CHAPTER 2

EXPERIMENTAL

This chapter describes the synthesis of hydroxyl-terminated polydimethylsiloxane, different types of bismaleimides namely N, N'-bismaleimido-4, 4'-diphenylmethane (BMI-1), 1,3-bis (maleimido) benzene (BMI-2), 1,2-bis (maleimido) ethane (BMI-3) and 1,6-bis (maleimido) hexane (BMI-4), preparation of siliconized epoxy prepolymers, siliconized epoxy bismaleimide blends, and fabrication of E-glass reinforced siliconized epoxy and siliconized epoxy – bismaleimide composites. It also deals with the experimental procedure for the studies of physico-chemical, mechanical, electrical, thermal and morphological properties of matrix systems and composites (Kossmehal *et al.*, 1995).

2.1   MATERIALS

Materials used for the development of siliconized epoxy / bismaleimide intercrosslinked network systems are:

(i)   epoxy resin LY 556 (diglycidyl ether of bisphenol-A, (DGEBA) Ciba-Geigy, epoxy equivalent = 180-190, viscosity 10,000 cP),

(ii)   hydroxyl - terminated polydimethylsiloxane (viscosity = 850 cP, M_w =18000)

(iii)   bismaleimides namely N, N'-bismaleimido-4, 4'-diphenylmethane (BMI-1), 1,3-bis (maleimido) benzene (BMI-2), 1,2-bis (maleimido) ethane (BMI-3) and 1,6-bis (maleimido) hexane (BMI-4)

(iv)   curing agent used for curing epoxy, siliconized epoxy and bismaleimide modified siliconized epoxy resins is diaminodiphenylmethane (DDM) (HT972, Ciba-Geigy, amine equivalent = 49.5 eq/kg)

(v)   Γ-aminopropyltriethoxysilane (A-1006, Union Carbide) a silane derivative is used as cross-linking agent,

(vi)   dibutyltindilaurate is used as catalyst

(vii)   8-mil bi-directional woven E-glass fabric is used as reinforcement

2.2   SYNTHESIS   OF   HYDROXYL-TERMINATED POLYDIMETHYLSILOXANE (HTPDMS)

Hydroxyl-terminated polydimethylsiloxane used for the development of siliconized epoxy matrix (Serier 1991) is derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany- Molecular weight 296.6, boiling point 175-176° C, refractive index-1.3968, density-0.956 g cm^{-3} and viscosity 2.5 cP at 25° C). Experimental set up used for the synthesis of hydroxyl – terminated polydimethylsiloxane is given in Figure 2.1. One litre of octamethylcyclotetrasiloxane and potassium hydroxide catalyst (0.22% on the weight of octamethylcyclotetrasiloxane) are taken in a five-necked round-bottom glass reactor.   The reaction is carried out in an inert atmosphere by purging nitrogen.   The temperature of the mixture   is   gradually raised   to 90° C   over   a   period   of   45   minutes   and   maintained at 90° C ± 1° C for six hours   in a   thermostatically   controlled oil bath. The reaction mixture is
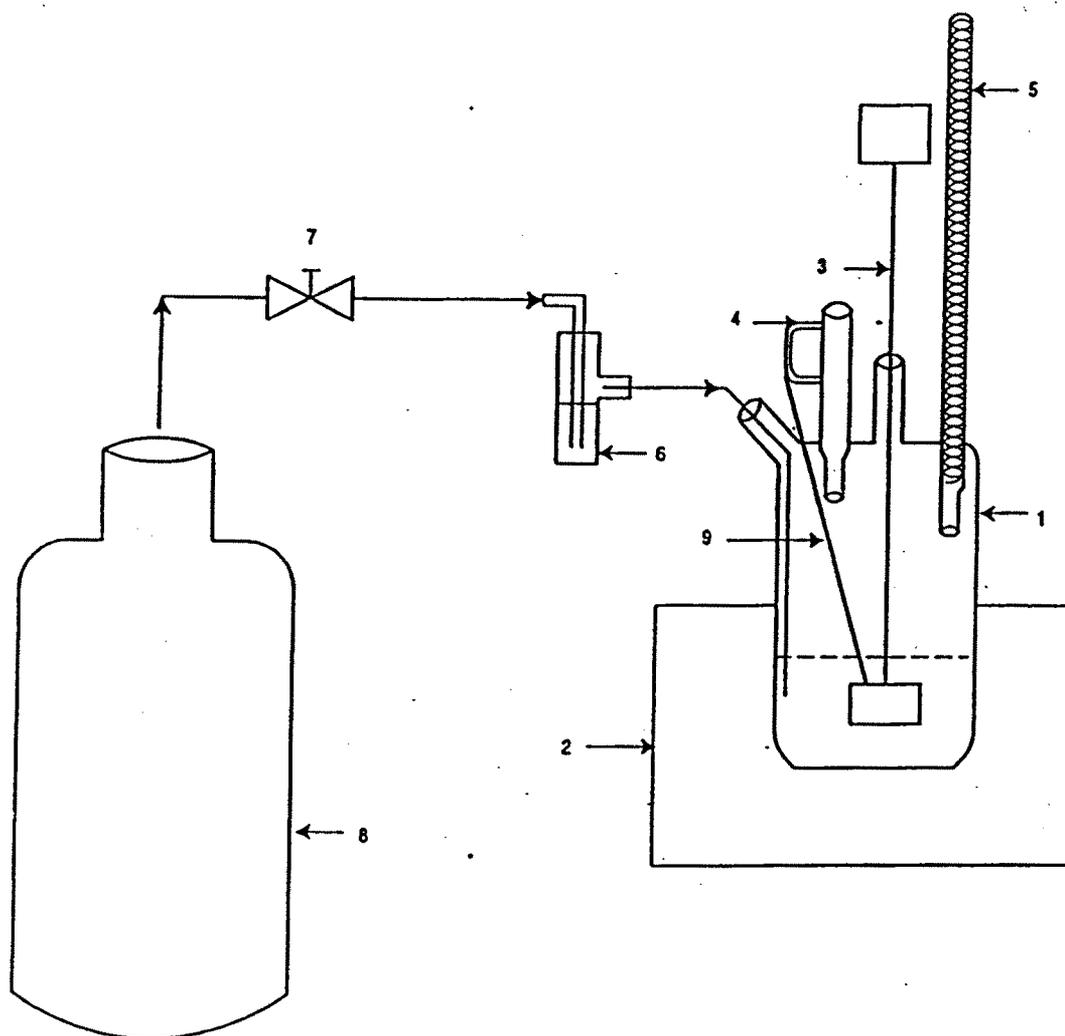
Figure 2.1   Schematic experimental setup for the preparation of hydroxyl-
terminated polydimethylsiloxane

1.   Reaction Kettle
2.   Heating mantle (500 W)
3.   Stainless steel stirrer (motor 0.06 HP)
4.   Dropping funnel
5.   Coiled condenser
6.   Moisture absorber (glycol)
7.   Valve
8.   Nitrogen cylinder
9.   Thermometer

slowly cooled to about 50°C. The unreacted octamethylcyclotetrasiloxane is removed by distillation under reduced pressure. The hydroxyl-terminated polydimethylsiloxane resulted from the reaction is cooled to room temperature. The percentage conversion of octamethylcyclotetrasiloxane to polymer is calculated based on the recovery of unreacted octamethylcyclotetrasiloxane (yield = 62%)(yield = (w_1-w_2) x $100/w_1$, where w_1 is the initial weight of octamethylcyclotetrasiloxane and w_2 is the weight of unreacted octamethylcyclotetrasiloxane). The viscosity of the hydroxyl-terminated polydimethylsiloxane is determined using Brookfield viscometer. Molecular weight of the polymer is determined using viscosity values (Molecular weight $m_v = 18000$).

2.3   SYNTHESIS OF AROMATIC BISMALEIMIDES

Aromatic bismaleimides namely N, N'-bismaleimido-4, 4'-diphenylmethane (BMI-1) and 1,3-bis (maleimido) benzene (BMI-2) were prepared from the corresponding amines (N, N'-diaminodiphenylmethane and m-phenylenediamine) 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, 1.0 mole (98.1 g) maleic anhydride and 0.5 mole of the desired aromatic diamine. Rapid formation of precipitate of the bismaleiamic 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 1.0-g nickel acetate and 25 ml triethylamine and the entire mixture heated slowly to reflux.
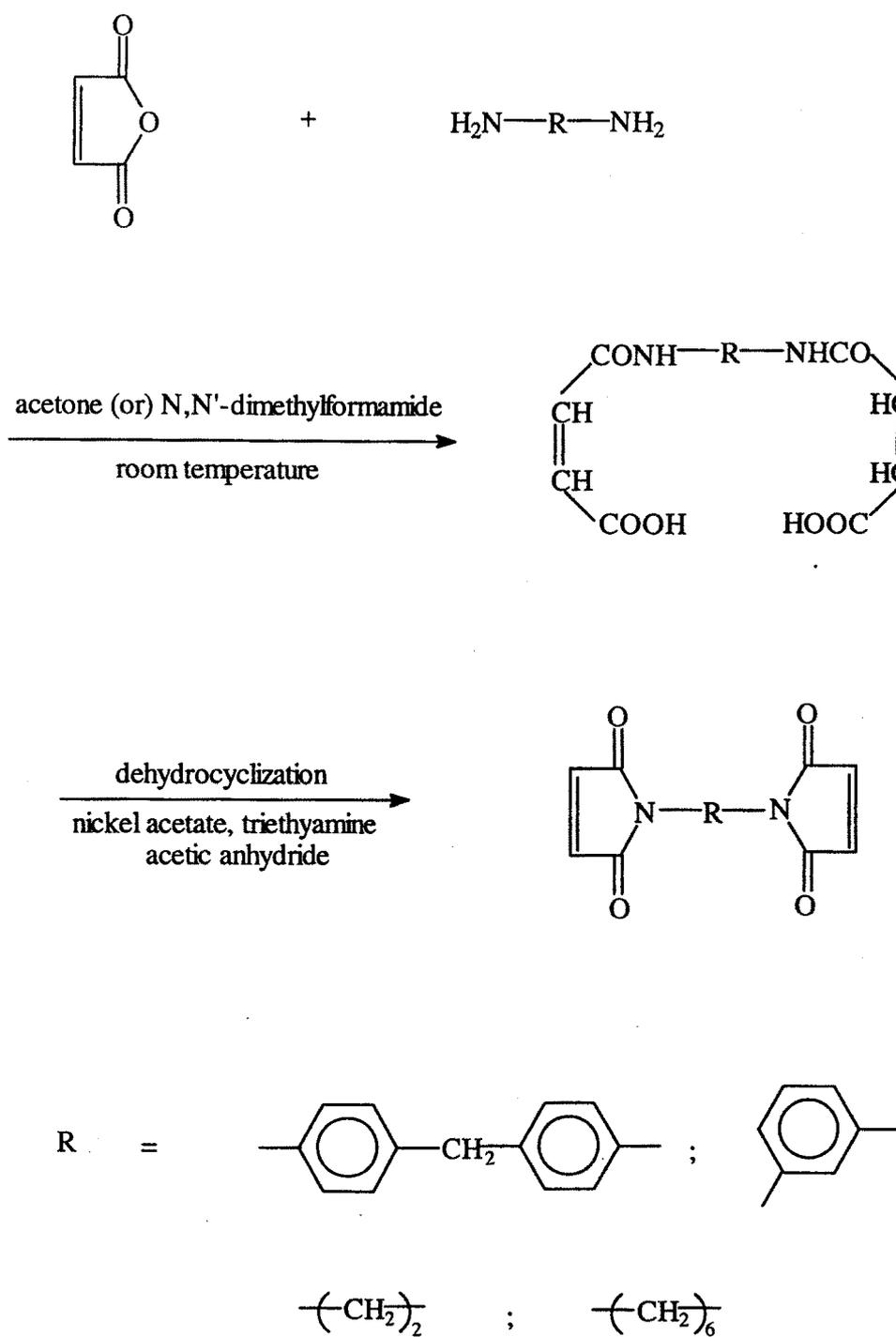
Figure 2.2 Synthesis bismaleimides

Then by means of pressure equalizing funnel 117.9 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.

2.4   SYNTHESIS OF ALIPHATIC BISMALEIMIDES

Aliphatic amine (0.25 mol) was added in one portion under stirring to a solution of maleic anhydride (49.0 g, 0.5 mol) in 150 ml of freshly distilled N,N-dimethyl formamide (DMF). The temperature of the solution rose to $105^{o}C$ and the opaque colour changes to yellow. Stirring was thereafter continued for 30 minutes at 90° C. Acetic anhydride (127.5 g, 1.0 mol), nickel (II) acetate, (0.5 g) and triethylamine (10.0 g) were then added to the reaction mixture and maintaining the system at $90^{\circ}C$ for another 30 minutes. Then, the solution was cooled to $40^{\circ}C$, poured into 2 litres of ice water and stirred for 10 minutes. The resulting brown precipitate was filtered off by suction, washed twice with one litre of water, again filtered-off by suction. In order to dry and further purification, the product was dissolved in 700 ml of acetone, dried with sodium sulphite, filtered, refluxed with 25 g of charcoal and filtered. The volume of the solution was reduced by evaporation to 300 ml and then kept at $0^{\circ}C$ for overnight. The precipitate was filtered off by suction and washed with small amount of cold acetone and dried.

2.5   PREPARATION OF SILICONIZED EPOXY PREPOLYMER

Fixed amount of epoxy resin, varying amounts of hydroxyl-terminated polydimethylsiloxane, stoichiometric amount of γ-aminopropyltriethoxysilane (with respect to hydroxyl groups of hydroxyl-terminated polydimethylsiloxane) and dibutyltindilaurate catalyst (Table 2.1)

epoxy resin ~~CH$_2$—CH—CH$_2$ +   NH$_2$ +   H$_2$C—CH—CH$_2$~~ epoxy resin
$\quad\quad\quad\quad\quad$ O $\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad$ O
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (CH$_2$)$_3$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Si(OEt)$_3$
$\quad\quad\quad\quad\quad\quad$ γ - aminopropyltriethoxysilane

epoxy resin ~~CH$_2$—CH—H$_2$C\N/CH$_2$—CH—CH$_2$~~ epoxy resin
$\quad\quad\quad\quad\quad$ HO $\quad\quad\quad$ | $\quad\quad\quad$ OH
$\quad\quad\quad\quad\quad\quad\quad\quad$ (CH$_2$)$_3$
$\quad\quad\quad\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad\quad\quad\quad\quad$ Si(OEt)$_3$

Siloxane prepolymer

epoxy resin ~~CH$_2$—CH—H$_2$C\N/CH$_2$—CH—CH$_2$~~ epoxy resin
$\quad\quad$ HO $\quad\quad$ | $\quad\quad$ OH
$\quad\quad\quad\quad$ (CH$_2$)$_3$

siloxane prepolymer $\quad$ siloxane prepolymer

siloxane prepolymer

Figure 2.3 Preparation of siliconized epoxy resin

were thoroughly mixed at 90^0 C for 10 minutes with constant stirring. The product was then degassed to remove ethanol formed during the condensation reaction between γ-aminopropyltriethoxysilane and hydroxyl-terminated polydimethylsiloxane.

Table 2.1 Composition of curing agent, crosslinking agent and catalyst.

Epoxy (wt%)	HTPDMS (wt%)	Amount of curing agent (g)	Crosslinking agent (g)	Catalyst (g)
100	0	27	-	-
100	5	27	0.05	0.1
100	10	27	0.09	0.1
100	15	27	0.14	0.1

HTPDMS – Hydroxyl-terminated polydimethylsiloxane

2.6 PREPARATION OF SILICONIZED EPOXY BISMALEIMIDE BLENDS

The stoichiometric amount of 4,4'-diaminodiphenylmethane was dissolved into siliconized epoxy resin at 90^0C under vigorous stirring. After complete dissolution, the calculated amount of bismaleimide was added. The agitation was continued at 100^0C until a homogeneous product was obtained. The product was subjected to vacuum to remove the trapped air and then cast and cured at 120^0C for one hour. The castings were then post cured at 180^0C for two hours and at 210^0C for one hour and finally removed from the mould and characterized.

2.7   FABRICATION OF COMPOSITES

E-glass fibre reinforced composites were prepared by hand lay-up technique using 8mil bi-directional woven E-glass fabric. Fabric pieces of size 20 X 12.5 cm weighing 130g is heated to 150°C in a hot air oven for 2 hours to remove moisture and then cooled to room temperature. Preweighed mixture of prepolymer with stoichiometric quantity of curing agent is applied over fabric by means of rubber roller. To ensure good resin distribution the fabrics were thoroughly wetted with the resin prior to the actual pressing and curing. Nine coated plies were laminated and then cured in hot press for one hour at 120 °C, two hours at 150 °C and one hour at 220°C at a pressure of 600 psi. The thickness of the composites was fixed at about 2.0 mm. The fibre volume fraction was maintained between 61/39 and 63/37 and was ascertained from burn out test.

2.8   CHARACTERIZATION

Mechanical, electrical and thermal characteristics of epoxy, siliconized epoxy, bismaleimides modified epoxy and bismaleimides modified siliconized epoxy matrices and E-glass fibre reinforced composites 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 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 extend 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 cross-head 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.

2.9.2   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.

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

$$= \quad L / bxD \tag{2.1}$$

Where, L is the load applied in N, b is the width in mm and D is thickness in mm.

2.9.3   Tensile modulus

Tensile modulus is given by the equation 2.2,

Tensile modulus   =   Tensile stress /Tensile strain

=   difference in load (N)/difference in extension (mm)

$$= \quad \Delta P / \Delta \delta \tag{2.2}$$

The results are presented in Tables 4.1 to 4.5.

2.9.4 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.

2.9.5 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 2.4,

$$\text{Flexural strength (S)} = PL / bd^2 \tag{2.4}$$

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)

2.9.6 Flexural modulus

Flexural modulus is a measure of stiffness. It is determined by using equation 2.5,

$$E = wl^3 / 48\delta I \tag{2.5}$$

Where, E is flexural modulus, w is load (N), l is the length of the specimen (50 mm), δ is the deflection in mm and $I = bd^3/12$ (b is width in mm and d is thickness in mm). The results are presented in Tables 4.1 to 4.5.

2.9.7 Hardness

Hardness of the composite material is measured using Durometer - Type D as per ASTM D2240. Specimens with 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 6mm radius for the indentor point. 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 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.

2.9.8 Plain strain fracture toughness

Plain strain fracture toughness has been measured by three-point bending specimen configuration as per the ASTM-E399-74 standard. The specimen dimensions: length, L = 64 mm; width, W = 10 mm; thickness, B = 3 mm; span length, s = 40 mm; crack length, a = 3.2 mm, P is load at break and K_{IC} is the fracture toughness. The results are presented in Tables 4.1 to 4.5.

$$K_{IC} = \frac{PS}{BW^{3/2}} \ f\,(a/w) \tag{2.6}$$

Where f(a/w) = 1.61.

2.10   ELECTRICAL PROPERTIES

Electrical properties namely, dielectric strength, arc resistance, volume 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 to produce 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/ mil)

$$= \text{breakdown voltage (V)/ thickness (mil)} \tag{2.7}$$

From the experimental data, dielectric strength is calculated using equation 2.7 and the results are presented in Table 5.1.

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 carbonization 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 to 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 higher the insulation resistance, the better the insulator.   In order to assess the performance of insulating material, the resistance offered by the polymeric material to electric current along a $1cm^2$ 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 is also defined as the ratio of the potential gradient parallel to the current in the material to the current density or simply 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.

2.10.4 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 $1cm^3$. It is determined on the flat surface of a specimen having thickness 3-mm.

From the experimental data, volume resistivity is calculated using equation 2.8.

$$\text{Volume resistivity} = \text{Area } x R_v / T \qquad (2.8)$$

Where, T is the thickness of specimen in cm R_v is volume resistance and Area in cm^2.

2.10.5 Surface resistivity

The surface resistance of a material is defined as the ratio of the direct voltage applied to the electrodes to that portion of the current between them that is primarily in a thin layer of moisture or other semiconducting 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 2.9 and the results are presented in Table 5.2.

$$R_s = R.P / g \qquad (2.9)$$

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

2.11 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 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 M Pa. 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.

2.12   DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimeter DSC 2910(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.

2.13   THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis of the polymeric matrices is carried out in TGA- Thermal Analyst 2000 (TA instruments USA) at a heating rate of 10°C per minute in an inert atmosphere to determine thermal degradation temperature and percentage weight loss.

2.14   WATER ABSORPTION

Test specimen when immersed in water for 24 hours at 30° C and the percentage of water absorbed by the specimen is calculated using equation (2.11) and the results are presented in Table 7.1.

$$\% \text{ Increase in weight} = (w_2 - w_1) \times 100 / w_1 \qquad (2.11)$$

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.

2.15   DETERMINATION OF GLASS FIBRE CONTENT

The glass fibre reinforced composites were burnt off and the glass fibre content is determined from the mass of the fibre left behind. A piece of composite conditioned at $25^{\circ}C$ at 50% relative humidity is weighed accurately (total mass = m_t). It is placed in a heat resistant crucible, the weight of which, m_o has been determined. The crucible and the composite sample are placed in an oven at $625^{\circ}C$. When combustion is complete (there is no longer any flame), glass fabric and charred residue remains.

The crucible and its contents are cooled in a desiccator to stop the fibre absorbing moisture and reweighed, m_1. The glass content of the composite material as a percentage of the total mass is calculated using equation (2.10).

$$m_f = (m_1 - m_0) \times 100 / m_t \qquad (2.10)$$

where, m_t = mass of the composite = mass of the glass fibre + mass of the resin

m_o = mass of the crucible

m_1 = mass of the crucible + mass of the residual glass

m_g = m_1 - m_0 = mass of the glass fibre and

m_f = percentage mass of fibre

2.16   VISCOSITY

The viscosity of the unmodified epoxy and siliconized epoxy prepolymer were measured at 30°C on a cone and plate set up with a 2.4 cm cone diameter at a 3° angle.

2.17 INFRARED SPECTRA (IR)

Infrared spectra are obtained from Perkin–Elmer Infrared Spectrometer. Infrared spectra are obtained for epoxy resin (Figure 2.4), epoxy resin cured with Υ-aminopropyltriethoxysilane (Figure 2.5) and Υ-aminopropyltriethoxysilane (Figure 2.6) to confirm the curing mechanism of interpenetrating polymer network formation. Purity of the synthesised bismaleimides namely N, N'-bismaleimido-4, 4'-diphenylmethane, 1,3-bis (maleimido) benzene, 1,6-bis (maleimido) hexane and 1,2-bis (maleimido) ethane were also confirmed by IR. The homopolymerzation of BMI in the presence of epoxy resin at lower temperature was confirmed using the IR spectrum (Figures 2.17 – 2.20)

2.18 NUCLEAR MAGNETIC RESONANCE SPECTRA (NMR)

The purity of the synthesised bismaleimides namely N, N'-bismaleimido-4, 4'-diphenylmethane, 1,3-bis (maleimido) benzene, 1,6-bis (maleimido) hexane and 1,2-bis (maleimido) ethane were confirmed by NMR.

2.19 SCANNING ELECTRON MICROSCOPY (SEM)

The fracture surfaces of specimens were coated with gold and examined under a scanning electron microscope (SEM (Leica Cambridge, Stereoscan Model 440).

Fractured surfaces were obtained from plain strain fracture toughness tested specimens using Instron testing machine (model 6025, UK), at a crosshead speed of 2 mm per minute. Excess material was removed from the other faces of the specimens by razor blade.