Thermo-mechanical properties of unsaturated polyester toughened epoxysiliconized iron (III) oxide nanocomposites

S Julyes Jaisingh*, V Selvamb, M Suresh Chandra Kumarb & K Thyagarajanc

*Department of Mechanical Engineering, St. Xavier’s Catholic College of Engineering, Nagercoil 629 003, India
bPolymer Nanocomposite Centre, Department of Chemistry & Research Centre, Scott Christian College, Nagercoil 629 003, India
cDepartment of Mechanical Engineering, Noorul Islam College of Engineering, Kumaracoil 629 180, India

Received 25 March 2013; accepted 12 August 2013

Novel siliconized iron (III) oxide nanoparticles reinforced unsaturated polyester (UP) toughened epoxy nanocomposites is prepared. The siliconized iron (III) oxide nanoparticles are improved thermal and mechanical properties of nanocomposites. Diglycidyl ether of bisphenol A (DGEBA) based epoxy resin is toughened with 5, 10 and 15% (by wt) of UP using benzoyl peroxide as radical initiator and 4, 4′-diaminodiphenylmethane (DDM) as curing agent. UP toughened epoxy systems are reinforced with 1, 3, and 5% (by wt) of siliconized iron (III) oxide nanoparticles. The thermal and mechanical properties, and microstructures of nanocomposites are investigated. Data results from thermal and mechanical studies indicate that the insertion of siliconized iron (III) oxide nanoparticles into UP toughened epoxy system enhances the thermal and mechanical properties. Morphology of the hybrid system reveals homogenous distribution of nanoparticles.

Keywords: Iron (III) oxide nanoparticles, Mechanical properties, Nanocomposites, SEM, Thermal properties

Epoxy resins are the most important class of thermosetting resins for many engineering applications due to their high strength and stiffness, good dielectric behavior, resistance to chemicals, corrosion and microbial organisms, low shrinkage during cure and good thermal characteristics.5-8 Diglycidyl ether of bisphenol A (DGEBA) is one of the most widely used epoxy resins and it has found many engineering applications. Among various inorganic nanoparticles, which based on iron (III) oxide nanoparticles are better for practical applications due to these iron (III) oxide nanoparticles are readily available and also give multifunctional properties. In the field of magnetic materials, solar energy conversion, and electrochromism, iron (III) oxide nanoparticles are used.5-8 Also the iron (III) oxide nanoparticles are used in ferrofluids, magnetic storage, magnetic refrigeration and color imaging. The effect of iron oxide nanoparticles on the thermal properties of polymer nanocomposites has been widely studied.9-15 Surface modification of iron nanoparticles by surfactants, e.g., by use of silane coupling agents, has been reported and it is necessary for proper polymer-filler interactions and improvement of the tensile strength of the nanocomposites.16,17

In our previous studies we observed the effect of reinforcing siliconized iron (III) oxide nanoparticles onto UP toughened epoxy matrix on electrical properties and glass transition temperature.18 In the present work, it is proposed to use unsaturated polyester as a toughening agent in order to improve the thermal properties of epoxy. It is observed that the introduction of UP into epoxy improved the thermal stability, but reduces the stress-strain properties. To prevent the loss of stress-strain properties, nanoparticles like siliconized iron (III) oxide was used as the reinforcement phase to the UP toughened epoxy system. The obtained hybrid nanocomposites were characterized by thermo gravimetric analysis (TGA), tensile and flexural properties and scanning electron microscope (SEM).

Experimental Procedures

Materials

Commercially available diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin LY556 (Ciba-Geigy Ltd., India) having epoxy equivalent of about 180-190, and 4,4′-diaminodiphenylmethane (DDM), epoxy curing agent were obtained from Ciba-Geigy Ltd., India. Unsaturated polyester (UP) resin (isophthallic acid, maleic anhydride and polypropylene glycol with 25% styrene having the

*Corresponding author (E-mail: singh_pec@rediffmail.com)
average molecular weight 2300-2600 g/mol, viscosity at 25°C = 600 cP) was procured from Naptha Resins and Chemicals, India. 3-aminopropyltrimethoxysilane (boiling point = 217°C, density = 0.946 g cm⁻³, $M_w$ = 221.3) and iron (III) oxide nanoparticles (having melting point = 565°C, density = 5.12, <50 nm) were obtained from Sigma Aldrich Inc., USA. Benzoyl peroxide, radical initiator was purchased from Merck India Ltd., India.

**Sample preparation**

**Preparation of hybrid UP toughened epoxy matrix**

A fixed amount of epoxy resin (100 g), varying amounts of unsaturated polyester resin (5, 10 and 15 g), a stoichiometric amount of 4,4'-diaminodiphenylmethane (27.2 g), with respect to epoxy resin and benzoyl peroxide (2 wt%) were mixed at 80°C for 10 min with constant stirring. The hybrid product was then degassed to remove the entrapped air and was then transferred into preheated mould kept at 100°C for 4 h and post-cured at 140°C for 3 h.

**Preparation of siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites**

The iron (III) oxide nanoparticles were siliconized by 3-aminopropylsilane. The epoxy resin was mixed with the desired amount of siliconized iron (III) oxide nanoparticles (1, 3 and 5 g) at 80°C. The nanoparticles filled epoxy resin, a known amount of unsaturated polyester resin (10 g), stoichiometric amount of 4,4'-diaminodiphenylmethane corresponding to epoxy equivalents and benzoyl peroxide were added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 100°C for 4 h. The castings were then post-cured at 140°C for 3 h and finally removed from the mould and characterized. The reaction between epoxy and siliconized iron (III) oxide nanoparticles are shown in Scheme 1.

**General characterization**

The thermal behavior of nanocomposites was performed with a thermo gravimetric analyzer (NETZSCH TG 209) under N₂ atmosphere. Sample was scanned from 0-600°C at a heating rate of 10°C min⁻¹. Tensile properties were measured according to ASTM-D3039 using universal testing machine (Instron, Model 6025 UK) at the cross-head speed of 10 mm/min. Five specimens were tested for each sample. Flexural properties were studied as per ASTM-D790 using universal testing machine (Instron, Model 6025, UK). Five specimens were tested for each sample. Hardness of the nanocomposite materials was measured using Durometer-Type D as per ASTM D2240. Surface morphology of fractured surface of the samples was performed using scanning electron microscope (Quanta-200 FEG, Netherland). The fractured surface of the samples was coated with gold before scanning.

**Result and Discussion**

**Thermo gravimetric analysis**

Figure 1 shows TGA curves of UP resin, epoxy, UP toughened epoxy and siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposite. The initial and final decomposition temperature for UP resin 296°C and 590.14°C, for neat epoxy 356.22°C and 586°C, for UP toughened epoxy 366°C and 592.14°C and for siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites 374°C and 592.22°C.

![Scheme 1](image_url)

Scheme 1—Reaction between epoxy and siliconized iron (III) oxide nanoparticles

![Fig. 1](image_url)

Fig. 1—TGA curves of (a) UP resin, (b) epoxy, (c) UP toughened epoxy (10:100) and (d) siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites (05:10:100)
respectively. Toughening the epoxy resin by UP improved the thermal stability and enhanced the degradation temperature. The delay in degradation caused by UP moiety is attributed to its cross-linked network structure of UP toughened epoxy system. The resistance to initial thermal degradation was improved after siliconized iron (III) oxide nanoparticles were reinforced, indicating a strong interaction between nanoparticles and UP toughened epoxy systems. Similar results were already reported on iron (III) oxide nanoparticles reinforced vinyl-ester resin composites. The existence of silane on the nanoparticles surface prevents the intimate contact of the iron (III) oxide nanoparticles with the epoxy resin by passivating the particle surface and thus may improve the thermal stability of the nanocomposites.

Mechanical properties

The tensile and flexural properties of epoxy, UP toughened epoxy, siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites are presented in Table 1. The introduction of 5, 10 and 15% UP (by wt) into epoxy resin decreased the tensile strength (8.8%, 16.1%, and 19.3%) and flexural strength (1.1%, 3.9%, and 6.4%) when compared with those of unmodified epoxy resin. This is due to the formation of chain entanglement in the UP epoxy matrix system. The incorporation of 1%, 3% and 5% (by wt) siliconized iron (III) oxide nanoparticles into UP toughened epoxy hybrid matrix enhances the value of tensile strength (34.6, 39.8 and 45.9%) and tensile modulus (26.8, 37.3 and 50.8%) due to the nanocomposites formation. The value of flexural strength and flexural modulus also increases (17.9, 40.8, 54.8% and 25.1, 36.5 and 45.5%) by the addition of 1, 3 and 5% (by wt) siliconized iron (III) oxide nanoparticles into UP toughened epoxy hybrid matrix. This is attributed to the improved nanoparticles dispersion and enhanced interaction between nanoparticles and polymer matrix. Therefore, the stress concentration is lower and the stresses can be more easily transferred from the matrix to nanoparticles. The intimate contact between the nanoparticles and the matrix also ensures a reduction of crack propagation. All the above features in the siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites definitely favor increases of the mechanical properties.

The values of hardness for 5, 10 and 15% (by wt) UP toughened epoxy systems were decreased to 78, 75 and 72 respectively due to the flexible ether group formation by the reaction of hydroxyl group of unsaturated polyester resin and the epoxide group of DGEBA resin. When the UP concentration increases the crosslinking density of the epoxy system decreases due to the formation of IPN structures. A significant improvement was observed in the values of hardness when 10% (by wt) UP toughened epoxy system was reinforced with 1, 3 and 5% (by wt) siliconized iron (III) oxide nanoparticles which confirm the effective network formation.

Morphology

The SEM micrographs of fractured surfaces of the unmodified epoxy system indicate smooth, glassy and homogenous microstructure (Fig. 2a). The SEM image of UP toughened epoxy system shows a homogenous structure (Fig. 2b) which confirms the effective blend between UP and epoxy resin. This further supports that there is no phase separation between the two components. Figure 2c shows the iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites. The iron (III) oxide nanoparticles are observed and found that they do not have regular shape

<table>
<thead>
<tr>
<th>Epoxy/UP/Iron (III) oxide/Si-iron (III) oxide Composition</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/00/00/00</td>
<td>67.75</td>
<td>2627.5</td>
<td>111.5</td>
<td>1924.2</td>
<td>82</td>
</tr>
<tr>
<td>100/05/00/00</td>
<td>63.4</td>
<td>2656</td>
<td>110.3</td>
<td>1840.4</td>
<td>78</td>
</tr>
<tr>
<td>100/10/00/00</td>
<td>59.5</td>
<td>2477</td>
<td>105.4</td>
<td>1760</td>
<td>75</td>
</tr>
<tr>
<td>100/15/00/00</td>
<td>57.6</td>
<td>2370</td>
<td>99.8</td>
<td>1660</td>
<td>72</td>
</tr>
<tr>
<td>100/10/01/00</td>
<td>55.87</td>
<td>2230</td>
<td>99.7</td>
<td>1680.4</td>
<td>73</td>
</tr>
<tr>
<td>100/10/03/00</td>
<td>54.72</td>
<td>2100</td>
<td>97.6</td>
<td>1564.2</td>
<td>82</td>
</tr>
<tr>
<td>100/10/05/00</td>
<td>52.86</td>
<td>2010</td>
<td>94.2</td>
<td>1332.4</td>
<td>86</td>
</tr>
<tr>
<td>100/10/00/01</td>
<td>71.8</td>
<td>2883.2</td>
<td>124.8</td>
<td>2150.6</td>
<td>87</td>
</tr>
<tr>
<td>100/10/00/03</td>
<td>76.8</td>
<td>3220.2</td>
<td>132.4</td>
<td>2274.4</td>
<td>92</td>
</tr>
<tr>
<td>100/10/00/05</td>
<td>82.2</td>
<td>3387</td>
<td>140.6</td>
<td>2402.8</td>
<td>96</td>
</tr>
</tbody>
</table>
and poor dispersion. This indicates low adhesion between nanoparticles dispersion in the polymer matrix. However, nanocomposites contain siliconized iron (III) oxide nanoparticles (Fig. 2d) have regular spherical shape and improve its dispersion in the polymer matrix. SEM images show the size of the nanoparticles does not change significantly after the siliconization. No observable void found which indicates a strong chemical interaction between the nanoparticles and polymer matrix which favours a more compact solid structure.

Conclusions
The various concentrations of siliconized iron (III) oxide nanoparticles reinforced UP toughened epoxy nanocomposites were prepared successfully. Incorporation of siliconized iron (III) oxide nanoparticles into UP toughened epoxy matrix systems increased tensile and flexural strengths and thermal stability. This reveals that there is chemical reaction between nanoparticles and the polymer matrix. Morphology of the siliconized iron (III) nanoparticles reinforced epoxy composites shows homogenous microstructure. It implies that functionalized nanoparticles only well dispersed into UP toughened epoxy matrix.

References