Chapter 3
Materials and Methods

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3.1 Introduction

This chapter deals with the materials and methods used for the fabrication of nanocomposites and the characterisation techniques used. The structural characterisation of the nanoparticles and the fabricated nanocomposites include FTIR, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). This chapter also discusses the characterisation techniques used to evaluate the thermal, mechanical, dielectric behaviour and EMI shielding performance of the composites.

3.2 Materials

3.2.1 Bismaleimide resin (BMI)

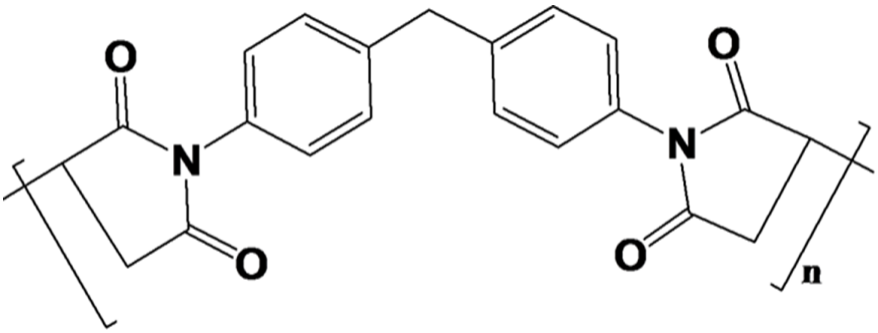

Figure 3.1 Structure of ABRON BR-720.

Bismaleimide resin (ABRON BR-720) purchased from ABR Organics Ltd., Hyderabad is a low molecular weight yellowish powder having imide structure with a melting point in the range of 70-90^{o}C and soluble in dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP). It has density 1.95 g/cm^3 and dielectric permittivity of 4 at 50 Hz.

3.2.2 Epoxy resin

Epoxy resin (Epofine-1564) and aliphatic amine hardener (Finehard 3486) were purchased from Fine Finish Organics Pvt. Ltd., Taloja. Diglycidyl ether of bisphenol A (DGEBA or DGEBPA), the most important class of epoxy resin is blended with BMI

resin to reduce the brittle nature of the latter. Epofine 1564 is one of the epoxy resin systems used for making high performance laminates. Its curing cycle is 24 hours at 25°C. Its viscosity is 200-300 mPas at 25°C.It has a tensile strength of 70-80 MPa. Its glass transition temperature is in the range 60-70°C.It has long pot life, low mix viscosity and excellent impact strength. Aliphatic hardener (Finehard-3486) of viscosity <50 mPas (density approximately equal to 0.94-0.95 g/cc) at room temperature (RT) was used.

The structure of epoxy resin is given in figure 3.2.

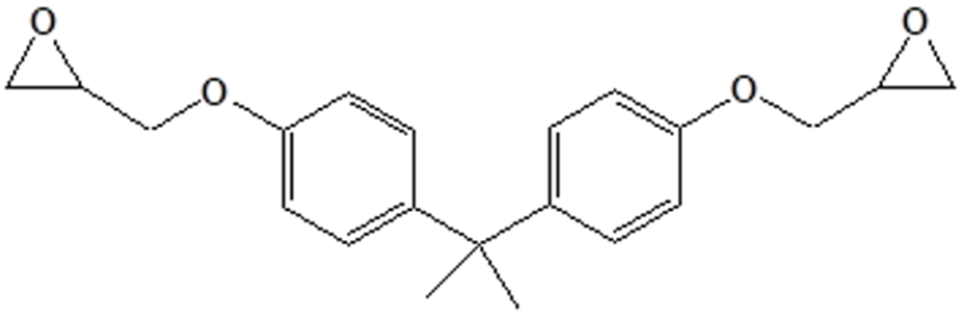

Figure 3.2 Structure of Diglycidyl ether of bisphenol A (DGEBA or DGEBPA).

3.2.3 Glass fibers

Two different glass fibers are used for reinforcing the fabricated BMI-epoxy nanocomposites and are denoted as EGF (E glass kiteboard unidirectional glass fiber) and SC-EGF (γ-aminopropyl triethoxy silane coated E glass fiber). EGF and SC-EGF were purchased from Urja Products Pvt. Ltd., India. E glass fibers are widely used in fiber reinforced polymer composite industry because of its excellent strength, good resistance to chemicals, moisture etc. To tailor the interface between the fiber and the matrix and to alter the mechanical properties of the fiber, a sizing (silane coupling reagent) is added to the glass fibers after production. This sizing protects the fibers during handling, improve the adhesion characteristics, moisture resistance and corrosion resistance. The organofunctional group and the alkoxy group can form strong bonds with the polymer matrix and with the filler particles respectively.

3.2.4. Tetrabutyl titanate $Ti(C_4H_9O)_4$

- Assay about 97 %
- Colourless odourless liquid

- Boiling point 312^0C
- Density 0.998 g/cm^3
- Purchased from Sigma Aldrich

3.2.5. Barium hydroxide octahydrate $Ba(OH)_2.8H_2O$

- Assay ≥ 98 %
- Melting point 78^0C
- Density 2.180 g/cm^3
- pH value 12.5
- Bulk density 900-1100 kg/m^3
- Solubility 72 g/litre
- Purchased from Sigma Aldrich.

3.2.6. Nitric acid

- Assay about 69 %
- Boiling point 120.5^0C
- Density 1.413 g/ml at 20^0C
- Purchased from Sigma Aldrich.

3.2.7. Sodium potassium tartarate tetrahydrate (Rochelle salt)

- Colourless, odourless crystals
- Density 1.79 g/cm3
- Melting point 75^0C
- Boiling point 220^0C

3.2.8. Multi walled carbon nanotube (MWCNT)

- MWCNT Type 5 multiwalled carbon nanotubes
- OD 30-50 nm
- Length10-30 µm
- Purchased from Sisco Research laboratories Pvt Ltd, Taloja, Maharashtra.

3.2.9. H_2O_2

- Colourless and clear liquid

- (30 % w/w) with stabilizer
- Formula weight 34.01 g/mol
- Storage temperature 2-8^{0}C
- Purchased from Sigma Aldrich

3.3. Methods

3.3.1. Preparation of BMI-epoxy nanocomposites

The conventional solvent method was found to be inappropriate for the preparation of composites due to the incomplete evaporation of the solvent DMF and the formation of blisters on the surface of the composite during solvent evaporation. Hand layup method was adopted for composite preparation in this study. BMI and Epoxy resin containing the nanofillers in the ratio 15:1.5 were mixed and grounded well. Unidirectional E glass fiber was used for reinforcement. The first glass fiber sheet is placed above the resin nanoparticle matrix and uniformly pressed using teflon rollers. The procedure was repeated upto four layers. Different samples of glass fiber reinforced BMI-epoxy nanocomposites were prepared by mixing the resin mixture with varying percentages of the nanofillers as mentioned in table 3.1. The composites were kept in press at 100°C for 10 minutes. The temperature was then raised to 120°C for 10 minutes followed by 140°C for another 10 minutes and finally compression moulded for 30 minutes at 180°C and 200 psi. The same procedure was adopted for the preparation of glass fiber reinforced BMI-epoxy composites without nanoparticles.

Table.3.1 Formulation for composite preparation.

Code	Weight Ratio
BMI -Epoxy	15:1.5
BMI -Epoxy-NP-1	15:1.5: 0.165
BMI -Epoxy- NP-2	15:1.5: 0.33
BMI -Epoxy- NP-3	15:1.5: 0.66
BMI -Epoxy- NP-4	15:1.5: 1.32
BMI -Epoxy- NP-5	15:1.5:2.64

3.3.2. Preparation of BMI-epoxy-MWCNT nanocomposites

Fabrication of nanohybrid BMI-epoxy composites with a constant concentration of MWCNT (5 weight %) and optimised weight % (2 and 3 weight %) of fillers such as BT, RS and BTOH were done using hand layup method followed by compression moulding.

3.3.3. Preparation of $BaTiO_3$ (BT) and surface hydroxylated $BaTiO_3$ (BTOH) nanoparticles

$BaTiO_3$ (BT) nanoparticles were synthesised by hydrothermal method and surface hydroxylated $BaTiO_3$ (BTOH) nanoparticles were prepared by H_2O_2 treatment of BT nanoparticles as discussed in chapter 4, section 4.2.1 and chapter 6, section 6.2.1.

3.3.4. Preparation of Rochelle salt crystals (RS)

Mechanical ball milling method was employed for breaking down the bulk Rochelle crystals into nano dimensions. Ball milling is a top-down method used for producing metallic and ceramic nanomaterials. Rochelle crystals were grounded well for 4 hours using a ball mill.

3.4 Characterisation studies

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) spectra of BMI, $BaTiO_3$, BMI-epoxy composites and BMI-epoxy-$BaTiO_3$ nanocomposites were obtained using ESEM Quanta 200 FEI from IISc Bangalore. Powder X-ray Diffraction (XRD) were recorded using an X-Ray diffractometer, Aeris, PANalytical- United Kingdom with Copper- K alpha radiation (1.5406 A^o) as the source to determine the morphology and composition of the synthesised $BaTiO_3$. FTIR spectra were recorded using IR Affinity-1S, Shimadzu, Japan. Mechanical properties such as tensile and flexural strength of BMI-Epoxy composites were measured using 50 KN UTM-1205. Thermogravimetric analysis (TGA) was carried out using Perkin Elmer Diamond and DSC using Mettler Toledo DSC 822E at a heating rate of 20°C/min from 40°C to 730°C.

Electrical studies included measurement of dielectric permittivity (ε_r), dielectric loss (tan delta) and ac conductivity using Keysight Technologies E4990A impedance Analyser 20 Hz to 10 MHz frequency range. Specimens for BDV were obtained by cutting the polymer composites in circular discs of thickness approximately 2 mm and

diameter approximately 75 mm and measurements were done using Hipotronics AC Dielectric test set as per ASTM D149. Small circular button shaped discs of approximately 12 mm diameter and approximately 2mm thickness were cut out to measure dielectric permittivity.

EMI shielding effectiveness of the composites was performed at the K band (18-26.5) using a KEYSIGHT PNA-L Network Analyzer N5234B 10MHz - 43.5GHz.

Figure 3.3 Specimen for dielectric strength measurement.

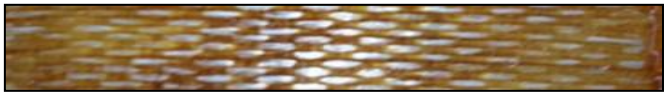

Figure 3.4 Specimen for tensile and flexural measurement.