Synthesis and Characterization of Polyurethane-layered Silicate Nanocomposites Using Tris(2-hydroxyethyl)ammonium Ions Attached Montmorillonite

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SUMMARY

Polyurethane-montmorillonite nanocomposites were successfully synthesized using novel tris(2-hydroxyethyl)ammonium ions attached montmorillonite. To enhance the interfacial interactions between the polyurethane and montmorillonite, first, sodium ions present in sodium montmorillonite layers were exchanged with tris(2-hydroxyethyl)ammonium ions and resulting modified montmorillonite was used during the synthesis of polyurethane. As tris(2-hydroxyethyl)ammonium ions are bigger than the sodium ions, during the modification, the distance between montmorillonite layers increased from 1.1 nm to 1.73 nm. X-ray diffraction and transmission electron microscopy results confirm the formation of exfoliated and intercalated polyurethane-montmorillonite nanocomposites. When compared to virgin polyurethane, polyurethane-montmorillonite nanocomposites show higher thermal stability and glass transition temperature.

INTRODUCTION

One of the major drawbacks of polyurethane (PU) is low thermal stability. However, silicate nanocomposite [1–3] show improved thermal stability. Apart from increased

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thermal stability, compared to virgin polyurethanes, polyurethane-montmorillonite (PU-MMT) nanocomposites show improved flame retardancy [4], improved gas barrier properties [5,6], increased modulus and tensile strength [7, 8] and higher mechanical properties [9]. The superior properties of PU-MMT nanocomposites are due to the intercalation and exfoliation of montmorillonite layered silicates with PU [10]. As PU is hydrophobic, and sodium montmorillonite (Na+-MMT) is hydrophilic in nature, compatibility of PU and Na+-MMT in PU-MMT nanocomposite is not good. To overcome this, Na+-MMT can be changed into hydrophobic by simple ion exchange of sodium cations with quaternary ammonium cations. As a result, MMT and PU are expected to be more compatible in PU-MMT nanocomposite. In addition to this, substituting functional groups at the quaternary ammonium cations can increase the interfacial interactions between inorganic MMT and organic polyurethane in PU-MMT nanocomposites [8, 11]. Depending on the strength of these interfacial interactions, mainly, intercalated and exfoliated nanocomposites are obtained. Intercalated nanocomposite results when polymer chains are completely penetrated inside the gallery of the layered silicates in a crystallographic regular fashion and exfoliated nanocomposites could be obtained when the silicate platelets are completely spread in the polymer matrix in a regular fashion at average distance depending on the silicate content. Due to the high aspect ratio of the silicate layers, exfoliated PU-MMT nanocomposites show better properties than the virgin polyurethane [12]. In addition, optical clarity is better in the exfoliated PU-MMT nanocomposites than the nanocomposites where the silicates layers remain as clusters [13, 14].

In recent years, various properties have been improved by incorporating the layered silicates into polyurethanes [15-17]. But, in most of the cases, PU-MMT nanocomposites have been synthesised by the physical mixing of alkyl or aryl modified layered silicates [18]. In few cases, PU-MMT nanocomposites have been prepared using layered silicates as pseudo chain extenders [19]. To increase the exfoliation, in the present investigation, tris(2-hydroxyethyl) ammonium ions functionalized layered silicates are used. As three hydroxyl functional groups are present on the modified MMT layered silicates, higher interfacial interactions between the polyurethane and MMT are expected in the resulting PU-MMT nanocomposites.

EXPERIMENTAL SECTION

Materials

Na+-MMT having cation exchange capacity (CEC) of 92.6 meq/100 g was purchased from Southern Clay Products, USA. Triethanolamine, tetrahydrofuran
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THF and dimethyl formamide (DMF) were purchased from SRL, India and used after purification. Toluene diisocyanate (TDI; mixture of 80% 2,4 and 20% 2,6 isomers) and dibutyltin dilaurate were used as received from Aldrich, U.S.A. Poly(tetramethyleneoxide) glycol of molecular weight 1000 (PTMG-1000; Aldrich, USA) was purified by heating at 105°C under reduced pressure for 3 hr just before use. All other chemicals used were of analytical grades and were used as received.

Synthesis of Tris(2-hydroxyethyl)ammonium Chloride (THEAC)

Synthesis of tris(2-hydroxyethyl)ammonium chloride was carried out by the reaction of triethanolamine with hydrogen chloride. In a 250 mL round bottom flask, triethanolamine dissolved in THF was taken and hydrogen chloride gas was passed through the solution slowly for 2 h. Resulting white precipitate was filtered, washed and dried. (Yield: 95% and M. P.: 174°C).

Preparation of THEAC Anchored MMT (THE-MMT)

Before the preparation of THE-MMT, first, Na+-MMT was purified according to the previously reported method [20]. The pure Na+-MMT was grounded into fine powder with the help of mortar and pestle, and sieved with 325 mesh. Purified Na+-MMT of 10 g (9.26 mmol) was then dispersed in one litre of deionized water and the resulting mixture was stirred overnight at 40°C to get homogeneous mixture. In a separate test tube, THEAC (11.11 mmol) was dissolved in deionized water and it was added drop-wise into the Na+-MMT dispersion for 1 h. As soon as THEAC solution was added into Na+-MMT dispersion, THE-MMT was separated out as white precipitate. The resulting mixture was further stirred for another 12 h in the same reaction conditions to achieve complete ion exchange. The resulting precipitate was filtered followed by washing three times with deionized water. The complete removal of Cl⁻ ions was confirmed by testing the filtrate using aqueous silver nitrate solution. At the end, the white precipitate was lyophilized to get the fine powder. The powder was again grounded and sieved with 325 mesh for further use. (Yield: 95%).

Preparation of PU-MMT Nanocomposites

Dried PTMG-1000 (0.005 mole) was taken in a 250 mL three necked round bottom flask, fitted with a mechanical stirrer, nitrogen inlet, dropping funnel and heated in an oil bath. When the temperature reached 65°C, TDI (0.011
mole) was added drop by drop with stirring. The temperature was then raised to 70°C and the reaction was allowed to proceed until the isocyanate content reached half of the initial value as determined by dibutylamine titration. Then, known quantity of THE-MMT (1%, 2%, 3% and 5% (w/w) based on the total weight of PTMG-1000 and TDI) was added to the NCO-terminated prepolymer and stirred for another 1 h. at the same temperature. Then, 1,4-butanediol (0.005 mole) was added followed by dibutyltindilurate (2 mole% of NCO), and the reaction mixture was stirred at 80°C. The reaction was allowed to proceed until complete disappearance of isocyanate group, which was monitored and confirmed by the Fourier-transform infrared (FT-IR) spectroscopy.

Characterization

FT-IR spectra were recorded as a KBr pellets on a Nicolet Impact 400 FT-IR spectrophotometer. X-ray diffraction (XRD) experiments were recorded using a Philips X’Pert diffractometer as well as a Bruker D8 high resolution diffractometer employing Cu Ka radiation at a scan rate of 1°/min. Transmission electron microscopy (TEM) was used to study morphology of the PU-MMT nanocomposites. For this, the nanocomposite samples were sectioned into ultrathin slices (< 90 nm) using a microtome equipped with a diamond knife and then mounted on 300 mesh copper grids. Images were recorded at Tecnai-12 TEM device operating at 200 kV. Differential scanning calorimetric (DSC) studies were carried out using a DSC Q200 instrument (TA Instruments, USA) at a heating rate of 10°C/min. under nitrogen atmosphere and thermogravimetric analysis (TGA) was carried out using a TGA Q50 instrument (TA Instruments, USA) at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Synthesis of THE-MMT

To prepare THE-MMT, first, THEAC was prepared by reacting triethanolamine with dry hydrogen chloride gas. Then, sodium ions present in Na+-MMT was exchanged with the quaternary ammonium ions of THEAC. The amount of THEAC for a cation-exchange reaction was calculated using the following equation [21]:

$$A = \frac{92.6}{100} \times \text{weight in g of Na}^+ - \text{MMT} \times 1.2 \times M_w \text{ of THEAC}$$
Where, $A$ represents the amount of intercalating agent used in gram, 92.6/100 represents the cationic exchange capacity (CEC) of 92.6 meq/100 g of MMT layers, and 1.2 (> 1) indicates the excess amount of intercalating agent used. THE-MMT was characterized by XRD, TGA and FT-IR spectroscopy. Figure 1a shows the X-ray diffraction pattern of the THE-MMT and Na⁺-MMT. Bragg’s equation, $n \lambda = 2d \sin \theta$, was used to calculate the basal $d$-spacing where $d$ is the spacing between diffractional lattice planes, $\theta$ is the diffraction position, and $\lambda$ is the wavelength of the X-ray (1×5405 Å). Diffraction (001) peaks for the Na⁺-MMT and THE-MMT are observed at 1.17 nm ($2 \theta = 7.5^\circ$) and 1.73 nm ($2 \theta = 5.65^\circ$) respectively. This indicates that tris(2-hydroxyethyl)ammonium groups are successfully incorporated into the MMT galleries resulting wider $d$-spacing in the THE-MMT. The complete absence of the parental peak reveals that there is no unmodified Na⁺-MMT present. The extent of incorporation of tris(2-hydroxyethyl)ammonium groups was also confirmed by TGA analysis. Figure 1b shows the TGA plots for the Na⁺-MMT and THE-MMT. This figure reveals that approximately 32% (wt/wt) of tris(2-hydroxyethyl)ammonium groups have been anchored on the surface of the layered silicates. Figure 2 shows FT-IR spectra of Na⁺-MMT and THE-MMT. The absorption peak for the terminal hydroxyl groups present in tris(2-hydroxyethyl)ammonium group is observed at 3410 cm⁻¹ and the -CH stretching vibrations of methylene
groups are absorbed at 2920 cm\(^{-1}\). Weak absorption peaks present in the FT-IR spectrum of THE-MMT confirm that tris(2-hydroxyethyl)ammonium groups are present inside the galleries of MMT.

If Na\(^+\) ion is completely replaced with quaternary ammonium ion, then there should not be any sodium cations present on the MMT surface. To check this, XPS analysis of Na\(^+\)-MMT and MEBAB-MMT was carried out and the results are presented in Figure 3. As MMT is a magnesium alumina silicate, the characteristic peaks due to O, Si, and Al are common in both the spectra. It is important to note that the peak due to Na 1s at 1072 eV disappeared in Figure 3b confirming the complete removal of Na\(^+\) cations from the surface of the MMT. In addition, the peak due to quaternary nitrogen (1s) is present at 400 eV. These results are clear evidences to confirm that quaternary nitrogens are adhered on the surface of MMT layers. Similar type of XPS results were also observed for Na\(^+\)-MMT and modified MMT in the literature [22].

Morphological Study of the PU-MMT Nanocomposites

The morphology of PU-MMT nanocomposites were carried out by TEM and XRD analysis. Figure 4 shows the X-ray diffraction pattern of PU-MMT.
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Figure 3. XPS spectra of (a) Na⁺-MMT and (b) THE-MMT

Figure 4. XRD patterns of the PU-MMT nanocomposites
nanocomposites with different THE-MMT content. The absence of the X-ray diffraction peak in between 2θ values of 3-10 confirmed that exfoliation of the layered silicates has been taken place successfully in PU-MMT nanocomposites. When intergallery d-spacing between the silicates layers increases more than 6-7 nm or when the silicate layers are dispersed into the polymer matrix randomly where two silicate planes are not diffracting the X-rays in an efficient way to get 2θ value, then XRD cannot be used to evaluate the nanocomposites morphology. In that case, TEM analysis is very useful to study the morphology of the nanocomposites.

Hence morphology of PU-MMT nanocomposites was again confirmed with the help of TEM. Figure 5a and b shows the bright field TEM images of PU-MMT 1.0, and PU-MMT 5.0 respectively. The bright region in the TEM micrographs represents the polymer matrix and dark line represents the montmorillonite silicate layers. TEM micrographs of all PU-MMT nanocomposites exhibit that silicate layers are dispersed in the polymer matrix thoroughly. As a result, the stacking of silicate layers is also lost. It is interesting to note that intercalated and exfoliated PU-MMT nanocomposites are formed when THE-MMT is used. The higher degree of exfoliation can be attributed to highly functional layered

Figure 5. Bright field TEM images of (a) PU-MMT 1.0 (b) PU-MMT 5.0
silicates which may help in the formation of strong interactions between the layered silicates and polymer matrix.

**Thermal Properties of PU-MMT Nanocomposites**

Thermal properties of PU-MMT nanocomposites were examined by DSC and TGA. Figure 6 shows the DSC curves for the PU-MMT nanocomposites with 1, 2, 3 and 5% content of THE-MMT. All $T_g$ values were obtained from the midpoint between onset and offset $T_g$ values. The $T_g$ values of the PU-MMT nanocomposites are higher than the pure polyurethane and it increases with increasing clay content. It is interesting to note that up to 10°C increase was observed when pure polyurethane was converted into PU-MMT nanocomposites. Similar type of results were observed for the thermosetting PU-MMT nanocomposites [23]. The higher $T_g$ values of PU-MMT nanocomposites is due to the reason that the mobility of polymer chains is restricted when they are in between the silicate layers. It has been observed that stronger the interactions between the silicate layers higher the $T_g$ values of the PU-MMT nanocomposites [4, 23].

![Figure 6. DSC curves of PU-MMT nanocomposites](image)

Thermal stability of PU-MMT nanocomposites was analysed by TGA under nitrogen atmosphere and compared with the thermal stability of pristine polyurethane. Figure 7 shows the TGA thermograms of pristine PU and PU-MMT
nanocomposites with different THE-MMT contents. The thermal degradation of PU occurs in two stages; the first stage is mainly due to the degradation of the hard polyurethane segments and the second stage is due to the degradation of the soft polyol segments [24]. As can be seen from the figure, thermal stability of PU-MMT nanocomposites is higher than the thermal stability of the pristine polyurethane [25, 26]. As the THE-MMT content increases, thermal stability of PU-MMT nanocomposites also increases. The kinetic study of the PU-MMT nanocomposites stability postulates that the thermal degradation mechanism of the layered silicate nanocomposites differ from the virgin polymers [27-29]. It was also postulated that when thermal degradation of the PU-MMT nanocomposites occurs, a silicate barrier formed gradually which may hinder the evaporation of the thermally volatile side products from the nanocomposites materials. Hence, the higher stability of PU-MMT nanocomposites is due to the good barrier property of silicate layers as well as restricted motion of the polymeric material inside the silicate galleries [30-31]. In general PU-MMT nanocomposites show approximately 50°C higher thermal stability as compared to the pristine polymer [32]. However, silicate layers could catalyse the thermal decomposition of PU-MMT nanocomposites. On the other hand, alkylammonium cations present on the surface of the layered silicates could leave via Hoffman elimination [33-35]. Initial weight loss in the TGA curves of PU-MMT nanocomposites are due to Hoffman elimination while it is absent in the pristine polymer. These results are the typical characteristics of the exfoliated and intercalated PU-MMT nanocomposites.
CONCLUSIONS

Interfacial interactions between the silicates layers and polymer chains are the key factor to enhance the exfoliation. Keeping this in mind, novel THEAC surface modifier was prepared to enhance the functionality of the silicate layers and was used for the surface modification of Na+-MMT. Modified THE-MMT was characterized by IR, XPS, XRD, and TGA successfully. Using THE-MMT, intercalated and exfoliated PU-MMT nanocomposites were successfully prepared and characterized by TGA, DSC, XRD and TEM analysis. Thermal analysis of PU-MMT nanocomposites reveals higher $T_g$ and higher thermal stability than the pristine polyurethane. Powder XRD and TEM analyses reveal the formation of intercalated and exfoliated PU-MMT nanocomposites.

REFERENCES