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Probing the role of surface treated montmorillonite on the properties of semi-aromatic polyamide/clay nanocomposites

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ABSTRACT

Semi-aromatic polyamide/organoclay nanocomposites were generated through solution blending technique. Surface modification of the montmorillonite clay was performed with *p*-amino benzoic acid for ample compatibilization with the polyamide matrix. The polymer chains were produced from the condensation of 4-aminophenyl sulfone with sebacoyl chloride. Interaction between the two phases was established by modifying the polymer chains with amine end groups using 1% surplus diamine near the completion of the reaction. The effect of clay dispersion and the interaction between clay and polyamide chains on the properties of nanocomposites were investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), tensile testing of thin films, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and water uptake measurements. The structural investigations confirmed the formation of delaminated nanostructures at low clay contents and disordered intercalated morphology at higher clay loadings. This morphology of the nanocomposites resulted in their enhanced mechanical and thermal properties. The tensile behavior and thermal stability significantly amplified while permeability decreased with increasing dispersibility of organoclay in the polyamide matrix.

1. Introduction

Natural montmorillonite (MMT) consisted of layered silicates carrying negative charges that formed ionic bonds with metal cations in interlayer of the clay. These silicates also contained dangling surface hydroxyl groups [1–4]. The presence of ionic bonds and the ability of forming hydrogen-bonding with water made MMT highly hydrophilic and hence neat MMT was difficult to be mixed with hydrophobic polymers. To improve the affinity of MMT toward organic molecules, it is necessary to modify the surface chemistry of MMT by replacing inorganic cations in the interlayer of silicates with various organic cationic molecules. The surface modification of the layered silicates increased interlayer spacing and became more uniform after intercalation with organic molecules. This surface treatment with organic molecules made MMT more miscible with polymer molecules. Thus, polymer molecules are allowed to enter the enlarged interlayer of organoclay for further intercalation or delamination. The surface modification of montmorillonite is a prerequisite for creating the desired morphology of nanocomposites and consequently resulting in enhanced properties of polymer nanocomposites. Organoclays have attracted much interest in many applications including polymer/clay nanocomposites, absorbents of organic pollution in ground water, coatings, paints, electrorheology and anticorrosion properties [5–10]. The surface characteristics of organoclays are very important for their applications. The compatibility between an organoclay and a polymer matrix is the key factor that determines the structure of the composite as a conventional microcomposite or nanocomposite. The nanocomposite may be classified as intercalated and exfoliated, depending on the degree of dispersion of the clay layers. The surface properties of organoclays are mainly determined by the surfactant used for cation exchange to modify originally hydrophilic clay. Consequently, polymer/clay nanocomposites exhibit superior properties including barrier, fire and mechanical at very low clay loading (<10 wt.%) dispersed at nanometer scale in the polymer matrix [11–28].

Polyamides are renowned for their excellent properties in terms of thermal stability, mechanical properties, high glass temperature and good resistance to solvents. Due to their high performance and superb properties, aromatic polyamides [29–32] and their

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composites [33,34] are widely utilized for defence and aerospace applications. The aliphatic analogues of these polymers are generally referred to as nylons used in many daily life applications. There is another class of glassy copolymer obtained from condensation of aromatic diacids and aliphatic diamines. These are often known as glass-clear nylons with exceptional properties such as good transparency, rigidity, thermal resistance, hardness, etc. and have many industrial applications. Some of their applications, however, require further property enhancements and the desired improvements can be obtained through incorporation of inorganic nano-fillers [35–37]. In recent years, polymer/clay nanocomposites, especially based on polyamides have attracted much attention because these hybrids have tremendous applications in coating, flame retarding, barrier and electronic materials [38–46]. However, nanocomposites based on semi-aromatic polyamides have been given no attention.

In the present work, nanocomposites of semi-aromatic polyamide with organoclay have been synthesized using solution blending technique. Polyamide was prepared by reacting 4-aminophenyl sulfone with sebacoyl chloride in anhydrous dimethyl acetamide (DMAc). These polymer chains were end-capped with amine groups using a slight excess of the diamine. Clay was modified with the ammonium salt of *p*-amino benzoic acid. The amine end group of swelling agent was changed into cations to interact chemically with the negatively charged silicate layers while free acid group reacted with the amine groups of the polyamide chains diffused into the space between the silicate layers of MMT upon heating. The interaction between the two phases through swelling agent rendered more permanent effect due to the larger number of polyamide chains connected to the organoclay, yielding tough and thermally stable nanocomposites. Thin composite films obtained by evaporation of the solvent were characterized for XRD, TEM, tensile strength, TGA, DSC and water absorption measurements.

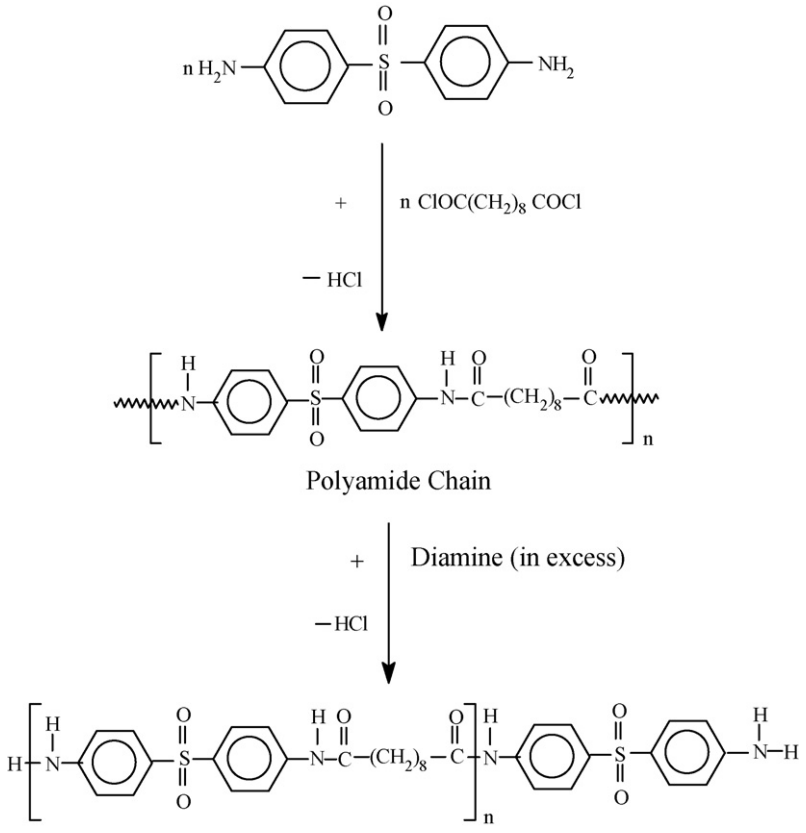
2. Experimental

2.1. Materials

4-Aminophenyl sulfone (APS) 97%, sebacoyl chloride (SCC) 97%, montmorillonite K-10 (cation exchange capacity of 119 mequiv./100 g), *p*-aminobenzoic acid (*p*-ABA) 99%, silver nitrate (99.9%) and *N*,*N*′-dimethyl acetamide (DMAc) >99% (dried over molecular sieves before use) were purchased by the courtesy of Aldrich and used as received. Triethylamine (TEA) ≥99.5% and hydrochloric acid >99% procured from Fluka were used as such.

2.2. Surface treatment of montmorillonite

For the preparation of nanocomposites, hydrophilic nature of clay was changed into organophilic using *p*-ABA as a swelling agent through ion exchange reaction. *p*-ABA was placed in a beaker containing water, followed by the addition of stoichiometric amount of concentrated hydrochloric acid for the conversion of amine group into cation. This solution was heated at 80 °C. In another beaker, MMT was dispersed in water at 80 °C. The dispersed MMT was then poured to the solution of ammonium salt of *p*-ABA and the mixture was agitated for 3 h at 60 °C. The precipitates of resulting organoclay were collected by filtration. These precipitates were washed thrice with distilled water to remove the residue of ammonium salt of *p*-ABA. The final product obtained was dried in a vacuum oven at 60 °C for 24 h. The dried cake was ground and screened with a 325-mesh sieve. The powder obtained was labeled as *p*-ABA–MMT employed for the preparation of the nanocomposites.



Scheme 1. Formation of amine end-capped semi-aromatic polyamide chains.