



Nano-boria reinforced polyimide composites with greatly enhanced thermal and mechanical properties via in-situ thermal conversion of boric acid



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ABSTRACT

High performance materials with excellent thermal stability and mechanical properties are highly required in high temperature area. The addition of inorganic particles is effective to improve the thermal and mechanical properties of polymers. In this work, B₂O₃ nanoparticles and their polymeric composites, B₂O₃/PI composite films, were formed by an in-situ thermal conversion. The morphology of B₂O₃/PI composite films were investigated by SEM, EDS and TEM. TGA and DMA were used to monitor the thermal properties of B₂O₃/PI composite films. The mechanical properties of the B₂O₃/PI composite films were characterized by tensile testing. The results indicated that the addition of B₂O₃ nanoparticles could significantly improve the thermal and mechanical properties of B₂O₃/PI composite films.

1. Introduction

Polyimides (PIs) possess outstanding mechanical properties, thermal stabilities and chemical resistance and are widely used in the fields of coating, aerospace, filtrations, adhesives, protective clothing, composites, electric and photonic applications [1,2]. Many efforts are made to improve the mechanical and thermal properties of PIs, such as copolymerization [3–5], blending [6], incorporation of heterocyclic units [7–13] and addition of inorganic particles [14–20].

Boron oxide (B₂O₃) is well-known for its super hardness [21], low thermal expansion [22], good flame retardant [23], and high thermal stability [24]. Polat and Kaynak incorporated B₂O₃ particles into nylon-6 to improve the flame retardancy and elastic modulus [25]. Kahraman et al. prepared B₂O₃/PI composites with improved thermal stability and flame retardancy [24]. However, both the B₂O₃/nylon-6 and B₂O₃/PI composites exhibited decrease in tensile strength. The reason could be the de-bonding, the poor compatibility and the poor load transfer efficiency between particles and matrix due to the large particle size (0.5–3 μm [24], 14.3–47.7 μm [25]).

In this work, B₂O₃ nanoparticles were incorporated into the PI matrix by an in-situ thermal conversion from boric acid in PAA matrix into B₂O₃/PI composites. Due to the excellent compatibility of boric acid and PAA, the resultant small B₂O₃ particles could be homogeneously distributed in the PI matrix and therefore significantly improved the thermal and mechanical properties of the B₂O₃/PI composites.

2. Experimental

The preparation of the B₂O₃/PI composite films was briefly described as following (Fig. S1) and detailed experimental information could be found in Supporting Information.

- 1) The polyamic acids (PAAs, 10 wt%) of 3,3',4,4'-biphenyltetracarboxylic dianhydride/4,4'-diaminobiphenyl (BPA-PAA, 5.1 dL/g) and 3,3',4,4'-biphenyltetracarboxylic dianhydride/4,4'-oxydianiline (ODA-PAA, 4.0 dL/g) in N, N'-Dimethylacetamide (DMAc) were synthesized according to our previous reports [6]. Equimolar BPA-PAA and ODA-PAA were mixed and diluted into 3.5 wt% blend-PAA (B-PAA) by DMAc.
- 2) Different amounts of H₃BO₃ were mixed with B-PAA solution (3.5 wt%).
- 3) H₃BO₃/B-PAA solutions were casting into films and then imidized with programmed protocol. During this process, PAA and H₃BO₃ were convert into PI and B₂O₃ respectively [24,26,27].

The corresponding samples with amounts of H₃BO₃ of 0, 1, 3, 4, 4.5, 5, 5.5, 6 and 7 wt% were designated as Bx-PAA and Bx-PI (x= 0, 1, 3, 4, 4.5, 5, 5.5, 6 and 7) in the following. Without special explanation, all the Bx-PI composite film means that the samples were imidized under 370 °C.

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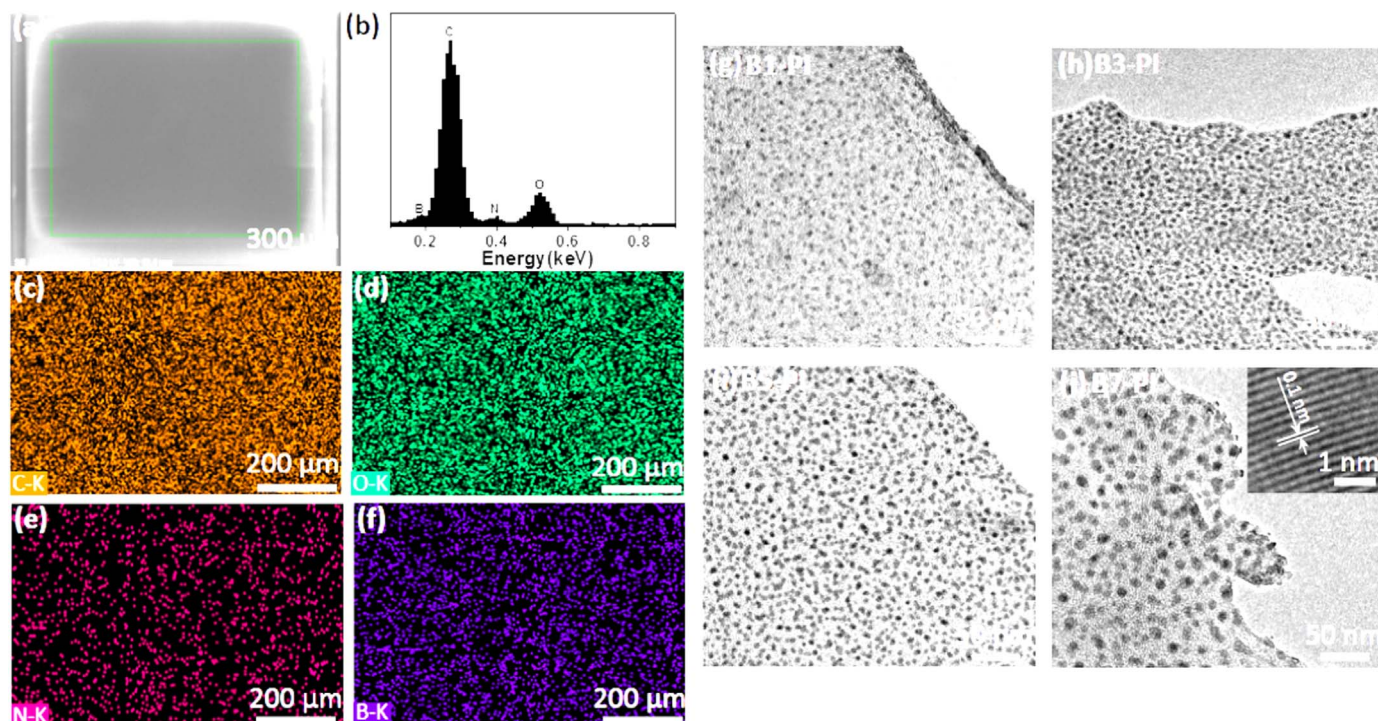
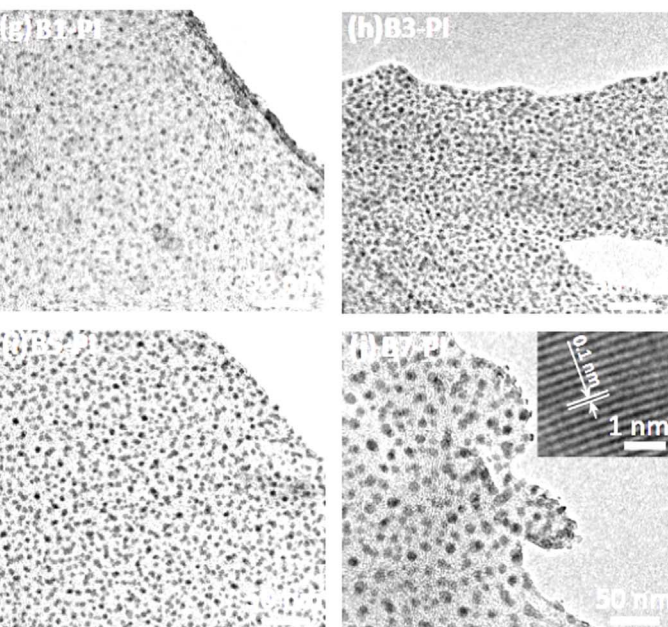


Fig. 1. Elements mapping of B5-PI (a-f), and TEM images (g-j) of Bx-PI. Insert of (d) shows the higher magnification of the particle.

3. Results and discussion

The B5-PI composite film exhibited smooth surface that no big particles and no cracks were observed (Fig. 1a) and uniform thickness of $20 \pm 5 \mu\text{m}$ (Fig. S2). EDS spectra confirmed the presence of boron elements (Fig. 1b). Further elements mapping on C, O, N and B proved the homogeneous distribution of B element in the composite film (Fig. 1c-f). TEM images showed detailed information about the morphology and distributions of B_2O_3 particles in the films (Fig. 1g-j). All the samples showed no aggregation, homogenous dispersion of particles in the films and no tiny voids between the particles and matrix. As the amount of H_3BO_3 increased from 1 to 7 wt%, the B_2O_3 particles grew bigger from $2.37 \pm 0.5 \text{ nm}$ to $4.40 \pm 0.81 \text{ nm}$ (Table S1), but all these sizes are much smaller than the previous reports ($0.5\text{--}3 \mu\text{m}$ [24], $14.3\text{--}47.7 \mu\text{m}$ [25]). High magnification image in Fig. 1j showed the lateral structure of the particle with lateral crystal size of around 0.1 nm , which was rarely observed in the previous reports with such low thermal treatment temperatures. Due to the increased particle size and the increased amount of H_3BO_3 , the specific number of particles per area first increased from 8218 to $9928 \mu\text{m}^{-2}$ and then decreased to $6788 \mu\text{m}^{-2}$ (Table S1). This quite small particle size and homogeneous distribution in the composite films could be attributed to the completely compatibility of H_3BO_3 and PAA solutions and the following in-situ thermal conversion.

TGA was used to characterize the thermal stabilities of the Bx-PI composite films. The H_3BO_3 was completely converted to boron oxide at around $350 \text{ }^\circ\text{C}$ (Fig. 2a), which is well agreed with the previous study [27]. The incorporation of B_2O_3 nanoparticles greatly increased the thermal stability of the Bx-PI composites that all the Bx-PI composites film exhibited 5% weight loss temperatures at least 40 and $20 \text{ }^\circ\text{C}$ higher than B0-PI in Ar and air, respectively (Fig. 2, Table 1). The B5-PI even possessed $T_{5\%}$ 74 and $61 \text{ }^\circ\text{C}$ higher than B0-PI in Ar and air, respectively. This significant improvement on the thermal stability could be attributed to the passivation of the carbon surface, the inhibition of physical blockage of active sites for oxidation probably by boron oxide and the formation of a glassy oxide residue above $450 \text{ }^\circ\text{C}$ [28–30].



For those materials with rigid backbone molecular structures, dynamic mechanical analysis (DMA) is efficient to measure the glass transition temperature (T_g) (Fig. 2c, Table 1). The B0-PI film showed a T_g of $300 \text{ }^\circ\text{C}$. As expected, the addition of B_2O_3 led to an increase of T_g in the range of $310\text{--}315 \text{ }^\circ\text{C}$. The increase of T_g could be attributed to the restriction of B_2O_3 particles to the segmental movement of the PI chains [31–33] and the decrease of the free volume of the hybrid composites [15], which are normally observed in other organic-inorganic nanocomposites [34].

The incorporation of B_2O_3 nanoparticles greatly improved the mechanical properties of the composite films (Fig. 3a, Table 1). As the amount of B_2O_3 increased, the tensile strength and modulus first increase and then decrease. The B5-PI composite film exhibited the highest tensile strength (δ) of $339.77 \pm 11.91 \text{ MPa}$ and modulus (E) of $3.43 \pm 0.05 \text{ GPa}$, 70% and 57% higher than B0-PI film ($\delta=199.74 \pm 8.79 \text{ MPa}$, $E=2.18 \pm 0.01 \text{ GPa}$), respectively. Further increasing the amount of B_2O_3 led to a slight decrease of δ and E , but still much higher than those of B0-PI film. Generally, the addition of inorganic fillers would lead to a decrease of the elongation at break (ϵ) and toughness of the composite films [16,18,35,36]. However, the Bx-PI composite films showed an increased ϵ and toughness. B5-PI composite film showed the highest ϵ of $63.52 \pm 2.78\%$ and toughness of $117.19 \pm 3.56 \text{ J/g}$, 31% and 143% higher than those of B0-PI film. The great improvement in mechanical properties could be due to the homogeneous distribution of particles, the very fine particle size and the strong interfacial interaction between B_2O_3 and PI matrix (Fig. 1g-j).

In addition, the imidization temperatures were also found playing important role on the mechanical properties and the particle morphology of the Bx-PI composite film. Take B5-PI composite film for example, when the temperature increased to $430 \text{ }^\circ\text{C}$, B5-PI composite film showed a decrease on the mechanical properties that the tensile strength, modulus, elongation at break and toughness were $273.04 \pm 1.51 \text{ MPa}$, $2.67 \pm 0.07 \text{ GPa}$, $54.82 \pm 0.40\%$ and $73.83 \pm 0.11 \text{ J/g}$, respectively, which were 20% , 22% , 14% and 37% smaller than the corresponding sample imidized at $370 \text{ }^\circ\text{C}$ (Fig. 3b and Table 1). As the imidization temperature increased to $430 \text{ }^\circ\text{C}$, the particle size increased

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