CHAPTER 2

EXPERIMENTAL WORK

This chapter describes the development of siliconization of iron (III) oxide nanoparticles, siliconization of iron (III) oxide nanoparticles reinforced with Unsaturated Polyester toughened epoxy nanocomposites, Glass and Kevlar fibre reinforced UP toughened epoxy/siliconized iron (III) oxide nanocomposites. It also describes experimental procedure for the studies of physico-chemical, mechanical, wear, electrical, thermal and morphological properties of nanocomposites. Experimental plan of the work is represented in Figure 2.1.

2.1 MATERIALS

I. The DGEBA based epoxy resin, LY 556 (epoxy equivalent of 185 g/eq and viscosity of 10,000 cP) and the hardener, 4,4’-diaminodiphenylmethane (DDM) were purchased from, Ciba-Geigy Ltd., India. Unsaturated polyester (isophthalic acid based, viscosity at 25°C = 2300-4000 cP, OH index = 24.4 eq/kg) was provided by Polyresins, India.

II. Iron (III) oxide nanoparticles with an average size of 50nm, 3-aminopropyltrimethoxysilane was purchased from sigmaAldrich India.

III. Glass fibre and Kevlar fibre were purchased from Ceat Ltd., India.
2.2 EXPERIMENTAL PLAN

Figure 2.1 Flow chart showing the experimental plan of the work
2.2.1 Preparation of Siliconized Iron (III) Oxide Nanoparticles

The siliconization of iron (III) oxide nanoparticles with 3-aminopropyltrimethoxysilane was carried out in a 250 ml 3-neck flask, equipped with a reflux condenser (Figure 2.13a), nitrogen inlet tube, dropping funnel, on a thermostated silicone bath. The reactions were performed in inert atmosphere (N$_2$ atmosphere), at dichloroethane reflux temperature (81°C) for 24 h. 20 ml dichloroethane, 0.3 g dibutyltin dilaurate (catalyst), 0.6367 g iron (III) oxide nanoparticle (2.7 mmol) and 4.73 g 3-aminopropyltrimethoxysilane (21.4 mmol) were added. The unreacted solvent and monomers were separated by vacuum distillation on a rotavapor at 35°C. Siliconized iron (III) oxide nanoparticles, washed with small amounts of toluene for the removal of siloxane oligomers formed during the reaction and with acetone for the separation of catalyst, were dried in vacuum at 35°C for 24 h (Park et al 2010). Figure 2.2 shows scheme of the siliconization of iron (III) oxide nanoparticles.

![Figure 2.2 Preparation of Si- Fe$_2$O$_3$ nanoparticles](image-url)
2.2.2 Development of UP Toughened Epoxy Matrix

Unsaturated polyester toughened epoxy matrix was developed by blending calculated amount of UP (5, 10, 15 and 20 wt. %) relative to the epoxy resin (100 w/w), stoichiometric amount of DDM (27.2 g) with respect to epoxy resin and benzoyl peroxide (2 wt. %) using a high speed stirrer at 80°C for 10 min. with constant stirring. The hybrid product was then degassed to remove the entrapped air and then transferred into a preheated mould (Figure 2.14) and kept at 100°C for 4 h and post cured at 140°C for 3 h and finally removed from the mould and characterized. 10 wt% of UP is considered for further studies since here the impact strength is near maximum.

2.2.3 Preparation of UP Toughened Epoxy Matrix Reinforced with Siliconized Iron (III) Oxide Nanoparticles

The epoxy resin (100 g) was mixed with the desired amount of siliconized iron (III) oxide nanoparticles (1, 3 and 5 wt %) at 70 °C for 24 h. To the Si-Fe$_2$O$_3$ nanoparticles filled epoxy resin, known amounts of unsaturated polyester resin (10 g) and benzoyl peroxide were added (2 wt.%) at 80 °C for 10 min. with (2000 rpm) 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 transferred into a preheated mould and cured at 100 °C for 4 h and post-cured at 140 °C for 3 h. Figure 2.3 shows the scheme for the reaction between epoxy and siliconized iron (III) oxide nanoparticles.
2.2.4 Preparation of Fibre Reinforced Siliconized Iron (III) Oxide Nanoparticles Filled with UP Toughened Epoxy Nanocomposites

The siliconized iron (III) oxide nanoparticles was mixed with UP toughened epoxy (1, 3, 5 wt %) respectively using mechanical stirring followed by sonication process (Figure 2.13b). The obtained epoxy mixture was reinforced with glass fibre. The epoxy resin mixture was applied on the both sides of the glass fibre. All samples were prepared using eight layers of glass fibre. In samples resin/fibre ratio was between 0.5 and 0.7. The obtained sample was placed in aluminum plates and clamped. Finally the sample was cured at 100°C for 4 h and post cured at 140°C for 3 h. The same procedures are followed for Kevlar fibre reinforced UP toughened epoxy nanocomposites.
2.3 CHARACTERIZATION

2.3.1 Physico-Chemical Properties

2.3.1.1 FT-IR spectroscopy

The Fourier transform infrared spectra (FT-IR) are recorded on a Shimadzu-1800S spectrophotometer using KBr pellets for solid samples. The viscous liquid samples were directly applied by dubbing on a KBr pellet. The structure and purity of epoxy, iron (III) oxide nanoparticles, UP toughened epoxy and siliconized iron (III) oxide nanoparticles reinforced epoxy nanocomposites were confirmed by FTIR.

2.3.1.2 XRD studies

X-Ray diffraction (XRD) data for nanocomposites were recorded at room temperature using Philips X’Pert PRO diffractometer with Cu K$_\alpha$ radiation at 40 kV/100 mA. The diffraction patterns were determined over a range of diffraction $2\theta = 0 – 100^\circ$.

2.3.1.3 Scanning electron microscope

The fractured surfaces of specimens were coated with gold and examined under a scanning electron microscope (FEG Quanta-200, Netherland). Fractured surfaces were obtained from tensile tested specimen.

2.3.1.4 Transmission electron microscope

Transmission electron microscope (TEM) was used to characterize the morphology (size and shape) of the as unmodified and siliconized iron (III) oxide nanoparticles. TEM was carried out in a JEM 100CX (JEOL) with an accelerating voltage of 100 keV.
2.4 MECHANICAL STUDIES

2.4.1 Tensile Properties of Nanocomposites

The tensile properties were tested on a Shimadzu Autograph (AG-I 50 kN) Universal Testing Machine (Figure A 1.1) (ASTM D 638 and ASTM D 3039 - Ref. Figure 2.4, 2.5 and 4.17 a, b 4.18 a, b and 4.19 a) at a constant rate of traverse of the moving grip of 5mm/min. The cast specimens were polished using emery paper prior to testing. One grip is attached to a fixed and the other to a movable (power driven) member so that they will move freely into alignment as soon as any load is applied. The test specimen was held tight by the two grips, the lower grip being fixed. The output data in the form of stress-strain graph and elongation, modulus and energy absorbed at various stages of the test directly appear on the console of the microprocessor and as a print out. The area under the stress-strain curve provides an indication of the overall toughness of the material at the particular temperature and rate of loading. The energy absorbed by the sample to break is a measure of the toughness. Five specimens were tested for each sample.

Figure 2.4 Tensile specimen as per ASTM D 638

Figure 2.5 Tensile specimen as per ASTM D 3039
2.4.1.1  **Tensile strength**

Tensile strength or tenacity is the stress at the breaking point. Tensile strength is obtained from the maximum load applied in breaking a tensile test piece divided by the original cross-sectional area of the test piece. Originally quoted as tons/sq.in. it is now measured as Newtons/sq.mm. Also termed Maximum Stress and Ultimate Tensile Stress

Tensile strength = Load at break / original cross-sectional area

\[ \sigma = \frac{P}{b \times d} \]  

(2.1)

where, P is the load applied in N, b is the width in mm and d is the thickness in mm

2.4.1.2  **Tensile modulus**

The stiffness of a material is the ability of material to resist bending. When a strip of material is bent, one surface is stretched and the opposite face is compressed. The more a material bends, the greater is the amount by which the stretched surface extends and the compressed surface contracts. Thus a stiff material wound is one that gave a small change in length when subject to tensile or compressive forces.

This means a small strain when subject to tensile or compressive stress and so a large value of stress/strain and hence a steep initial gradient of the stress strain graph. This gradient is called the tensile modulus (or modulus of elasticity), Symbol E: Bolton (1998)

\[ \text{Tensile modulus } E = \frac{\text{Stress}}{\text{Strain}} = \frac{\Delta P}{\Delta l} \]  

(2.2)
After the tensile testing the fractured samples were examined using JEOL Scanning Electron Microscope (SEM).

2.4.1.3 Elongation at break

Ductility is a qualitative, subjective property of a material and the measurement of ductility is of interest to indicate to the designer, in a general way, the ability of the metal to flow plastically before fracture. The conventional measures of ductility that are obtained from the tension test are the engineering strain at fracture (usually called elongation) and the reduction of area at fracture. In this investigation, the elongation of the specimen at break has been calculated by the following expression Budinski (1998).

\[
\text{Elongation} \, \%(\%) = \left( \frac{L_f - L_0}{L_0} \right) \times 100
\]

(2.3)

Where \( L_f \) is the final gauge length after failure and \( L_0 \) is the initial gauge length before loading (here the gauge length has been maintained as 60 mm).

2.4.1.4 Reduction in area

Another measure of ductility which is sometimes used is the percent reduction in area, defined as

\[
\text{Percent reduction in area} = 100 \times \frac{A_0 - A_B}{A_0}
\]

(2.4)

where \( A_0 \) and \( A_B \) denotes the original cross-sectional area of the specimen and its minimum cross-sectional area at rupture.
2.4.1.5 Poisson’s ratio

A homogeneous slender bar is axially loaded, the resulting stress and strain satisfy Hooke’ law, as long as the elastic limit of the material is not exceeded. In all engineering materials, the elongation produced by an axial tensile force P in the direction of the force is accompanied by a contraction in any transverse direction. All materials considered will be assumed to be both homogeneous and isotropic, i.e., their mechanical properties will be assumed independent of both position and direction. It follows that the strain must have the same value for any transverse direction. Therefore, in the loading we must have $E_y=E_z$. This common value is referred to as the lateral strain. An important constant for a given material is its Poisson’s ratio,

$$\mu = \frac{\text{Lateral strain}}{\text{Linear strain}} (2.5)$$

2.4.2 Flexural Properties

The flexural properties were tested on a Shimadzu Autograph (AG-I 50 kN) Universal Testing Machine (Figure A.1.2) (ASTM D 790 - Ref. Figure 2.6, 5.12, 5.13a, b, c and d) at a constant rate of traverse of the moving grip of 1.3 mm/min. The cast specimens in the form of rectangular bars were polished using emery paper prior to testing. The depth and width of the specimen was measured nearest to 0.01 mm. The support span should be 16 times the depth of the specimen. The specimen was centered on the supports with the long axis of the specimen perpendicular to the loading nose and
supports. The load was applied to the specimen and flexural strength and modulus were recorded. Five specimens were tested for each sample.

![Figure 2.6 Flexural specimen as per ASTM D 790](image)

### 2.4.2.1 Flexural strength

Flexural strength, also known as modulus of rupture, bend strength, or fracture strength, is measured in terms of stress, and thus is expressed in units of pressure (or stress, the two being equivalent). The value represents the highest stress experienced within the material at its moment of rupture. In a bending test, the highest stress is reached on the surface of the sample.

For a rectangular sample under a load in a three-point bending setup where the loading span is one-third of the support span

\[
\sigma_f = \frac{3PL}{2bd^2}
\]  

where

- \( \sigma_f \) is the Flexural strength (MPa)
- \( P \) is the load (force) at the fracture point (N)
- \( L \) is the length of the support (outer) span (mm)
- \( b \) is width of the bar (mm)
- \( d \) is thickness of the bar (mm)
2.4.2.2 Flexural modulus

The flexural modulus is a measure of stiffness. It is determined by using the following equation

\[ E_f = \frac{PL^3}{48\delta I} \] (2.7)

where, \( E_f \) is flexural modulus, \( P \) is load (N), \( L \) is the length of the specimen (50 mm), \( \delta \) is the deflection in mm and moment of inertia, \( I = \frac{bd^3}{12} \) (b is width in mm and d is thickness in mm)

2.4.3 Impact Strength

Impact strength is defined as toughness or the ability of a rigid material to withstand a sharp blow, such as that from a hammer. Impact strength is determined using impact strength tester as per ASTM D 256 (Figure 2.7). Five specimens were tested for each sample.

![Figure 2.7 Impact specimen as per ASTM D 256](image)

The pendulum was released and the force consumed in breaking the sample was calculated from the height of the pendulum reached on the follow through using the following formula.

\[ \text{Impact strength} = \frac{\text{Energy absorbed (J)}}{\text{Thickness of the sample (m)}} \] (2.8)
2.4.4 Wear Properties

The wear specimens were prepared by machining the nanocomposites as square plate of 6mm x 6mm x 3mm size. The counterwear material was a hardened alloy steel disc. Wear tests were performed using a wear tester (MPD Friction & Wear Tester) by following a pin-on-disc (Figure 2.8, Figure 2.9 (a) and (b) procedure of ASTM G99 (ASTM). Sliding speed was fixed at 0.18 m/s and applied load were 1, 5 and 10 N, respectively.

![Figure 2.8 Wear testing experimental setup](image)

![Figure 2.9 (a) Position of pin on disc](image)  ![Figure 2.9 (b) Pin with specimen](image)
2.4.5 Hardness

Hardness of the material is measured using Durometer – Type D as per ASTM D 2240 using specimens with 3 mm thickness. The specimen is placed on a hard horizontal surface. The durometer is held in a position in the point of indentor at least 12mm from any edge of the specimen. The Durometer has a pointed indenter projecting below the base of the presser foot. When the indenter is pressed into the plastic specimen so that the base rests on the plastic surface, the amount of indentation registers directly on the dial indicator. Hardness is determined at five different positions on the specimen at least 6 mm apart and arithmetic mean is taken.

2.4.6 Water Absorption

Test specimen were immersed in water for 24 hours at 30° C and the percentage of water absorbed by the specimen was calculated using Equation :

\[
\% \text{ Increase in weight} = \frac{(w_2 - w_1)}{w_1} \times 100
\]  

(2.9)

where, \( w_1 \) is the initial weight of the sample and \( w_2 \) is weight of sample after immersion in water for 24 hours at 30° C.

2.4.7 Electrical Characteristics

2.4.7.1 Dielectric strength

The dielectric strength of an insulating material is defined as the maximum voltage required producing a dielectric-breakdown and is expressed in volts per unit of thickness such as V/mm. The higher the dielectric strength, the better the quality of an insulator. Dielectric strength is determined as per
ASTM D 149 in a dielectric strength tester. Figure 2.10 shows the dielectric strength specimen.

![Dielectric strength specimen as per ASTM D 149](image)

Dielectric strength of specimens is determined by step by step test using heavy cylindrical brass electrodes on the plane surfaces of specimen disks having 100-mm diameter and 2.5-mm thickness, kept immersed in insulating oil, to prevent splash over during the test.

\[
\text{Dielectric strength (V/mm) =} \frac{\text{Breakdown voltage (V)}}{\text{Thickness (mm)}} \quad (2.10)
\]

2.4.7.2 Dielectric constant

Dielectric constant for the samples was determined per ASTM D149 using Shearing Bridge at 50 Hz. The diameter and thickness of the specimens were 55 mm and 4 mm respectively.
2.4.7.3 Volume and surface resistivity

The volume and surface resistivity of the moulded samples were determined as per ASTM D 257-83 using a Sigma MM87, Million Mega Ohm Meter at 500V for 60 seconds at room temperature. The diameter and thickness of the specimen were 110 mm and 4 mm respectively. Figure 2.11 Shows volume and surface resistivity specimen.

![Volume and surface resistivity specimen as per ASTM D257](image)

2.4.7.4 Arc resistance

Arc resistance is measured as per ASTM D 495 (Figure 2.12) and is the ability of the insulating material to resist the action of a high voltage electrical arc, usually stated in terms of time required to form material electrically conductive. Failure is characterized by carbonization of the surface, tracking, localized heating to incandescence, or burning. Arc resistance of coating materials can be improved substantially by the addition of inorganic fillers.
In this test, a high voltage arc (15 kV) is struck between two electrodes placed on the test specimen of 3 mm thickness, the initial current being a few milli amperes. The arc is interrupted by a timer, the ‘on’ and ‘off’ intervals being carefully defined. As the test progress the ‘off’ period decreases until finally, in later stages the arc is continuous and its severity is increased by increasing the arc current. The materials are classified by their time to failure.

2.4.8 Thermal Properties

2.4.8.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) were performed on a NETZSCH TG 209 thermogravimetric analyzer between 0 and 600 °C with a 10 ºC min⁻¹ heating rate under nitrogen flow rate of 20.0 ml min⁻¹. TGA is used to determine thermal degradation temperatures and percentage weight. The first derivative of primary thermogravimetric curves, representing rate of weight loss, were determined from tangents for the weight loss curves.
2.4.8.2 Differential scanning calorimetry (DSC)

The thermal behavior of hybrid matrices and nanocomposites were studied using NETZSCH DSC 200 thermal analyzer under nitrogen flow in the temperature range 0°C to 300 °C, with a heating rate of 10 °C/min. The glass transition temperature of each sample was taken the midpoint of the step in the scan.

Figure 2.13 Experimental setup (a) Reflux condenser

Figure 2.13 (b) Sonicator
Figure 2.14 Types of moulds used for specimen preparation