CHAPTER – 5

Synthesis and Characterization of Polymer Clay Nanocomposites

5.1. INTRODUCTION:

Nanocomposites are generally defined as composites in which the components are combined in at least one dimension (i.e. length, width or thickness) in the size range of 1-100 nm [1]. The reasons behind the interest are the changes in physical and chemical properties of the polymer layered silicates, in comparison to neat polymer [2-4]. They also exhibit improved mechanical and thermal properties [5], enhanced ionic conductivity [6] and gas permeability resistance [7] compared to conventional microcomposites. Nanocomposites are also used as catalyst [8]. Investigations on nanocomposite materials were started by researchers at Toyota Research Laboratories from 1987 [9, 10]. They prepared Nylon 6 - clay nanocomposites by the polymerization of ε-caprolactam in the interlayer gallery region of organoclays [9]. The filler used was Montmorillonite. Organoclay is a product obtained by the modification of the hydrophilic surface of the clay through the use of organic surfactant. Numerous other researchers later used this concept for nanocomposites based on epoxides [11], polystyrene [12], poly (1-caprolactone) [13], silicone rubber [14], polyimide [15], polybenzoxazole [16], polyurethane [17].

The most frequently used clay in nanocomposites is usually a type of smectite clay such as Montmorillonite, which is an aluminous silicate mineral with sodium ions present between the clay layers because of its small particle size (<10 µm) and ease of intercalation [18, 19]. The Montmorillonite crystal lattice consists of about 1 nm thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets [20]. This space between the clay layers is referred to as the clay gallery. The Na-Montmorillonite clay is hydrophilic and expands the interlayer spaces readily when immersed in water. The clay surface can be converted from hydrophilic to organophilic via cation exchange of Na⁺ with alkylammonium ions.
including primary, secondary, tertiary and quaternary alkylammonium cations under proper conditions [21]. The space between the silicate layers depends greatly on the length of the alkyl chain and the ratio of cross-sectional area to available area per cation [22]. The conversion of hydrophilic inorganic clay to a hydrophobic organoclay also improves the interfacial adhesion properties between the organic and inorganic phases when a hydrophobic polymer matrix is involved.

The composites can be classified into intercalated and exfoliated nanocomposites, depending on the structure of dispersed clay platelets in the polymer matrix. Intercalated structures are self-assembled, well-ordered multilayered structures where the extended polymer chains are inserted into the gallery space of the clays [23, 24]. This leads to an expansion of the interlayer spacing. In an exfoliated structure, individual silicate sheets lose their layered geometry as a result of delamination, and dispersed as nanoscale platelets in a polymer matrix (Fig. 5.1) [24]. However, fully exfoliated structure is rarely seen in practice. An exfoliated structure as shown in Fig. 5.1 is an idealized reference morphology that arises from only looking at local scale. In reality, the morphology is mixed intercalated/exfoliated structure.

X-ray diffraction (XRD) is commonly used for the characterization of the structure of nanocomposites. For an intercalated structure, the (0 0 1) characteristic peak tends to shift to lower angle region due to the expansion of the basal spacing. Although the layer spacing increases, there still exists an attractive force between the silicate layers to stack them in an ordered structure. In contrast, no peaks are observed in the XRD pattern of exfoliated polymer nanocomposites due to loss of the structural regularity of the layers [24].

The PLS nanocomposite can be prepared via several routes including in situ polymerization [25, 26], solution blending [27], or melt intercalation method [28]. Out of these three, the melt intercalation method is by far the most versatile and widely employed procedure, as it does not require the use of organic solvents and can be realized with the processing operations commonly adopted for the parent polymers. It involves the thermal treatment, in most cases under shear, of clay/polymer mixtures, at temperatures above the polymer softening point.
Fig. 5.1: Schematic diagram of 2:1 phyllosilicates and the polymer clay nanocomposites
5.2. EXPERIMENTAL:

5.2.1. Preparation of Polystyrene-Montmorillonite Clay Nanocomposites:

The polystyrene-Mont clay nanocomposite were synthesized by the following two methods, viz

i) Method of intercalation of polymer from solution, and

ii) Melt intercalation method.

5.2.1.1. Method of intercalation of polymer from solution:

In this method pristine Na – Mont clay was used. The clay was organically modified by an alkylammonium cation (tetrabutylammonium bromide) exchange.

50 mL of 0.5 M solution of tetrabutylammonium bromide in H$_2$O was prepared by dissolving 8.059 g of the ammonium salt in 50 mL of H$_2$O.

0.1 g of finely-ground polystyrene was added to the above solution. The resulting mixture was vigorously stirred for 1 hr. 0.5 g of Na – Mont clay was added to the mixture. The mixture was then ultrasonicated for 15 min. The solvent was allowed to evaporate at ambient temperature by keeping the mixture at r.t. for a few days.

5.2.1.2. Melt intercalation method:

In this method, both pristine and organically modified Na – Mont clay were used for the synthesis.

5.2.1.2.1. From pristine Na-Mont clay:

0.3 g of the Na – Mont clay and 0.15 g of polystyrene were mechanically mixed. The mixture was heated in an oven at 165 °C.
5.2.1.2.2. From Organically Modified Na – Mont Clay:

5.2.1.2.2.a. Organic modification of Na – Mont Clay:

8.059 g of tetrabutylammonium bromide was dissolved in 50 mL of H₂O. 0.5 g of Na – Mont clay was added to this solution and stirred for 2 hr. The solution was centrifuged, washed the residue with H₂O and dried at 100 °C in an air oven.

5.2.1.2.2.b. Synthesis of the Nanocomposite:

0.1 g of finely-powdered polystyrene and 0.3 g of the above prepared organically modified Mont clay were thoroughly mixed using mortar and pestle and then formed into some small pellets using a hydraulic press to form nanocomposite.

The pellet was heated at 165 °C for three different time periods—— 35 min, 70 min and 105 min.

5.2.1.2.3. Synthesis of Nanocomposite at Different Compositions of Polystyrene and Clay:

8.059 g of tetrabutylammonium bromide was dissolved in 50 mL of H₂O. 0.8 g of Na – Mont clay was added to this solution and stirred for 2 hr. The solution was centrifuged, washed the residue and dried at 100 °C.

0.15 g of finely powdered polystyrene and 0.3 g of the above modified clay were mixed thoroughly and formed pellets. The pellet was heated at 165 °C for 70 min in an air oven.

Similarly, a pellet formed from the powdered mixture of 0.2 g of polystyrene and 0.3 g of the organically modified clay was heated at 165 °C for 70 min.

5.3. RESULTS AND DISCUSSION:

5.3.1. Characterization of the Polymer Clay Nanocomposites:

The polymer clay nanocomposite was identified by XRD measurement substantiated by IR spectroscopy, TEM and thermal analysis.
5.3.1.1. FT-IR Study :

The IR spectrum of the polymer clay nanocomposite is shown in the Fig. 5.2. The band at 3426 cm\(^{-1}\) is due to H-O-H vibrations of absorbed water. The band at 2850 cm\(^{-1}\) is due to –CH\(_2\) symmetric stretching and the band at 2920 cm\(^{-1}\) is due to –CH\(_2\) asymmetric stretching. The band at 400-600 cm\(^{-1}\) is due to \(\nu\) (O-Si-O) bending or deformations of the clay framework. The band at 754 cm\(^{-1}\) is due to –CH out-of-plane bending vibration of the phenyl ring [29]. The 1032 cm\(^{-1}\) band shows the (Si – O – Si) stretching vibration.

![Fig. 5.2 : IR Spectrum of Polymer Clay Nanocomposite](image)

5.3.1.2. Powder XRD Study :

In case of pristine clay (Fig. 5.3) the most intense peak at \(2\theta = 5.6035\) was observed for the (001) plane which corresponds to an interlayer spacing (d) of 15.7584 Å. In case of nanocomposite synthesized by the method of intercalation of polymer from solution (Fig. 5.4), the most intense peak was observed at \(2\theta=5.0256\) which corresponds to an interlayer spacing of 17.5691 Å. This increase in the d-spacing of the silicate layers of the clay in the sample demonstrates the intercalation of polystyrene in the clay. The average crystalline size was calculated as 11.55 nm.
The characteristic peak of the nanocomposite synthesized by the melt intercalation method from the pristine Na – Montmorillonite appears at 2θ=5.6035, with little change of its position (Fig. 5.5). This suggests that direct intercalation of polymer in Na-Montmorillonite is not very effective and it is necessary to modify the Montmorillonite to organo-clay.

Whereas when organic modification was done by tetrabutylammonium bromide, as shown in the Fig. 5.6, the characteristic intense peak of the clay shifted to a lower value of 2θ = 5.38. The corresponding d- value is 16.4126 Å. The shifting of the 2θ to a lower value indicates intercalation of polymer.

When the synthesized nanocomposite was heated at 165 °C for 35 min, two peaks are observed at 2θ~3.125 and 6.025. The most intense peak at 2θ~3.125 corresponds to interlayer (d_{001}) ~28.2512 which is greater than the previous one. This means that the intercalation has increased when the sample was heated at 165 °C. The other peak at 2θ~6.025 is probably due to higher order peak of the most intense peak [30]. When the time of heating increased from 35 min to 70 min and 105 min, the 2θ value shifted from 3.125 to 3.025 and consequently the d-spacing increased from 15.7584 Å to 29.19 Å. Thus, the extent of intercalation reached very high values when the time of heating is increased to 105 min. The crystalline size calculated for the nanocomposite is found to be in the range of 6-9 nm.

When the compositions of polystyrene and clay are different (Fig. 5.7), it is observed that there occurred a high degree of intercalation of polystyrene between the clay layers. Even in the organically modified clay, the maximum intense peak has a 2θ value of 2.396 indicating an interlayer separation (d) of 36.8383 Å. While in case of the polystyrene-clay nanocomposite, the 2θ value corresponding to the maximum intense peak is the same, i.e., 2.388, which denotes a value of d=36.9693Å. Thus, the degree of intercalation is higher at a higher percentage of polystyrene.
Fig. 5.3: XRD pattern of Na-Montmorillonite

Fig. 5.4: XRD pattern of Nanocomposite Synthesized by the Method of Intercalation of Polymer from Solution
Fig. 5.5: XRD pattern of Nanocomposite Synthesized by the Melt Intercalation Method without Organic Modification

(a) = Nanocomposite heated for 70 min
(b) = Nanocomposite heated for 35 min
(c) = Nanocomposite heated for 105 min
(d) = Nanocomposite dried at r.t.

Fig. 5.6: XRD pattern of Nanocomposite Synthesized by the Melt Intercalation Method Heated at Different Temperature
5.3.1.3. Study of Thermal Stability of the Nanocomposite:

The TGA-DTA plots of pure polystyrene and the nanocomposite are shown in the Figs. 5.8 and 5.9 respectively.

The TGA curve of pure polystyrene shows only one mass loss stage which corresponds to the decomposition of 99.27% of polystyrene. Its decomposition started at 300 °C and completed at about 460 °C. The maximum weight loss occurred at about 411.74 °C.

The TGA curve of the nanocomposite showed four mass loss stages. The first one in the range of 50 to 150 °C corresponds to dehydration of absorbed water [31]. The second one in the range of 200 to 300 °C corresponds to the decomposition of 6.053% of tetrabutylammonium bromide [32]. The third one representing 33.71% loss of mass corresponds to the decomposition of polystyrene. Its decomposition started at about 300 °C and completed at around 490 °C. The maximum weight loss
occurred at 412.11 °C. This implies an improvement in the thermal stability of the polystyrene in the nanocomposite compared to pure polystyrene.

The fourth mass loss stage in the range of 500 – 650 °C may be due to loss of OH lattice water of the clay [31].

The endothermic peak in the DTA curve of the nanocomposite at about 891.32 °C denotes a physical change such as phase transformation.

![Fig.5.8](a) TGA-DTA (b) only TGA of pure polystyrene

![Fig.5.9](a) TGA-DTA (b) only TGA of Nanocomposite dried at 165 °C
5.3.1.4. Characterization of the Nanocomposite by TEM:

The TEM image of the nanocomposite synthesized by the melt intercalation method is shown in the Fig. 5.10. The particle size of the nanocomposite synthesized by this method was in the range of 1.3 – 4.0 nm, while in case of nanocomposite synthesized by the method of intercalation of polymer from solution, the particle size was found to be 2 – 5 nm.

![TEM image of the Nanocomposite Synthesized by the Melt Intercalation Method](image)

5.4. CONCLUSIONS:

A nanocrystalline polymer clay nanocomposite has been synthesized by a simple melt intercalation method involving Na-Montmorillonite, Tetrabutylammonium bromide and polystyrene. The crystalline size of the synthesized nanocomposite was found to be 6-9 nm while its particle size was 1.3-4.0 nm.
5.5. REFERENCES :


