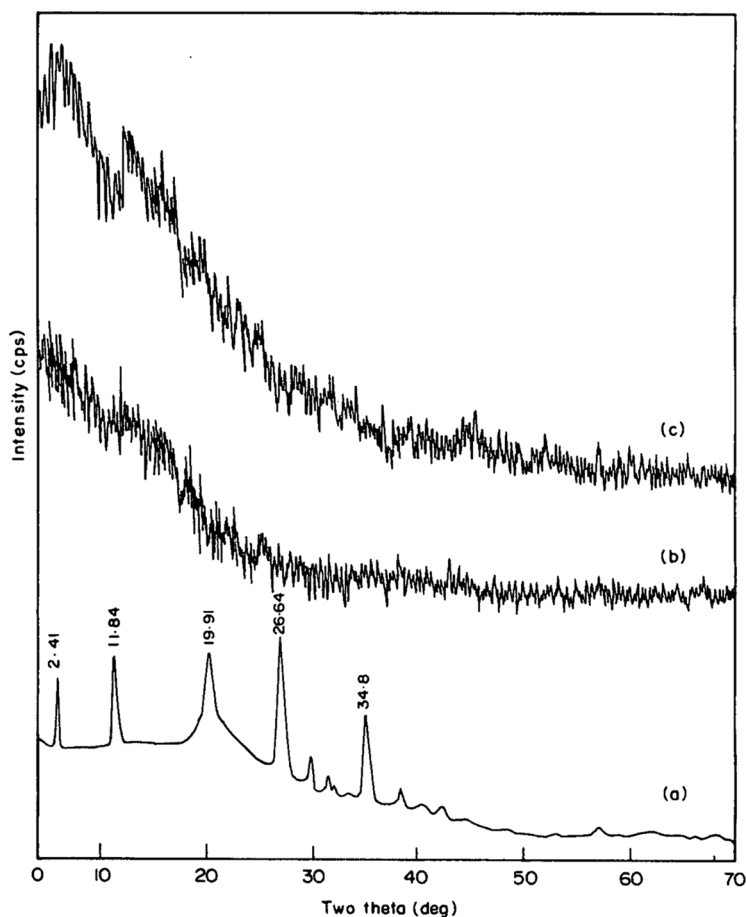
FIGURE 5 XRD patterns of a) organo-modified MMT clay, b) epoxy-clay (100:3) and c) epoxy-VEO-clay (100:10:3).
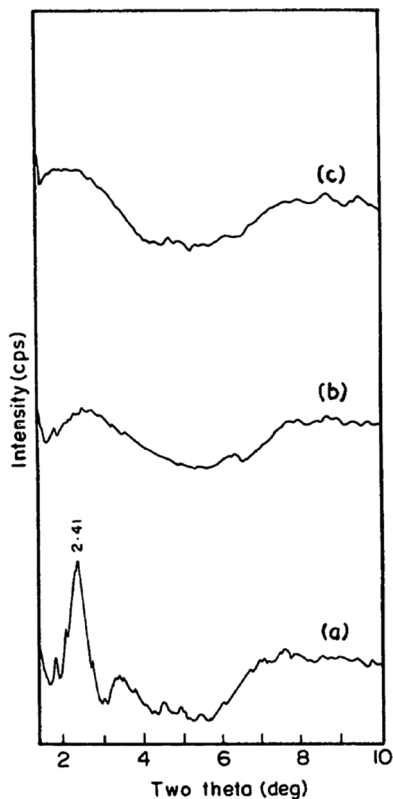
FIGURE 6 XRD patterns of a) organo-modified MMT clay, b) epoxy-clay (100:3) and c) epoxy-VEO-clay (100:10:3) at low angle.

compute the crystallographic spacing. The XRD patterns of organoclay-filled VEO-epoxy systems suggested the formation of exfoliated nano hybrids (Figures 5c and 6c). The clay layers are exfoliated and dispersed evenly throughout the epoxy matrix [36,39]. This is due to the compatibility of VEO-epoxy resin with the layered silicates, and the VEO-epoxy chain penetrates into the gallery and expands the nano size to some extent [38]. From Figures 5(b, c) and 6(b, c) it is observed that the 001 reflections of the clay are absent in the cured product, indicating the delamination of the crystal structure of clay, which in turn confirms the formation of exfoliated nanocomposites [23,40]. It is also evident that the swelling period of organoclay in epoxy resin influences the formation of exfoliated nanocomposites. The longer swelling time favors the exfoliated of the clay. The introduction

of nanoclay into a matrix system has significant effect on mechanical properties. The addition of nanoclay to the unmodified matrix increases the mechanical properties to an appreciable extent. The increase in mechanical strength is attributed to the formation of exfoliated nanocomposites.

CONCLUSIONS

Vinyl ester oligomer-toughened epoxy, organophilic MMT clay-filled epoxy and organophilic MMT clay-filled VEO-toughened epoxy hybrid nanocomposites were developed. The thermal properties such as *Tg* and HDT of VEO-toughened epoxy and organophilic clay-filled VEO-epoxy systems have been compared with those of unmodified epoxy systems, and a decreasing trend with VEO was observed, whereas the thermal stability was increased with increasing VEO content. The mechanical studies inferred that the incorporation of vinyl ester oligomer into epoxy resin improved the impact strength with a slight increase in the tensile and flexural strength, whereas the incorporation of organophilic clay increased the storage modulus and stress-strain properties greatly according to its percentage content, along with a large improvement in impact strength. The fractured surfaces of the organophilic clay and vinyl ester oligomer-toughened epoxy system showed the presence of homogeneous microstructures. The XRD patterns of organophilic clay-filled hybrid VEO-epoxy systems suggested the formation of exfoliated nanocomposites, which cause a drastic improvement in mechanical behavior. The VEO-toughened epoxy matrix systems and nanocomposites exhibited better thermo-mechanical properties and good resistance to water absorption properties than that of unmodified epoxy system. The hybrid matrix systems developed in the present work can be used to fabricate advanced composite components for engineering and aerospace applications for better performance and enhanced longevity.

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