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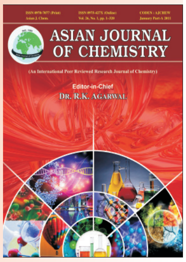

Synthesis and Characterization of Polymer-Layered Silicate Nanocomposites

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The polystyrene-montmorillonite clay nanocomposite was synthesized from montmorillonite clay by two different methods. The synthesized nanocomposites were characterized by FT-IR, XRD and TEM. The thermal stability of the synthesized nanocomposite was studied by TGA-DTA.

Keywords: Na-montmorillonite clay, Polystyrene, Tetrabutyl ammonium bromide, Nanocomposite materials.

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[1,2]. The reasons behind the interest are the physical and chemical properties of the polymer layered silicates, as these properties are dramatically different from their bulk counterparts[3]. They also exhibit improved properties when compared to micro- and macro-composites[4,5]. Montmorillonite, hectorite and saponite are the most commonly used layered silicates for the preparation of pillared layered silicates (PLS) nanocomposites[6]. To render layered silicates miscible with other polymer matrices, the hydrophilic silicate surface should be converted into an organophilic one, by the intercalation of quaternary ammonium salt[4]. Montmorillonite clay has been extensively used for preparation of nanocomposites because of its small particle size (<10 μm) and ease of intercalation[7,8]. The montmorillonite clay, whose lamella is constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, exhibits a net negative charge on the surface of layers[9]. The cation such as Na^+ or Ca^{2+} is intercalated in between the layers to compensate the net negative charge. The increase in interlayer spacing that occurs with swelling of the montmorillonite clay in water is large and enables particles of large size to penetrate in to the inter layers[10,11].

Pillared layered silicates nanocomposites can be synthesized by three ways, *viz*. intercalation of polymer, *in situ* intercalative polymerization and melt intercalation method. Out of these three the third method has great advantages over the other two as in this method no solvent is required.

In this paper, we report the synthesis of pillared layered silicate nanocomposites by using melt intercalation method as well as the method of intercalation of polymer from solution. The synthesized materials are characterized by XRD, FT-IR, TEM and TGA-DTA.

EXPERIMENTAL

The materials used are: (i) Wyoming montmorillonite clay obtained from Source clay, USA; (ii) Polystyrene obtained from LOBA Chemie (molecular weight = 13.15 × 10^4); (iii) Tetrabutylammonium bromide obtained form E-MERCK.

Synthetic procedure: The polystyrene-montmorillonite clay nanocomposite were synthesized by the following two methods, *viz.*

(1) Method of intercalation of polymer from solution: In this method pristine Na-montmorillonite (MMT) clay was used. Although the clay was not organically modified, an alkylammonium cation (tetrabutylammonium bromide) capable of serving as an organic modifier was used as a component of the solution.

0.1 g of finely ground polystyrene was added to a solution of 50 mL 0.5 M tetrabutylammonium bromide in H_2O. The mixture was vigorously stirred for 1 h. 0.5 g of Na-mont clay was added to it and the mixture was ultrasonicated for 15 min. The solvent was allowed to evaporate at ambient temperature by keeping the mixture at room temperature for a few days.

(2) Melt intercalation method: In this method, both pristine and organically modified Na-Mont clay were used for the synthesis:

(i) From pristine Na-Mont clay: 0.3 g of the clay and 0.15 g of polystyrene were mechanically mixed. The mixture was heated in an oven at 165 °C; (ii) From organically modified Na-Mont clay:

(a) Organic modification of Na-Mont clay: 0.5 g of Na-Mont clay was added to a solution of 50 mL 0.5 M tetrabutylammonium bromide in H_2O and stirred vigorously for 2 h. The solution was centrifuged, washed and dried at 100 °C in an oven. 0.3 g of this organically modified clay was thoroughly mixed with 0.1 g (or 0.15 or 0.2 g) of finely ground polystyrene using mortar and pestle and then formed into some small pellets using a hydraulic press. The pellet was heated at 165 °C for different time periods (*i.e.*, 35, 70 and 105 min).

RESULTS AND DISCUSSION

FT-IR data: The IR spectrum of the polymer clay nanocomposite is shown in the Fig. 1. 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 ν(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[12]. The 1032 cm^{-1} band shows the (Si-O-Si) stretching vibration.

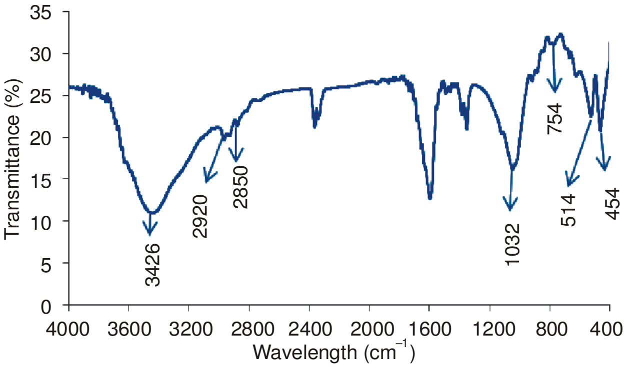

Fig. 1. IR Spectrum of polymer clay nanocomposite

XRD analysis: In case of pristine clay (Fig. 2) the most intense peak at 2θ = 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. 3), the most intense peak was observed at 2θ = 5.02562° 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.

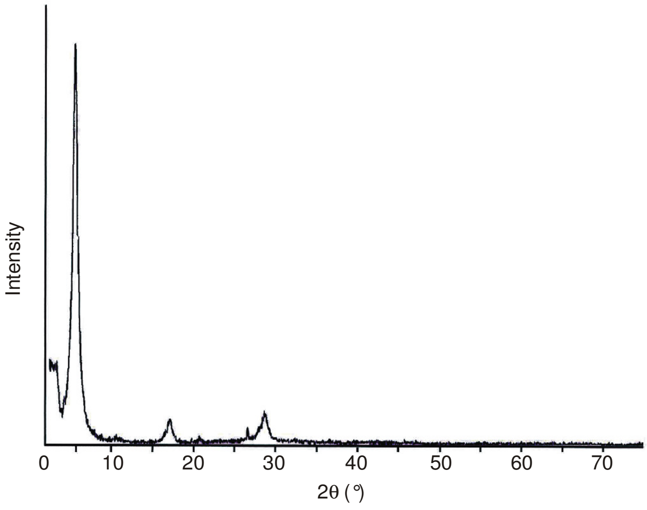

Fig. 2. XRD pattern of Na-mont

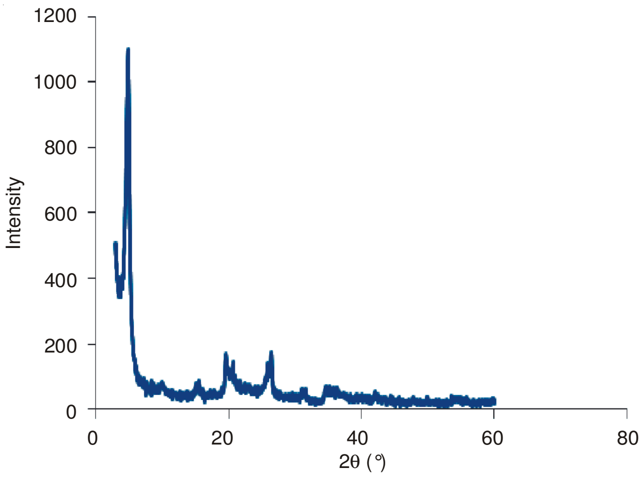

Fig. 3. XRD of Nanocomposite synthesized by method of intercalation of polymer from solution

The nanocomposite synthesized by the melt intercalation method from the pristine Na-mont the characteristic peak appears at 2θ = 5.6035° (Fig. 4). This means that no intercalation takes place when the clay is not organically modified.

Whereas when organic modification was done by tetrabutylammonium bromide, as shown in the Fig. 5, the characteristic intense peak of the clay shifted to a lower value of 2θ = 5.38°. The corresponding d-value is 16.4126 Å.

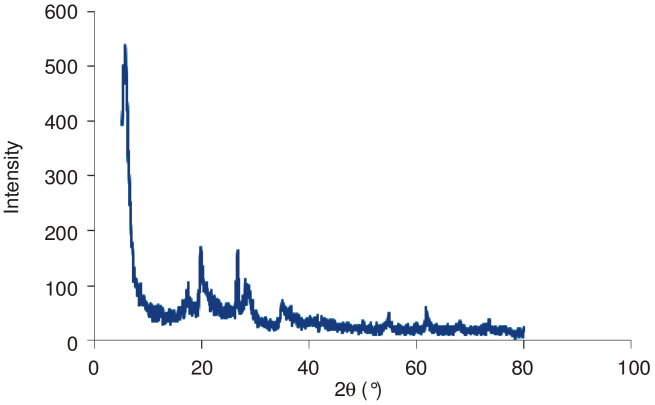

Fig. 4. XRD of Nanocomposite synthesized by the melt intercalation method without organic modification

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})-28.25 Å. 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[13]. 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 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.

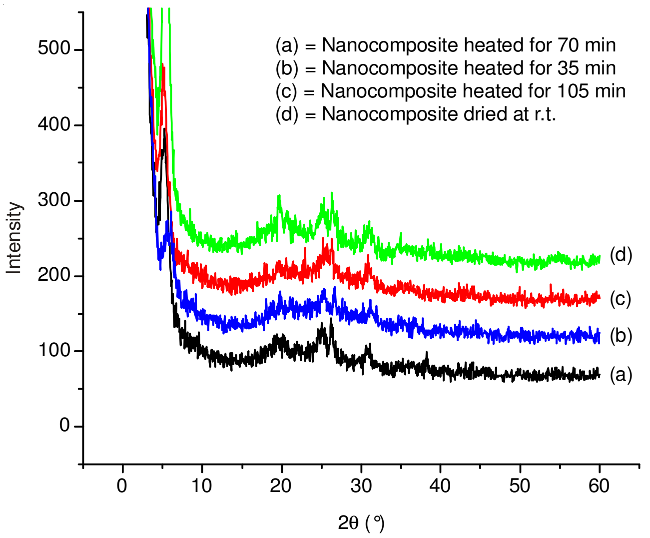

Fig. 5. XRD of nanocomposite synthesized by the melt intercalation method heated at different temperature

When the compositions of polystyrene and clay are different (Fig. 6), 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 36.83 Å. While in case of the polystyrene-clay nanocomposite, the 2θ value corresponding to the maximum intense peak is the same, *i.e.*, 2.38°, which denotes a value of d = 36.9693 Å. Thus, the degree of intercalation is higher at a higher percentage of polystyrene.

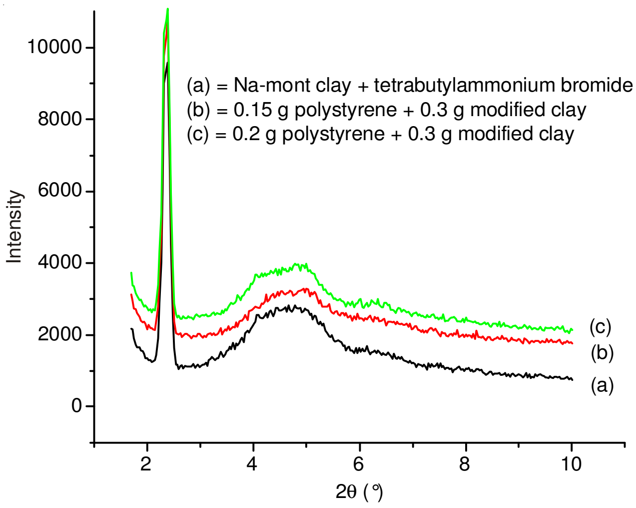

Fig. 6. XRD pattern of nanocomposite at different composition

Characterization of the nanocomposite by TEM: The TEM image of the nanocomposite synthesized by the melt intercalation method is shown in the Fig. 7. The particle size of the nanocomposite synthesized by this method was in the range of 1.3-4 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.

Study of thermal stability of the nanocomposite: The TGA-DTA plots of pure polystyrene and the nanocomposite are shown in the Figs. 8 and 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 °C.

The TGA curve of nanocomposite-6 showed four mass loss stages. The first one in the range of 50 to 150 °C corresponds to dehydration of absorbed water[13]. The second one in the range of 200 to 300 °C corresponds to the decomposition of 6.053 % of tetrabutylammonium ion[14]. The third one repre-

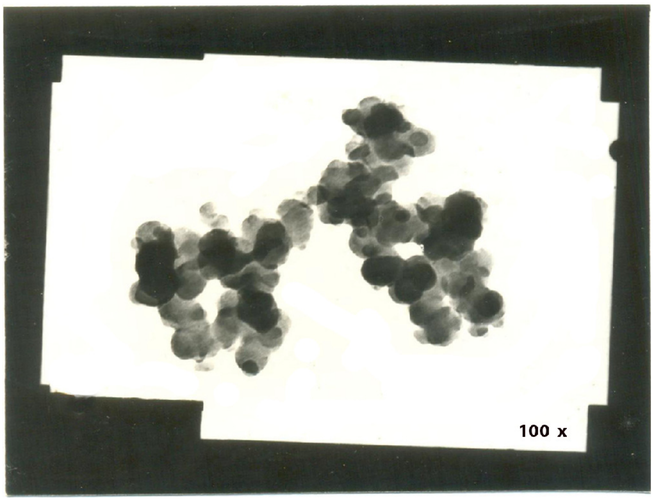

Fig. 7. TEM image of the nanocomposite synthesized by melt intercalation method

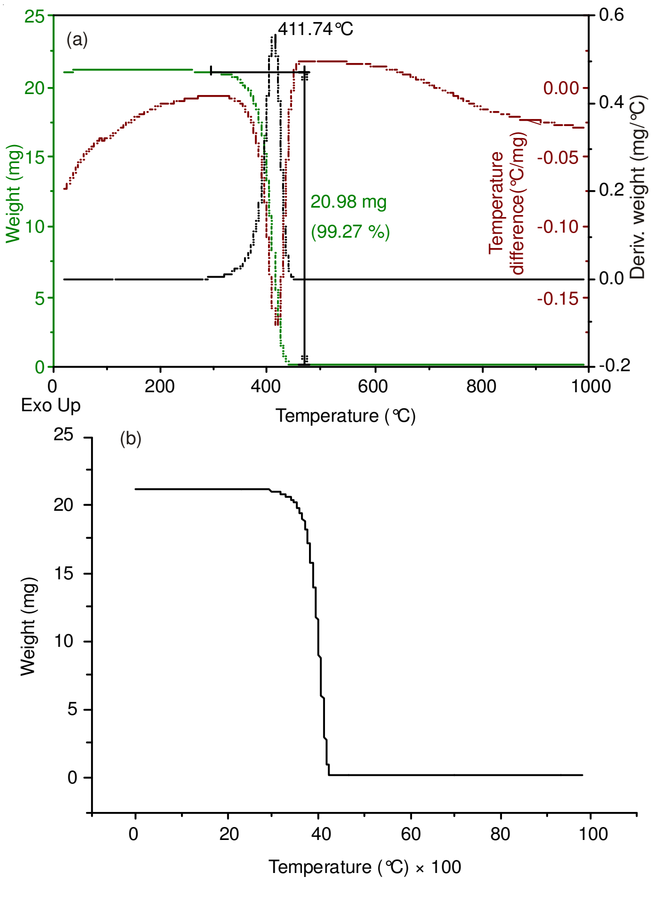

Fig. 8. (a) TGA-DTA (b) only TGA of pure polystyrene

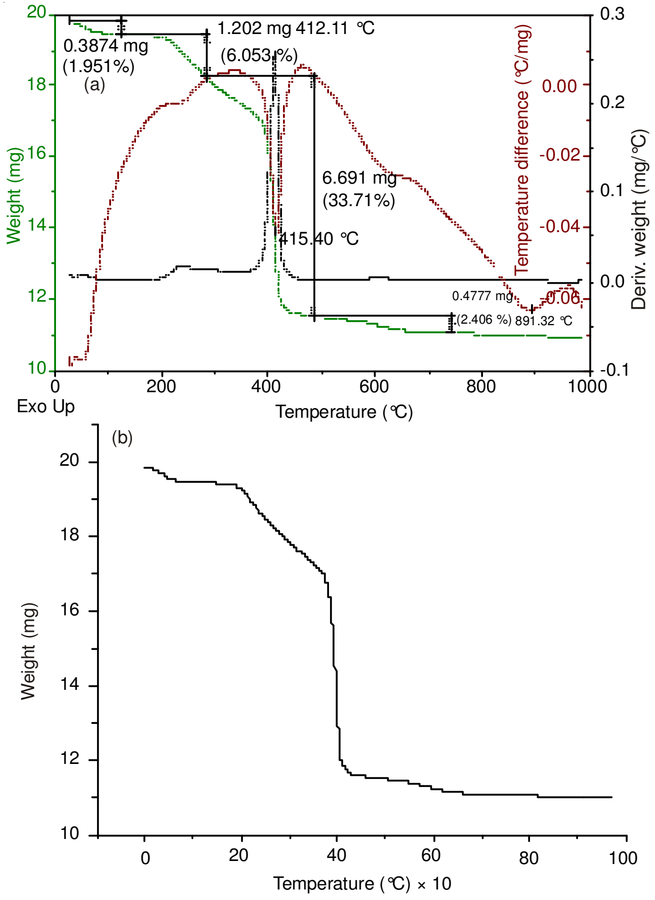

Fig. 9. (a) TGA-DTA (b) only TGA of nanocomposite dried at 165 °C

senting 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 °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 which may be due to loss of OH lattice water of the clay[15].

The endothermic peak in the DTA curve of the nanocomposite at about 891 °C denotes a physical change such as phase transformation of the clay.

Conclusion

Montmorillonite clay can be used for the preparation of nanocomposite. The nanocomposite synthesized of crystalline size is found to be in the range of 6-9 nm and the particle size is found to be in the range of 1.3-4 nm.

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