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Synthesis and Characterization of Borax-Polyimide for Flame Retardant Applications

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Polyamide-borax composites were prepared from solution of polyimide and the borax using *N*-methyl-2-pyrrolidone as a solvent. The Polyimide-borax composites films (PI-BX) characterized by FTIR, SEM and x-ray. The borax content significantly influences thermal behavior of the polymeric films, such as glass transition and decomposition temperatures of polyimide-borax composites. The glass transition temperatures of the composites were higher than that of the original polyimide. The flammability properties of them were demonstrated by cone calorimeter and indicate that the borax composites have significantly decreased in heat release rate, and mass loss rate. The PI-BX composites appears very good the flame retardant properties.

Keywords: borax; composites; flame retardant properties; polyimide

Introduction

Borax, also known as sodium borate, sodium tetraborate, or disodium tetraborate, is an important boron compound, a mineral, and a salt of boric acid.[1] Borax has a wide variety of uses. It is a component of many detergents, cosmetics, and enamel glazes. It is also used to make buffer solutions in biochemistry, as a fire retardant, as an anti-fungal compound for fiberglass, as an insecticide, as a flux in metallurgy, and as a precursor for other boron compounds.[2–5]

Polyimide composites have been proposed or are being used for numerous applications, ranging from sensors to advanced optoelectronic devices.[6–8] Understanding the impact of fillers on the composite mechanical properties is critical to the success of all of these applications. Consequently, a large number of research groups are focused on developing a general framework for predicting, or at least, understanding how the chemistry and morphology of the polymer matrix synergizes with the surface chemistry, the size, and the shape of a scale filler to define mechanical properties.[9–13]

In this study, novel polyimide-borax hybrid composite films has been developed from the poly (amic acid) of (1R,3S)-(+)-1,2,2-trimethyl-1,3-bis(p-dimethylamino benzyliden amino)-cyclopentane with different weight percentages (1, 3, 5 wt %) of borax using *N*-methyl-2-pyrrolidone (NMP) as aprotic solvent. Since it has long been known that borax exhibits excellent flame-retarding property, the prepared polyimide-borax composite films were characterized for their structure, morphology, and thermal behavior employing Fourier transform infrared spectroscopy (FTIR), scanning electron micrograph (SEM), and thermal analysis (TGA/DSC) techniques. These studies showed the homogenous dispersion of borax in the polyimide matrix with an increase in the thermal steadiness of the composite films on borax loadings. And the total heat release was only affected by the presence of borax in the polyimide matrix.

Experimental Part

Materials

All chemicals were purchased from Aldrich and used after purification. NMP was

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distilled over CaH_2 under reduced pressure and stored over 4 Å molecular sieves. Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA) that was sublimed at 250 °C under reduced pressure, PMDA were used after crystallization from the appropriate solvents. The dianhydride was dried under vacuum at 120 °C prior to use. Standard borax was purchased from Aldrich (229946) and used without any further purification. All solvents were also dried by using suitable procedures.

Measurements

Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu DSC-60 and TGA-50 thermal analyzers, respectively.

Chemical composition analysis by EDAX was performed with an EDAX; Rönteck xflash detector analyzer associated to a scanning electron microscope (SEM, Leo-Evo 40xVP). Incident electron beam energies from 3 to 30 keV had been used. In all cases, the beam was at normal incidence to the sample surface and the measurement time was 100 s. All the EDAX spectra were corrected by using the ZAF correction, which takes into account the influence of the matrix material on the obtained spectra.

Synthesis of the Monomer (1R,3S)-(+)-1,2,2-Trimethyl-1,3-Bis(p-Dimethylamino Benzyliden Amino)-Cyclopentane (2)

(1R,3S)-(+)-1,2,2-trimethyl-1,3-diaminocyclopentane (**1**) was prepared from (1R,3S)-(+)-camphoric acid according to literature.[14] A mixture of toluene (50 ml), *p*-dimethylaminobenzaldehyde (3.28 g, 22 mmol), (1R,3S)-(+)-1,2,2-trimethyl-1,3-diaminocyclopentane (**1**) (1.56 g, 11 mmol) and *p*-toluenesulfonic acid (0.01 g) was stirred under reflux for 4h. After evaporation of the solvent, the crude product was recrystallized from toluene (20 ml)/hexane (5 ml) to give a yellow solid. Yield 2.81 g (63%), mp 196 °C, $\nu_{(C=N)} = 1556\,cm^{-1}$, $[\alpha]_D^{20} = +110$ (c 0.4 in CH_2Cl_2).

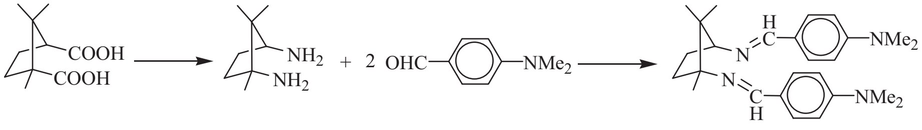
^1H NMR (δ,$CDCl_3$): 0.89 [s, 3H, CH_3]; 0.93 [s, 3H, CH_3]; 1.20 [s, 3H, CH_3]; 1.73, 2.01 and 2.28 [m, 4H, CH_2CH_2]; 3.49 [t, 1H, $J = 8.4$ Hz, CH]; 3.00 [s, 12H, $N(CH_3)_2$]; 6.70 and 7.65 [m, 8H, Ar-H]; 8.15 [s, 2H, $CH{=}N$]. $^{13}C\{H\}$ NMR (δ,$CDCl_3$): 18.91, 21.15 and 25.00 [$3CH_3$]; 40.56 and 40.62 [$N(CH_3)_2$]; 28.35, 34.56, 49.28 and 70.62 [$C_{cyclopentane}$]; 111.94, 112.06, 125.43, 126.52, 129.28, 129.72, 152.09 and 155.74 [$C_{aromatic}$]; 159.11 [$CH{=}N$]. Anal. calcd. for $C_{26}H_{36}N_4$; C:77.22, H:8.91, N:13.86; Found; C:77.05, H:8.70, N:13.64.

Polyimide Synthesis

Polyimide synthesis was performed as follows: (1R,3S)-(+)-1,2,2-trimethyl-1,3-bis(p-dimethylamino benzyliden amino)-cyclopentane (2) (5 mmol) was dissolved in N-methyl-2-pyrrolidone (NMP) (15 mL) in a 50 mL Schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. Pyromellitic dianhyrides (PMDA) (1.09 g, 5 mmol) was added to the amine solution and stirred overnight to give a viscous solution. After being stirred for 3h, the solution was heated to reflux at 145 °C for 15 h. During polyimidization process, the water generated from the imidization was allowed to distill from the reaction mixture together with 1–2 mL of xylene. After being allowed to cool to ambient temperature, the solution was diluted with NMP and then slowly added to a vigorously stirred solution of 95% ethanol. The precipitated polymer was collected via filtration, washed with ethanol, and dried under reduced pressure at 150 °C. The polymer was isolated with 93% yield.

Synthesis of the PI-BX Composites

HNO_3 treated positively charged borax was added into the polyimide solution at 145 °C with fixed ratio, and the synthesis process lasted for 4 h. As shown in Scheme 1, polyimide-borax composites with different ratios of borax unit (1, 3, 5% weight percent). The mixture was stirred and allowed to evaporate slowly at 25 °C for



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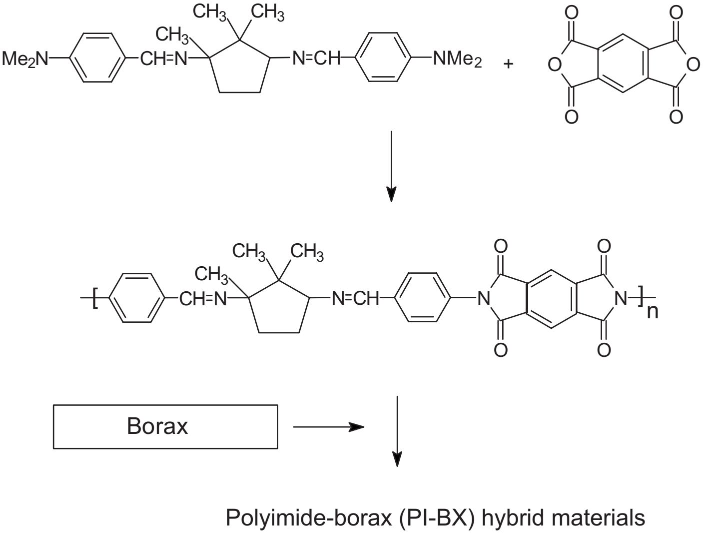
Scheme 1.
The synthetic route for the preparation of the monomers.

12 h and cure at 200 °C for 8 h under vacuum to ensure total imidization of monomers to polyimide. After curing, smooth, stiff and hazel to brown film was obtained.

Results and Discussion

Polyimide-borax hybrid composite films has been developed from the polyimide solution of (1R,3S)-(+)-1,2,2-trimethyl-1,3-bis(p-dimethylamino benzyliden amino)-cyclopentane with different weight percentages (1, 3, 5 wt %) of borax using *N*-methyl-2-pyrrolidone (NMP) as aprotic solvent. Using a combination by dissolving the polyimide and borax particles. We have demonstrated the formation of composites with uniform particle dispersion. The influence of borax on heat releasing capacity was analyzed. Heat releasing capacity of composites was reduced compared to polyimide itself. The microstructures and morphology of the as obtained samples were studied by infrared spectra (IR), scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS) and thermogravimetric analysis (TGA).

The intermediates and polymers were characterized by FT-IR spectra. The results are in agreement with the proposed structures. FTIR spectra were collected in order to determine whether borax particles were incorporated into the polyimide matrix respectively. Figure 1 displays the FTIR absorption spectra of pure PI and PI-BX composites with various borax content and are recorded between 4000 and 650 cm^{-1}. The characteristic absorption peak are 1780 cm^{-1} (C=O, asymmetric stretch),



Scheme 2.
Synthesis of the polyimide and PI-BX composites.

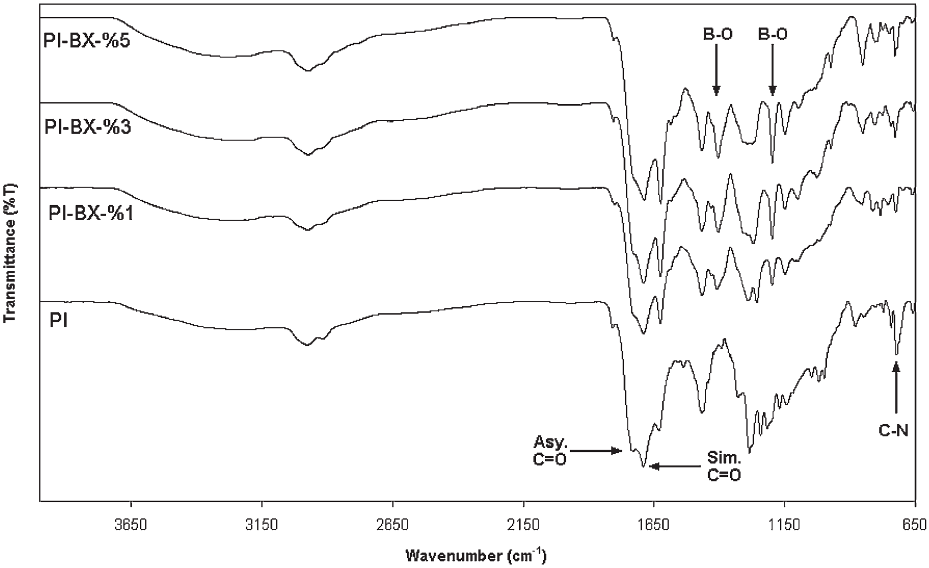


Figure 1.
FTIR spectra of the PI and PI-BX composites.

1720 cm^{-1} (C=O, symmetric stretch), 730–725 cm^{-1} (C–N bending), 1390 and 1150 cm^{-1} (B–O stretching) are clearly presented. The intensity of absorption peak is increased with borax content.[15–19]

All composites were subjected to DSC measurements for the purpose of examining miscibility. Figure 2 shows the DSC thermograms of all composites exhibiting only one T_g from all composition. A single T_g strongly implies that all these composites are homogenous. Figure 2 shows the dependence of the T_g on the composition of these copolymers, increasing the borax content results in T_g increase than average values.

TGA analysis of PI-borax composites were given in Figure 3. Their thermal decom-

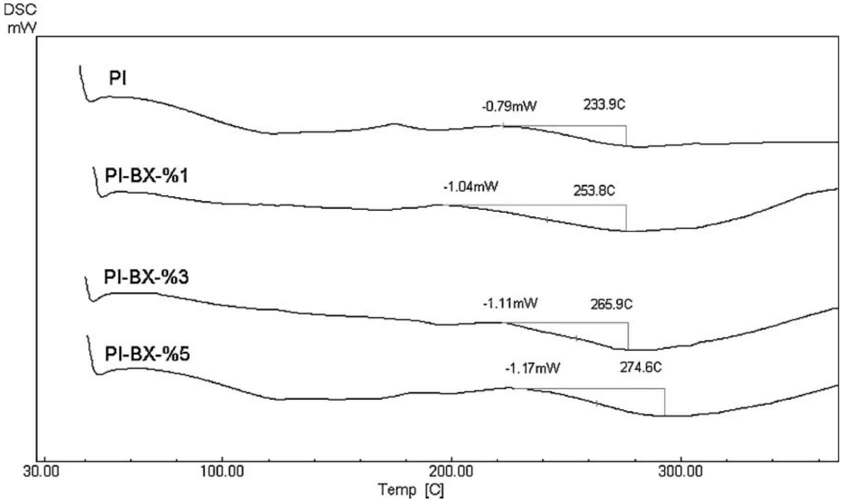


Figure 2.
DSC of pure PI and PI-BX composites with different loadings of borax in polymer (1 to 5%).

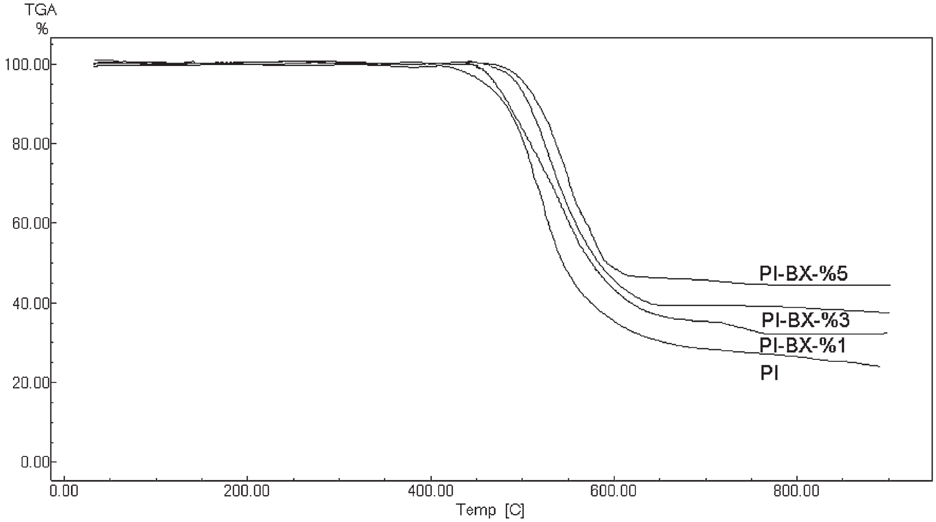


Figure 3.
TGA of pure PI and PI-BX composites with different loadings of borax in polymer (1 to 5%).

position temperatures (T_d = temperature at 5% mass loss) were measured via thermogravimetric analysis (TGA) and showed that the introduction of borax into polymer backbones increased thermal stability.

Figure 4 and 5 shows the SEM photographs of the fracture surface of composite

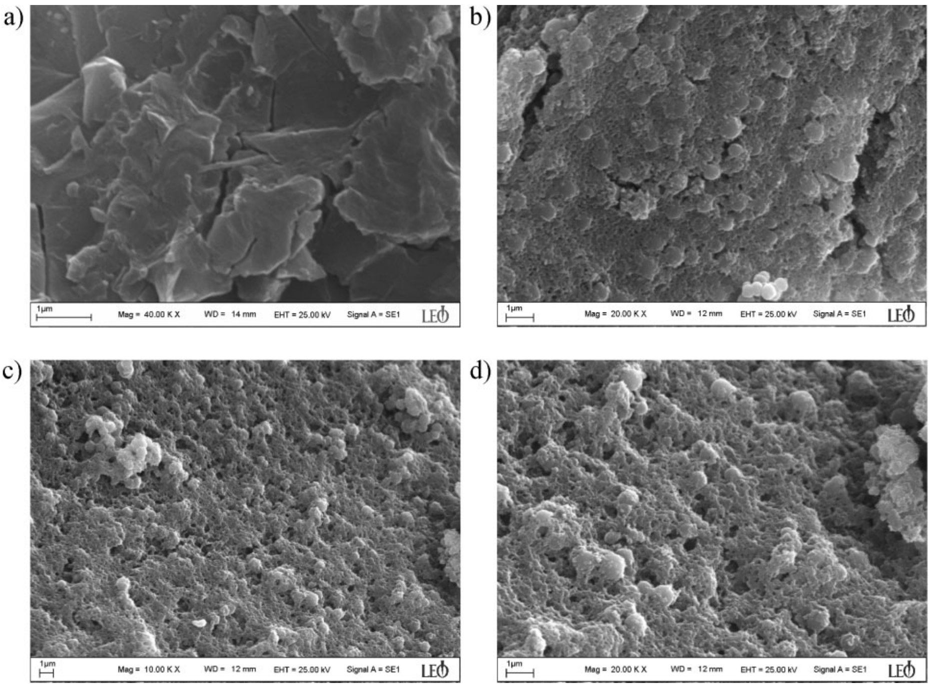


Figure 4.
SEM image of pure PI (a) and PI-BX composites with different loadings of borax in polymer (b) 1%, (c) 3%, (d) 5%.

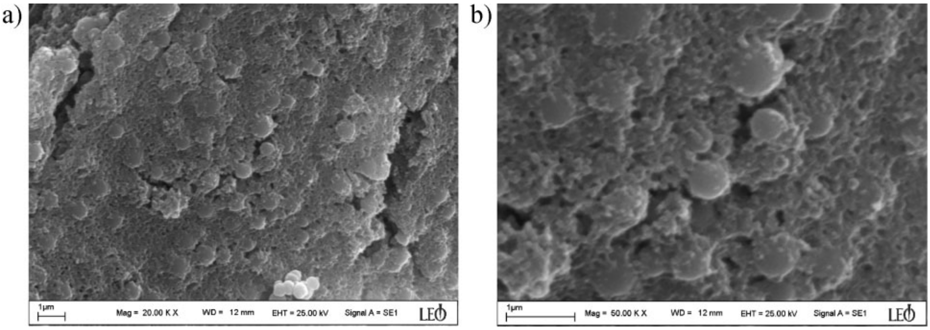


Figure 5.
SEM image of PI-BX%1 composites. Low (a) and high (b) magnification.

films. It can be clearly seen that the particles (borax) with a diameter of 400–700 nm distribute uniformly in the polymer matrix for the hybrid films with 1 and 5 wt% of borax. In addition, we can also see that the borax particles are imbedded in polymer matrices, indicating that the borax has good compatibility and interfacial interaction with polyimide matrix, which favors for the improvement of thermal and mechanical properties of hybrids.

EDX studies (Figure 6–7) demonstrated borax particles appear to be dispersed randomly, although the particles do appear to form aggregates at increasing particle loadings. Borax particles showed mosaic micro-pattern and particles surrounded by polyimides. Controlling more than a single type of particles in specific positions can provide an opportunity to utilize unique properties of each type of borax particles. The intensity of absorption peak boron and sodium in EDX spectrum of the PI-BX is increased with borax content.

A total of four samples (PI, PI-BX%1, PI-BX%3 and PI-BX%5) were analyzed by

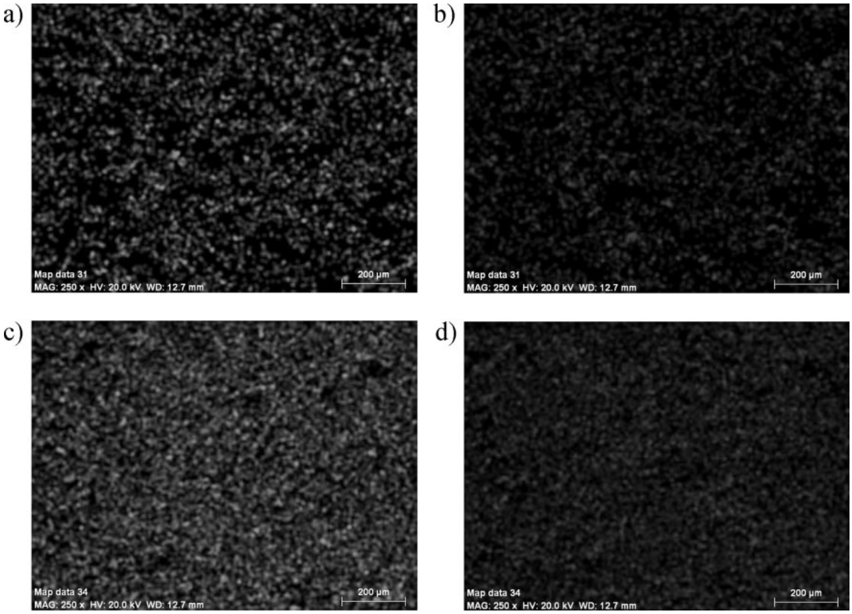


Figure 6.
EDX mapping of the PI-BX-%1 boron (a), PI-BX-%1 Sodium (b), PI-BX-%5 boron (c) and PI-BX-%5 Sodium(d).

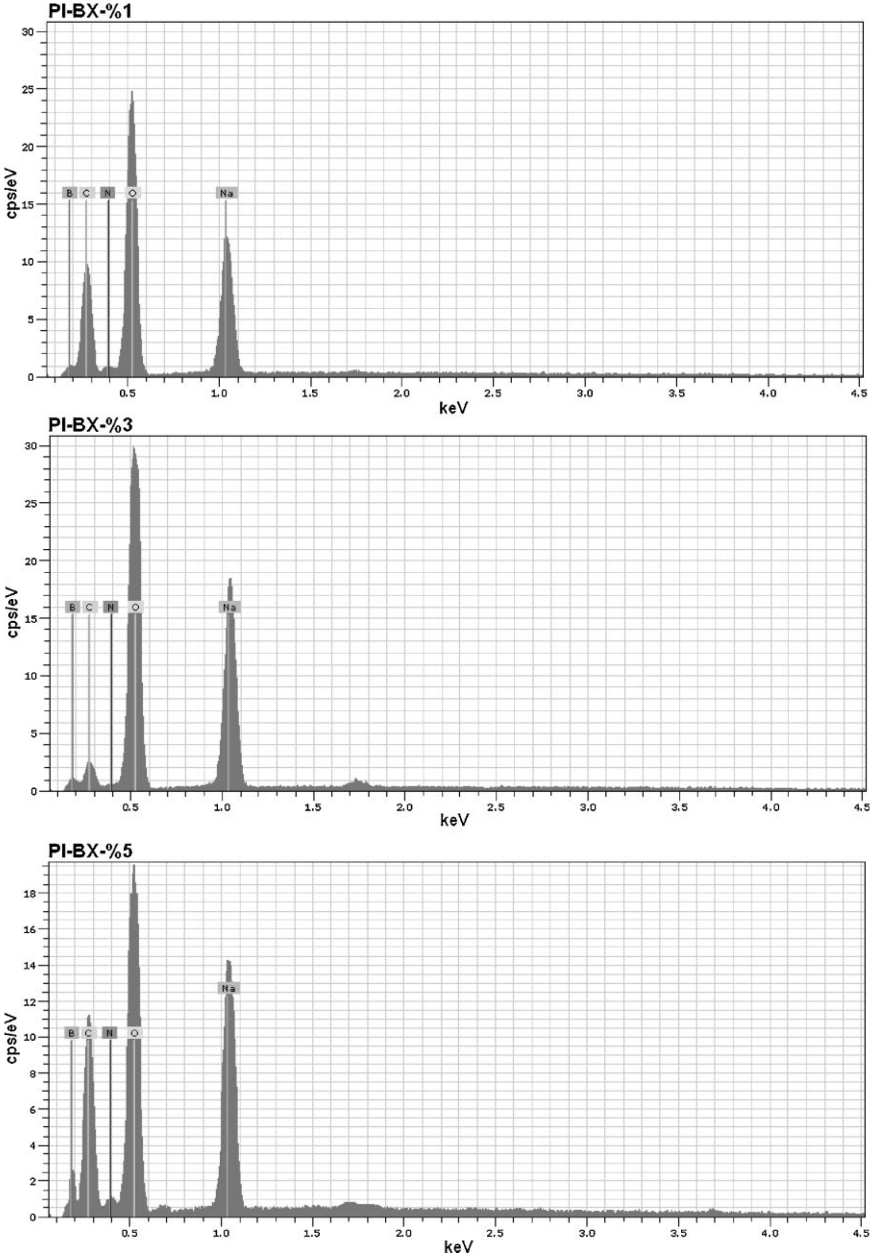


Figure 7.
EDX of PI–borax composites with different loadings of borax in polymer (1, 3 and 5%).

cone calorimeter to compare the effects of borax particle on polymer flammability, and the results of them are shown in Figure 8, respectively. When compared the pure polyimide control, all the samples show reduced Heat release rates (HRR) and peak HRR values.

Figure 8. Heat release rates of pure PI, and PI-BX composites with different loadings of borax in polymer 1%, 3%, 5%.

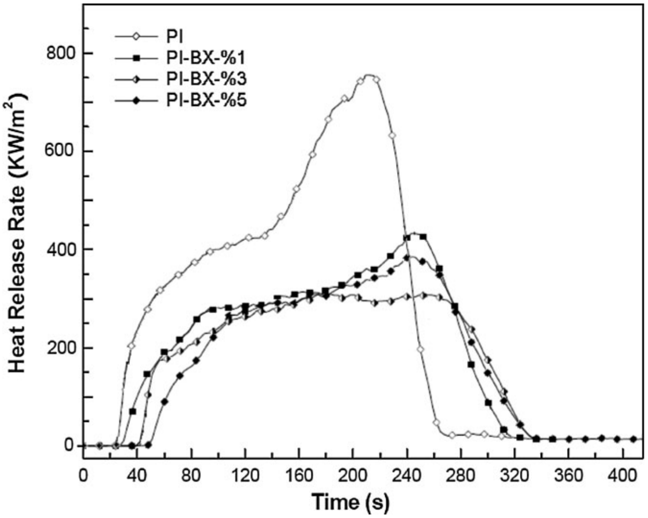


Figure 8.
Heat release rates of pure PI, and PI-BX composites with different loadings of borax in polymer 1%, 3%, 5%.

Conclusion

The PI-BX composites were prepared from polyimide and borax. The borax as 400–700 nm particles distributes homogeneously in polyimide matrix. The incorporation of borax causes a decrease in thermal stability of hybrid films. It also points that the addition of borax shows higher Tg as compared with pure PI. PI-BX composites appear very good the flame retardancy, which have significantly decreased in heat release rates (HRR) and mass losses rates (MLR).

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