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Phosphonium modified clay/polyimide nanocomposites

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Abstract. In this study, octyltriphenylphosphonium bromide [OTPP-Br] was prepared from the reaction of triphenylphosphine and 1-bromooctane. The modification of clay was done by ion exchange reaction using OTPP-Br in water medium. Poly(amic acid) was prepared from the reaction of 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-Oxydianiline (ODA). Polyimide(PI)/clay hybrids were prepared by blending of poly(amic acid) and organically modified clay as a type of layered clays. The morphology of the Polyimide/phosphonium modified clay hybrids was characterized by scanning electron microscopy (SEM). Chemical structures of polyimide and Polyimide/ phosphonium modified clay hybrids were characterized by FTIR. SEM and FTIR results showed that the Polyimide/ phosphonium modified clay hybrids were successfully prepared. Thermal properties of the Polyimide/phosphonium modified clay hybrids were characterized by thermogravimetric analysis (TGA).

1. Introduction

Polyimide (PI) is one of the most important super-engineering materials because of its mechanical properties and its thermal stability [1-5]. Electronic industry is the typical extensive applications of polyimides including interlayer insulation films, buffer coating, films, alpha-ray shielding films, and alignment films for liquid crystal displays [1, 6-7].

The mechanical and thermal properties of polymers are generally improved by the addition of inorganic additives. The challenges in this area of high performance organic/inorganic hybrid materials are to obtain significant improvements in the interfacial adhesion between the polymer matrix and the reinforcing material since the organic matrix is relatively incompatible with the inorganic phase [8-9].

Clays are widely used in various areas of science. The use of clay in polyimide (PI) nanocomposites has attracted considerable attention in the field of materials science and technology [10]. Polyimide/organically modified clay nanocomposites appear as a material possessing improved tensile properties, thermal stability [11].

In order to disperse hydrophilic clay silicate layers into the hydrophobic polymer matrix, either the clay or the polymer need to be modified to enhance their compatibility. In practical purpose the first one is chosen, for its simplicity and better dispersion of clay layers into the polymer matrix. To make the clay compatible to the polymer matrix, bulky ions such as quaternary ammonium, quaternary phosphonium, and imidazolium are generally incorporated into the clay galleries. The choice of the modifier is based on the processing temperature of the nanocomposites and desired property in the final nanocomposites [11].

In this study, the modification of clay was performed by the incorporation of octyl triphenylphosphonium bromide into clay's interlayer spaces. We prepared poly(amic acid) from the reaction of 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-Oxydianiline (ODA). Polyimide-clay hybrids (nanocomposites) were prepared by blending poly(amide acid) and organically modified clay.



2. Materials and methods

2.1. Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-Oxydianiline (ODA) were purchased from Sigma-Aldrich and were desiccated under vacuum overnight at 120°C. N.N. Dimethylformamide (DMF) was also purchased. Clay was obtained from a local supplier. The composition of the clay is given in Table I.

2.1. Methods

2.1.1. Preparation of octyl triphenylphosphonium bromide

Octyl triphenylphosphonium bromide were prepared from poly(amic acid), according to reference [10]. A solution of 1-bromooctane(0.02 moles) and triphenylphosphine(0.04 moles) was heated under reflux for 24 hours and continuous stirring. The mixture was then cooled and the yellow product was filtered, washed with diethyl ether and then dried at room temperature for 24 hours. Preparation route to octyl triphenylphosphonium bromide is given in Figure 1.

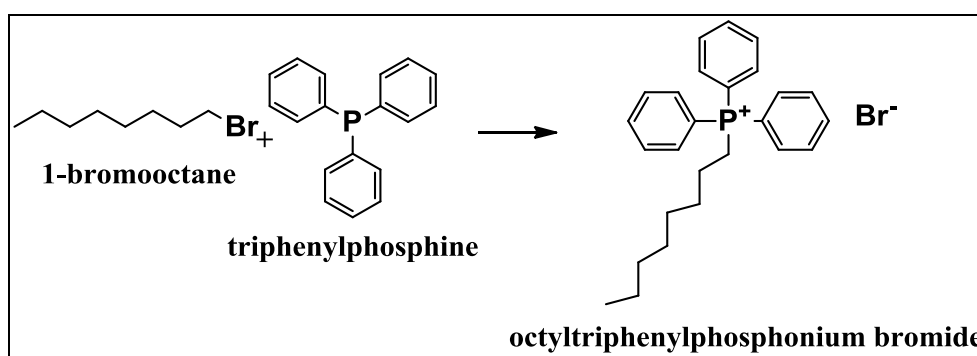


Figure 1. Preparation of octyl triphenylphosphonium bromide

2.1.2. Modification of the clay

Modification of clay was performed according to [12]. The clay was dispersed in 100 mL distilled water at 80 °C and stirred for 1h. A solution containing phosphonium salt with 70 mL distilled water was then added drop wise into suspension over a period of 10 min. The stirring was continued at the same temperature for 2h. The phosphonium modified clay was then filtered by using vacuum pump and washed distilled water to remove impurities and then dried at 100 °C for 24 h. The composition of clay can be seen in Table 1.

Table 1. Compositon of unmodified Clay

<i>Metal Oxides</i>	<i>Percent weight (%)</i>
SiO ₂	62.01
Al ₂ O ₃	15.21
Fe ₂ O ₃	6.58
CaO	1.19
MgO	2.28
K ₂ O	1.13
Na ₂ O	1.59

2.1.3. Preparation of BTDA-ODA polyimide films

BTDA-ODA films were prepared from poly (amic acid), according to [13]. In order to synthesis poly(amic acid) (PAA) solutions, ODA(0.01 moles) was firstly put into a flame dried three-neck flask containing 16 mL of DMF under a nitrogen purge. After ODA was fully dissolved in DMF,

bonds, respectively. After modification of clay, new peaks were observed in the FTIR spectrum. As can be seen in Fig. 3, the peaks at 2975 and 2855 cm^{-1} belong to the $-\text{CH}_2$ and $-\text{CH}_3$ of the groups of the octyl moiety. Moreover in this spectrum the peak at 1629 cm^{-1} can be attributed to the aromatic double bonds. These newly formed peaks prove that octyl triphenylphosphonium bromide was successfully intercalated between the layers of clay.

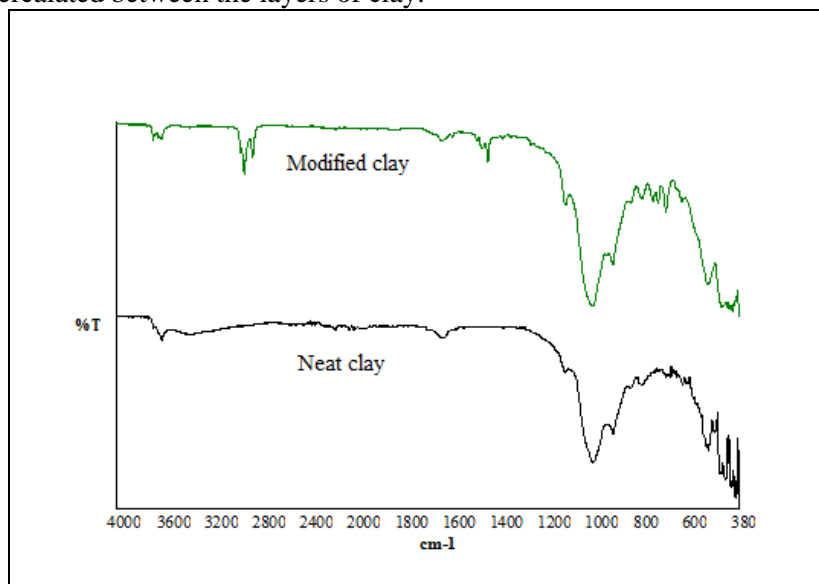


Figure 3. The FTIR spectra of neat clay and modified clay

4.2. Polyimide/PI-composite Synthesis

The FTIR spectra of PAA, PI and PI/clay composite are given in Figure 4. In the spectrum of PAA, the characteristic amide bonds stretching were found at 1660 cm^{-1} . After imidization this amide carbonyl peak was completely disappeared, indicating the full imidization. Moreover the spectrum of PI displays the characteristic carbonyl groups at around 1780 and 1715 cm^{-1} . When modified clay was incorporated into PI matrix, these carbonyl groups were slightly shifted. This can be attributed to the interactions between clay and PI. Also it can be interpreted that this situation is a result of the good dispersion of clay owing to the organophilic octyl groups.

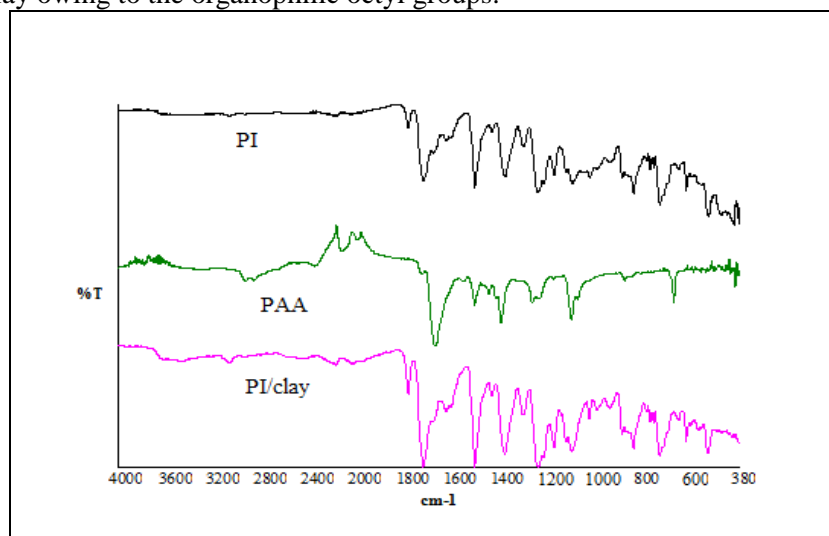


Figure 4. The FTIR spectra of PAA, PI and PI/clay composite

4.3. Thermo-gravimetric analysis

Thermal stability of the clay-PI composite was characterized by TGA under nitrogen atmosphere. The TGA spectra of PI and PI-clay composite are given in Figure 5. As can be seen the addition of phosphonium modified clay was found to improve the thermal stability of neat PI. The onset degradation temperature of neat clay was 480 degrees while it was shifted to 500 degrees when 3 wt. % clay was added. Moreover the maximum weight loss temperature of the composite PI was also higher than that of pure PI. The char yields of the PI and PI-Clay composite films were also collected at 750 degrees. As expected the char yield of the composite films produced more char than BTDA-ODA PI films. Thus it can be said that the addition of octyl triphenylphosphonium salt modified clay not only dispersed well in the organic PI matrix, it also improved the thermal properties of PI.

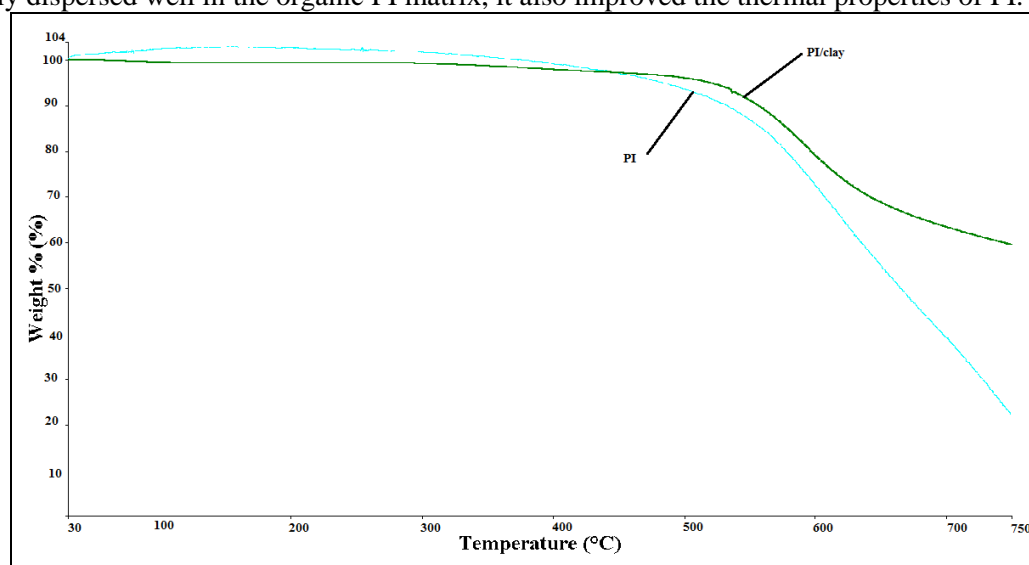


Figure 5. TGA spectra of PI and PI-clay composite

4.4. SEM analysis

The surfaces of PI and polymer film are normally investigated by means of the SEM technique. SEM micrographs of PI and PI/Clay films were given in Figure 6 from which obvious differences can be observed. Figure 6 show that the pure PI film has a very smooth surface. Surface roughness in nanocomposite increased with respect to pristine polyimide. It can be clearly seen that the particles (clay) are distributed uniformly in the polymer matrix for the hybrid film containing 3 wt % of clay.

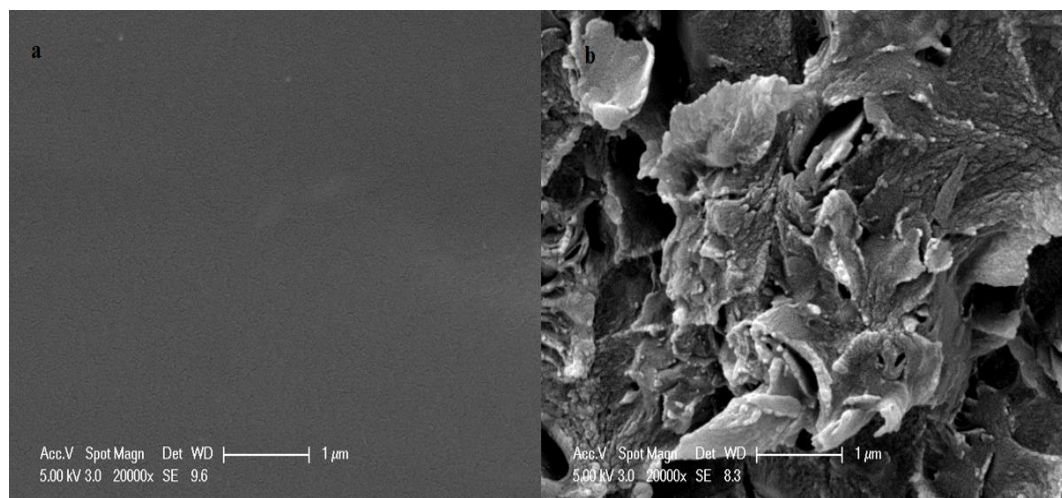


Figure 6. SEM micrographs of a) pristine PI and b) the PI/clay film

5. Conclusions

Clay has been modified using octyl triphenylphosphonium bromide. The modified clay was characterized by using FTIR spectroscopy and TG analysis. FTIR spectra show that phosphonium salt is successfully intercalated into the interlayer of clay. Thermal stability of PI/modified clay film with appropriate clay content was better than this of original PI film. Morphology study with scanning electron microscopy showed that the surface roughness in nanocomposite increased with respect to pristine polyimide.

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