Preparation of Polyimide-Clay Nanocomposites and Their Performance

S. M. M. Alam[1]

College of Textile Technology, Tejgaon, Dhaka-1208, Bangladesh

Abstract

A series of polyimide (PI)-organically modified clay nanocomposites were made to enhance tensile modulus, thermal stability of PI. PI was made from 3, 3′, 4, 4′-biphenyl tetracarboxylic dianhydride (BPDA), p-phenylediamine (PDA). Montmorillonite (MMT), one type of layered clay, was treated by dodecylamine salt. XRD indicated that organically modified montmorillonite (OMMT) layers were exfoliated and dispersed into PI-film. Tensile measurements indicated that small amount of OMMT (up to 3%) increased tensile modulus nicely. The glass transition temperatures (T_g) of the nano-composites are higher than those of pristine PI. Thermal gravimetric analysis (TGA) showed that nanocomposites have higher decomposition temperatures in comparison with the original PI.

Keywords: Polyimide; Organically modified clay; Nanocomposites; Dodecylamine.

1. Introduction

Organic-inorganic nanocomposites usually have unique properties because of the combination of advantages of inorganic materials like rigidity, low co-efficient of thermal expansion (CTE), high thermal stability and the advantages of organic polymers like flexibility, dielectricity, process ability etc. Due to the distribution at nano-meter size, organic-inorganic composites often exhibit some special mechanical, electronic properties which extend their application to many new sectors [1-4].

Among organics, PI is well-known as high performance polymer which exhibits outstanding dielectric, mechanical properties, thermal stability and low CTE. Among different types of PIs, rigid PI prepared from 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylediamine (PDA) (Scheme 1) are widely used in microelectronics and aerospace industries because of its unique features like high modulus, low CTE and good mechanical strength, low solvent swelling and moisture uptake and spontaneous in-plane orientation. PIs possess limitations for much higher performance applications in which inorganic materials are used, because of their intrinsic nature as

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[1] *E-mail:* dalim70@yahoo.com

organic materials [5]. Inorganic materials exhibit excellent thermal stability and high modulus. Thus, the formation of nanocomposites of PI with inorganic materials has been suggested to meet the demands of balanced properties for both organic and inorganic materials. Different types of inorganics like layered silicate (clay), silica etc. can be used to prepare PI-inorganic nanocomposites. The most commonly used clay in the preparation of polymer/clay nanocomposites is montmorillonite (MMT). The layer of MMT is 1 nm thick and about 100 nm in length. The building blocks of MMT are silicon-oxygen tetrahedra ($Si_2O_5^{-2}$) and aluminum octahedral $Al(OH)_6^{-3}$. The repeat unit contains two tetrahedral and one octahedral layer. The MMT layer has permanent negative charge because of the isomorphous substitution of, for instance, Mg^{2+} for Al^{3+} or, rarely, Al^{3+} for Si^{4+}. These net negative charges are balanced by charge-balancing cations such as sodium, potassium et al. between the clay layers in the gallery space. The ions are loosely bound to the silicate layers and exchangeable, which provide the common way to modify the silicates with organic cation to form an organic-inorganic complex. In order to disperse the hydrophilic MMT well into organic polymers, Na ions on its surface should be exchanged by organic cations through ion-exchange process to render the surface hydrophobic. This modified MMT is called organically modified montmorillonite (OMMT) [6]. Thus, there will be hydrophobic environment into the clay galleries to accommodate the hydrophobic poly(amic acid). The presence of carboxyl groups may enhance the interaction between OMMT and poly(amic acid) through hydrogen bonding [7, 8].

Also, organic ammonium salts can provide functional groups that can react or interact with the monomers or polymers to improve the interfacial strength between clay and the polymer matrix [9]. In the present study, PI (BPDA/PDA)/OMMT nanocomposites were made with different ratio of clay (1, 3, 5 and 10%). The performance (mainly thermal and mechanical properties) of the nanocomposite films was also studied.
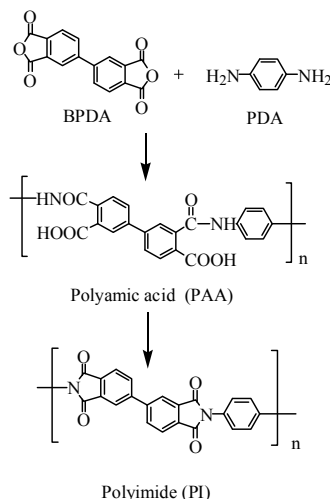
Scheme 1. Preparation of PI.

2. Experimental

2.1. *Reagents*

Kunipia-F, a Na^+-montmorillonite, was supplied by Kunimine Ind. Co., Japan with cation exchange capacity (CEC) of 119 meq/100g. OMMT was prepared from MMT by ion-exchange reaction using dodecylamine ($H_2N(CH_2)_{11}CH3$) following the reported method [7]. BPDA from UBE Industries Ltd., Japan and PDA from Tokyo Kasei Kogyo Co. Ltd, Japan was purified by sublimation. N-Methyl-2-Pyrrolidone (NMP) from Osaka Chemicals, Japan was dried by distillation under reduced pressure over sodium hydride. The HCl (35% strength) as received from Kishida Chemical Company, Japan was used. Polyamic acid (PAA) was prepared from BPDA and PDA in presence of NMP to prepare PI-OMMT nanocomposites.

2.2. *Preparation of PI-clay nanocomposite*

PI-OMMT nanocomposites with different weight percentage of OMMT (1, 3, 5 and 10%) were prepared according to the reported method [14].

2.3. *Measurements*

IR spectra were obtained with spectrophotometer named JASCO Spectrophotometer model FT/IR-420. DSC was recorded using Rigaku Thermo Plus 2DSC8230 at a heating rate of 10˚C/min under nitrogen. TGA was performed with Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5˚C/min under argon. Dynamic mechanical analysis (DMA) was conducted on ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35Hz at a heating rate of 4°C/min. XRD was measured in reflection mode using an X-ray diffractometer (Rigaku model RINT2000) using CuKα radiation. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a cross-head speed of 1mm/min using film of 2 cm long. Transparency of the films was checked by JASCO V-550 UV/vis Spectrophoto-meter where thickness of all films were about 0.03 mm.

3. Results and Discussion

3.1. *Preparation of OMMT*

Ammonium salt of dodecylamine was used for ion exchanging of the Na^+ ions on the MMT surfaces to render the surface hydrophobic. Thus, there will be hydrophobic environment into the clay galleries to accommodate the hydrophobic PAA. XRD measurements (Fig. 1) showed that the interlayer spacing of MMT (0.28 nm) was increased (0.69 nm) after surface treatment with dodecylamine. MMT with higher interlayer spacing after surface treatment is called OMMT.

3.2. *Morphological study*

XRD patterns of different PI films are shown in Fig. 2. With the increase of the OMMT loading 5 and 10%, the hybrid shows a slight pick corresponding to the basal spacing suggesting that a small part of OMMT was not dispersed in the molecular level and aggregates. The PI-10%OMMT related composites became darker due to aggregation of OMMT. Transparency of all composites was checked by UV-spectrophotometer. From UV-spectra, it was found that the transparency became respectively 80, 76.7, 66.9, 52, 44.3% in case of 0, 1, 3, 5, 10% OMMT related composites at 700 nm wave length. The pristine PI transparency is 80%, which is reduced in presence of OMMT.
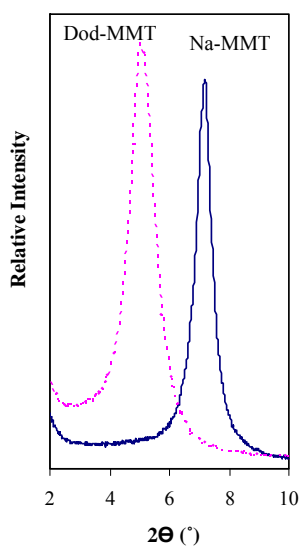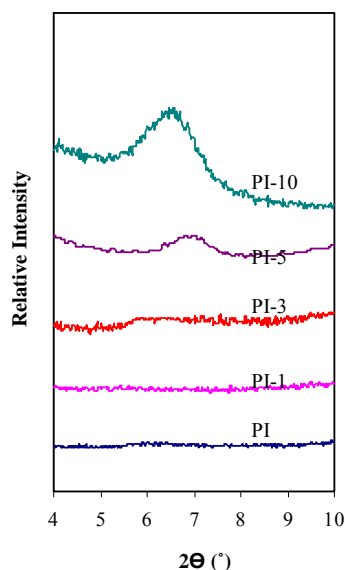

Fig. 1. XRD of MMT and OMMT.

Fig. 2. XRD of various PIs.

4. Performance of PI-inorganic composites

4.1. *Tensile properties of PI-inorganic composites*

Inorganics has higher rigidity than organics with brittleness which is a manifestation of the properties of composite. Pristine PI tensile modulus was 8.2 GPa which became 10.3, 11.5, 6.5, 3.5 GPa for PI-OMMT (1-10%) composites due to the reinforcement effect attained by the dispersion of clay nanolayers in PI (Fig. 3). At higher contents of clay (5, 10%), the layered silicate was not exfoliated due to less reinforcement effect which decreased the modulus of the hybrids. The pristine PI tensile strength is about 340 MPa. After inclusion of OMMT (1-10%), the strength became 390 MPa (for PI-1 composite), 332 MPa (for PI-3 composite), 210 MPa (for PI-5 composite), and 165 MPa (for PI-10 composite). Small amount of inorganic (1%) increased the strength of organic-inorganic

hybrid which is natural for interfacial interaction. OMMT decreased the elongation at break% of the composite films due to the brittle behaviour of clay.
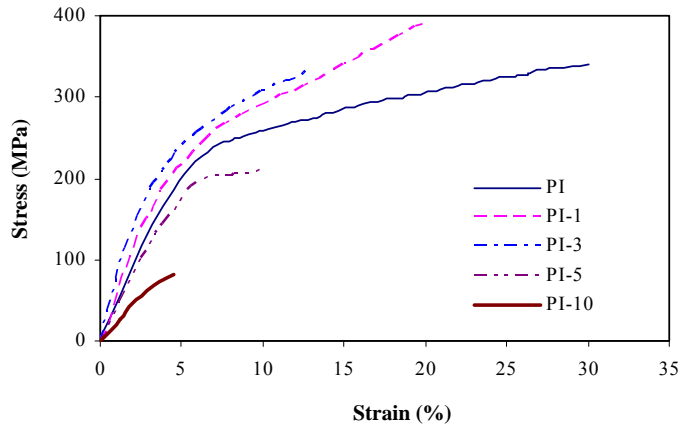

Fig. 3. Tensile properties of various PIs.

4.2. *Thermal properties of PI-clay nanocomposites*
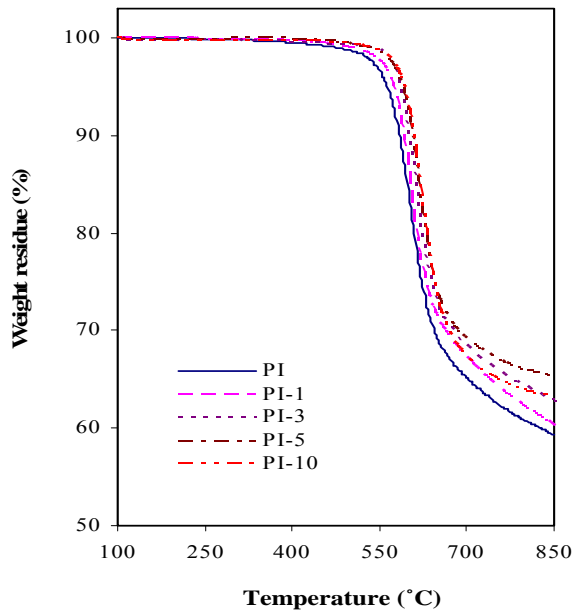

Fig. 4. TGA of various PIs.

TGA was recorded for PI-inorganic nanocomposites to monitor the effect of OMMT on the thermal properties. In case of PI-OMMT nanocomposites, the 5 and 10% degradation temperature (T_5, T_{10}) showed that the thermal stability of the PI-films was enhanced by the incorporation of the clay nanolayers. The pristine PI T_5, T_{10} temperatures are about 563 and 583˚C which became 573, 590˚C; 586, 599˚C; 589, 606˚C; 590, 607˚C after adding 1 to 10% OMMT (Fig. 4). The initial decomposition of fully aromatic polyimide is accompanied by the volatilization of carbon dioxide. The clay nanolayers, which dispersed homogeneously into PI, prevent the permeability of volatile degradation products out from the material and create delayed decomposition of PI [15, 16]. Weight of residue% of pristine PI at 800°C is ~ 60.8% which became about 62.2, 64.3, 65.9, 63.8% after adding various ratios of OMMT in PI-OMMT (1-10%) nanocomposites. Higher residue also indicated the higher thermal stability of composites than pristine PI.

4.3. *Dynamic mechanical analysis (DMA) of PI-OMMT nanocomposites*

The viscoelastic properties of the composites were studied using DMA. The storage modulus (E'), loss modulus (E'') and tan δ were measured for PI-OMMT nanocomposites (Fig. 5). The presence of inorganic increased the glass transition temperature (T_g) of the PI-inorganic nanocomposites in comparison with the neat PI. The
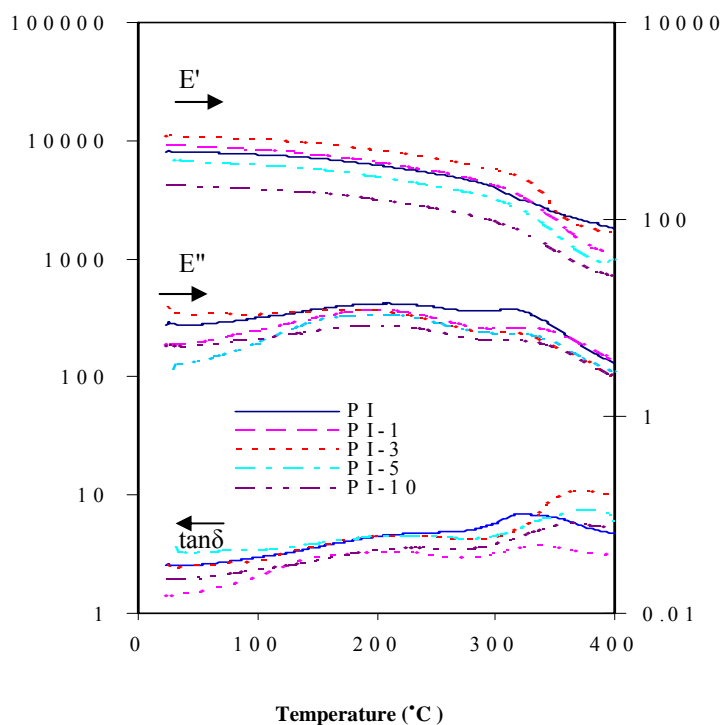

Fig. 5. DMA of various PIs.

surface treatment of MMT maximize the adhesion between polymer-inorganic surfaces and the nanometer size of inorganic restricts the segmental motion near the organic-inorganic interface. The storage modulus at room temperature from DMA is 8.0 GPa which became 9.0, 10.8, 6.6, 4.1 GPa after inclusion of OMMT (1-10%). At 3% OMMT, the PI-OMMT nanocomposites showed the highest modulus due to the maximization of attraction between OMMT and PI. The aggregation of OMMT decreased the modulus of PI-5, PI-10 composites. T_g of pristine PI is 311°C from E'' and 321°C from tanδ. The presence of OMMT into PI-OMMT nanocomposites increased the T_g like 322, 345, 326, 320°C from E" and 340, 377, 376, 369°C from tanδ after adding 1, 3, 5, 10% OMMT.

5. Conclusions

PI-clay nano-composites where MMT was dispersed at the molecular level were prepared with poly(amic acid) precursor of BPDA-PDA and various ratio of OMMT. As seen from XRD patterns, the nanocomposite films had special structure exhibiting exfoliated silicate layers with homogeneous dispersion of small contents (1, 3%) of MMT. These results suggest that the PI-clay nanocomposite could be classified as an exfoliated nanocomposite. Because of this special structure, the PI-clay nanocomposites showed a marked improvement in mechanical and thermal properties. Due to the homogeneous dispersion of clay nanolayers and their reinforcement with PI, the tensile modulus and tensile strength of the composite films were enhanced. T_g of the nanocomposites were higher than that of the pristine polyimide. The nanocomposites have higher thermal stability when compared to pristine polyimide. Generally, at 1, 3% of clay loading, the polyimide-clay nanocomposites showed prominent balance in properties concerning the modulus, T_g and thermal stability.

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