CHAPTER 2

EXPERIMENTAL

This chapter describes the synthesis of four different types of bismaleimides namely N,N’-bismaleimido-4,4’-diphenylmethane (BMI-1), 1,3-bismaleimido benzene (BMI-2), 3,3’-bis(maleimidophenyl) phenylphosphine oxide (BMI-3) and 1,1’-bis(4-maleimidophenyl) cyclohexane (BMI-4) and preparation of polysulfone modified epoxy, preparation of bismaleimide modified epoxy, bismaleimide modified polysulfone epoxy, polyethersulfone modified epoxy, bismaleimide modified polyethersulfone epoxy and organo clay filled polysulfone modified epoxy nanocomposites. It also deals with the experimental procedure for the studies of physico-chemical, mechanical, electrical, thermal and morphological properties of modified epoxy matrix systems and organoclay filled modified epoxy systems.

2.1 MATERIALS

Materials used for the development of bismaleimide modified polysulfone – epoxy and organoclay filled modified epoxy systems are

(i) Epoxide resin LY 556 (diglycidyl ether of bisphenol-A, (DGEBA) Ciba-Geigy, epoxy equivalent = 180-190, viscosity 10,000 cP) and 4,4’-diaminodiphenylmethane (DDM, epoxy curing agent) are obtained from Ciba Geigy Ltd., India.
(ii) Bisphenol – A based polysulfone (Mw = 15000 g/mol, Tg = 195 °C) supplied by Shauguang chemical factory, Shanghai, China was used as received and the structure is given in Figure 2.1.

(iii) Hydroxyl terminated polyethersulfone (Mw = 1.38 KDa, Tg = 225 °C) received from Jilin University, China was used as received and its structure is given in Figure 2.2.

(iv) Bismaleimides namely N,N’-bismaleimido-4,4’-diphenylmethane (BMI-1), 1,3’-bismaleimido benzene (BMI-2), 3,3’-bis(maleimidophenyl) phenylphosphine oxide (BMI-3) and 1,1’-bis(4-maleimidophenyl)cyclohexane (BMI-4) were synthesized as per reported procedures (Crivello 1976 and Ashok Kumar et al 2001).

(v) Montmorillonite used for the nanocomposites preparation was obtained from Aldrich (USA) and was organically modified for the development of nanocomposites based on modified epoxy systems.

2.2 SYNTHESIS OF BIS(3-AMINOPHENYL) PHENYLPHOSPHINE OXIDE

Triphenylphosphine oxide (27.8 g, 0.1 M) was placed in a 500 ml RB flask equipped with stirrer and nitrogen atmosphere and 200 ml of 96% H₂SO₄ was added. The reaction system was cooled to -5 °C with an ice bath. A solution of 14.5 g (0.4 M) of fuming nitric acid in 100 ml of H₂SO₄ was added drop wise over a period of 2 hrs. The reaction system was kept at 25°C for another 8 hrs. The reaction solution was hydrolyzed over ice. After the melting of ice, the mixture was extracted with chloroform
and washed with aq. NaHCO₃ until neutral pH. The solvent was removed. The solid product (Bis(3-nitrophenyl)phenylphosphine oxide) was recrystallized from absolute ethanol (Yield - 70%)

25 g of bis(3-nitrophenyl)phenylphosphine oxide was placed in a 1000 ml RB flask with 180 g of powder SnCl₂.2H₂O. A solution of 200 ml fuming HCl in 400 ml ethanol was introduced into the flask. The reaction mixture was stirred at room temperature for 5 hrs. The solution was concentrated and then neutralized by 25% aqueous solution of NaOH. The resulting solution was extracted with chloroform. The organic layer was collected and concentrated under a reduced pressure. The product was recrystallized from CH₂Cl₂ to get a pure product (Yield 95%). The synthesis route of 3,3’-bis(maleimidophenyl)phenylphosphine oxide is presented in Scheme 2.1.

2.3 SYNTHESIS OF 1,1’-BIS(4-AMINOPHENYL) CYCLOHEXANE

To a three necked round bottom flask, a mixture of 30 mL of H₂O, 30 mL of concentrated HCl (0.36 mol), and 9.8 g (0.1 mol) of cyclohexanone was stirred in an ice bath, and 20.49 g (0.22 mol) of aniline was dropped within 20 minutes under nitrogen atmosphere and refluxed for 24 hours. The mixture was poured slowly into 300 mL of 15% Na₂CO₃ solution; the precipitate formed was filtered and washed with water until a neutral pH was obtained. The product was recrystallized from isopropyl alcohol. Yield 70%, melting point 112°C (Gao et al 2003). The synthesis route of 1,1’-bis(4-amino phenyl) cyclohexane is presented in Scheme 2.2.
Figure 2.1 Bisphenol-A based polysulfone

Figure 2.2 Polyethersulfone

Scheme 2.1 Synthesis of bis(3-aminophenyl)phenylphosphine oxide
Scheme 2.2 Synthesis of 1,1'-bis(4-amino phenyl) cyclohexane

2.4 SYNTHESIS OF BISMALEIMIDES

Bismaleimides namely N,N’-bismaleimido-4,4’-diphenylmethane (BMI-1), 1,3-bis (maleimido) benzene (BMI-2), 3,3’-bis(maleimidophenyl) phenylphosphine oxide (BMI-3) and 1,1’-bis (4-maleimidophenyl) cyclohexane (BMI-4) were prepared from the corresponding amines N,N’-diaminodiphenylmethane, 1,3 diaminodiphenyl benzene, bis-(3-amino phenyl)phenylphosphine oxide, 1,1’-bis(4-amino phenyl) cyclohexane and maleic anhydride by using acetic anhydride as the dehydrating agent with nickel acetate and triethylamine as catalysts.

To a one litre three-necked flask fitted with paddle stirrer, reflux condenser and nitrogen inlet, were added, 600 ml acetone, 0.5 mole (49.05 g) maleic anhydride and 0.25 mole of the desired aromatic diamine. Rapid formation of precipitate of the bismaleimic acid occurred on mixing the reactants together, and the mixture was allowed to stand for 30 minutes to complete the reaction. To the reaction vessel were now added 0.5-g nickel acetate and 12.5 ml triethylamine and the entire mixture heated slowly to reflux. Then by means of pressure equalizing funnel 59 ml acetic anhydride was added to the refluxing reaction mixture and heating was continued for an additional three hours. The reaction mixture was diluted with 500 ml water
and chilled to crystallize the bismaleimide. The resulting bismaleimide was filtered and recrystallized from toluene. The synthesis route for different bismaleimides is presented in Scheme 2.3.

2.5 PREPARATION OF POLYSULFONE - EPOXY PREPOLYMER

The hybrid polysulfone epoxy matrices were prepared by dissolving varying percentages (4, 8, 12% by wt) of bisphenol-A based polysulfone and tetramethyl ammonium hydroxide (TMAH) in known amount (100% by wt) of epoxy resin with continuous stirring at 150°C for two hours. The blend obtained was degassed under vacuum for half an hour and then cooled to 90°C. Then the stoichiometric amount of 4,4’-diaminodiphenylmethane was added to the blend with continuous stirring until a homogeneous liquid was obtained. The product was subjected to vacuum to remove the trapped air, and poured into a preheated mould. The samples were cured successively at 120 °C for 2 hours and post-cured at 180°C for 2 hours and finally removed from the mould and characterized.

2.6 PREPARATION OF BISMALEIMIDE MODIFIED POLYSULFONE – EPOXY MATRICES

The calculated amount of bismaleimide was dissolved into polysulfone-epoxy blend under vigorous stirring. The stoichiometric amount of 4,4’-diaminodiphenylmethane (with respect to epoxy) was added. The agitation was continued at 100°C until a homogeneous product was obtained. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120°C for 3 hours. The castings were then post cured at 180°C for 2 hours and finally removed from the mould and characterized.
Scheme 2.3 Synthesis of bismaleimides
2.7 DEVELOPMENT OF ORGANOCLAY FILLED POLYSULFONE MODIFIED EPOXY NANOCOMPOSITES

2.7.1 Purification of montmorillonite clay

A known amount (25 g) of the crude montmorillonite clay was first dispersed into 5 litres of 1N solution of NaCl with constant stirring for 24 hours at 70°C. Upon centrifugation of the solution at high speed an opaque whitish layer accumulates in the bottom of the centrifuge tubes beneath a translucent gel. The gel was isolated and washed several times with deionised water until no chloride was detected in the centrifugate which was ascertained by testing with one drop of 0.1N AgNO₃ solution. The purified clay was dried at 70°C and stored in desiccator.

2.7.2 Intercalation of the alkylammonium ions

15 g of the purified montmorillonite clay was dispersed into 1200 ml of distilled water at 80 °C. 5.7 g of cetylammonium bromide in 300 ml distilled water was poured in the hot mixture of montmorillonite and water and stirred vigorously for 1 hour at 80 °C. A white precipitate formed, was isolated by filtration and washed several times with a hot water/ethanol (1:1) mixture until no chloride was detected in the filtrate by one drop of 0.1 N AgNO₃ solution. The cetylammonium ion exchanged montmorillonite was then dried 10 days at 75 °C, ground with a mortar and pestle, and then the < 50 µm fraction was collected. The organophilic clay was stored in desiccator.

2.7.3 Determination of cation exchange capacity

The cation exchange capacity (CEC) of montmorillonite clay was first measured by determining the amount of alkylammonium salt being
retained by the organoclay after careful washing. The dried organophilic clay along with a sample of its corresponding untreated clay was ignited at 1000°C in an electric furnace. From the differences in the loss on ignition of the sample and blank and the molecular weight of the alkylammonium salt, the milli equivalents of the organic substance retained by the clay were calculated and these values are taken as its Cation Exchange Capacity.

2.7.4 Preparation of organoclay filled epoxy nanocomposites

Prior to curing, the epoxy resin and polysulfone - epoxy was mixed with the desired amount of organophilic clay at 70°C for 24 hours. A stoichiometric amount of the curing agent corresponding to epoxy equivalents was added. The product was subjected to vacuum to remove the trapped air and then cast and cured at 140°C for 3 hours. The castings were then post cured at 200°C for 2 hours and finally removed from the mould and characterized.

2.8 CHARACTERIZATION

Mechanical, electrical and thermal characteristics of unmodified epoxy, polysulfone modified epoxy, bismaleimides (BMI-1, BMI-2 and BMI-3) modified polysulfone-epoxy, bismaleimide (BMI-2) modified polyethersulfone epoxy, organoclay filled polysulfone-epoxy nanocomposites are tested as per ASTM standards.

2.9 MECHANICAL CHARACTERISTICS

Mechanical properties such as, tensile strength, tensile modulus, flexural strength, flexural modulus, hardness and plain strain fracture toughness of modified epoxy matrix samples are studied as per ASTM standards.
2.9.1 Tensile properties

Tensile strength is a measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the materials stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Tensile properties are studied as per ASTM-D3039 using Instron testing machine (Model 6025 UK), at 10-mm/minute crosshead speed, using specimen with a width of 25 mm, length of 200 mm, and thickness of 3 mm. A distance of 115 mm is kept in between the grips. The test specimen is prepared by machining operation. Five specimens are tested for each sample.

2.9.1.1 Tensile strength

Tensile strength or tenacity is the stress at the breaking point of test specimen. Tensile strength is obtained from the experimental data using equation 2.1.

\[
\text{Tensile strength} = \frac{\text{load at break}}{\text{original cross-sectional area}} = \frac{L}{b \times D} \tag{2.1}
\]

where, \(L\) is the load applied in N, \(b\) is the width in mm and \(D\) is thickness in mm.

2.9.1.2 Tensile modulus

Tensile modulus is given by the equation 2.2,

\[
\text{Tensile modulus} = \frac{\text{Tensile stress}}{\text{Tensile strain}} = \frac{\text{difference in load (N)}}{\text{difference in extension (mm)}} = \frac{\Delta P}{\Delta \delta} \tag{2.2}
\]
2.9.2  Flexural properties

Flexural properties are studied as per ASTM D790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length using Instron testing machine (Model 6025 UK), at 10 mm/minute cross-head speed.

2.9.2.1  Flexural strength

Flexural strength is the maximum stress developed when a bar shaped test piece acting as a simple beam, is subjected to a bending force perpendicular to the bar. Flexural strength is calculated from the data using equation 2.3,

\[
\text{Flexural strength (S)} = \frac{PL}{bd^2}
\]

(2.3)

where,  
\(P\) = load at a given point on the deflection curve (N)  
\(L\) = length of the support span (mm)  
\(d\) = width of the bar (mm)  
\(b\) = depth of the beam (mm)

2.9.2.2  Flexural modulus

Flexural modulus is a measure of stiffness. It is determined by using equation 2.4,

\[
E = \frac{wl^3}{48\delta I}
\]

(2.4)

where, \(E\) is flexural modulus, \(w\) is load (N), \(l\) is the length of the specimen (50 mm), \(\delta\) is the deflection in mm and \(I = \frac{bd^3}{12}\) (\(b\) is width in mm and \(d\) is thickness in mm).
2.9.3 Hardness

Hardness of the composite material is measured using Durometer - Type D as per ASTM D2240. The sample specimens are 3 mm in thickness. The surface of the specimen is flat over sufficient area to permit presser foot to contact the specimen over an area having 6 mm radius for the indenter point. The specimen is placed on a hard horizontal surface. The Durometer is held in a position in the point of indenter at least 12 mm 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 in to 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.

2.9.4 Izod Impact Strength

The Izod impact strength of each sample was tested as per ASTM D 256-88(model 6025, UK). All samples were tested unnotched so that they would be more sensitive to the transition between ductility and brittleness. Specimens, having thickness 3.2 mm with 10 mm cross-section and 64 mm long were clamped in the base of the pendulum testing machine so that they cantilevered upward. The pendulum was released and the force consumed in breaking the sample calculated from the height the pendulum reached on the follow through.

2.10 ELECTRICAL PROPERTIES

Electrical properties namely, dielectric strength, arc resistance and surface resistivities of matrix samples are studied as per ASTM standards.
2.10.1 Dielectric strength

The dielectric strength of an insulating material is defined, as the maximum voltage required for producing a dielectric breakdown. Dielectric strength is expressed in volts per unit of thickness such as V/mil. Dielectric indicates electrical strength of a material as an insulator, is a very important characteristic of an insulating material. The higher the dielectric strength, the better the quality of an insulator. Dielectric strength is determined as per ASTM D149 in a dielectric strength tester and is expressed in kV/mm.

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

Dielectric strength (V/mm) = breakdown voltage (V)/ thickness (mm) (2.5)

From the experimental data, dielectric strength is calculated using equation 2.5.

2.10.2 Arc resistance

Arc resistance 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 carbonisation of the surface, tracking, localized heating to incandescence, or burning. Resistance to arcing or tracking depends upon the type of plastic materials such as phenolics that tend to carbonize easily and therefore have relatively poor arc resistance. Plastics such as alkyds, melamines and
fluorocarbons are excellent arc-resistant materials. Arc resistance of plastics can be improved substantially by the addition of fillers such as glass, mineral, wood flour, asbestos and other inorganic fillers. It is measured as per ASTM D495 on test specimen of thickness 3.2 mm.

In this test, a high voltage arc (15 kV) is struck between two electrodes placed on the test specimen, the initial current being a few milliamperes. The arc is interrupted by a timer, the ‘on’ and ‘off’ intervals being carefully defined. As the test progresses, 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 of failure.

2.10.3 Resistivity

The primary function of an insulator is to insulate current carrying conductors from each other as well as from ground and to provide mechanical support for components. Naturally, the most desirable characteristic of an insulator is its ability to resist the leakage of the electric current. The resistivity is higher, the insulation is better. In order to assess the performance of insulating material, the resistance offered by the polymeric material to electric current along a 1cm² surface or through the thickness is determined using a resistivity meter as per ASTM D 257.

Volume resistance is defined as the ratio of the direct voltage applied to two electrodes that are in contact with a specimen to that portion of the current between them that is distributed through the volume of the specimen. In other words, the volume resistance is the resistance to leakage through the body of the material. Volume resistance generally depends upon the material. It also defined the ratio of the potential gradient parallel to the current of the material to the current density or if simple stated, the volume
resistivity of a material is the electrical resistance between the opposite faces of a unit cube for a given material and at a given temperature.

For measuring the volume resistance ($R_v$) of a flat specimen of thickness 3-mm, a guard electrode having the shape of a ring is kept in position in concentric with another guarded electrode on the other faces of specimen. An unguarded electrode is kept on the other face of the specimen. The guard electrode effectively equalises the field between the guarded and unguarded electrode and drains the surface and the volume currents of the specimen into the earth.

2.10.3.1 Volume resistivity

Volume resistivity is a measure of resistance of electrical dc current through the thickness of an insulating specimen. It is expressed in ohm cm, which is a unit of resistance between two opposite faces of 1 cm$^3$. It is determined on the flat surface of a specimen having thickness 3 mm.

From the experimental data, volume resistivity is calculated using equation 2.6.

$$\text{Volume resistivity} = \frac{\text{Area} \times R_v}{T} \quad (2.6)$$

where, $T$ is the thickness of specimen in cm, $R_v$ is volume resistance and area in cm$^2$.

2.10.3.2 Surface resistivity

The surface resistance of a material which is defined as the ratio of the direct voltage applied to the electrodes to that portion of the current
between them is primarily in a thin layer of moisture or other semi conducting material that may be deposited on the surface. In other words, surface resistance is the resistance to leakage along the surface of an insulator. Surface resistivity can also be defined as the ratio of potential gradient parallel to the current, along its surface to the current per unit width of surface. It is expressed in ohm and is determined on the flat surface of a specimen having thickness 3-mm. From the experimental data, surface resistivity is calculated using equation 2.7 and the results are presented in Table 5.2.

\[ R_s = \frac{R \cdot P}{g} \]  \hspace{1cm} (2.7)

where, R is the surface resistance, P is the diameter of the electrode and g is the thickness of the material.

### 2.11 THERMAL CHARACTERISTICS

#### 2.11.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimeter NETZSCH DSC 200PC (TA instruments USA) is used to determine the glass transition temperature (\( T_g \)) and curing exotherm with a heating rate of 10 °C per minute, the measurements are carried out from 0 °C to 300 °C under inert atmosphere.

#### 2.11.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the polymeric matrices is carried out in TGA-Thermal Analyst NETZSCH STA 409PC (TA instruments USA) at a heating rate of 10 °C per minute in an inert atmosphere to determine thermal degradation temperature, percentage weight loss and char yield formation.
2.11.3 Ageing Characteristics

Test samples were heated at 135° C in an air circulating oven for 72 hours. After cooling to room temperature, the dimensions of each specimen were measured. The tensile properties of these samples were determined according to ASTM D 412-87 using a Zwick Universal Testing Machine at a crosshead speed of 500 mm per minute.

2.11.4 Heat Distortion Temperature (HDT)

It is also called Deflection Temperature of polymeric material Under Flexural Load (DTUL). Determination of heat distortion temperature is carried out as per ASTM D648-72 using heat distortion temperature apparatus. The specimens of size 120 mm in length, 13-mm in thickness and 5 mm in width, are kept in an oil-bath under a load of 1.82 MPa. The temperature is raised at a rate of 2 °C per minute and the temperature is noted when the specimen deflected by 0.25 mm.

2.11.5 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical behaviour of both unmodified and modified epoxy resins was studied in a Metravib viscoanalyser. Each sample was scanned from 0 °C to 300 °C at a heating rate of 3 °C/min. During heating, the samples were subjected to strain at a frequency of 10Hz while the storage modulus (E’) and the damping factor (tan δ) were recorded. The temperature corresponding to the maximum in tan δ versus temperature plots was recorded as the measurement of the glass transition temperature (Tg)
2.12 WATER ABSORPTION BEHAVIOUR

Test specimen (ASTM D 570) was immersed in water for 24 hours at 30\(^\circ\) C and the percentage of water absorbed by the specimen is calculated using equation (2.8) and the results are presented in Table 7.1.

\[
\% \text{ water absorption} = \left(\frac{w_2-w_1}{w_1}\right) \times 100
\]  
(2.8)

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\(^\circ\)C.

2.13 SPECTROSCOPIC INVESTIGATIONS

2.13.1 Infrared Spectra (IR)

Infrared spectra are obtained from Perkin–Elmer Infrared Spectrometer (Model RX1). The purity and structure of bismaleimides were confirmed by FTIR. The homopolymerization of BMI in the presence of epoxy resin at lower temperature was confirmed using the IR spectrum.

2.13.2 Nuclear Magnetic Resonance Spectra (NMR)

The purity and structure of the synthesised bismaleimides were confirmed by NMR. \(^1\)H and \(^{13}\)C spectra were recorded on a Bruker 400 MHz NMR spectrometer with dimethylsulfoxide-d6 (DMSO-d6)/CDCl\(_3\) as solvent.

2.14 SCANNING ELECTRON MICROSCOPY (SEM)

The fractured surfaces of specimens were coated with gold and examined under a scanning electron microscope JEOL JSM (Model 6360).
Fractured surfaces were obtained from impact strength tested specimens using Instron testing machine (model 6025, UK), at a crosshead speed of 2 mm per minute.

2.15 X-RAY DIFFRACTION ANALYSIS (XRD)

The X-ray diffraction technique is the most direct and simple method to evaluate the spacing between the clay layers. XRD patterns were obtained using an X-ray diffractometer (X’pert, Philips) equipped with Cu, Kα radiations and a curved graphite crystal monochromator. Diffraction data were collected at 0.001°/S steps between 10 and 70°C, and were used to determine changes in gallery heights in the organoclay before and after polymer intercalation.