CHAPTER III
MATERIALS AND METHODS

3.1. Materials

The epoxy resin (diglycidyl ether of bisphenol A, DGEBA) LY 556 having epoxy equivalent about 180-190 and 4,4’-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy Ltd., India. Unsaturated polyester resin (manufactured using phthalic acid, maleic anhydride and propylene glycol with 25% styrene having the average molecular weight 2,300-2,600 g/mol and viscosity of 600 cP) and benzoyl peroxide were supplied by Polyresins, India. Montmorillonite, cetylammmonium bromide and ethylenediamine were purchased from sigma Aldrich Inc., USA. Sodium chloride, nitric acid, thionyl chloride and tetrahydrofuran were provided by Central Drug House, New Delhi, and Polycarbonate membrane filters with 0.2 m pore size was used for filtration of carbon nanotubes. The silanes \( \gamma \)-glycidoxy-propyl-trimethoxysilane (gGPTS), tetraethoxysilane (TEOS) and aminopropyl(diethoxysilane were from Anabond limited, Chennai. N,N-Dimethyl formamide was obtained from E-Merck, India. All the reagents were used as received unless specified. Double distilled water was used throughout the study.

3.1.1. Purification of solvents

3.1.1a. N, N-Dimethyl formamide

N, N-Dimethyl formamide (E-merck) was stirred with freshly dried copper sulphate overnight and distilled under reduced pressure. The fraction boiling at 75°C/12 mm Hg was collected.
3.1.1b. Tetrahydrofuran

Tetrahydrofuran (1L) was shaken with sodium hydroxide pellets and distilled. The distillate was dried over anhydrous calcium sulphate. The mixture was refluxed for 6 Hrs on a water bath and distilled. The fraction boiling at 65°C was collected and stored over metallic sodium wire.

3.1.1c. Ethyl alcohol

Rectified spirit was refluxed with freshly ignited and cooled calcium oxide for 6 hrs, set aside overnight and then distilled. The fraction boiling at 78°C was collected. The distillate was refluxed with few magnesium turnings for 6 hours and distilled.

3.1.2. Materials for composite preparation

3.1.2a. Epoxy resin

The term ‘epoxy resin’ refers to both the prepolymer and its cured resin/hardener system. The former is a low molecular weight oligomer that contains one or more epoxy groups per molecule (more than one unit per molecule is required if the resultant material is to be crosslinked). The characteristic group, a three-membered ring known as the epoxy, epoxide, oxirane, glycidyl or ethoxyline group is highly strained and therefore very reactive. Epoxy resins can be cross-linked through a polymerization reaction with a hardener at room temperature or at elevated temperatures (latent reaction) [1]. The three dimensional view and chemical structure of the typical epoxy are as given under.
3D view of epoxy resin

The base material used is the diglycidyl ether of bisphenol A, (DGEBA, LY 556) having epoxy equivalent about 180–190.

Structure of DGEBA

3.1.2b. Unsaturated polyester resin

A polyester family characterized by ethenic unsaturation in the polyester backbone that enables subsequent hardening or curing by co-polymerization with a reactive monomer in which the polyester constituent has been dissolved. Unsaturated polyesters are made by agitating a mixture of glycols, unsaturated dibasic acids or anhydrides in a heated kettle. In order to control the reaction and to modify the properties saturated dibasic acid, or anhydride, e.g., isophthalic acid or phthalic anhydride may be used. After the removal of water and cooling, the fluid polyester may be dissolved in a reactive monomer in the same kettle, or it may be shipped to users who add the monomer and catalyst in their plants. Styrene is the
most widely used reactive monomer. A peroxide catalyst is generally used for the final co-polymerization.

The structure of the hydroxyl terminated polyester in styrene used for the toughening of epoxy resin is represented as:

![Structure of hydroxyl terminated polyester](image)

### 3.1.2c. Curing agent

The addition of the primary amine to an epoxide group leads to the formation of a hydroxyl group and a secondary amine, which continues until the primary amine groups are exhausted. Further the crosslinking through the addition of secondary amines with epoxy groups, where the macromolecules develop a three-dimensional network. One of the most common side reactions is etherification where a hydroxyl group reacts with an epoxide group, forming an ether linkage and a further hydroxyl group. The extent to which etherification takes place during cure depends on the structure and chemistry of the resin and hardener, as well as the cure conditions. When the branched structures extend throughout the whole system, the gel point is reached. At this characteristic point, the crosslinked resin does not dissolve in a suitable solvent of the parent resin, although a soluble (sol) fraction may still be extractable. Further, diffusion-controlled cure is required to increase the degree of crosslinking and to finally produce a structural material with a mechanical modulus of a vitrified or glassy solid material. The point at which the glass transition temperature of the growing network reaches the cure temperature is known as vitrification. The structure of the
amine hardener 4,4′-diaminodiphenylmethane used for the hardening of polymer matrix is represented as:

\[
\begin{align*}
\text{Structure of 4,4′-diaminodiphenylmethane}
\end{align*}
\]

3.1.2d. Montmorillonite

The commonly used layered silicates for the preparation of polymer layered silicates (PLS) nanocomposites belong to the same general family of 2:1 layered or phyllosilicates. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Fig. 3.1). The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al\(^{3+}\) replaced by Mg\(^{2+}\) or Fe\(^{2+}\), or Mg\(^{2+}\) replaced by Li\(^+\)) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not fixed, but varies from layer to layer, and must be considered as an average value over the whole crystal [2].
Figure: 3.1. Schematic diagram showing the structure of 2:1 phyllosilicates and the polymer clay nanocomposites
3.1.2f. Nanosilica by sol-gel method

Nano-silica is the most commonly used tool for the preparation of nanocomposites. The sol-gel process has provided promising potential for the preparation of a variety of organo-inorganic hybrid materials at the molecular level. The in-situ development of a three-dimensional cross-linked inorganic network structure using an organic precursor such as an alkoxide, M(OR)$_4$, can be carried out within the polymer matrix [3]. The Nano-SiO$_2$ particles are hydrophilic because of surface OH groups and so need to be modified with organic surfactant treatment [4].

3.1.2g. Multiwalled carbon nanotube

CNT is a cylindrical molecule composed of carbon atoms. A major feature of the structure is the hexagon pattern that repeats itself periodically in space. As a result of the periodicity, each atom is bonded to three neighboring atoms. Such structure is mainly due to the process of $sp^2$ hybridization [2] during which one $s$-orbital and two $p$-orbitals combine to form three hybrid $sp^2$-orbitals at 120° to each other within a plane. This covalent bond (referred to as the $\sigma$ bond) is a strong chemical bond and plays an important role in the impressive mechanical properties of CNT’s. In addition, the out-of-plane bond (the $\pi$-bond) that is relatively weak contributes to the interaction between the layers in MWCNTs, and between SWCNT’s in SWCNT bundles. Of course, the bonding is not purely $sp^2$ in nanotubes, as curving the graphene sheet into a tube re-hybridizes the $\sigma$ and $\pi$ orbitals, yielding an admixture [5]. A typical MWCNT structure is illustrated as:
3.2. EXPERIMENTAL

To prepare UP toughened epoxy nanocomposites, several strategies have been considered as given below.

3.2.1. Processing Techniques

3.2.1a. Intercalative and/or exfoliation polymerization

In this process, the layered expanded C-MMT or exfoliated layered nanosheets are swollen within the liquid monomer or a monomer solution, so that the polymer formation can then occur in between the silicate layers. The polymerization can then be initiated by the process of curing, by the use of a suitable hardener. Despite the availability of different curing agents (hardener), 4,4’-diaminodiphenylmethane (DDM) is used because of its high temperature processing range, considering the fact that when the layered expanded C-MMT are mixed with the polymer matrix in the molten state, the chosen polymer can diffuse into the interlayer space or galleries of expanded silicate layers and yield either an intercalated or an exfoliated polymer/layered silicate nanocomposite. This methodology is solvent-free and cost-effective. The advantage of this technique is that a well-dispersed intercalated or exfoliated polymer/layered silicate nanocomposite is generally obtained. It is also assumed
that intensive stirring such as ball-milling and sonication needed to break down the expanded silicate layers help the polymer chains intercalate into silicate layers to form a polymer/silicate nanocomposite.

3.2.1b. Surface modification of nanoparticles

The tiny particles are easy to agglomerate due to their large specific surface area. Moreover, the hydrophilic nanoparticles and the hydrophobic polymer are not compatible in nature. Consequently, the so-called nanocomposites sometimes contain a number of loosened clusters of nano-fillers, where the polymer binder is impoverished. This may make properties of nanoparticle-filled composites even worse than conventional microcomposites. Extensive material loss would thus occur due to disintegration and crumbling of the particle agglomerates under tribological conditions. It is therefore necessary to break down these nanoparticle agglomerates in order to produce nanostructured composites. In this context, control and/or manipulation of surface properties of nano-fillers are critical. By considering the above facts, MMT, nanosilica and MWCNTs are subjected to surface modification and used as suitable fillers for the epoxy/UP resin.

3.2.1c. Solvent free polymerization

Solvents are often the largest sources of wastes in chemical syntheses and processes. Many solvents are themselves toxic, flammable, and explosive. Eliminating their use reduces safety and storage hazards. Eliminating the need to purchase and then treat large amounts of solvent may also provide substantial economic benefits. Eliminating the use of solvents can dramatically reduce the amount of waste and volatile organic compound (VOC) emissions that are produced in a process. Using a solvent in composite preparation will lead to the formation of volatile gases during the curing process, which in turn causes voids and affect
the mechanical properties of the composites. In the present study nanocomposites are prepared by solvent (diluents) free technique.

3.2.1d. High energy mixing

There are a number of methods to prepare uniformly dispersed nanoparticle reinforced composites. Here we combine mechanical mixing, ball milling and ultrasonication to ensure a homogeneous dispersion of nanoparticles in the polymer resin.

3.2.2. Preparation of Clay minerals as fillers

3.2.2a. Purification of Montmorillonite

The purification of montmorillonite was achieved by sedimentation centrifugation and drying. A portion of the montmorillonite was crushed in a mortar in order to obtain a fine powder. The clay was dispersed in deionised water using an ultrasonic bath for ten minutes. The dispersion was stirred overnight. As stirring stopped, particles started to sediment, when the solution containing particles still in suspension (which are less than \( \approx 2 \mu m \)) was siphoned off. This solution was subjected to 20000 rpm during 15 minutes so that particles sedimented rapidly in the centrifugal field. Particles were then redispersed in a small amount of purified water. The concentrated solution obtained was dried at 50\(^\circ\)C in a ventilated oven for 4 days. [6]

3.2.2b. Preparation of Na-Montmorillonite

In order to increase swelling properties of montmorillonite (MMT), sodium activation was performed. Montmorillonite clay was first dispersed in 1N solution of sodium chloride and stirred. The stirring was continued for 24 hours at 70\(^\circ\)C. Upon centrifugation of the solution at high speed, an opaque layer accumulated 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 by testing with one drop of 0.1 N silver nitrate solution. The purified clay (Na-MMT) was dried at 70°C and stored in a desiccator.

3.2.2c. Intercalation of alkyl ammonium ions

The Na-exchanged clay was dispersed in desired quantity of distilled water at 80°C. Then cetyl ammonium bromide was mixed with the hot solution and stirred vigorously for one hour at 80°C. A white precipitate formed, was isolated by filtration and washed several times with hot water/ethanol (1:1) mixture until no chloride was detected in the filtrate by one drop of 0.1N silver nitrate solution. The alkylammonium ion exchanged montmorillonite (C-MMT) was then dried for several days at 75°C, ground with mortar and pestle, and then stored in a desiccator [7]. The possible types of intercalation of cetyl ammonium ions in the clay galleries are given as:

The possible intercalation of cetyl ammonium ions in clay galleries
3.2.2d. Preparation of silanated montmorillonite

A mixture of 400 ml of EtOH/H$_2$O (75:25) was introduced in a three necked flask. Sodium montmorillonite (1.5g) was added to the solvent together with a large excess of glycidyl-propyl-triethoxysilane (5 g). The mixture was heated at 80$^\circ$C and kept under stirring for 4 h. Then the clay mineral was filtered and washed carefully with ethanol. The resulting product (G-MMT was dried in oven at 80$^\circ$C overnight [8]. The two step reaction of silanation on montmorillonite is described as:

\[ \text{HYDROLYSIS} \]
\[ \text{CONDENSATION} \]

Mechanism of silanation of Montmorillonite
Grafting and/or intercalation are possible during silanation (Fig: 3.2).

**Figure: 3.2. The possible grafting/intercalation of cetyl ammonium ions in clay galleries**
3.2.3. Silica as filler

3.2.3a. Preparation of silica nanoparticles

Methanol as medium and ammonium hydroxide as catalyst were mixed in 2L resin kettle, followed by dropwise addition of tetraethoxysilane (TEOS) in methanol, carried out for 3h at room temperature. The particles obtained were centrifuged and de-ionized water added to remove the catalyst. The washed powder was vacuum dried at 100°C for 3 days [9] and further heated to 600°C for 30 min and then to 1000°C for 2 h in a muffle furnace.

3.2.3b. Modification of silica surface with amine group

Ten grams of the synthesized silica particles were mixed with 120 ml of the solution of aminopropyldiethoxysilane in toluene. The silica powder (A-silica) was centrifuged, washed repeatedly with toluene and dried at 150°C in vacuum for 6 h.

3.2.4. Multiwalled Carbon nanotube as filler

3.2.4a. Functionalization of carbon nanotubes

Purification of MWCNT was first performed with a selective oxidation step at 530°C in air for 60 min to remove amorphous carbon. After being oxidized with a mixture of H\textsubscript{2}SO\textsubscript{4} (98%)/HNO\textsubscript{3} (68%) (3:1, v/v) at 60°C for 4 h, the carboxylated MWCNTs were filtered and washed with deionized water until pH was 7 and dried in vacuum oven. One hundred and fifty milligrams of carboxylated MWNTs were stirred in 30 ml of a 20:1 mixture of thionyl chloride (SOCl\textsubscript{2}) and dimethylformamide (DMF) at 70°C for 24 h. After the acyl chlorination, the MWCNTs were centrifuged and washed repeatedly with anhydrous tetrahydrofuran (THF). The remaining solid was dried under vacuum. One hundred milligrams of acyl-chlorinated MWCNTs were reacted with 50 ml of ethylenediamine solution at 100°C for 2 days [10]. After cooling to room temperature, the MWCNTs were
washed with ethanol to remove excess diamine. Finally, the black solid (A-MWCNT) was
dried at room temperature overnight under vacuum (Scheme.1).

![Scheme 1](image.png)

Scheme 1. Formation of amine functionalized carbon nanotubes

### 3.2.5. Preparation of composites

#### 3.2.5a. Preparation of neat epoxy

A fixed amount of epoxy resin (100 g), a stoichiometric amount of melted DDM
(27.2 g), with respect to epoxy resin was mixed with constant stirring under a mechanical
stirrer. The hybrid product was then degassed to remove the entrapped air and was then
transferred into a preheated mould and kept at 100°C for 4h and post cured at 140°C for 3h

#### 3.2.5b. Preparation of hybrid unsaturated polyester toughened epoxy resin.

A fixed amount of epoxy resin (100 g), varying amounts of unsaturated polyester
resin (5, and 10 g), benzoyl peroxide (2 wt%) with respect to unsaturated polyester, were
mixed with constant stirring for 6 hrs to get even distribution of unsaturated polyester resin in
epoxy resin. Then a stoichiometric amount of melted DDM (27.2 g), with respect to epoxy
resin was added with the above mixture and stirred. The hybrid product was then degassed to
remove the entrapped air and transferred into a releasing agent-coated and preheated mould
kept at 100°C for 4h and post cured at 140°C for 3h [12], when a toughened epoxy network
results [scheme 2].
Scheme 2: Formation of UP toughened Epoxy network
3.2.5c. Preparation of organophilic MMT clay-filled epoxy nanocomposites

Prior to curing, the epoxy resin was mixed with the desired amount of (1, 3, 5 and 7 wt%) organophilic nanoclay at 70°C for 24 h [13]. A stoichiometric amount of the curing agent 4,4′ diaminodiphenylmethane corresponding to epoxy equivalents was melted and added to the above mixture and stirred. The product was subjected to vacuum to remove the trapped air and then cast and cured at 140 °C for 3h. The castings were then post-cured at 200 °C for 2 h and finally removed from the mould for characterization.

3.2.5d. Preparation of silanated MMT clay-filled epoxy nanocomposites

Prior to curing, the epoxy resin was mixed mechanically with the desired amount of (1, 3, 5 and 7 wt%) silanated nanoclay at 70 °C for 24 h fitted with a condenser. A stoichiometric amount of the curing agent 4,4′ diaminodiphenylmethane corresponding to epoxy equivalents was added. The product was subjected to vacuum to remove the trapped air and at higher clay loadings, a foam of tiny bubbles appeared during degassing and was removed [14]. The mixture was then cased and cured at 140 °C for 3 h. The castings were then post-cured at 200°C for 2 h and finally removed from the mould before characterization.

3.2.5e. Preparation of amine-modified silica-filled epoxy nanocomposites

The epoxy resin (100g) was mechanically mixed with the desired amount of amine-modified silica particles (1, 3, 5 and 7%) at 80°C for 24h and sonicated for 30 minutes [15]. A stoichiometric amount of curative DDM (27.2g) corresponding to epoxy equivalents was heated and added to the above mixture at 80°C. The product was subjected to vacuum for removing the trapped air and then casted and vacuum-cured at 100°C for 4h. The casting was then post-cured at 140°C for 3h and finally released from the mould and then characterized.
3.2.5f. Preparation of amine-modified MWCNT filled epoxy nanocomposites

Prior to curing, the epoxy resin was mechanically mixed with the desired amount of (0.1, 0.3, 0.5 and 0.7 wt%) amine-modified MWCNT at 80°C for 24 h. The resulting mixture was ball milled for another 24 h to enhance the homogenous dispersion of carbon nanotubes in the resin and hence blending character [16], and further sonicated with SCS1200 sonicator (33KHZ/50 W) for 30 minutes. A stoichiometric amount of the melted curing agent 4,4’-diaminodiphenylmethane corresponding to epoxy equivalents was added. The product was subjected to vacuum to remove the trapped air and then injected into the mold, which was maintained at 100°C, under a low pressure (85 cm Hg) [17] and cured at 100 °C for 4 h. The castings were then post-cured at 140 °C for 3 h and finally removed from the mould and characterized [Scheme 3].
3.2.5g. Preparation of organophilic MMT/UP/epoxy nanocomposites

Different amounts of cetyl ammonium substituted MMT (C-MMT) from 1 to 7wt% (1, 3, 5 and 7) were introduced into the 10 wt% UP mixed epoxy resin along with the initiator, mechanically stirred for 24 h. Then the resulting mix was ball milled using a vertically rotating ball mill at room temperature for 10 h to enhance the exfoliated clay structure to get an effective nanocomposite. A stoichiometric amount of curing agent with respect to epoxide groups was melted and added to the DGEBA/UP/C-MMT mixture (kept at 90°C) under constant stirring and sonication for 15 minutes. The product was then subjected to vacuum to remove the trapped air and the ternary mixture was then transferred to the preheated mould for curing and vacuum-cured at 100°C for 4h. The castings were then post-cured at 140°C for 3h and finally removed from the mould and characterized.

3.2.5h. Preparation of silanated MMT/UP/epoxy nanocomposites

Different amounts of silanated MMT (G-MMT) from 1 to 7wt% were introduced into the 10 wt% UP mixed epoxy resin along with the initiator and mechanically stirred for 24 h. Then the resulting mix was ball milled using a vertically rotating ball mill at room temperature for 10 h to enhance the exfoliated clay structure to get an effective nanocomposite. A stoichiometric amount of curing agent with respect to epoxide groups was melted and added to the DGEBA/nanoparticle mixture, (kept at 90°C) continuously stirred and sonicated for 15 minutes. The product was then subjected to vacuum to remove the trapped air and then the ternary mixture was transferred to the mould for curing and vacuum-cured at 100°C for 4h. The castings were then post-cured at 140°C for 3h and finally removed from the mould and characterized.
3.2.5i. Preparation of amine-modified silica/UP/epoxy nanocomposites

The epoxy resin (100g) was mechanically mixed with the desired amount of amine-modified silica (A-silica) particles (1, 3, 5 and 7wt.%) at 80°C for 24h and sonicated for 30 minutes. To the above nanosilica-filled epoxy resin, 10g of unsaturated polyester resin and benzoyl peroxide were added (2 wt%) at 50°C for 10 min with constant stirring. A stoichiometric amount of curative DDM (27.2g) corresponding to epoxy equivalents was heated and added to the above mixture at 80°C. The product was subjected to vacuum for removing the trapped air and then casted and vacuum-cured at 100°C for 4h. The casting was then post-cured at 140°C for 3h and finally released from the mould and then characterized.

3.2.5j. Preparation of amino modified MWCNT hybrid unsaturated polyester toughened epoxy nanocomposites

The epoxy resin (100g) was mechanically mixed with the desired amount of amine modified carbon nanotube (A-MWCNT) particles (0.1, 0.3, 0.5 and 0.7 wt%) at 80°C for 24h and sonicated for 30 minutes with SCS1200 sonicator (33KHZ/50 W). To the above-filled epoxy resin, 10wt% of unsaturated polyester resin and benzoyl peroxide (2wt% with respect to UP) were added at 50°C with constant stirring for 10 min. The resulting mixture was ball-milled for 24 hours and sonicated for 30 minutes. A stoichiometric amount of melted curative agent DDM (27.2g) corresponding to epoxy equivalents was added to the above mixture kept at 80°C. The product was subjected to vacuum to remove the trapped air, injected by VARTM process into a preheated mould kept at 100°C and vacuum-cured at 100°C for 4h. The casting was then post-cured at 140°C for 3h and finally removed from the mould and characterized (Scheme 4).
Scheme 4. Preparation of amine modified MWCNT hybrid unsaturated polyester toughened epoxy nanocomposite
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3.3. Characterization

Continuing with the chain in materials research, both the development of synthetic materials and structure-properties models of nanocomposites require an adequate structural, thermal, mechanical, morphological and hydrophobic characterization of the materials. The testing and characterization of composites were carried out as per ASTM standards. FT-IR spectroscopy and Raman spectroscopy were preferred for functional identification, XRD for crystalline studies, DSC and TGA for thermal behavior and Mechanical tests (Tensile properties, flexural properties and impact strength) morphology (SEM) and hydrophobic behavior, by standard methods.

3.3.1. FT-IR spectroscopy

Nicolet Impact 400 FT-IR spectrometer was used to examine the structure of the fillers, monomers and composites. The spectra of samples were recorded by making pellets with potassium bromide (E-merck, IR grade). All the spectra were recorded at a resolution of 4 cm\(^{-1}\) with maximum scans. A background spectrum was run before recording the spectrum for each sample. The spectral calibration of the instrument was made using a polystyrene film at regular intervals of time.

3.3.2. XRD

X-ray diffraction patterns were obtained for diffraction angle 2θ from 0 to 10° by using a Rigaku X-ray diffractometer, with Cu-K\(\alpha\) radiation and a curved graphite crystal monochromator, to compute the crystallographic spacing, (d). X-rays primarily interact with electrons in atoms and the diffracted waves from the array of atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of
sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distance between crystal planes. Bragg's law $n\lambda=2dsin\theta$, enables the calculation of interplanar distance.

X-ray diffraction patterns of diffraction angle 2θ from 10 to 70° as standard and 0.5 to 10° as low angle was recorded using a Rich Seifert (Model 3000) X-ray powder diffractometer. The diffractometer was equipped with a Copper target ($\lambda= 1.5405 \text{ A}^\circ$) radiation using Guinier type camera employed as a focusing geometry and a solid-state detector. Curved nickel crystal was used as a monochromator and the step width (scanning speed) used was 2θ=0.04°/min.

The crystallite size of the polymer domain in nm scale (L), can be estimated from X-ray peak broadening of the (hkl) diffraction peak using Scherrer formula

$$L = \frac{k\lambda}{\beta_{1/2} \cos \theta} \quad \text{(1)}$$

where k is the Scherrer shape factor, here k=0.89; $\lambda$ the X-ray wavelength (0.15405 A°); $\theta$ the diffraction angle; $\beta_{1/2}$ the measured full-width at half-maximum (FWHM) of the experiment

3.3.3. Raman spectroscopy

Raman spectroscopy is non-destructive and readily available, and measurements can be made over a wide range of temperatures or pressures. It can provide unique information about vibrational and electronic properties of the material. Though not a direct method, it can still be used to determine the structure of the material and allows the identification of materials through the characteristic vibrations of certain structural parts. Because the Raman intensity of a vibration or phonon in a crystal depends on the relative directions of the crystal
axis and the electric wave polarization of the incident and scattered light, it may also be used to determine the orientation of nanotubes in polymer matrices or within nanotube bundles.

Raman spectra were recorded with a Dilor LABRAM-1B multi-channel confocal microspectrometer.

3.3.4. Thermo gravimetric analysis

Thermogravimetric Analysis (TGA) is a quantitative technique where a sample is placed in a furnace on a sensitive balance and heated, typically at a rate of 10 °C. The furnace environment is controlled by continuously purging the system with air or nitrogen as required. A characteristic curve obtained displays the mass against temperature that provides information regarding the composition of the sample. Organic polymers heated in air will burn and release combustion products with consequent continuous decrease in mass until all the sample has burned giving a balance reading of close to zero depending on any inorganic impurities that may be present. In a composite under investigation, where the filler material is thermally more stable than the polymer matrix, it can withstand higher temperatures.

Thermo-gravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA instruments, USA) at a heating rate of 10 °C per min in nitrogen atmosphere.

3.3.5. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is an advanced technique to measure the heat flow through a sample as the sample is heated at a controlled rate. Heat flow is dependent on sample morphology. If the material is amorphous, a shift in the baseline will be observed when the amorphous chains are given enough thermal energy to facilitate movement of the chains. Thus the material changes from a rigid, glassy state to more rubbery state as the chains become more flexible and a change in heat capacity occurs. The
temperature at which this change in material properties occurs is referred to as the glass transition temperature, \( T_g \). If the material is crystalline, a peak in the heat flow occurs as the crystals melt or crystallize. Since melting is an endothermic process, it is observed as an endothermic peak which returns to the baseline upon termination of melting. Conversely, crystallization appears as an exothermic peak.

Glass transition temperature (\( T_g \)) of the samples was determined using a DSC Netzsch (TA instruments, USA) in the temperature range between 50 and 250 °C at a heating rate of 10 °C per min in nitrogen atmosphere.

3.3.6. Tensile properties

3.3.6a. Tensile strength

The maximum nominal stress sustained by a test specimen being pulled from both ends, at a specified temperature and at a specified rate of stretching is a measure of mechanical strength. When the maximum nominal stress occurs at the yield point it shall be designated tensile strength at yield. When it occurs at break, it shall be designated tensile strength at break.

3.3.6b. Tensile Modulus

It is the ratio of change in stress to change in strain within the elastic limits of the material. The ratio is calculated from the stress expressed in force per unit cross-sectional area, and the strain expressed as a fraction of the original length. Modulus so calculated is equivalent to the force required to strain the sample 100% of its original length, at the rate prevailing below the elastic limit.
The tensile (stress-strain) properties were determined using INSTRON (model 3365, UK) as per ASTM D 3039 at 10 mm/min cross-head using specimen with a width of 25 mm, length of 200 mm and thickness of 3 mm. Six specimens were tested for each sample.

3.3.7. Flexural properties

3.3.7a. Flexural strength

The maximum calculated stress in the outermost fibers of a test bar subjected to three-point loading at the moment of cracking or breaking.

3.3.7b. Flexural modulus

The ratio, within the elastic limit, of the applied stress in the outermost fibers of a test specimen in three-point, static flexure, to the calculated strain in those outermost fibers is flexural modulus.

The flexural properties were measured (INSTRON, model 3365, UK) as per ASTM D 790 using specimen with dimensions 3 mm in depth, 10 mm in width and 90 mm in length at 10mm/min cross head speed. Six specimens were tested for each sample.

3.3.8. Impact strength

The quantitative measure of the ability of a material to withstand shock loading is a standard test for impact strength. For plastics the test is usually either the Izod or Charpy test described in ASTM 256, and the result is calculated as the energy expended (work done) in breaking a specimen of unit thickness. Specimens of both tests are usually notched on the wide opposite that where they are struck, though the notch position may be reversed and unnotched specimens may be tested. To provide a much simpler stress distribution free of notch effects, researchers have developed the tensile-impact test [18].
3.3.9. Hydrophobic character

Plastic materials when immersed in water for a stipulated time and at a specified temperature (usually room temperature), they absorb water to some extent, varying from almost zero in the case of polytetrafluoroethylene and polyolefins, to complete dissolution for some types of polyvinyl alcohol and polyethylene oxide. Water absorption can cause swelling, leaching of additives, plasticizing and hydrolysis, which in turn can cause discoloration, embrittlement, stress cracking, lowering of mechanical and electrical properties, and reduced resistance to heat and weathering.

The hydrophobic behavior of the samples was tested as per ASTM D 570. The cured specimens (dimensions: 60 mm square, 3 mm thickness) were immersed in distilled water for 48 h. Specimens were tested after the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g. The percentage of the change in mass was calculated by using the formula:

\[
\text{Change in mass \%} = \frac{M - Mo}{Mo} \times 100
\]

Where, Mo represents the dried weight of the specimen and M the weight of the specimen.

3.3.10. Morphological studies

In order to obtain the microscopic characterization of the fractured surface of specimen, scanning electron microscopy (SEM; JEOL JSM Model 6360), was used on the principle that a finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen. SEM provides topographical and elemental information at magnifications from 10x to 100,000x with virtually unlimited depth of field.
3.4. References


[9] SungtackKang, Sung Il Hong, Chul Rim Choe, Min Park, Soonho Rim, Junkyung Kim. Polymer 42, 879 (2001)


