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Synthesis and properties of polybenzoxazole–clay nanocomposites

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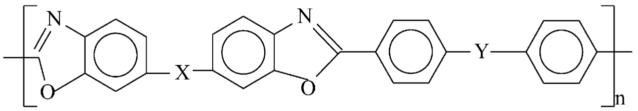
Abstract

A novel polybenzoxazole (PBO)/clay nanocomposite has been prepared from a PBO precursor, polyhydroxyamide (PHA) and an organoclay. The PBO precursor was made by the low temperature polycondensation reaction between isophthaloyl chloride (IC) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane with an inherent viscosity of 0.5 dl/g. The organoclay was formed by a cation exchange reaction between a Na^+-montorillonite (Na^+-Mont) clay and an ammonium salt of dodecylamine. The PHA/clay was subsequently thermal cured to PBO/clay. Both X-ray diffraction and transmission electron microscope analyzes showed that the organoclay was dispersed in the PBO matrix in a nanometer scale. The in-plane coefficient of thermal expansion (CTE) of PBO/clay film decreased with increasing amounts of organoclay. The CTE of PBO/clay film containing 7 wt% clay was decreased by 21% compared to the pure PBO film. Both of the glass transition temperature (T_g) and the thermal decomposition temperature of PBO/clay increased with increasing amounts of organoclay. The thermal decomposition temperature and the T_g of PBO/clay containing 7 wt% clay increased to 12 and 16 °C, respectively. © 2002 Published by Elsevier Science Ltd.

Keywords: Nanocomposite; Polybenzoxazole; Organoclay

1. Introduction

Polybenzoxazoles (PBOs) are a class of heterocyclic polymers with properties similar to polyimides. They all have excellent thermal stability, high mechanical properties, and superior chemical resistance [1–4]. The general structures of PBOs are shown in the following



where X, Y could be O, $C(CF_3)_2$, $C(CH_3)_2$, CO, etc. Unlike polyimides, PBOs do not possess polar carbonyl groups in their backbones, so they have lower water absorption and dielectric constant than polyimides. They are more suitable for use in the microelectronic industry as buffer coatings in IC chips, interlayer dielectrics for multilayer electronic devices, substrates for flexible printed circuit board and tape automatic bonding, and high-end electronic packaging materials [5–7].

Like the polymeric materials in general, PBOs have much higher CTEs than that of other inorganic and metallic materials (e.g. silicon chip and copper foil). When they are used in the applications mentioned earlier, the mismatch in CTEs results in warpage and cracking in the products. A common method to address this problem involves using molecular design to adjust the structures of PBOs to lower their CTEs. However, it is necessary to synthesize new monomers to achieve this goal, and that is very expensive and tedious. A novel and economical approach to reduce the CTE is by the addition of a small amount of nano-dispersed organoclay to polymeric materials. Due to the high surface to volume ratio of the nano-dispersed clay, the thermal expansion and contraction of polymer molecules are highly restricted, which can effectively reduce their CTEs [8–11]. The purpose of our research is to develop PBO/clay nanocomposites with lower CTEs for microelectronic applications.

2. Experimental

2.1. Materials

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BisAPAF) was purchased from Chriskev Company (USA). Isophthaloyl chloride (IC) was obtained from Aldrich and dried under vacuum at 60 °C for 24 h before use. Anhydrous *N*-methylpyrrolidone (NMP) and pyridine were obtained from Aldrich and used without further purification.

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Na^+-montmorillonite clay with a cation-exchange capacity of 95 mequiv./100 g was supplied by Pai Kong Co. (Tauyan, Taiwan). Dodecylamine (DOA) and dimethylacetamide (DMAc) were obtained from Aldrich.

2.2. Preparation of organoclay

In a 2000 ml beaker, 10 g of montmorillonite was added to 800 ml of water and stirred vigorously for 1 h. In another 500 ml beaker, 0.69 g of concentrated HCl was added to 200 ml water and then 3.52 g of DOA was added and stirred until dissolved. The solution was added to the montmorillonite suspension and stirred vigorously at 80 °C for 3 h. After the cation exchange reaction, the montmorillonite was collected by filtration and repeatedly washed with deionized water until no AgCl precipitate could be seen in the filtrate when it was titrated with 0.1N $AgNO_3$. The montmorillonite was dried at 80 °C in a vacuum oven for 24 h. It was ground and screened with a 325-mesh sieve. The clay was designated as DOA-Mont.

2.3. PBO precursor synthesis

A typical preparation of BisAPAF-IC poly(hydroxyamide) (PHA) precursor proceeds as follows. To a dry 250 ml three-necked flask equipped with a nitrogen inlet and mechanical stirrer were added 5.21 g (14.24 mmol) of BisAPAF, 2.25 g (28.48 mmol) of pyridine and 50 g of anhydrous NMP. After the BisAPAF was completely dissolved, the solution was cooled to 5 °C with ice water and 2.89 g (14.24 mmol) of IC was added slowly to the solution. After complete addition, the reaction mixture was stirred at room temperature for 16 h. The resulting viscous solution was added dropwise to 1 l of stirring water. The precipitated polymer was collected by filtration, washed with methanol, and then dried in a vacuum oven at 80 °C for 24 h.

2.4. Preparation of PBO/clay nanocomposites

A representative 5 wt% clay loading PBO/clay nanocomposite was prepared as follows. In a 200 ml beaker, 0.15 g of DOA-Mont clay was mixed with 10 g of DMAc and stirred vigorously for 12 h. In another three-necked flask equipped with a mechanical stirrer were added 3 g of BisAPAF-IC PHA and 10 g of DMAc; the mixture was stirred until BisAPAF-IC PHA was dissolved. The DOA-Mont solution was then added to the polymer solution and stirred vigorously for 6 h to form a PHA/clay solution with a solids content of 13%. The solution was coated on a glass plate with a doctor knife and dried in a vacuum oven at 80 °C for 16 h. The dried PHA/clay film was further heated in a high temperature oven in air at 350 °C for 1 h to give the PBO/clay nanocomposite.

2.5. Characterization

FTIR spectra were recorded on a Jasco model 460 FTIR Spectrometer. ^1H NMR spectra were recorded on a Brucker Advance 600 Spectrometer using dimethyl sulfoxide-d_6 as solvent. The inherent viscosity was measured using a Cannon-Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dl in NMP at 30 °C. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Model Q500 at a heating rate of 10 °C/min under nitrogen. The in-plane coefficients of thermal expansion (CTEs) were determined on a TA Instrument Thermal mechanical Analyzer (TMA) model 2940 at a heating rate of 5 °C/min in nitrogen under a force of 0.1 N. The glass transition temperature (T_g) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C/min under nitrogen. X-ray diffraction (XRD) experiment was conducted on a Rigaku D/MAX-IIIV X-ray Diffractometer using Co Kα radiation. The samples for transmission electron micrograph (TEM) study were prepared by placing PBO/clay films in an epoxy resin and curing the resin at 70 °C overnight. The cured epoxies containing PBO/clay were microtomed with a diamond knife into 70 nm thick slices and placed on a 200-mesh copper grid and examined with a Zeiss 10 C TEM using an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Preparation of organoclay

In order to improve the dispersion of clay in the polymer matrix, the hydrophilic Na^+-montmorillonite was treated with the ammonium salt of DOA to form an organoclay. The reaction is shown in Scheme 1.

This kind of treatment has been reported by Yano et al. for the preparation of polyimide–clay nanocomposite [8,12]. Fig. 1 shows the XRD curves of Na^+-montmorillonite and organoclay in the region $2\theta = 2–10°$. The curve of the original Na^+-montmorillonite has a peak at $2\theta = 6.95°$ which corresponds to an interlayer spacing of 12.7 Å, and the curve of organoclay has a peak at $2\theta = 4.88°$ which corresponds to an interlayer spacing of 18.1 Å. The result implied that the organoclay has been swelled by the ammonium ion of DOA and has a larger interlayer spacing than the original Na^+-montmorillonite. The increase of interlayer spacing helps the polymer molecules to intercalate the clay.

3.2. Preparation of PBO precursor

Similar to polyimides, most PBOs are insoluble in common organic solvents. In this study, we chose two commercially available monomers, BisAPAF and IC, to

$$Na^+\text{-Mont} + RNH_3^+Cl^- \longrightarrow RNH_3^+\text{-Mont} + NaCl$$

R = dodecyl

Scheme 1. Reaction of ammonium salt of DOA and Na^+-montmorillonite.

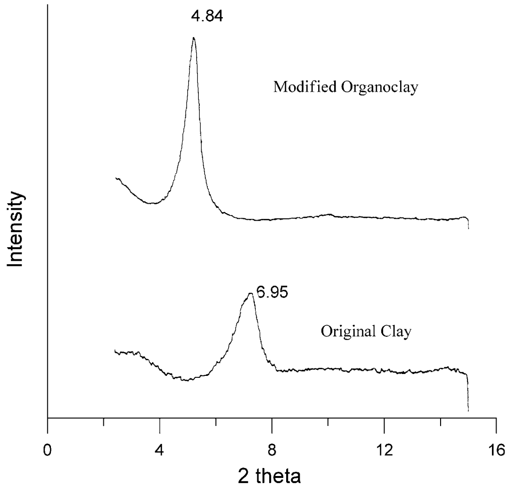


Fig. 1. XRD patterns of Na^+-montorillonite and organoclay.

prepare the PBO/clay nanocomposite. Although the BisAPAF-IC PBO possesses the hexafluoropropylidene group and the 1,3-phenylene linkage in the backbone, it is not soluble in most common organic solvents [3,13]. However, its precursor, BisAPAF-IC PHA, is soluble in most organic solvents. So we synthesized the PBO/clay nanocomposite from its soluble precursor, PHA, and converted it to the PBO composite by thermal cyclization. The soluble PHA was synthesized from the reaction of IC and BisAPAF at 5 °C in anhydrous NMP. The inherent viscosity of the polymer was 0.5 dl/g measured at 30 °C in NMP at a concentration of 0.5 g/dl. The formation of PHA was confirmed by IR and ^{1}H NMR spectra as shown in Figs. 2(a) and 3. The polymer exhibited a broad absorption band at 3400–3100 cm^{-1} due to amino (N–H) and hydroxyl (OH) groups and a strong carbonyl absorption at 1650 cm^{-1} in IR spectrum [14]. The ^{1}H NMR spectrum of the polymer also showed the hydroxyl (10.4 ppm) and amino (9.8 ppm) groups [15].

3.3. Preparation of PBO/clay nanocomposites

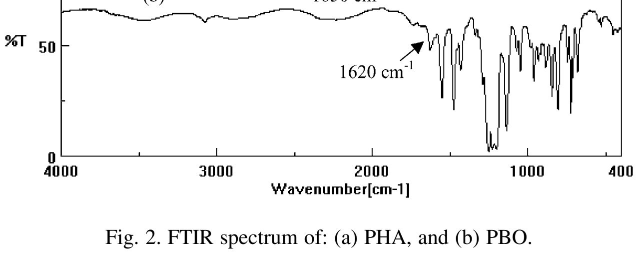


Fig. 2. FTIR spectrum of: (a) PHA, and (b) PBO.

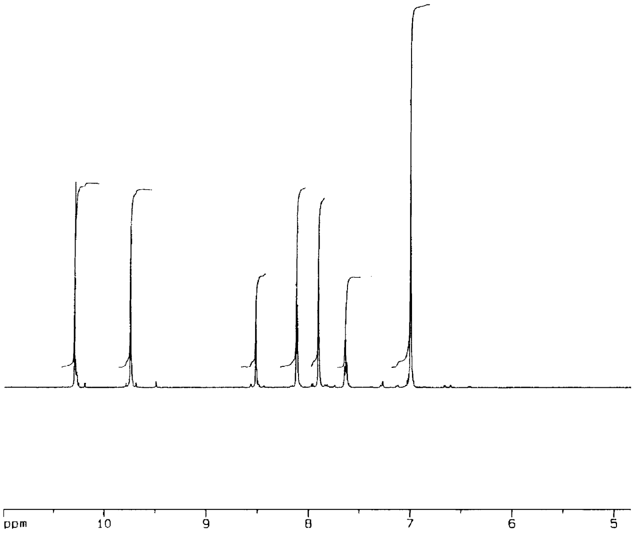
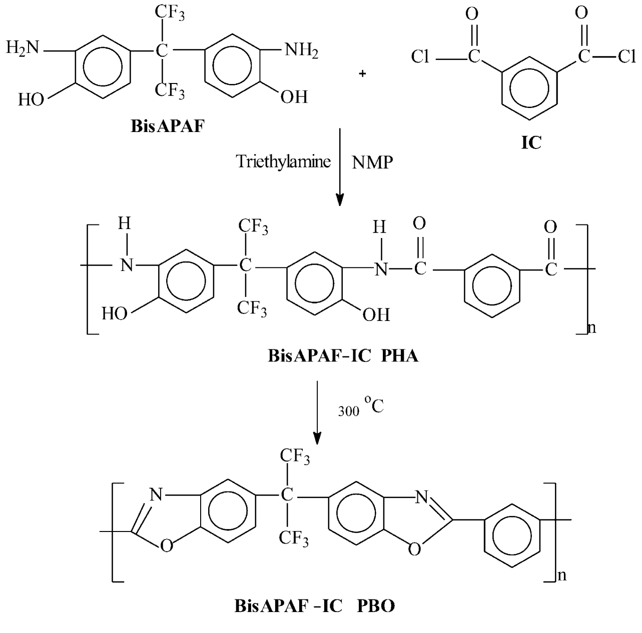


Fig. 3. ^{1}H NMR spectrum of PHA.

To improve the dispersion of organoclay in the PHA matrix, the organoclay was first dispersed in DMAc solvent to make a suspension. After the PHA was dissolved in DMAc, the clay suspension was added to polymer solution and stirred vigorously to obtain a homogeneous mixture. The PHA/clay film was obtained from solution casting and dried at 80 °C under vacuum. The final PBO/clay nanocomposite was obtained by heating the film at 350 °C to form a benzoxazole ring. The two-step reaction of producing PBO is shown in Scheme 2. The dehydrative cyclization of PHA to form a benzoxazole ring was confirmed by the disappearance of the broad absorption of 3400–3100 and 1650 cm^{-1} and by the appearance of a new characteristic absorption of benzoxazole ring at 1620 cm^{-1} in IR spectrum (Fig. 2(b)) [14]. The XRD curves of 1–7 wt% organoclay/PBO films are shown in Fig. 4. They do not show any diffraction peak in $2\theta = 2$–10°. This indicates the possibility of having exfoliated silicate layers of



Scheme 2. Two-step synthesis of BisAPAF-IC PBO.

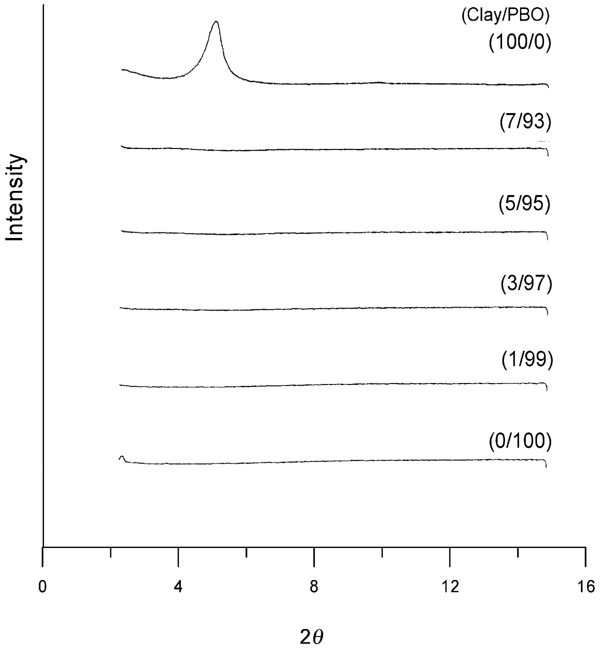


Fig. 4. XRD patterns of PBO/clay nanocomposites.

organoclay homogeneously dispersed in the PBO matrix. A TEM of 5 wt% organoclay/PBO film (Fig. 5) further supports that the organoclay is dispersed randomly in the PBO matrix in a nanometer scale. The estimated size of the silicate sheets is ca. 1 nm in thickness and ca. 50–300 nm in length.

Fig. 5. TEM of 5 wt% PBO/clay nanocomposite.

Table 1
Thermal properties of PBO/clay nanocomposites

Contents of clay (wt%)	CTE (μm/m °C)[a]	T_g (°C)[b]	Decomposition temperature (°C)[c]
0	48.3	314	513
1	44.6	320	517
3	43.5	324	519
5	39.9	329	522
7	38.3	330	525

[a] In-plane CTE measured by TMA at a heating rate of 5 °C/min in nitrogen under a force of 0.1 N.
[b] Temperature at 5% weight loss in nitrogen.
[c] Measured by DSC at a heating rate of 20 °C/min in nitrogen.

3.4. Properties of PBO/clay nanocomposites

Using an extension probe on a TMA, the in-plane CTEs of the PBO/clay films with different clay loading were able to be measured (Table 1). As the amount of the clay increases, the CTE decreases accordingly. The CTE of PBO/clay film was decreased by 21% compared to the pure PBO film when 7 wt% clay was added. The result showed that the addition of a small amount of organoclay could decrease the CTE of PBO. Due to the fact that PBO/clay films were not thick enough, the out-of-plane CTEs could not be measured reproducibly and accurately by using an expansion probe.

The thermal stability of PBO/clay nanocomposites was studied by TGA under nitrogen. The 5% weight loss temperatures of the nanocomposites increased with the amount of clay added as shown in Table 1. It was found that the 5% weight loss temperature increased 12 °C when 7 wt% clay was added. The results showed that the organoclay could slightly increase the thermal stability of PBO. The glass transition temperatures of PBO/clay nanocomposites are given in Table 1. The T_g also increased with increasing amounts of clay. It increased 16 °C when 7 wt% clay was added. The results indicated that the mobility of PBO molecules was restricted by the nano-dispersed organoclay.

Due to the insolubility of the BisAPAF-IC PBO in common organic solvents, the PBO/clay nanocomposite can only be prepared by a two-step method. However, through the incorporation of some specially synthesized monomers, such as 2,2-bis(4-carbonyl chloride benzene)-1,1,1,3,3,3-hexafluoropropane or 4,4′-oxydibenzoyl chloride, the resulting PBOs are soluble in NMP [3,13]. In this case, it is possible to prepare the PBO/clay nanocomposites through a single step synthesis by using these organosoluble PBOs, which will be our future research works.

4. Conclusions

A novel PBO/clay nanocomposite has been synthesized from a polyhydroxyamide and a clay which was intercalated with an ammonium salt of DOA. The PHA/clay was converted to the PBO/clay by thermal cyclodehydration.

Both of the XRD and TEM data indicate that the clay was dispersed in the polymer matrix at a nanometer scale. The CTE of the nanocomposite was decreased and the thermal stability and the T_g were increased with the addition of a small amount of clay. Combining the excellent physical and chemical properties of PBO and the high reinforcement effect of the nano-dispersed clay, the PBO/clay nanocomposites could find wide applications in microelectronic industry.

Acknowledgements

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