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Sonochemical Synthesis of Polymethylmethacrylate-Halloysite Nanotube by Solution Casting Method

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ABSTRACT
Halloysite nanotubes (HNTs) are naturally occurring hollow nanotubes which are widely investigated as these materials have attractive features and results in improved properties of resulted nanocomposites. In this present work, we have successfully synthesized polymethylmethacrylate-HNT nanocomposites by solution casting method using ultrasound energy in a greener, safer, faster, and facile way. The effect of clay loading and ultrasound energy on the structure, morphology, and thermal properties of nanocomposites were investigated by X-ray diffraction, Fourier transform and infrared (FT-IR), scanning electron microscopy (SEM), and differential scanning calorimetry. According to the experimental results, nanocomposites synthesized on utilizing ultrasound revealed complete exfoliation of filler into the polymer matrix. Furthermore, sonication time of 60 minutes resulted in uniform distribution of particle as observed by SEM. Increase in sonication time resulted in decrease in glass transition temperature (T_g) of nanocomposites due to the breaking of polymer chains due to excessive temperature and pressure generated during sonication. FT-IR analysis broadcasted presence of HNTs in the polymer matrix, and hence, the confirmed successful incorporation of HNTs in the polymer matrix.

Key words: *Ultrasound energy, Solution casting, Halloysite nanotube, Polymethylmethacrylate.*

1. INTRODUCTION

Polymer nanocomposites are gaining ample attention of researchers around the world as these materials offers various advantages such as improved mechanical properties (strength, stiffness), improved dimensional stability, decreased gas, water and hydrocarbon permeability, increased thermal stability, flame retardancy and less smoke emission, improved chemical resistance and surface appearance, increased transparency, reduced weight and can be used widely for construction, transportation, electronics products and many other applications and it is difficult to obtain these properties separately from individual components [1-4]. Nanocomposite is characterized by the size of particles in dispersed phase which are lesser than 100 nm. Consequently, nanocomposites have relatively large surface areas and interact strongly with a polymer matrix, and hence, possess unique properties that are not typically shared by their traditional composite counterparts.

Polymethylmethacrylate (PMMA), an amorphous thermoplastic, is well known for its optimistic properties such as chemical resistance, transparency, flexibility, high strength, surface protection, good weather ability, and dimensional stability [5-7]. Further, PMMA can resist both acidic and alkaline environments and is tolerant to many non-polar solvents as well as inorganic reagents [8]. However, its application is restricted in many areas due to its poor thermal stability and its mechanical-dynamical performance at high temperatures. Hence, addition of nanoparticles such as clays, carbon nanotubes (CNTs), and various other fillers to polymer matrix is being identified as an approach to overcome this limitation [9,10]. Recently, polymer-clay nanocomposites are widely investigated as these materials exhibit enhanced properties. Addition of clay to polymers is believed to drastically improve the thermal, mechanical, and various other properties of polymers. Halloysite nanotubes (HNTs) are naturally occurring aluminosilicates that are achieving considerable interest in the field of research as a result of their low cost and attractive properties. The length of these materials varies between 1 and 15 μ, inner diameter varies from 10 to 50 nm, and outer diameter ranges between 50 and 100 nm. These materials exhibit close similarity to kaolinites in chemistry and CNTs in structure and cause significant

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improvement in various polymer properties. Polymer nanocomposites can be synthesized in three ways according to the filler material, and processing techniques; however, in this study, we have adopted solution casting method as this method provides an opportunity to adopt techniques such as extrusion and injection molding for processing, and bestows good control on the homogeneity of the constituents, which aids in understanding of process and morphology of nanocomposites. It also provides better knowledge about the structure, dynamics, and stability of the synthesized nanocomposites, which can provide molecular insight and lead to the design of materials with desired properties [11]. In solution intercalation method, homogeneous three-component mixture of polymer, clay, and solvent is prepared using heating and mechanical or ultrasonic mixing for reinforcement of filler into the polymer matrix in the presence of solvent. Once the composites are synthesized the solvent is allowed to evaporate. During evaporation of the solvent, the clay platelets rearrange themselves into tactoids and get incorporated into the polymer. The objectives of the present work were to synthesize PMMA-HNT nanocomposites by the solution method assisted by ultrasound energy and to scrutinize the effects of reinforcing HNTs into the polymer matrix and sonication time on morphology and thermal stability of PMMA-HNT nanocomposites.

2. EXPERIMENTAL

2.1. Materials

PMMA and HNTs were used as polymer matrix and filler, respectively, and were procured from Sigma-Aldrich. Toluene was used as solvent to serve as medium for interaction between polymer and clay. Probe type ultrasonicator containing titanium horn and frequency of 20 kHz and 500 W capacity was used for the study, and it was operated at 55% amplitude to deliver 375 W power.

2.2. Synthesis of PMMA-HNT Nanocomposites

For synthesis of nanocomposites, in our study, 10 wt.% of HNTs were dispersed in 50 ml beaker containing 10 ml of toluene and was magnetically stirred for 1 h and sonicated for 1 h. In another beaker 2 g of PMMA was dissolved in 10 ml of toluene and stirred magnetically for 1 h and sonicated for 1 hr. Both the solutions were then mixed and sonicated for 120 min. Samples were withdrawn for 30 min to analyze the effect of sonication on synthesized nanocomposites. The solution was then poured into glass Petri dishes and dried at room temperature for 24 h. The resulting thin films were named as PMMA-HNT. The similar procedure was repeated without HNTs for comparison as named as PMMA.

3. CHARACTERISATION

The structure of nanocomposites was analyzed by X-ray diffraction (XRD) analysis using RIGAKU diffractometer, and data were collected in 2θ ranging between 10°C and 65°C. Morphology of nanocomposites was analyzed by Jeol JSM scanning electron microscope. Fourier transform and infrared analysis were carried on Bruker spectrometer, and data were collected between 4000 and 400 cm^{-1} in attenuated total reflectance mode. The differential scanning calorimetry (DSC) analysis was done to understand the thermal behavior of nanocomposites on reinforcing halloysites into the polymer matrix and was carried out using Perkin–Elmer Pyrus 1 DSC at heating rate of 10°C min^{-1} from 0 to 200°C in the presence of nitrogen flow.

4. RESULTS AND DISCUSSION

4.1. Studies on Structure of Nanocomposites

Figure 1 interprets the structure of synthesized nanocomposites. It can be observed that nanocomposites synthesized on utilizing ultrasound showed reduction in peaks and increased in intensity representing exfoliation of HNTs into the polymer matrix and increase in number of particles, respectively. Thus, there is reduction in agglomerates of HNTs, which further aids in uniform dispersion of filler into the polymer.

4.2. Studies on Morphology of Nanocomposites

Figure 2 visualizes the scanning electron microscopy (SEM) images of nanocomposites synthesized in the presence and absence of ultrasound. It can be observed that nanocomposites synthesized in the absence of ultrasound resulted in agglomerated morphology,

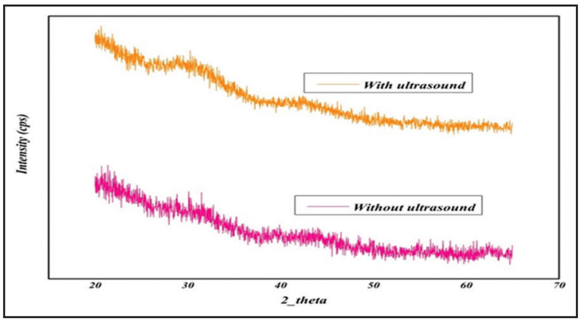

Figure 1: X-ray diffraction patterns of polymethylmethacrylate-halloysite nanotube nanocomposites with and without sonication.

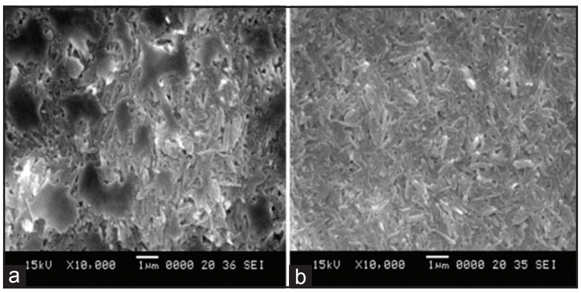

Figure 2: Scanning electron microscopy analysis of: (a) Without sonication and (b) with sonication.

whereas those synthesized with ultrasound showed the uniform dispersion of nanotubes across the specimen; this is due to high frequency and intensity that is generated by sound waves that tears apart the agglomerations and results in uniform distribution of nanotubes.

4.3. Studies on Functional Groups on Nanocomposites

The most significant feature of HNTs is the presence of characteristic peaks at 3692, 3623 ascribes Al–OH, and 1030, 909 cm^{-1} represents Si–O. The presence of these peaks on the synthesized nanocomposites indicated the presence of HNTs in PMMA matrix. Hence, these results indicate that the solution casting assisted by ultrasound successfully produced PMMA-HNT nanocomposites.

4.4. Studies on Thermal behavior of Nanocomposites

The thermal behavior of synthesized nanocomposites was analyzed by DSC analysis. The results showed an increase in glass transition temperature on the incorporation of HNTs into the polymer matrix. This is because HNTs create tortuous path and obstructs heat flow into the polymer. However, increase in sonication time caused decrease in T_g of synthesized nanocomposites this is to breaking of polymer chains due to high temperature and pressures generated during sonication. Hence, it can be concluded that sonication time of 60 min is optimum to synthesize nanocomposites with good thermal properties.

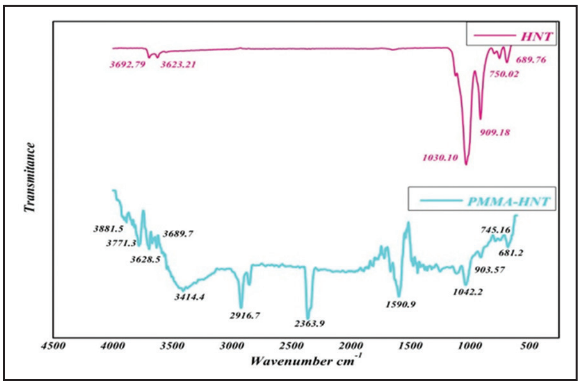

Figure 3: Fourier transform and infrared analysis of nanocomposites.

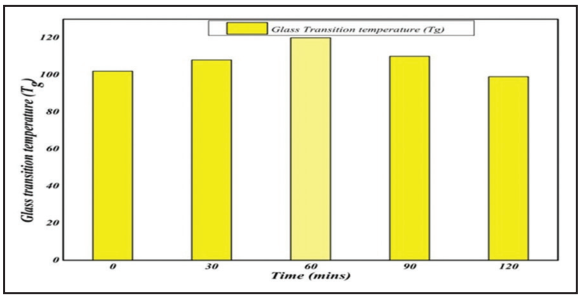

Figure 4: Differential scanning calorimetry analysis of nanocomposites synthesized at various times.

5. CONCLUSION

Nanocomposites of PMMA matrix reinforced with HNTs were successfully synthesized by ultrasound assisted solution method. XRD analysis revealed complete exfoliation of HNTs into the polymer matrix. SEM results broadcasted uniform dispersion of HNTs on sonication due to high energy produced during sonication. Fourier transform and infrared analysis confirmed encapsulation of HNTs into the polymer matrix. DSC analysis indicated increase in T_g on sonicating for 60 min, further increase in sonication caused decrease in T_g due to breaking of polymer chains.

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***Bibliographical Sketch**

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