Chapter 2
Materials and Experimental Techniques

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Abstract
This chapter gives a detailed description about the materials and experimental techniques used for the preparation of nanocomposites. The different characterization techniques employed are also described.
2.1 Materials

2.1.1 Polypropylene (PP)

Polypropylene homopolymer (REPOL H200MA) with a melt flow index of 25 g/10 min (230°C/2.16Kg) was purchased from Reliance Industries limited, Mumbai, India.

2.1.2 Polystyrene (PS)

General purpose Polystyrene (MFI (200°C/5Kg) is 12 g/10 min) was obtained from Supreme Petrochem Ltd India.

2.1.3 Modified kaolin nanoclays

Modified kaolin nanoclays were obtained from English India Clays Limited Veli, Thiruvananthapuram, Kerala, India. The clays had a bulk density of 0.2-0.3 g/cc and a BET specific surface area of 28-30 m²/g. The samples used were unmodified kaolin nanoclay (Nanocaliber 100), vinyl silane modified nanoclay (Nanocaliber 100V - N100V), dialkyl silane modified nanoclay (Nanocaliber 100 Z- N100Z), mercapto silane modified kaolin nanoclay (Nanocaliber 100 M denoted as N100M) and amino silane modified kaolin nanoclay (Nanocaliber 100 A- N100A).

2.1.4 Glass fibers

E- Glass fiber: E-Glass fiber with a diameter of 13 µm, Specific Gravity-2.6 g/cm³, tensile strength-3.5 GPa, tensile modulus-72 GPa was obtained from Sharon Industries Ltd, Kochi, India.

AR glass fiber (Alkali resistant glass fiber): Cem-FIL® 54 with a diameter of 10 µm, specific gravity: 2.68 g/cm³, tensile Strength: 1,700 MPa
and modulus of elasticity: 72 GPa was obtained from Sharon Industries Ltd, Kochi, India.

2.1.5 Vinyltriethoxysilane (VTES)

Vinyltriethoxysilane (98%) was supplied by Lancaster synthesis, East gate, England.

2.1.6 Itaconic acid

Itaconic acid (Figure 2.1) pure AR with molecular weight of 130.10, melting range of 165-167°C was supplied by Spectrochem Pvt. Ltd. India

![Figure 2.1 Structure of itaconic acid](image)

2.1.7 Dimethyl itaconate

Dimethyl itaconate (Figure 2.2) (97%) with molecular weight of 158.16, boiling point of 207-208°C was supplied by Alfa Aesar.

![Figure 2.2 Structure of dimethyl itaconate](image)
2.1.8 Other chemicals

Glacial acetic acid was obtained from Spectrochem Pvt. LTD Mumbai. Sodium hydroxide (NaOH) pellets purified obtained from SDFCL, Sd fine – chem limited. Sodium hypochlorite solution about 4%w/v available chlorine was supplied by Merck specialties private limited.

2.2 Methodology

2.2.1 Composite preparation

A thermo Haake Rheomix 600 (Figure 2.3) mixing chamber with a volumetric capacity of 69cm$^3$ fitted with roller rotors was used for melt mixing of polymers with fillers. In the chamber, the roller rotors rotate in opposite directions in order to affect a shearing force on the material mostly by shearing the material against the walls of the mixing chamber. The granules in the desired proportion were fed to the chamber through a vertical chute with a ram. There is a small clearance between the rotors which rotate at different speeds at the chamber wall. In these clearances dispersive mixing takes place. The shape and motion of the rotors ensure that all particles undergo high intensive shearing flow in the clearances. The mixer consists of three sections and each section is heated and controlled by its own heater and temperature controller. It is designed to maintain very accurate and uniform temperature profiles throughout the mixer.
Since mechanical dissipation heat is developed in the small gap between rotors and chamber, the heat conducts to the center bowl and raises the set temperature. In this case, the heater at the center bowl is automatically shut off and circulation of cooling air is activated [1].

Three types of composites (nanoclay composites, short glass fiber/nanoclay hybrid composites and cellulose nano fiber composites) were prepared by this method. A mixing time of 8 minutes at a counter rotating rotor speed of 50 rpm was used for the mixing of the samples.

**2.2.2 Preparation of test specimen**

The hot mix from the mixing chamber was immediately pressed using a hydraulic press at a pressure of 100kg/cm² and the resulting sheets were cut to small pieces. The test specimen were prepared using injection DSM Micro 10cc Injection Molding Machine (Figure 2.4), with a barrel temperature of 190°C. The specimens were molded at identical conditions and the properties were taken as the average property of six samples.
2.2.3 Characterization Techniques

2.2.3.1 X-ray Diffraction (XRD)

The samples were analyzed in a Bruker AXS D8 Advance X-Ray Powder Diffractometer (Cu Kα radiation) in order to find the change in basal spacing of composites. The samples were scanned in the range of 3-80° at increment step of scanning 0.020° at a wave length of 1.5406 Å and Ni filter open at 30kV and 20mA. The particle size was calculated by the Scherer’s Equation 

\[ t = \frac{K \lambda}{B \cos \theta} \]

where \( t \) = crystallite thickness, \( \lambda \) = X-ray wavelength, \( B \) = Full width half max (FWHM) of the diffraction peak, \( \theta \) = diffraction angle and \( K \) = Scherer’s constant. It provides information on the changes of the inter-layer spacing of the clay upon the formation of clay nanocomposites. The formation of an intercalated structure should result in a decrease in \( 2\theta \), indicating an increase in d-spacing and if the complete exfoliation takes place, no peak is shown in the XRD pattern and the broadening of the peak is considered to be result of partial exfoliation [2].
2.2.3.2 Scanning Electron Microscopy (SEM)

SEM is a very useful tool to investigate the morphology of fractured surfaces. In SEM, the electron beam incident is scanned across the specimen surface causes various phenomena of which the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is a one- to- one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of the surface is progressively built up on the screen. The SEM observations reported in the present study were made on the fracture surface of the tensile specimens. Morphology of the tensile fractured surfaces of the specimens was investigated by using JEOL Model JSM 6390LV scanning electron microscope (SEM). The samples were subjected to gold sputtering prior to electron microscopy to give the necessary conductivity [3].

2.2.3.3 Thermogravimetric analysis (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time while the substance is subjected to a controlled temperature programme. The sample was placed in a temperature programmed furnace. Thermal stability was analyzed using TGA Q-50 of TA instruments under N₂ atmosphere. The samples weight of about 5–7 mg was heated at a rate of 20°C/min from ambient temperature to 600°C. The corresponding weight changes were noted with the help of an ultra-sensitive microbalance. The data of weight loss versus temperature and time was
recorded online in the TA Instrument's Q series Explorer software. The
analysis of the thermogravimetric (TG) and derivative thermogravimetric
(DTG) curves were done using TA Instrument's Universal Analysis 2000
software version 3.38.

The oxidation index (OI) was calculated based on the weight of
carbonaceous char as related by the empirical equation:

\[
\text{OI} \times 100 = 17.4 \times 0.4CR 
\] ................................. (2.1)

2.2.3.3.1 Kinetic analysis of thermal decomposition

To evaluate the thermal stability and kinetic parameters of the sample,
non-isothermal thermal degradation kinetics was used. The reaction rate can
be described in terms of reaction mechanism, \( f(\alpha) \); where \( \alpha \) is the degree of
conversion; \( \alpha = W_0 - W_t/W_0 - W \) [\( W_0 \) is the initial weight of the sample,
\( W_t \) is the weight remaining at a given temperature \( T \), \( W \) is the final weight] and a temperature –dependent function, \( k(T) \):

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) .................................................. (2.2)
\]

By substituting the Arrhenius equation in the temperature dependent term
\( k(T) = A\exp(-E_a/RT) \),

\[
\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) .................................................. (2.3)
\]

Where \( \alpha \) is the conversion degree or fractional weight loss, \( t \) is the reaction
time, \( A \) is the pre-exponential factor, \( R \) is the gas constant, \( T \) is the absolute
temperature, \( E_a \) is the apparent activation energy and \( f(\alpha) \) is the reaction
model.
If the constant heating rate of TGA process is set as $\beta = \frac{dT}{dt}$, the conversion degree $\alpha$ can be expressed as the function of the temperature. The temperature is dependent on the heating time. Therefore,

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \frac{d\alpha}{dt} \quad \ldots \quad \text{(2.4)}$$

$\beta$ is the heating rate in TGA. The combination of equation (2.3) & (2.4) gives the following relationship

$$\frac{d\alpha}{\beta} = A \exp \left( -\frac{E_a}{RT} \right) f(\alpha) \quad \text{........................................ (2.5)}$$

Rearranging the equation (2.5)

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp \left( -\frac{E_a}{RT} \right) dT \quad \text{........................................ (2.6)}$$

Eq.2.6 is the basic relation to determine the kinetic parameters on the basis of TG data.

After the integration of previous equation, $g(\alpha)$ can be obtained,

$$g(\alpha) = \int^0_\alpha d\alpha / f(\alpha) = \frac{A}{\beta} \int^{\alpha}_0 \exp \left( -\frac{E_a}{RT} \right) dT \quad \text{........................................ (2.7)}$$

where $g(\alpha)$ is the integral conversion function. The left hand side of the equation can be resolved in terms of the reaction mechanism that better fits the decomposition process. The Table 2.1 shows the expressions of $g(\alpha)$ corresponding to each one of the mechanism functions $f(\alpha)$ and “n” is the reaction order [4,5].
Table 2.1 Algebraic expressions of functions $f(\alpha)$ and $g(\alpha)$ and its corresponding mechanisms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>$f(\alpha)$ function</th>
<th>$g(\alpha)$ function</th>
<th>Mechanism model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1-\alpha)^n$</td>
<td>$[1-(1-\alpha)]$</td>
<td>Phase boundary-controlled reaction(plane symmetry)</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>$2[1-(1-\alpha)^{1/2}]$</td>
<td>Phase boundary-controlled reaction (contracting area)</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>$3[1-(1-\alpha)^{1/3}]$</td>
<td>Phase boundary-controlled reaction (contracting volume)</td>
<td></td>
</tr>
<tr>
<td>$Fn$</td>
<td>$(1-\alpha)$</td>
<td>-$\ln(1-\alpha)$</td>
<td>Reaction order with $n=1$</td>
</tr>
<tr>
<td>$1/n(1-\alpha)^{1-n}$</td>
<td>$1-1-(1-\alpha)^{1/2}$</td>
<td>$1-(1-\alpha)^{1/3}$</td>
<td>$n$ th Reaction order with $n=1/2, 1/3$</td>
</tr>
<tr>
<td>An</td>
<td>$[-\ln(1-\alpha)]^{(1-n)}(1-\alpha)$</td>
<td>$[-\ln(1-\alpha)^n]$</td>
<td>Random nucleation and growth of nuclei(Avrami-Erofeev equation) $n=2/3, 1/2, 1/3, 1/4$</td>
</tr>
<tr>
<td>Pn</td>
<td>$1/n(\alpha)^{1-n}$</td>
<td>$\alpha^n$</td>
<td>Power law $n=1/4, 1/3, 1/2, 3/2$</td>
</tr>
</tbody>
</table>

The integral in the right hand side has no analytical solution and several kinds of approximation are generally used. Flynn–Wall–Ozawa [6], Friedman [7], Kissinger [8], Freeman-Carroll [9] and other researchers have used several differential and integral methodologies, involving either a single thermogram or multiple thermograms with different heating rates have been developed. In the present investigation, three different non isothermal methods are used for the computation of the kinetic parameters. The three well-known kinetic methods such as Broido (BR), Horowitz-Metzger (H-M) and Coats-Redfern (C-R) methods are applied in this study and their main equations are given below [10].
I. Horowitz-Metzger (HW) method

\[
\ln \left[ \ln \left( \frac{1}{1-\alpha} \right) \right] = \frac{E_a \theta}{RT_s^2} \ \\
\text{............................................ (2.8)}
\]

where \(E_a\) is the activation energy, \(\theta = T - T_s\), \(T_s\) the DTG peak temperature and \(T\) the temperature corresponding to weight loss. Plot of \(\ln [-\ln (1-\alpha)]\) verses \(\theta\) should give a straight line whose slope is \(\frac{E_a}{RT_s^2}\).

II. Coats – Redfern (CR) method

\[
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left[ \frac{AR}{\beta E_a} \left( 1 + \frac{2RT}{E_a} \right) - \frac{E_a}{RT} \ \\
\text{............................................ (2.9)}
\]

where \(\alpha\) is the fraction of the sample decomposed at temperature \(T\), \(A\) is the frequency factor, \(\beta\) is the heating rate, \(E_a\) is the activation energy and \(R\) is the gas constant. A plot of \(\ln [g(\alpha)/T^2]\) {where \(g(\alpha)\) is the integrated from of various kinetic model equation as given in Table 2.1} against the reciprocal of absolute temperature \(1/T\) gives the slope for evaluation of activation energy.

III. Broido’s method (BM)

\[
\log(-\log(1-\alpha)) = -\left( \frac{E_a}{2.303R} \right) \left( \frac{1}{T} \right) + C \ \\
\text{.............................. (2.10)}
\]

where \((1-\alpha)\) is the fraction of initial molecules not yet decomposed, \(T\) the peak temperature of the derivative curve of TG, \(R\) the universal gas constant and \(E_a\) is the activation energy which can be calculated from the plot of \(\log(-\log(1-\alpha))\) verses \(1/T\).

2.2.3.4 Dynamic mechanical analysis (DMA)

DMA is used for studying the viscoelastic behavior of polymers. A sinusoidal stress is applied and the strain in the material is measured,
allowing one to determine the complex modulus [11]. Dynamic mechanical analysis measures the mechanical properties of materials as a function of time, temperature and frequency. Dynamic mechanical analysis was carried out using a dynamic mechanical analyzer (DMA Q-800, TA instruments). Rectangular shaped specimens of dimension 35 X 4 X 3 mm³ were used. DMA tests were conducted at a frequency of 1 Hz. A temperature ramp was run from 38 to 125°C at a heating rate of 3°C/min. Storage modulus, loss modulus and tan δ are used to generate the information about crystalline as well as amorphous nature in polymers. The variation of these components as a function of temperature is used to study the molecular motion in the polymers.

The storage modulus measures the stored energy, representing the elastic portion, and the loss modulus measures the energy dissipated as heat, representing the viscous portion. For viscoelastic materials, the modulus is a complex quantity.

\[
E^* = E' + iE''
\]

(2.11)

\[
E' = \text{storage modulus corresponding to the elastic response to the deformation and it is a measure of stiffness.}
\]

\[
E'' = \text{loss modulus corresponding to the plastic response to the deformation and it is associated with the dissipation of energy as heat when material is deformed.}
\]

\[
\frac{E''}{E'} = \tan \delta, \text{ useful for determining the occurrence of molecular transition such as glass transition temperature.}
\]
2.2.3.5 Mechanical properties

(a) Tensile properties

Tensile properties were evaluated using Shimadzu Autograph AG-I series universal testing machine at a crosshead speed of 50 mm/min with a load cell capacity of 10KN, according to ASTM D 638. The length between the jaws at the start of each test was fixed to 50 mm. A minimum of five samples were tested in each composite and the average results were recorded.

(b) Flexural properties

The flexural test measures the force required to bend a beam under three point loading conditions. Flexural modulus is used as an indication of material’s stiffness when flexed. The data is used to select materials for parts that will support loads without flexing. Flexural strength was measured by three point loading system using UTM (Shimadzu AG-1) with a load cell capacity according to ASTM D 790. The flexural properties were determined using rectangular shaped samples at a crosshead speed of 5mm/min. A minimum of five samples were tested in each sample and the average results were recorded.

The flexural strength is given by

\[
S = \frac{3PL}{2bd^2} \tag{2.12}
\]

Where \( S \) = flexural strength, \( P \) = maximum load at the moment of break, \( b \) = width of the specimen, \( L \) = length of the span and \( d \) = the thickness of the specimen.
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The maximum strain \( r \) in the outer fibers is given by

\[
r = \frac{6Dd}{L^2}
\]

\[(2.13)\]

where, \( D \) is the deflection.

The flexural modulus is calculated from the slope of initial portion of the flexural stress strain curve

\( \text{(c) Impact strength} \)

The impact strength describes the ability of a material to absorb shock and impact energy without breaking. The impact strength is calculated as the ratio of impact absorption to test specimen cross-section. Toughness is dependent upon temperature and the shape of the test specimen. The area under the stress-strain curve is directly proportional to the toughness of the material. Higher the impact strength of the material, higher will be the toughness and vice versa.

The Izod impact strength of the injection molded samples was determined as per ASTM D 256. The test was carried out using REIL IMPACTOR JUNIOR (CEAST) machine with a pendulum of 4kJ and striking velocity of 3.4m/s. Sample is clamped vertically in the base of the machine. A pendulum swings on its track and strikes the sample. The energy lost as the pendulum continuous on its path is measured from the distance of follow through. The impact energy is directly read from the machine.

\[
\text{Impact strength} = \frac{\text{Impact energy (J)}}{\text{Thickness (m)}}
\]

\[(2.14)\]
(d) Hardness

Durometer hardness test measures the penetration of a specified indentor into the material under specified conditions of force and time. Hardness of the test samples were determined using Durometer hardness Shore D according to the ASTM D 2240. The specimen is first placed on a hard flat surface. The indentor for the instrument is then presses into the specimen making sure that it is parallel to the surface.

2.2.3.6 Melt Flow Index (MFI)

Melt flow index is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in 10 minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. Melt Flow Index (MFI) is a measure of the plastic’s ability to flow and it is inversely related to melt viscosity. The melt flow index of the test samples was determined using a CEAST Modular Line Melt Flow Indexer, according to ASTM D1238 (230°C/2.16kg). MFI is used to determine how a polymer will process. The apparatus is reheated to a specified temperature and the material loaded into the cylinder from the top and a specified weight is applied on a piston. The weight exerts a force on the molten polymer and it immediately starts flowing through the die. A sample of the melt is taken after desired period of time and is weighed accurately. MFI is expressed as grams of polymer/10 minutes of total time of the test [12].

2.2.3.7 Differential scanning calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and
reference is measured as a function of temperature. It is used to investigate thermal transitions, such as phase changes, crystallization, melting, glass transitions of a material as a function of temperature [13]. When the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. Heat flow i.e. heat absorption (endothermic) or heat emission (exothermic), is measured as a function of time or temperature of the sample and the result is compared with that of a thermally inert reference. The materials, as they undergo changes in chemical and physical properties, which are detected by transducers, which changes into electrical signals that are collected and analyzed to give thermograms. The melting and crystallization parameter, such as melting point ($T_m$), Heat of fusion ($\Delta H_f$), temperature of crystallization ($T_c$), and Heat of crystallization ($\Delta H_c$) were used for the comparison of composites.

DSC measurements were made on a DSC Q 100 (TA instruments). The samples were heated from 30°C to 250°C at the rate of 50°C/min and kept at isothermal for 3 minutes in order to remove the thermal history, cooled from 250°C to room temperature then reheated from room temperature to 250°C at heating rate of 10°C/min under nitrogen atmosphere

Based on the mechanism of operation, DSCs can be classified into two types: heat-flux DSC and power-compensated DSC. In a heat flux DSC, the sample material, enclosed in a pan and an empty reference pan are placed on a thermoelectric disk surrounded by a furnace. The furnace is heated at a linear heating rate, and the heat is transferred to the sample and reference
pan through the thermoelectric disk. In a power-compensated DSC, the sample and reference pans are placed in separate furnaces heated by separate heaters. The sample and reference are maintained at the same temperature, and the difference in thermal power required to maintain them at the same temperature is measured and plotted as a function of temperature or time [14].

References


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