

Preparation and characterization of flame retardant and proton conducting boron phosphate/polyimide composites

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ABSTRACT

In this study novel flame retardant boron phosphate (BPO₄)/polyimide composites were prepared. 4,4'-Oxydianiline (ODA) was reacted with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) in dimethyl formamide (DMF) and mixed with BPO₄ particles to obtain a series of polyamic acids, meanwhile, corresponding polyimides were synthesized via the thermal imidization technique. The amount of BPO₄ in the composite films was varied from 0 wt% to 10 wt%. The structure, thermal and surface properties of the polyimide films were characterized by means of ATR-FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The flame retardancy of the composite materials was examined by limiting oxygen index (LOI) measurements and UL-94 VTM tests. Result showed that the LOI values of composites increased from 28 to 39. Furthermore, proton conductivity of polyimide films was measured by the four probe technique. The composite membrane containing 3 wt% of BPO₄ showed a conductivity of 0.4 mS/cm at room temperature.

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1. Introduction

Polyimides are widely used in aerospace, microelectronic, coating, composite, fiber and photonic applications due to their outstanding thermal, mechanical and electrical properties in addition to their excellent chemical and radiation resistance [1–3]. On the other hand, due to rapid developments in technological and industrial applications, polyimides with enhanced properties and unique functions are needed [4]. Thus, in recent years, in order to improve several properties of polyimides, preparation of polyimide composites has become of great importance. Al₂O₃ [4], clay [5,6], silica [7], Eu₂O₃ [8], carbon nanotubes [9], titania [10], sodalite [11], BaTiO₃ [12], silver [13] and aluminum nitride [14] are only a small number of the inorganic additives used in polyimide composites.

Although, polyimides are inherently fire resistant to some extent, it is desired to increase their thermo-oxidative stability and flame retardancy properties for certain applications. Flame retardancy of polyimides can be enhanced by using either flame retardant monomers such as phosphine oxide containing diamines [15] or using inorganic fillers. For instance, A. B. Morgan and S. Putthanarat [16], investigated the flame retardancy and the thermal stability of alumina, silica, graphite particles and carbon nanofibers

containing polyimides. J. Liu et al., prepared polyimide (BTDA–ODA)/silica composites and found that when 20 wt% of silica was introduced to polyimides, limiting oxygen index values could be increased up to 37 [17]. In another study, zinc borate nanoparticles were incorporated into polyimide matrix and an enhancement in the thermal stability of the nanocomposites was observed [18].

Boron phosphate (BPO₄) is a white solid which belongs to the class of orthophosphates. In the chemical structure of BPO₄, PO₄ and BO₄ groups are tetrahedrally linked by shared oxygen atoms and form a three dimensional network [19]. It is an effective catalyst for dehydration reactions [20] and also it is used as a phosphating agent for various metals [21,22]. Its catalytic properties were also investigated for the decomposition of dichlorodifluoromethane [23]. Besides, it was used as an additive in glass and ceramic production [24,25]. It has been proved that boron phosphate is a good flame retardant additive due to its low cost, low toxicity and reduced smoke generation [26]. It was used as a flame retardant for acrylic resins [26], polysiloxanes [27], polypropylene [28] and polyamides [29]. Furthermore, in recent years boron phosphate has found application in fuel cell membranes, owing to its proton conductivity in the presence of water [19,30–33]. The addition of boron phosphate to sulfonated polyether ether ketones (SPEEK) resulted in a five fold increase in proton conductivity [33].

To authors' best knowledge there are no published studies on boron phosphate/polyimide composites. The first goal of this study was to prepare boron phosphate containing polyimides and to

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investigate their flame retardant properties. Also it was aimed to investigate the potential use of these novel composite films as fuel cell membranes due to the proton conductivity of boron phosphate. First, boron phosphate particles were synthesized via the calcination of equimolar amounts of boric acid and phosphoric acid. Then BPO₄ particles were dispersed in BTDA–ODA polyamic acid solutions. Finally boron phosphate/polyimide composites were prepared by thermal imidization. Thermal properties of composites were investigated by TGA and DSC measurements. The effect of boron phosphate on the mechanical properties of the composites was investigated by tensile measurements. In order to assess the flame retardancy of the composites, LOI measurements and UL-94 VTM tests were carried out. The surface topology of the films was observed by a scanning electron microscope (SEM). Moreover, water uptake and proton conductivity of the membranes were investigated.

2. Experimental

2.1. Materials

4,4'-Oxydianiline (ODA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and dimethyl formamide (DMF) were purchased from Sigma Aldrich and used without further purification. Boric acid and phosphoric acid were provided by Merck.

2.2. Characterization methods

FTIR spectrum was recorded on Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer.

Mechanical properties of polyimide films were determined by standard tensile stress–strain tests to measure modules, ultimate tensile strength and elongation at break. Standard tensile stress–strain experiments were performed at room temperature on a Materials Testing Machine Z010/TN2S, using a crosshead speed of 2 mm/min.

Thermogravimetric analyses (TGA) of polyimide films were performed using a Perkin–Elmer Thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 to 750 °C with heating rate of 10 °C/min under air atmosphere and also char yields at 900 °C in nitrogen were collected with a heating rate of 20 °C/min.

DSC measurements were performed using Pyris Diamond DSC. Samples were run from 30 to 400 °C with a heating rate of 10 °C/min. Glass transition temperatures were obtained from the second heating scan.

The flammability characteristics of composites were determined by LOI and UL-94 VTM tests. The LOI values of the polyimide materials were measured by using an FTT (Fire Testing Technology) type instrument.

SEM imaging of the films were performed on Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and applying a gold coating.

The transmission spectra of the hybrid coatings were recorded in the wavelength range of 300–800 nm using a Shimadzu 3100 UV–vis–NIR spectrometer.

Since BPO₄ is conductive in the presence of water, it is very important to measure water absorption capacity of polyimide composite membranes. For the determination of water uptake of membranes, samples were first dried at 100 °C for 1 day in vacuum. Then dried polyimide films were weighed (M_{dry}). Afterwards membrane samples were immersed in distilled water for 24 h at room temperature. Then films were removed and water droplets on the surface of the films were wiped gently with a soft tissue paper. The samples were immediately weighed (M_{wet}). Water uptake was calculated using the following equation:

$$\text{Water uptake(\%)} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100$$

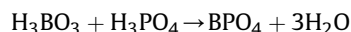
Proton conductivity measurements were recorded using a Gamry (Gamry Series G 750) Potentiostat/Galvanostat/ZRA with Gamry Framework software system v.4.3 model EIS300. EIS (electrochemical impedance spectroscopy) measurements were carried out in potentiostatic mode over the frequency range of 0.1 Hz–10⁵ Hz with amplitude of 5–50 mV potential. All experiments were measured after 100 s delay time. EIS spectra were analyzed with Echem Analyst 4.0 software. Membrane samples were kept in distilled water for 24 h at room temperature prior to testing. Membranes were fixed between two platinum electrodes in a Teflon® frame (BekkTech Conductivity Clamp) and proton conductivities were measured at ambient temperature. Conductivity measurement of fully hydrated membranes was carried out with the cell immersing in distilled water. The proton conductivity, σ , in these experiments was calculated from the following equation:

$$\sigma = \frac{L}{R \times W \times T}$$

where L is the distance between the two electrodes, T and W are the thickness and width of the membrane and R is the resistance value measured. The membrane resistances were obtained from Nyquist plots by extrapolating the impedance data to the real axis on the high frequency side.

2.3. Synthesis of BPO₄

BPO₄ was synthesized from the reaction between equimolar amounts of boric acid and phosphoric acid, according to the procedure given elsewhere [19,30]. Briefly, appropriate amounts of H₃PO₄ and H₃BO₃ were stirred continuously at 120 °C until a thick mass was formed. After that it was kept at this temperature for 4 h without stirring. Then it was calcinated for 12 h at 410 °C. The obtained solids were washed with distilled water and separated by centrifugation. The dried samples were ground and then sieved with a 60 mesh standard sieve to control particle diameter to less than 250 µm. This relatively high calcination temperature produces crystalline BPO₄ particles [19].



2.4. Synthesis of polyamic acids (PAA)

To synthesize polyamic acid (PAA) solutions, ODA (9,0108 g, 0.045 mol) was first put into a flame dried three-neck flask containing 80 ml of DMF under a nitrogen purge. The flask was then immersed in an ice/salt bath (–5 to 0 °C). After ODA was completely dissolved in DMF, BTDA (9,8154 g, 0.045 mol) was added to the flask batch by batch. The mixture was stirred at this temperature for 3 h than stirred overnight at room temperature to obtain a viscous PAA solution. The solid concentration was afforded as 20 (wt/wt) %.

2.5. Synthesis of BTDA/ODA–BPO₄ polyimide composites

The procedures for preparing polyamic acid and polyimide hybrid films are shown in Scheme 1. BPO₄ free polyimide membranes were prepared by casting viscous PAA solutions on clean dust-free glass plates. Then thermal imidization was performed stepwise at 80, 100, 150, 200, and 300 °C for 1 h at each temperature. Composite membranes were prepared by adding appropriate amounts of BPO₄ (0.5 wt%, 1 wt%, 3 wt%, 5 wt% and 10 wt%) into PAA solutions. For instance, for the preparation of 1 wt% BPO₄

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