ORIGINAL ARTICLE

Mechanical and thermal studies of unsaturated polyester-toughened epoxy composites filled with amine-functionalized nanosilica

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Abstract The inter-crosslinking networks of unsaturated polyester (UP)-toughened epoxy-nanosilica hybrid nanocomposites have been developed. Epoxy resin was toughened with 5 and 10% (by wt) of unsaturated polyester using benzoyl peroxide as radical initiator and 4,4′-diaminodiphenylmethane (DDM) as a curing agent at appropriate condition, and the resulting product was identified by FT-IR spectra. Unsaturated polyester-toughened epoxy system (10%) was further filled with 1, 3, 5 and 7% (by wt) of amine-functionalized nanosilica particles prepared by sol–gel method. Modified nanosilica-filled hybrid UP–epoxy matrices developed in the form of casting were characterized for their thermal, mechanical properties and water absorption capacity according to ASTM standards. The degree of dispersion of nanosilica in the matrices was investigated by SEM technique. Mechanical testing data indicate that the introduction of UP into epoxy resin has improved the impact strength. Significant improvement in the flexural properties, tensile properties and impact strength were observed in the UP–epoxy blends with increase in the percentage of amine-modified nanosilica particles. The T_g value decreases with UP toughening and increases with concentration of modified nanosilica on the UP–epoxy matrix. The water absorption behavior is found to decrease with UP toughening and concentration of modified nanosilica on the UP–epoxy matrix.

Introduction

Epoxy resins are widely used mainly due to their thermal, mechanical, chemical and corrosion resistance. A favorable property of epoxy resins is the low viscosity in the uncured state that enables the resin to be processed without the use of high pressure equipments. The main drawback of epoxy systems is their inherent brittleness. Most of the techniques for toughness improvement are based on the addition of rubbers or thermoplastic modifiers (Cicala and Recca 2008). However, modification of epoxy resin with elastomers improved its impact properties with degradation in some of the physical properties at high temperature regions (Preghenella et al. 2005).

The addition of nanoparticles has exhibited high potential for proven mechanical properties of polymers. Battistella et al. (2008) obtained an increase of 54% of fracture toughness by filling an epoxy resin with 0.5 vol% of fuming silica modified with 3-aminopropyltrimethoxy silane. Ragosta et al. (2005) found that adding 10 wt% of TiO_2 nanoparticles within epoxy resin increased fracture toughness by a considerable percentage. Zhanhu Guo et. al. (2007) studied the effect of functionalized ZnO nanoparticle on the optical and mechanical properties of vinyl resin. Zhang and Singh (2004) established that Al_2O_3 (micro-nano) particles enhance the fracture toughness with polyester matrix, strongly influenced by the particle matrix adhesion.

Hussain et al. (2007) obtained an increase of 47% of the tensile modulus in filling an epoxy with 5 wt% of clay. Choi et al. (2005) obtained a maximum tensile strength and

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Young's modulus resulting in 5 wt% of cup-stacked carbon nanotubes filling in epoxy. Chisholm et al. (2005) observed an average of 20–30% increase in mechanical properties with 1.5 wt% loading of carbon/SiC on epoxy resin. Rajulu et al. (2003) used epoxy and polyester as coating materials and observed that alkali-treated epoxy and polyester-coated fibers showed an increase in tensile strength of 55 and 88%, respectively, over the uncoated fibers.

The present work attempts to improve the mechanical behavior of epoxy resin by toughening with unsaturated polyester and reinforcing the toughened matrix with amine-modified nano silica particles.

Experimental

Materials

Unsaturated polyester resin (isophthalic acid based) with viscosity 2,300–2,400 cP and analytical-grade benzoyl peroxide were supplied by Polyresins, India. Diglycidyl ether of bisphenol-A (DGEBA) by Ciba-Geigy Ltd., India was used as the epoxy resin. 4, 4′-Diaminodiphenylmethane (DDM) obtained from Ciba-Geigy Ltd. was used as curing agent. Aminopropyldiethoxysilane and tetraethoxysilane (TEOS) were supplied as gift samples by Anabond Limited, Chennai. Dry toluene, methanol and ammonium hydroxide were provided by the Central Drug House, New Delhi. De-ionized water was used throughout the study.

Preparation of silica nanoparticles

Methanol as medium and ammonium hydroxide as catalyst were mixed in 2-L resin kettle, followed by dropwise addition of TEOS in methanol, carried out for 3 h at room temperature. The particles obtained were centrifuged and de-ionized water was added to remove the catalyst. The washed powder was vacuum dried at 100°C for 3 days (Huimin Lu et al. 2006) and further heated to 600°C for 30 min and then to 1,000°C for 2 h in a muffle furnace.

Modification of silica surface with amine group

Ten grams of the synthesized silica particles was mixed with 120 ml of the solution of aminopropyldiethoxysilane in toluene. The silica powder was centrifuged, washed repeatedly with toluene and cured at 150°C in vacuum for 6 h.

Preparation of hybrid unsaturated polyester-toughened epoxy resin

A fixed amount of epoxy resin (100 g), varying amounts of unsaturated polyester resin (5 and 10 g), a stoichiometric amount of melted DDM (27.2 g) with respect to epoxy resin, and benzoyl peroxide (2 wt%) with respect to unsaturated polyester, were mixed with constant stirring. The hybrid product was then degassed to remove the entrapped air and then transferred into a preheated mold kept at 100°C for 4 h and post-cured at 140°C for 3 h.

Preparation of amine-modified silica/UP/epoxy nanocomposites

The epoxy resin (100 g) was mechanically mixed with the desired amount of amine-modified silica particles (1, 3, 5 and 7%) at 80°C for 24 h and sonicated for 30 min. To the above nanosilica-filled epoxy resin, 10 g of unsaturated polyester resin and benzoyl peroxide were added (2 wt%) at 50°C for 10 min with constant stirring. A stoichiometric amount of curative DDM (27.2 g) corresponding to epoxy equivalents was heated and added to the above mixture at 80°C. The product was subjected to vacuum for removing the trapped air and then casted and vacuum cured at 100°C for 4 h. The casting was then post-cured at 140°C for 3 h and finally released from the mold and then characterized.

Characterization

The IR spectra were recorded on a Perkin-Elmer (Model RX1) FT-IR spectrometer, with KBr pellets. Glass transition temperature (T_g) of the samples was determined using a DSC Netzsc (TA instruments, USA) in the temperature range 50–250°C at a heating rate of 10°C per min in nitrogen atmosphere. The tensile (stress–strain) properties were determined using INSTRON (model 3365, UK) as per ASTM D 3039 at 10 mm min^{-1} cross-head using specimen 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 3365, UK) as per ASTM D 790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length at 10 mm min^{-1} cross-head speed. The unnotched Izod impact strength of each sample was studied as per ASTM D 256. All these parameters were arrived at as a mean of six samples.
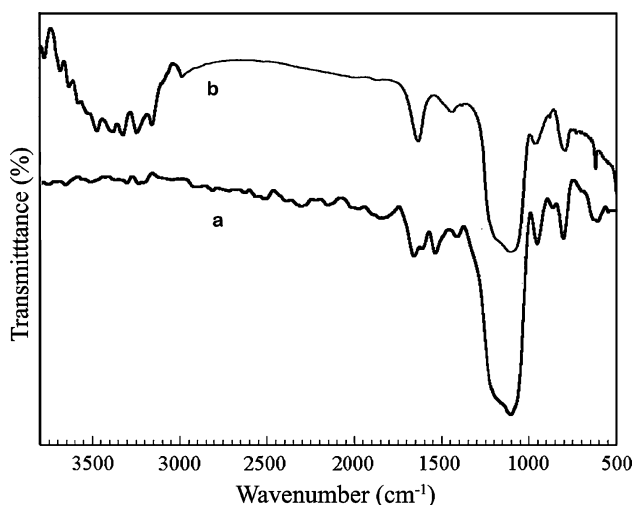
The water absorption behavior of the samples was tested as per ASTM D 570. The cured specimens (dimensions: 60-mm square, 3-mm thickness) were immersed in distilled water for 48 h. Specimens were removed and the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g. The morphology of fractured surface of the samples was scanned using scanning electron microscope (SEM; JEOL JSM Model 6360).

Results and discussion

FT-IR spectroscopy

The characteristic IR absorption peaks observed for nanosilica and amine-modified nanosilica are shown in Fig. 1. Figure 1a shows that on heating the silica particles up to 1,000°C, most of the silanol groups are eliminated leading to the only peak of –Si–O–Si– (1,100 cm^{-1}). A broad band (in Fig. 1b) between 3,100 and 3,700 cm^{-1}, related to the presence of Si–OH and –NH$_2$ (Si–NH$_2$), was detected. The band at around 1,100 cm^{-1} is attributed to the –Si–O–Si– bond stretching in the tetrahedral unit of the SiO$_2$ matrixes (Huimin Lu et al. 2006). The signal at 1,648 cm^{-1} is due to the bending vibration of water molecules adsorbed on the silica surface.

Figure 2 is the FT-IR spectra of the epoxy resin and the 10 wt% unsaturated polyester-modified epoxy resin. The strong IR absorption peak due to the C=C stretching of aromatic ring occurred at 1,611 cm^{-1} (Fig. 2a, b). The peaks at 2,965 cm^{-1} represent the aliphatic C–H stretching of epoxy and UP–epoxy resin (Fig. 2a, b). An asymmetric stretching of methylene occurs at 2,929 cm^{-1} (Fig. 2a, b). The broad peaks at around 3,400–3,500 cm^{-1} indicate the presence of hydroxyl group of epoxy resin (Fig. 2a, b) and the peaks between 920 and 770 cm^{-1} suggest the presence of asymmetric stretching of the epoxide ring. The 914 cm^{-1} is strongly attributed to the stretching absorption of C–O in the epoxide ring (Fig. 2a) and this absorption clearly disappeared after curing (Fig. 2b). The network structure formed between UP and epoxy resin shows the reaction of epoxide ring of epoxy resin with the hydroxyl group of unsaturated polyester and is further confirmed by

the decrease in the intensity of the epoxy band at 914 cm^{-1} (Ashok Kumar et al. 2001).

Thermal property

The glass transition temperature (T_g) of unmodified epoxy and UP-toughened epoxy systems are presented in Table 1. The value of the glass transition temperature of the epoxy system is decreased, with increasing concentration of UP. This is explained by the chain lengthening and flexibility behavior of unsaturated polyester 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 chain entanglement in the matrix system, leading to reduction in the values of T_g, since T_g is associated with mobility of the molecule (Brown et al. 2000). The incorporation of amine-modified nanosilica into UP-toughened epoxy systems increased the glass transition temperature. The increase in the values of T_g is due to the reaction between the amine group of nanosilica and the epoxy resin and enhanced the curing temperature (Kang et al. 2001). This could be due to the effective crosslinking of amine-modified nanosilica with the UP-toughened epoxy resulting in the formation of nanocomposites.

Mechanical properties

The observed values for tensile and flexural properties of unmodified epoxy, UP-toughened epoxy and amine-modified silica-filled UP-toughened epoxy are presented in Table 2. The introduction of 5 and 10% of UP (by wt) into

Fig. 1 FT-IR spectra nanosilica (**a**) and amine functionalized nanosilica (**b**)
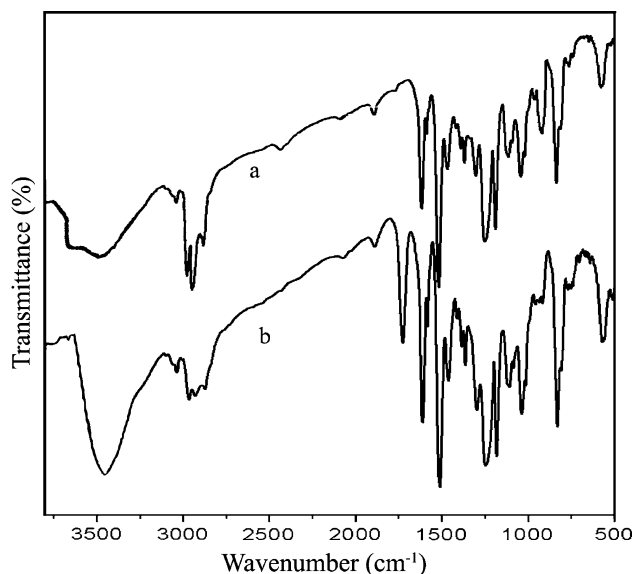
Fig. 2 FT-IR spectra of unmodified epoxy resin (**a**) and UP-toughened epoxy matrix cured by DDM with the composition (100:10) (**b**)

Fig. 3 SEM images of **a** neat
epoxy, **b** UP-toughened epoxy,
c 1 wt% amine-silica/UP/epoxy,
d 5 wt% amine-silica/UP/epoxy
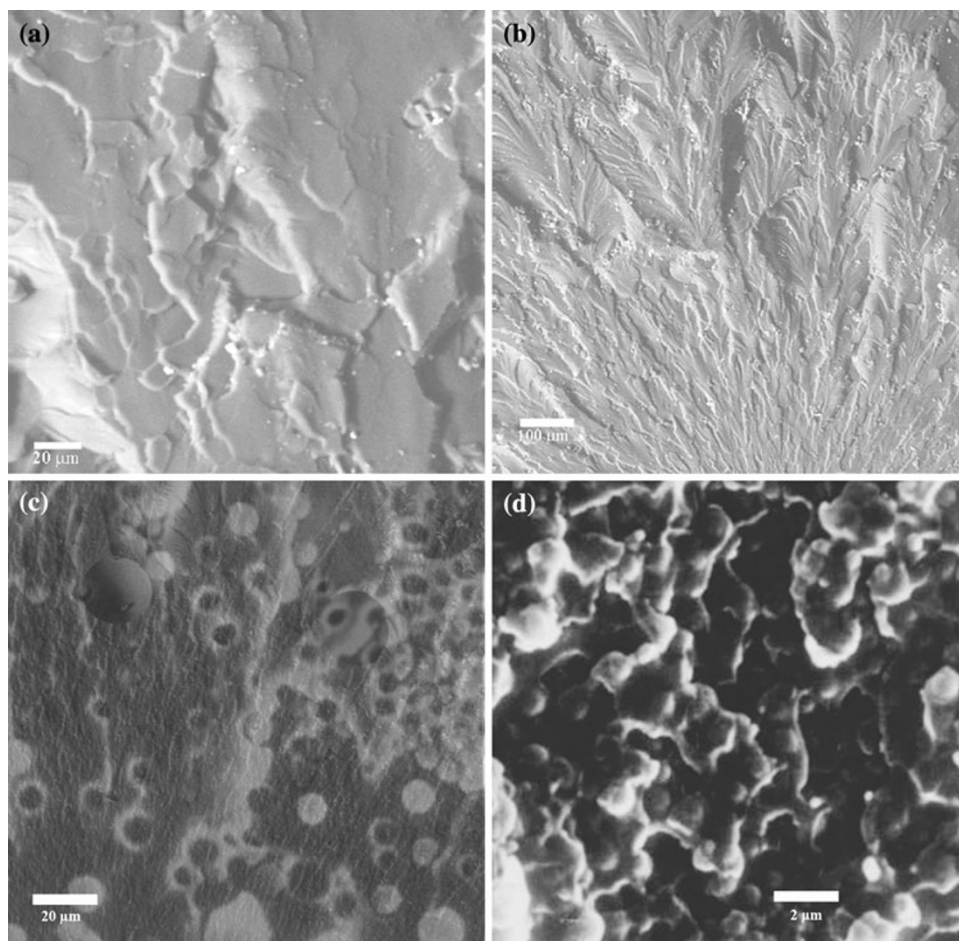
Table 1 Glass transition temperature of hybrid UP–epoxy nanocomposites

Epoxy/UP/modified silica composition	Glass transition temperature (°C)
100/00/00	168
100/05/00	151
100/10/00	144
100/10/01	150
100/10/03	159
100/10/05	164
100/10/07	167

epoxy resin decreased the tensile strength (3.6 and 7.4%) and flexural strength (2.5 and 7.9%), compared to the unmodified epoxy resin, due to the formation of chain entanglement in the UP–epoxy matrix system (Chozhan et al. 2007). The introduction of amine-modified nanosilica particles on UP–epoxy matrix improved the values of tensile strength and flexural strength according to their percentage content (Table 2). The introduction of 1, 3, 5 and 7% (by wt) amine-modified nanosilica into 10% UP-toughened epoxy resin increased the tensile strength

(9.4, 17.2, 24.9 and 28.5%) and flexural strength (11.8, 18, 29.2 and 38.2%). Like tensile and flexural strength, the values of tensile and flexural modulus also follow a similar trend (Table 2).

The incorporation of 5 and 10% (by wt) UP into epoxy resin enhanced the impact strength to 5.1 and 14.7% according to the percentage concentration of UP, due to the formation of entangled network structure developed in the unsaturated active sites of polyester-toughened epoxy system. Further, the incorporation of modified silica into the UP–epoxy systems also increased the impact strength due to the flexibility imparted by the plasticization effect of modified silica (Table 2). The introduction of 1, 3, 5 and 7% (by wt) modified silica into 10% UP-toughened epoxy resin increased the impact strength to 17, 27.4, 34.5 and 43.3%, respectively. The loss of tensile and flexural strength/modulus of epoxy matrices due to the addition of UP was overcome by the addition of modified silica.

Water absorption

The incorporation of unsaturated polyester into epoxy resin decreased the percentage water uptake, according to the

Table 2 Mechanical properties of hybrid UP–epoxy nanocomposites

Epoxy/UP/modified silica	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
100/00/00	67.3	2,807.17	109.4	1,858.79	102.43
100/05/00	64.9	2,710.17	106.7	1,822.43	107.62
100/10/00	62.3	2,619.05	100.8	1,743.73	117.49
100/10/01	73.6	3,051.44	122.3	2,075.17	119.76
100/10/03	78.9	3,278.69	129.1	2,199.42	130.49
100/10/05	84.1	3,510.61	141.3	2,411.20	137.72
100/10/07	86.5	3,641.67	151.2	2,569.79	146.83

Table 3 Water absorption of hybrid UP–epoxy nanocomposites

Epoxy/UP/modified silica composition	Water absorption (%)
100/00/00	0.1341
100/05/00	0.1279
100/10/00	0.1201
100/10/01	0.1194
100/10/03	0.1072
100/10/05	0.0947
100/10/07	0.0639

percentage concentration (Table 3) due to its inherent hydrophobic nature. Further, the incorporation of modified silica into epoxy and UP-toughened epoxy systems also reduced the percentage water uptake due to reduction in permeability behavior influenced by the nanocomposite structure.

Morphology

Comparison of the SEM images (Fig. 3a, b) of the surfaces of nanocomposites, UP-toughened epoxy and neat epoxy matrix shows that the epoxy and unsaturated polyester are strongly interconnected with no major macroscopic phase separation revealing a smooth, glassy and homogeneous microstructure without any plastic deformation. The image of fractured surfaces of unsaturated polyester-modified epoxy matrices filled with 1% (by wt) amine-modified silica nanoparticles shows a uniform dispersion of particles in the matrix and that the particles are in nanometer scale (Fig. 3c). The silica particles present are in spherical shape with an average particle size of 300–400 nm.

Conclusion

Unsaturated polyester-toughened epoxy matrix systems with varied concentration were developed. Mechanical studies inferred that the incorporation of unsaturated polyester into epoxy resin enhanced their impact strength. Amine-modified nanosilica/UP/epoxy nanocomposites were prepared. The incorporation of amine-modified silica into UP–epoxy matrices steadily improved the tensile, flexural and impact strength and exhibited good resistance to water absorption. The incorporation of amine-modified silica into UP–epoxy matrix greatly improved the glass transition temperature. The SEM images of the epoxy and unsaturated polyester-modified epoxy matrix strongly reveal smooth, glassy and homogeneous microstructure without plastic deformation and an equal dispersion of nano-sized fillers on the matrix. The hybrid amine-modified nanosilica-filled UP–epoxy matrix systems developed in the present work can be used to fabricate advanced composite components for engineering and airspace applications for better performance.

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