Preparation and characterization of new polyamide/montmorillonite nanocomposites containing azo moiety in the main chain

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Abstract Two new samples of polyamide/montmorillonite reinforced nanocomposites containing 4,4'-azobenzoic acid moiety in the main chain were synthesized by a convenient solution intercalation technique. Polyamide (PA) 4 as a source of polymer matrix was synthesized by the direct polycondensation reaction of 4,4'-azobenzoic acid 2 with 4,4'-diamino diphenyl ether 3 in the presence of triphenyl phosphite (TPP), CaCl2, pyridine and N-methyl-2-pyrrolidone (NMP). Morphology and structure of the resulting PA-nanocomposite films 4a and 4b with 10 and 20% silicate particles were characterized by FTIR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of clay dispersion and the interaction between clay and polymeric chains on the properties of nanocomposites films were investigated by using UV–vis spectroscopy, thermogravimetric analysis (TGA) and water uptake measurements.

1. Introduction

Polymer-clay nanocomposites typically exhibited good mechanical, thermal and gas barrier properties, which are superior to those of the corresponding pure polymers (Biswas and Ray, 2001; McNally et al., 2003; Shen et al., 2004; Gain et al., 2005; Gonzalez et al., 2005; Lopez et al., 2005; Nah et al., 2002; Huang et al., 2001; Hu et al., 2001). Unique properties of the nanocomposites are usually observed when the ultra fine silicate layers are homogenously dispersed throughout the polymer matrix at nanoscale. The uniform dispersion of silicate layers is usually desirable for maximum reinforcement of the materials. Due to the incompatibility of hydrophilic layered silicates and hydrophobic polymer matrix, the individual nanolayers are not easily separated and dispersed in many polymers. For this purpose, silicate layers are usually modified with an intercalating agent to obtain organically modified clay prior to use in nanocomposite formation (Zulfiqar et al., 2007; Kausar et al., 2007). Also thermally stable polyamides (PA)s have received much attention over the past decade, owing to...
increasing demands for high-performance polymers materials for several applications such as high strength, high-modulus fibers, high-temperature coating and high-efficiency semi-permeable membranes. But, due to their low solubility, their applications have been restricted (Mallakpour and Kolahdoozan, 2008; Hsiao et al., 2004, 2006; Al-Ghamdi et al., 2006; Higashi et al., 2004). Much effort has been made to create structurally modified aromatic polyamides having better characterization in terms of both solubility and processability with retention of their high thermal stability (Faghihi et al., 2010a,b,c). Thus, to overcome these processing problems various approaches have been carried out by incorporating flexible units such as –NHCO–, –O–, N=N and –SO2–, some of which are commercialized. On the other hand introduction of flexible chains into the PAs backbone, the use of meta-oriented monomers and the synthesis of PAs with non-coplanar units in the polymer chains, resulted in a number of modified PAs. Another strategy is based on the introduction of bulky side groups into the polymer chains (Ayala et al., 2005; Mallakpour and Rafiee, 2008).

In this article two PA-nanocomposite films with 10% and 20% silicate particles containing 4,4’-azobenzoic acid moiety in the main chain were prepared by using a convenient solution intercalation technique.

2. Experimental

2.1. Materials

4-Nitrobenzoic acid, 4,4’-diaminodiphenyl ether, acetic acid, triphenyl phosphite (TPP), CaCl2, pyridine and N-methyl-2-pyrrolidone (NMP) were purchased from Merck Chemical Company and used without previous purification. Purified organically-modified Cloisite 20A (Where HT is Hydrogenated Tallow) supplied by Southern Clay Products (TX), were used as polymer nano reinforcement. The organic modifiers and the interlayer distance of the clays are shown in Table 1 to account the structural modifications of the functional points.

2.2. Equipment

1H-NMR spectrum was recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy Series FTIR 5000 spectrophotometer (England). UV–vis spectra were recorded at 25 °C in the 250–700 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer in NMP solution using cell lengths of 1.0 cm. Thermal gravimetric analysis (TGA and DTG) data were taken on a Mettler TA4000 System under N2 atmosphere at a rate of 10 °C/min. The morphology and structure of nanocomposite film were investigated on Cambridge S260 scanning electron microscope (SEM). X-ray diffraction (XRD) were performed on Philips X-Pert (Cu–Kα radiation, x = 0.15405 nm). The water absorption of PA-nanocomposite films were carried out using a procedure under ASTM D570-81 (Zulfiquar and Sarwar, 2008).

2.3. Monomer synthesis

4,4’-Azobenzoic acid 2 was prepared according to a typical procedure shown in Scheme 1 (Faghihi and Hagibeygi, 2003).

### Table 1 Organic modifiers and interlayer distance of the clays.

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>Organic modifiers</th>
<th>Concentration of organic modifier [meq/100 g clay]</th>
<th>Interlayer distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite®20 A</td>
<td>CH3N=HT</td>
<td>95</td>
<td>1.77</td>
</tr>
</tbody>
</table>

2.4. Polymer synthesis

Into a 100 mL round bottomed flask was placed a mixture of 4,4’-azobenzoic acid 2 (0.002 mol), 4,4’-diaminodiphenyl ether 3 (0.002 mol), 0.60 g of calcium chloride, 1.0 mL of triphenyl phosphate, 1.0 mL of pyridine and 4.0 mL NMP. The mixture was heated for 1 h at 60 °C, 2 h at 90 °C and then refluxed at 140 °C for 8 h until a viscous solution was formed. Then it was cooled to room temperature and 30 mL of methanol was added to reaction mixture. The precipitate was formed, filtered off and washed with methanol. The resulting polyamide 4 was dried under vacuum. The inherent viscosity of this polymer in a solution of DMF was 0.55 Dl/g. Elemental analysis for C26H18N4O3, Calcd. C, 71.88; H, 4.18; N, 12.90; found, C, 70.99; H, 4.15; N, 12.82.

2.5. PA-nanocomposite synthesis 4a and 4b

PA-nanocomposites 4a and 4b were produced by solution intercalation method. Two different amounts of organoclay particles (10 and 20-wt%) were mixed with appropriate amounts of PA solution in N-methyl-2-pyrrolidone (NMP) to yield particular nanocomposite concentrations. To control the dispersibility of organoclay in polyamide matrix, constant stirring was applied at 25 °C for 24 h. Nanocomposite films were cast by pouring the solutions for each concentration into Petri dishes placed on a leveled surface followed by the evaporation of solvent at 70 °C for 12 h. Films were dried at 80 °C under vacuum to a constant weight. Scheme 1 shows the flow sheet diagram and synthetic scheme for PA-nanocomposites film 4a and 4b.

2.6. The water absorption analysis

The water absorption of PA-nanocomposite films was carried out using a procedure under ASTM D570-81 (Zulfiquar and Sarwar, 2008). The films were dried in a vacuum oven at 80 °C to a constant weight and then weighed to get the initial weight (W0). The dried films were immersed in deionized water at 25 °C. After 24 h, the films were removed from water and then they were quickly placed between sheets of filter paper to remove the excess water and the films were weighed immediately. The films were again soaked in water. After another 24 h soaking period, the films were taken out, dried and weighed for any weight gain. This process was repeated again and again till the films almost attained the constant weight. The total soaking time was 168 h and the samples were weighed at regular 24 h time intervals to get the final weight
The percent increase in weight of the samples was calculated by using the formula \[
\left( \frac{W_f - W_0}{W_0} \right) \times 100\%.
\]

3. Results and discussion

3.1. Monomer synthesis

4,4'-Azobenzoic acid 2 was synthesized from the reduction of 4-nitrobenzoic 1 acid by glucose in a basic solution (Scheme 1).

The chemical structure of diacid 2 was confirmed by FTIR and \(^1\)H-NMR spectroscopy. In the FT-IR spectrum of diacid 2, peaks appearing at 2500–3400 cm\(^{-1}\) (acid O–H stretching) and 1709 cm\(^{-1}\) (C=O acid) confirmed the presence of carboxylic groups in this compound (Fig. 1). The \(^1\)H-NMR spectrum of diacid 2 shows H(a) protons relevant to O–H carboxylic groups at 12.0 ppm and peaks between 8.2 and 8.19 ppm related to aromatic protons (Fig. 2).

3.2. Polymer synthesis

Polyamides 4 were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid 2, and diamine 3 by using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). PA 4 was obtained in good yield (99%) and had an inherent viscosity (0.55 dL/g) in a solution of DMF. The structure of the resulting polymer 4 was confirmed as PA by using FTIR spectroscopy and elemental analyses. The resulting polymer has an absorption band at 1680 cm\(^{-1}\) due to amide carbonyl groups. Absorption bands between 3350 and 3500 cm\(^{-1}\) demonstrated the presence of the amide N–H stretching absorption in this polymer (Fig. 3). The elemental analysis value of the resulting polymer was in good agreement with the calculated values for the proposed structure.

3.3. PA-nanocomposite films

PA-nanocomposite films were transparent and have light orange color. The incorporation of organoclay changed the color of films to dark orange color. Moreover, a decrease in the transparency was observed at higher clay contents.

3.4. FT-IR spectroscopy analyses

FT-IR spectrum of PA-nanocomposite films 4a and 4b showed the characteristic absorption bands of the Si–O moieties at 1040 and 1035, Mg–O moieties at 465 and 454 cm\(^{-1}\), respectively. The incorporation of organic groups in PA-nanocomposite films was confirmed by the presence of peaks at 3280 and 1650–1662 (amide N–H stretching and carbonyl group) (Fig. 3).
3.5. X-ray diffraction analysis

Fig. 4 shows the XRD patterns of PA-nanocomposite films 4a and 4b containing 10 and 20-wt% of silicate particles. These results indicated significant expansion of the silicate layer after insertion of PA chains. The shift in the diffraction peaks of PA-nanocomposite films confirms that intercalation has been taken place. This is direct evidence that PA-nanocomposites have been formed as the nature of intercalating agent also affects the organoclay dispersion in the polymer matrix. Usually there are two types of nanocomposites depending upon the dispersion of clay particles. The first type is an intercalated polymer clay nanocomposite, which consists of well ordered multi layers of polymer chain and silicate layers a few nanometers thick. The second type is an exfoliated polymer-clay nanocomposite, in which there is a loss of ordered structures due to the extensive penetration of the polymer chain into the silicate layer. Such parts would not produce distinct peaks in the XRD pattern (Bharadwaj, 2001). In our PA-nanocomposite films there are coherent XRD signal at 5.80° and 4.21° related to 10 and 20 wt% nanocomposite films, respectively.

3.6. Scanning electron microscopy

The surface morphology of the PA-nanocomposite films prepared by solution intercalation technique is compared by SEM analyses. Fig. 5 shows the morphological images of 10 and 20 wt% nanocomposite films, respectively. The SEM images show that the PA matrix has a smooth morphology. Also SEM micrographs of PA-nanocomposite containing 10 and 20 wt% clay platelets were uniformly distributed without agglomeration.
3.7. Optical clarity of PA-nanocomposite films

Optical clarity of PA-nanocomposite films containing 10 and 20 wt% clay platelets and neat PA was compared by UV–vis spectroscopy in the region of 300–800 nm. Fig. 6 shows the UV–vis transmission spectra of pure PA and PA-nanocomposite films containing 10 and 20 wt% clay platelets. This spectrum shows that the UV–visible region (500–800 nm) is affected by the presence of the clay particles and exhibiting low transparency reflected to the primarily intercalated composites. Results
shows that the optical clarity of PA-nanocomposite films system is significantly lower in the neat PA system.

3.8. Thermogravimetric analysis

The thermal properties of PA-nanocomposite films containing 10 and 20 wt% clay platelets and neat PA were investigated by using TGA in nitrogen atmosphere at a rate of heating of 10 °C/min, and thermal data are summarized in Table 2. These samples exhibited good resistance to thermal decomposition, up to 265–380 °C in nitrogen, and began to decompose gradually above this temperature. $T_5$ for these polymers ranged from 190 to 220 °C and $T_{10}$ for them ranged from 240 to 290 °C (temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂, respectively), and residual weights at 600 °C ranged from 53.20% and 62.31% in nitrogen, respectively (Fig. 7). Incorporation of organoclay into the PA matrix also enhanced the thermal stability of the nanocomposites. Fig. 5 shows the TGA thermograms of PA-nanocomposites under nitrogen atmosphere. Thus, we can speculate that interacting PAs chains between the clay layers serve to improve the thermal stability of nanocomposites. The addition of organoclay in polymeric matrix can significantly improve the thermal stability of PA.

3.9. Water absorption measurements

The PA under investigation contains polar amide groups in the backbone that have the tendency to uptake water through hydrogen bonding. Thus water absorption measurements become necessary for neat PA and PA-nanocomposite films and data are shown in Table 2. In the water permeability studies, we found that the incorporation of clay platelets into PA matrix results in a decrease of water uptake relative to pure PA by forming the tortuous path of water permeant. Water permeability depends on length, orientation and degree of delamination of layered silicate (Zulfiqar and Sarwar, 2008). It should be noted that a further increase in clay concentration resulted in an enhanced barrier property of nanocomposites which may be attributed to the plate-like clays that effectively increase the length of the diffusion pathways, as well as decrease the water permeability.

<table>
<thead>
<tr>
<th>Polyamide</th>
<th>$T_5$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>Char yield (%)</th>
<th>Water uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>190</td>
<td>240</td>
<td>53.20</td>
<td>7.38</td>
</tr>
<tr>
<td>4a</td>
<td>197</td>
<td>250</td>
<td>57.80</td>
<td>5.16</td>
</tr>
<tr>
<td>4b</td>
<td>220</td>
<td>290</td>
<td>62.31</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$^a,b$ Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N₂, respectively.

$^c$ Percentage weight of material left undecomposed after TGA analysis 600 °C.
4. Conclusions

The PA-nanocomposites were successfully prepared using solution intercalation method. The structure and the uniform dispersion of organoclay throughout the PA matrix were confirmed by FTIR, XRD and SEM analyses. The optical clarity and water absorption property of PA-nanocomposites were decreased significantly with increasing the organoclay contents in PA matrix. On the contrary the thermal stability of PA-nanocomposites was increased significantly with increasing the organoclay contents in PA matrix. The enhancements in the thermal stability of the nanocomposites films 4a and 4b caused by introducing organoclay may be due to the strong interactions between polymeric matrix and organoclay generating well intercalation and dispersion of clay platelets in the PA matrix.

References
