Chapter 3

Experimental details and Characterization

This chapter describes in detail about the experimental details and various characterization techniques used in this work.

3.1 MATERIALS

The hBN powder (Grade – NX5, mean particle size – 5 microns) was procured from Momentive Performance Materials, India. Ethyl alcohol, graphite powder, potassium permanganate (KMnO₄), concentrated sulphuric acid (97% H₂SO₄) and hydrogen peroxide (H₂O₂), sodium hydrosulphite (NaHS), dimethyl formamide (DMF) were of analytical grade obtained from S. D. Fine Chemicals, India, and used without further purification. The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) (Lapox L-12, Atul Ltd, India.) was used as the matrix material. The amine hardener, N,N-Bis (2-aminoethyl) ethane-1,2-diamine (Lapox K-6, Atul Ltd., India.), was used as a crosslinker for the epoxy. Polyvinylpyrrolidone (PVP), a non-ionic surfactant was supplied by Sigma Aldrich.

3.2 EXPERIMENTAL

3.2.1 SYNTHESIS OF hBN NANOPATELETS

The hBN nanoplatelets were prepared according to the simple chemical exfoliation method suggested by Du et al (2013). In a typical chemical exfoliation experiment, 3 g of hBN powder was added into 75 mL of concentrated H₂SO₄ and stirred continuously. Thereafter, 0.75 grams of KMnO₄ was added slowly to the above stirring solution with the reaction vessel immersed in an ice bath. After this, the suspended solution was stirred continuously for 12 h. Subsequently, 30 mL of H₂O₂ was added into
the above stirred suspension. The exfoliated hBN was filtered and washed with deionized water to remove metal ions until the pH value of the filtrate was 7. The final product was dried in a vacuum oven at 80°C for 12 h. The exfoliated hBN prepared using this protocol is referred as ‘hBN nanoplatelets’ in this work. The yield of hBN nanoplatelets was 2.1 grams.

![Figure 3.1: Schematic of steps involved in epoxy/hBN nanoplatelets nanocomposites processing.](image)

3.2.2 SYNTHESIS OF GRAPHENE NANOPlatelets

Graphene nanoplatelets oxide was synthesized using improved method of synthesis of graphene oxide proposed by Tour et al., 2010. For the improved method, a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and KMnO₄ (18.0 g, 6 wt equiv). This produced a slight exotherm of 35-40 °C. Then, the reaction was heated to 50 °C and stirred for 12 h. The reaction vessel was cooled to room temperature. Further, ice (400 mL) with 30%
H₂O₂ (3 mL) was poured into vessel. The mixture was washed repeatedly with ethyl alcohol. Graphene nanoplatelets oxide was dried in vacuum oven overnight. For reduction of graphene nanoplatelets oxide, 1 mg/ml of graphene nanoplatelets oxide was suspended in water by sonicating it for one hour. Thereafter, NaHS was added to the mixture for reduction of graphene nanoplatelets oxide. The obtained graphene nanoplatelets were dried overnight at 80 °C under vacuum.

3.2.3 EPOXY/hBN NANOCOMPOSITES

The hBN nanoplatelets reinforced epoxy nanocomposites were prepared by using the procedure shown in Fig. 3.1. The desired quantity of hBN nanoplatelets was mixed in 25 ml ethyl alcohol using probe sonication (Sonics Vibra Cell, VCX-130, 43% of the maximum output power of 130 Watts and frequency of 20 KHz) for 30 minutes in an ice bath. Then, the mixture of hBN nanoplatelets and ethyl alcohol was mixed with epoxy, and probe sonicated for another 30 minutes in an ice bath. Further, the epoxy hBN nanoplatelets and ethyl alcohol mixture was heated at 80°C for 2 hours over magnetic stirrer in order to evaporate the ethyl alcohol form the mixture. Thereafter, epoxy hBN nanoplatelets solution was ball milled using 10 mm diameter tungsten carbide balls at speed of 200 rpm for 2 hours followed by degassing for 24 hours. Then the desired quantity of hardener was added (in the ratio of 100:10 by volume of resin), and gently stirred to minimize the formation of air bubbles followed by casting it in open mould. After that, it was first cured at room temperature for 24 hours. Subsequently, further post curing was carried out in hot air oven at 70°C for 7 hours. The weight of hBN nanoplatelets in epoxy nanocomposites was controlled at 0.1, 0.2, 0.4 and 0.6 wt. %. Similar process was followed for the pure epoxy sample preparation without mixing hBN nanoplatelets.

3.2.4 EPOXY/PVP MODIFIED hBN NANOCOMPOSITES

The 0.1 wt.% of PVP was mixed with 25 ml ethyl alcohol. In this PVP solution, the desired quantity of hBN nanoplatelets was mixed using probe sonication for 30
minutes in an ice bath. Then, the mixture of PVP-hBN was mixed with epoxy, and probe sonicated for another 30 minutes in an ice bath. Thereafter removal of ethyl alcohol, ball milling, degassing, addition of hardener and curing is the same process as described in Fig. 3.1. The weight content of hBN nanoplatelets in PVP modified hBN nanoplatelets reinforced epoxy nanocomposites was controlled at 0.1, 0.2, 0.4 and 0.6 wt. %.

3.2.5 EPOXY/GRAPHENE NANOPLATELETS AND EPOXY/PVP MODIFIED GRAPHENE NANOPLATELETS NANOCOMPOSITES

![Figure 3.2: Schematic of steps involved in processing of epoxy/graphene nanoplatelets nanocomposites.](image)

Graphene nanoplatelets reinforced epoxy nanocomposites were prepared according to the steps shown in Fig. 3.2. Initially, a desired weight percent of graphene nanoplatelets was dissolved in 25 ml ethyl alcohol by probe sonicking it for 30 min in an ice bath. Further, this solution was added into epoxy and again probe sonicated for 30 min in an ice bath. Thereafter, the mixture was heated over the magnetic stirrer at 80°C for 2 hours for evaporation of ethyl alcohol from the mixture. Then, the epoxy/graphene nanoplatelets mixture was ball milled for 2 hours using 10 mm diameter tungsten carbide balls and at 200 rpm. The ball milled epoxy/graphene nanoplatelets mixture was degassed
for 24 hours in a vacuum oven. In degassed epoxy/graphene nanplatelets mixture, the hardener N,N-Bis (2-aminoethyl) ethane-1,2-diamine was added (in the ratio of 100:10 by volume of resin), and mixed together by gently stirring so as to minimise the air bubble formation. The resultant mixture was cast into an open mould and cured at room temperature for 24 hours. The cured epoxy nanocomposites were post cured at 70°C for 7 hours in hot air oven. Addition of graphene nanplatelets in epoxy matrix was controlled at 0.025, 0.05, 0.1 and 0.2 wt.%.

For PVP modified graphene/epoxy nanocomposites preparation, similar protocol was followed. PVP was mixed directly into the ethyl alcohol (0.1 wt.% of PVP in 25 ml ethyl alcohol). Addition of PVP modified graphene nanplatelets in epoxy matrix was controlled at 0.025, 0.05, 0.1 and 0.2 wt. %. In case of pure epoxy sample preparation, similar protocol was followed without mixing of graphene.

3.2.6 1:1 RATIO OF 0.1 WT% OF GRAPHENE AND hBN REINFORCED EPOXY HYBRID NANOCOMPOSITES

Initially, a desired weight percent of graphene and hBN nanplatelets was dissolved in 25 ml ethyl alcohol by probe sonicating it for 30 min in an ice bath. Further, this solution was added into epoxy and again probe sonicated for 30 min in an ice bath. Thereafter, the mixture was heated over the magnetic stirrer at 80°C for 2 hours for evaporation of ethyl alcohol from the mixture. Then, the epoxy/graphene and hBN nanplatelets mixture was ball milled for 2 hours using 10 mm diameter tungsten carbide balls and at 200 rpm. The ball milled epoxy/graphene and hBN nanplatelets mixture was degassed for 24 hours in a vacuum oven. In degassed epoxy/graphene and hBN nanplatelets mixture, the hardener N,N-Bis (2-aminoethyl) ethane-1,2-diamine was added (in the ratio of 100:10 by volume of resin), and mixed together by gently stirring so as to minimise the air bubble formation. The resultant mixture was cast into an open mould and cured at room temperature for 24 hours. The cured epoxy nanocomposites were post cured at 70°C for 7 hours in hot air oven. Addition of graphene and hBN nanplatelets in epoxy matrix was controlled at 0.1 wt. %.
For PVP modified graphene and hBN nanoplatelets/epoxy nanocomposites preparation, similar protocol was followed. PVP was mixed directly into the ethyl alcohol (0.1 wt.% of PVP in 25 ml ethyl alcohol). Addition of PVP modified graphene and hBN nanoplatelets in epoxy matrix was controlled at 0.1 wt. %. In case of pure epoxy sample preparation, similar protocol was followed without mixing of graphene.

3.3 CHARACTERIZATION

3.3.1 X-RAY DIFFRACTION

X-ray diffraction (XRD) studies were carried out on a BRUKER, Germany (D8 Advance). The incident X-rays (λ=1.54 nm) from the Cu-target was monochromatized using a Ni filter. XRD patterns were recorded with a step scan with step size of 0.02° between 5° and 40° (2θ).

3.3.2 THERMAL CHARACTERIZATION

Thermogravimetric analysis (TGA) was performed on a Q500 from TA instruments with a heating rate of 10°C/min in the temperature range of 25 to 900°C with the nitrogen and air flow of 50 ml/min. The amount of the sample used is 6-8 mg. Based on the original weight loss dependence of the temperature, the first derivative data, i.e. DTG data were accordingly obtained. Differential scanning calorimetric (DSC) measurements were carried out using a DSC Q200 from TA instruments. The cast samples of about 5 mg were dried in a vacuum oven prior to experiment. Temperature and transition heat were calibrated with indium standard. The heating run all samples were recorded in the temperature range from 25 °C to 235 °C at a scan rate of 10 °C/min under nitrogen atmosphere.

3.3.3 MORPHOLOGICAL CHARACTERIZATION
The morphology of the graphene and hBN nanoplatelets was examined by JEOL JEM 2100 high resolution transmission electron microscope (HRTEM). Scanning electron microscopy (SEM) analysis was performed with Hitachi S3400, operated at 15 KV with gold sputtering on the tensile fractured samples.

3.3.4 MECHANICAL PROPERTIES CHARACTERIZATION

Three-point bending flexural tests were conducted according to ASTM D790 using Instron tensile tester (8801). Dimensions of specimen were 137 mm (length) 10 mm (width) and 3.1 mm (thickness). The tests were performed at a cross-head speed of 2 mm/min. At least five specimens from each sample were tested.

3.3.5 SPECTROSCOPIC CHARACTERIZATION

FTIR spectroscopic analysis was carried out with (IRAffinity-1, SHIMADZU, resolution 0.5 cm⁻¹) for the film samples in the scanning range of 400 to 4000 cm⁻¹. UV-Vis-NIR spectroscopy analysis was carried out with HITACHI U-2800 spectrophotometer.