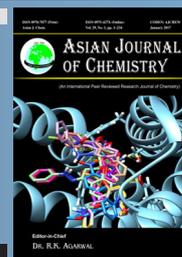




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Sonochemical Synthesis of Cetyl Trimethylammonium Bromide Modified Halloysite Nanotubes-Polystyrene Nanocomposites by Solution Casting Method†

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This paper reports the surface modification of halloysite nanotubes (HNTs) using cetyl trimethylammonium bromide (CTAB) and propitious incorporation of CTAB-HNTs into polystyrene matrix by ultrasound-assisted solution casting method. The effect of surface modification and sonication on the structure, morphology and thermal behaviour of the modified halloysite nanotubes and synthesized nanocomposites was also investigated. X-ray diffraction data stipulated increase in d-spacing on surface modification and revealed complete exfoliation as a result of sonication. Scanning electron microscopy portrayed uniform distribution of clay in the polymer matrix due to combined effect of surface modification as well as sonication. Fourier transform and infrared results manifested halloysite nanotubes, cetyl trimethylammonium bromides and polystyrene major peaks in the synthesized nanocomposites confirming intercalation of cetyl trimethylammonium bromide in halloysite nanotubes interlayers and encapsulation of CTAB-HNT into the polymer, DSC analysis displayed enhancement in glass transition temperature (T_g) indicating increase in thermal stability, hence these can improved properties with potential applications.

Keywords: Halloysite nanotubes, Cetyl trimethylammonium bromide, Surface modification, Ultrasound, Solution casting method.

INTRODUCTION

Industrialization and modernization always demands better products and better services. Nanocomposites are group of materials that exhibit improved mechanical, chemical, electrical, optical, thermal, barrier and various other properties. Among various existing nanocomposites, polymer-clay nanocomposites have provoked tremendous research interest as they are economical than other nanomaterials in cost and drastically enhance assorted polymer properties. Halloysite nanotubes have been classed among clay materials that are widely investigated as a result of their promising prospects in synthesizing new structural and functional materials. These materials possess optimistic properties like natural availability, nanotubular structure, lumen spaces and have tunable surface chemistry. Also, halloysite nanotubes have hollow lumen, high surface area and large aspect ratio hence, they form low-density nanocomposites on combining with polymer matrix and thus substituting larger quantities of materials like glass or carbon fibres [1]. Halloysite nanotubes possess gibbsite octahedral sheet (Al-OH) groups on the interior surface and their exterior surface has siloxane (Si-O-Si) groups, this chemistry dictates

a positively charged lumen and a negatively charged outer surface in pH interval 2-8 [2]. The interlayer spacing of halloysite nanotubes is approximately 7 Å, but if there is presence of water in the interlayer, this spacing will increase to 10 Å. Hydrated halloysite nanotubes consists of double layers of Si-centered tetrahedral and Al-centered octahedral layers with presence of water monolayer between both layers. As a result of mismatch between the siloxane and gibbsite layers, nanotube form of halloysite nanotubes is formed [3]. Halloysite nanotubes contain OH⁻ polar groups on their inner lumen making them highly hydrophilic and have very few functional groups on their exterior structure, which aids them to separate from agglomerates and promotes their dispersion in polymer. Although uniform dispersion of halloysite nanotubes into the polymer matrix has been reported in literature [4-6], lower activity of halloysite nanotubes external surface hinders interfacial interaction, which lowers dispersion and reinforcement efficiency. Surface modification of clay has become an urgent necessity as these have highly hydrophilic interior and exterior surfaces that severely restrict its usage in many applications. To overcome this drawback and to enhance the performance of halloysite nanotubes, surface modification of halloysite

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nanotubes is reported in the literature [7,8]. This converts hydrophilic nanotubes to organophilic materials and hence increases the compatibility between clay and polymer, which in-turn meliorates polymer properties. Surface of halloysite nanotubes can be selectively modified by using ionic surfactants [9]. Surfactants play a major role in synthesizing nanoparticles by adsorbing onto the surface of halloysite nanotubes; forming nanoparticles, lowering its surface energy and improving its wettability and thus prevents aggregation.

Ultrasonication has been reported to be intensified source for dissipation of energy for synthesis of polymer-clay nanocomposites and yields constructive results because cavitations generated by ultrasound results in shearing action that aids in homogenous dispersion of clay into the polymer as well as causes exfoliation [10,11]. Further, ultrasonication enhances movement of clay into the polymer matrix by increasing the interlayer spacing and hence promotes better interaction between clay and polymer. Hence in the present work the surface of halloysite nanotubes was modified using cetyl trimethylammonium bromide (CTAB). Since CTAB has positively charged head group, the surfactant was selectively adsorbed onto the external surface of halloysite nanotubes and forms tubular nanoparticles with a hydrophobic shell and a hydrophilic cavity. Further these CTAB modified halloysite nanotubes were reinforced into polystyrene matrix by ultrasound assisted solution casting method using toluene as solvent.

EXPERIMENTAL

Polystyrene was used as polymer matrix it had mol weight of 280000, density of 1.04 g/cc and softening temperature of 99 °C. Halloysite nanotubes were procured from Sigma Aldrich. Toluene was provided by MERCK and CTAB was obtained from Sisco Research Laboratories.

Surface modification of halloysite nanotubes by CTAB:

CTAB-HNT was prepared by ion exchange method using CTAB solution. 1000 mL of deionized water was taken in 2 L beaker and 10 g of halloysite nanotubes was dispersed into this solution by vigorously stirring overnight using magnetic stirrer. In a separated beaker 5 g of CTAB was dissolved in 100 g of deionized water and stirred magnetically for 30 min and this suspension was slowly added to overnight stirred solution and was magnetically agitated for 24 h. The suspension was centrifuged at 10000 rpm for 15 min, washed with distilled water to remove excess Br⁻ and was dried at 105 °C until constant weight loss was observed and labelled as CTAB-HNT.

Synthesis of PS-CTAB-HNT and PS-HNT nanocomposites:

Polymer nanocomposites of polystyrene matrix were prepared by addition of 10, 20, 30 wt % of CTAB-HNT in 20 mL of toluene. The suspension was stirred magnetically for 1 h and sonicated for 1 h. Then, 2 g of polystyrene was added and again stirred magnetically for 1 h and sonicated for different time interval to study effect of sonication time on properties of resultant nanocomposites. The mixture was cast into petri dishes and allowed to dry for 24 h at room temperature, solvent was evaporated and thin films were obtained. These composites were labelled as PS-CTAB-HNT. The procedure was repeated using unmodified halloysite nanotubes for comparison and was labelled as PS-HNTs.

Characterization: The structure of nanocomposites was monitored using XRD using RIGAKU Ultima-IV diffractometer and data regarding the intensity was recorded in the 2 θ range of 5°-65° at a step of 0.02° and a 2 s count time using Cu-K α ($\lambda = 1.542 \text{ \AA}$) radiation. The surface morphology of halloysite nanotubes, CTAB-HNT and nanocomposites synthesized with halloysite nanotubes and CTAB-HNT were examined using JEOL JSM-6360LV SEM. A pinch of halloysite nanotubes, CTAB-HNT and small section of thin film was stuck to carbon tape on standard Al mounts then sputtered with a thin conductive layer of gold. FT-IR analysis was performed on BRUKER spectrophotometer and data was collected in the range of 4000-400 cm⁻¹ using ATR mode. Thermal behaviour of synthesized nanocomposites was determined using Perkin-Elmer Pyrus DSC at heating rate of 10 °C min⁻¹ from 0-200 °C under nitrogen flow.

RESULTS AND DISCUSSION

X-ray diffraction of CTAB-HNT: X-ray diffraction analysis data provide information on changes in interlayer spacing of clay layers. Fig. 1 shows the XRD patterns of pristine halloysite nanotube and CTAB-HNT, which were studied in the range of 2 θ (5-65)°. For pristine halloysite nanotube the characteristic peak (001) appeared at 2 θ value of 12.11 which corresponds to d value of 7.3 Å, as calculated using Bragg's law and for CTAB-HNT this peak appeared at lesser 2 θ value 11.79 corresponding to d spacing of 7.5 Å. The increase in interlayer spacing is mainly due to existence of large hydrophobic groups on the surfactant and due to reduction in the surface energy of halloysite nanotubes [12]. Also, the surfactant which got adsorbed onto the surface of halloysite nanotubes increased the wettability of halloysite nanotubes making them hydrophobic and hence it can be seen in Fig. 1 that there was increase in intensity of CTAB-HNT representing increase in number of nanoparticles and hence, decrease in agglomerates.

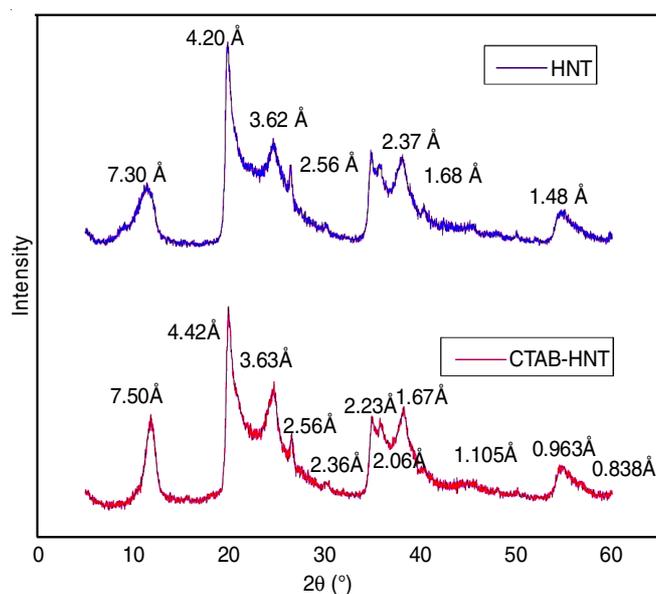


Fig. 1. XRD of halloysite nanotube (HNT) and cetyl trimethylammonium bromide halloysite nanotube (CTAB-HNT)

X-ray diffraction of polystyrene-HNT and polystyrene-CTAB-HNT: Fig. 2a shows the structure of nanocomposites synthesized using halloysite nanotube with and without modification. It can be noticed that nanocomposites synthesized on using CTAB-HNT did not show presence of significant peaks on comparing with those synthesized without clay modification meaning complete exfoliation of clay into the polymer matrix thus suggesting improved properties. Also, ultrasound energy further aids in exfoliating halloysite nanotubes into the polymer matrix.

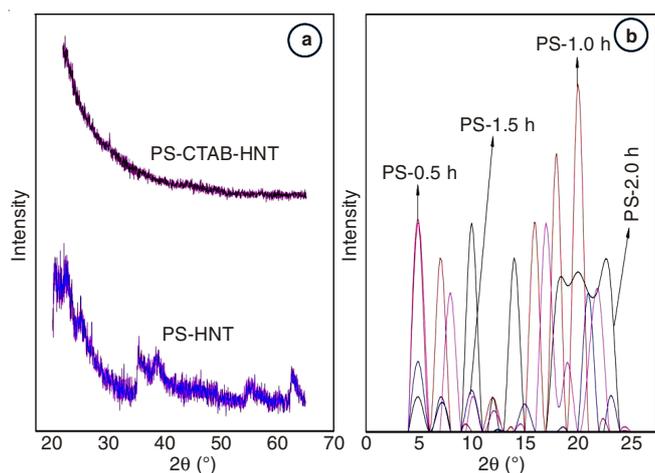


Fig. 2. XRD of (a) Nanocomposites synthesized using halloysite nanotube and CTAB-HNTs, (b) Nanocomposites synthesized at various time intervals

X-ray diffraction of nanocomposites with different sonication time: X-ray diffraction was also done to analyze structural characteristics of nanocomposites, which were synthesized at different sonication times. Fig. 2b shows the values of 2θ and d-spacing for PS-CTAB-HNT composites prepared at different sonication time using toluene as solvent. It can be analyzed that sonication time of 1 h synthesized nanocomposites with maximum peak intensity indicating greater intercalation and increase in number of nanoparticles formed. Sonication time of 30 min was not sufficient for sequencing of polymer chains between the interlayers. Increase in sonication time may cause the polymer chains to enter between the clay layers with random orientation due to instability of structure of clays.

SEM of halloysite nanotube and CTAB-HNT: SEM analysis was done to determine shape, size and study morphology of nanocomposites. Fig. 3 shows the micrographs of pristine halloysite nanotube and CTAB-HNT. Intramolecular forces within the particles caused particle aggregation as depicted in Fig. 3a whereas on treatment with CTAB *i.e.* Fig. 3b there was decrease in agglomerates of halloysite nanotubes, as the surface of halloysite nanotubes was made hydrophobic due absorption of ammonium salts onto the surface of halloysite nanotubes due to ion-exchange mechanism.

SEM of nanocomposites: To observe dispersion of the particles, nanocomposites, which were prepared using toluene and sonicated for 1 h were examined using SEM. As seen in Fig. 4b incorporation of 10 % CTAB-HNT with polystyrene matrix resulted in uniformly dispersed morphology in compa-

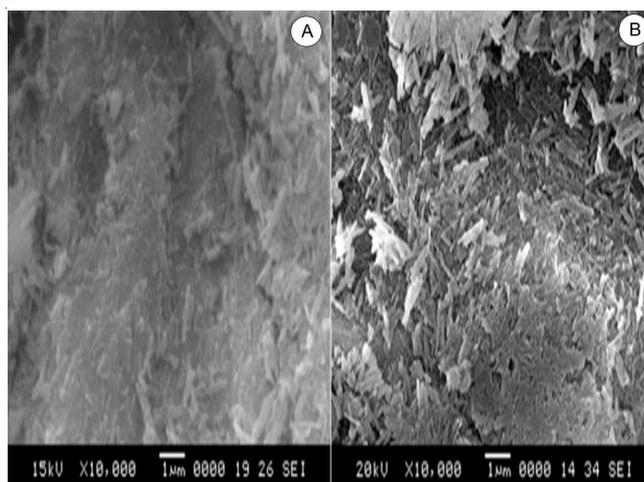


Fig. 3. SEM of (a) halloysite nanotubes (b) CTAB-HNTs

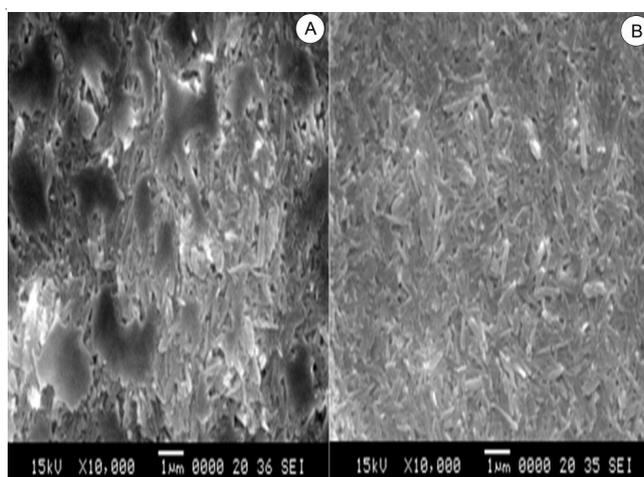


Fig. 4. SEM of (a) PS-HNTs (b) PS-CTAB-HNTs

parison with that synthesized without clay modification (Fig. 4a). The size of filler material was in nanoscale and shape was tube shaped.

Fourier transform and infrared (FT-IR): The characteristics peaks of halloysite nanotube (Fig. 5a) and CTAB (Fig. 5b) are present in Fig. 5d, thus confirming the adsorption of surfactant onto the surface of halloysite nanotube. Also, the incorporation of CTAB-HNT into the polymer matrix was confirmed by the presence of halloysite nanotube (Fig. 5a) major peaks, polystyrene major peaks (Fig. 5b) in the resultant nanocomposites as portrayed in Fig. 5e.

Studies on thermal behaviour: DSC traces of pure polystyrene, PS-HNT and PS-CTAB-HNT with 10, 20 and 30 wt % clay loading are portrayed in Fig. 6. Glass transition temperature (T_g) of pure polystyrene, PS-HNT-10 % were estimated to be 84 and 99 °C, respectively, whereas T_g of PS-CTAB-HNT at 10, 20 and 30 wt % were, 104, 95 and 90 °C, respectively. PS-CTAB-HNT-10 % nanocomposites showed higher T_g than that of pure polystyrene and PS-HNT, when the content of the CTAB-HNT is only 10 wt %, the T_g is evidently improved and is believed to restrict the intercalated polymer chains between the sheets of the halloysite nanotube, which prevents the segmental motions of the polymer chains, another reason for increase in T_g is uniform distribution of halloysite nanotubes

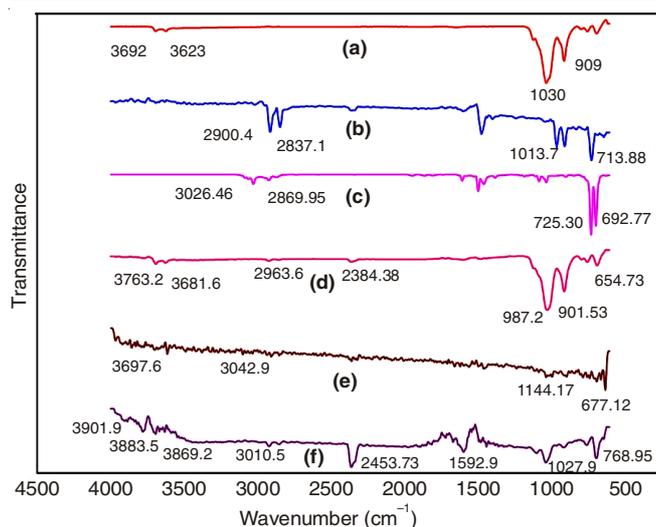


Fig. 5. FT-IR analysis of (a) halloysite nanotube, (b) CTAB, (c) polystyrene, (d) CTAB-HNT, (e) PS-HNT, (f) PS-CTAB-HNT

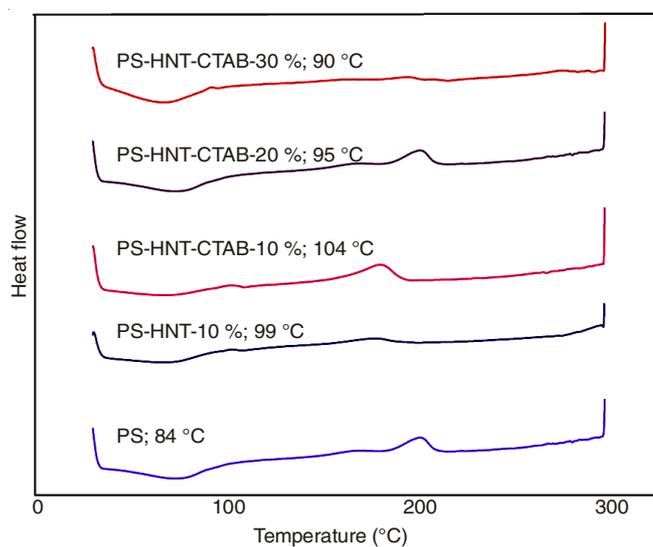


Fig. 6. DSC plots of polystyrene, PS-HNT, PS-CTAB-HNT-10 %, PS-CTAB-HNT-20 %, PS-CTAB-HNT-30 %

on modification with CTAB which creates tortuous path for heat to pass through it thus enhancing thermal properties. On the other hand, T_g decreases with increase in halloysite nanotube content because of difficulty in dispersing and hence, reducing the thermal properties. Thus, it can be confirmed

that the 10 wt % itself can be effective on improving the T_g of the polystyrene and hence thermal stability.

Conclusion

Nanocomposites with polystyrene matrix reinforced with pristine clay and modified clay were synthesized using ultrasound assisted solution intercalation method using toluene as solvent. Ultrasound plays a crucial role in uniformly dispersing filler in polymer matrix, also sonication time of 1 h provided best dispersion, sonication time less than 1 h was not sufficient for order and regularity of chains. Also, increase in sonication time beyond 1 h may break the polymer chains that would lead to degraded properties of composites. Modification of halloysite nanotube was done using CTAB and the successful intercalation into the clay gallery was observed by XRD analysis. The increase in d-spacing for halloysite nanotube and CTAB-HNT was from 7.3 to 7.5 Å. FT-IR results confirmed successful adsorption of CTAB onto the surface of halloysite nanotubes as well as encapsulation of CTAB-HNT in the polystyrene matrix. The increase in glass transition temperature was observed by adding clay particles as observed by DSC results and 10 % loading itself was found to be effective for improving thermal properties of composites.

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