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## RESEARCH LETTER

### Elevation of charring level of polyamide-6,6 films via ionic introduction of phosphoric acid and boric acid esters

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Phosphorus and boron containing materials have the feature of increasing char formation, which can be effectively used as flame retardants especially in textiles. This paper discusses the ionic addition of phosphorus and boron esters to polyamide-6,6 (PA66), and its effect on the charring level. A mixture of phosphoric acid–boric acid ester at different degrees of esterification (ED) was prepared and two theoretical mechanisms for the esterification reaction were suggested. Ionically grafted polymer films were prepared by introducing the ester of highest ED to PA66–formic acid solution via three different processes: open air (cold) grafting, ultraviolet irradiation grafting, and hot vacuum oven grafting. Thermogravimetry was conducted for all synthesized esters and films, and the formation of new bonds between the ester and PA66 was verified using Fourier transform infrared spectroscopy.

**Keywords:** phosphoric acid; boric acid; esterification degree; charring; polyamide-6,6; ionic grafting

#### Introduction

When exposed to heat, polymers degrade via thermal and thermal–oxidative decomposition processes. The resulting compounds comprise a mixture of combustible volatiles and noncombustible gasses. The type of produced volatiles is subject to the chemical nature of the polymer. Reducing the hazard associated with the degradation and burning of organic polymers via promotion of carbonization is one of the most important methods for enhancing the flame-retardant effect of polymers. Production of char not only decreases the production of flammable volatiles but also makes a flame and heat barrier between the heat source and the treated substrate (1–5).

Polyamide fibers have been widely used in textiles due to their excellent features (e.g. mechanical properties, resistance to shrinkage, low cost, and pleasant esthetics). However, it forms melting drips during burning, which can lead to the spread of fire (6–8). Subbulakshmi et al. (7) studied the addition of flame-retardant chemicals during spinning of Nylon fiber. In the current study, ionic introduction of a mixture comprising potential flame retardants to Nylon-6,6 (polyamide-6,6, PA66) dope was investigated as a preliminary research toward spinning flame-retardant Nylon fibers in the future.

El Garf et al. (9) worked on phosphorylation of Nylon-6 using a halogenated phosphorus-containing

flame retardant. Yang et al. (10) studied the mechanism of bonding a hydroxy-functional organophosphorus oligomer to PA66 fabric using formaldehyde derivatives of urea and melamine. However, the use of flame retardants based on formaldehyde derivatives, antimony oxide, and halogenated compounds has been strictly restricted due to environmental concerns (11–13).

Phosphorus- and boron-containing materials are known to be both environmentally friendly and effective for providing increased char formation for various substrates such as textiles (14, 15). During the burning process, phosphorus compounds decompose to water and phosphorus oxides, which can dehydrate the polymeric matrix and produce phosphoric acids (PhAs). The resulted acids will again produce water and phosphorus oxides. Consequently, the reaction between phosphorus oxides with polymeric structure results in the formation of a high melting point char acting as a heat barrier against the source of heat (9, 10, 16–18). Boron-containing materials form a glass-like cover over polymeric substrates through degradation. The provided shielding effect stops the further flame propagation by excluding oxygen molecules during combustion (19).

According to Dorn et al. (20), the simultaneous use of borate- and phosphate-containing materials may result in enhanced flame-retardant effect for polymeric

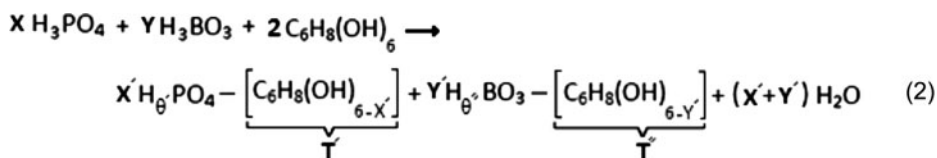
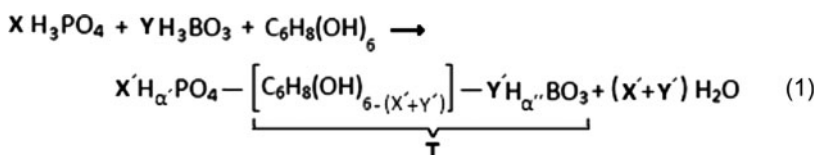
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substrates. However, they did not suggest any method for permanent and durable flame-retardant treatments. In addition, neither esterification mechanism nor the correlation between esterification degree (ED) and charring level was investigated. The ester preparation technique by Dorn et al. was adopted as the first experimental step. This paper investigates the esterification mechanism of PhA and boric acid (BA), reacting with mannitol, charring level, and the possibility of ionic bonding between PhA–BA ester mixture and PA66.

### Theory

A series of reactions were suggested based on the ionic nature of the used compounds and the existing possibilities for forming new bonds between the mannitol and the mixture of PhA and BA.

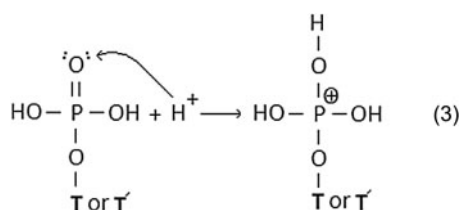
Considering mannitol as a polyol capable of reacting with acids, PhA and BA, the esterification reaction may be either simultaneous or separate. In the simultaneous esterification reaction, it is assumed that both PhA and BA molecules can attach to the same mannitol molecule. This possible reaction is shown in Scheme 1. In the separate esterification reaction, PhA and BA molecules separately attach to two different mannitol molecules, Scheme 2.



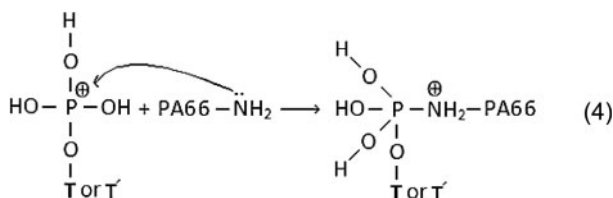
where  $X$ ,  $Y$ ,  $X'$ , and  $Y'$  are the reaction coefficients,  $\alpha'$ ,  $\alpha''$ ,  $\theta'$ , and  $\theta''$  (can be 0, 1, or 2) are the number of remaining hydrogen atoms on the grafted phosphate and borate residues, respectively. The summation of  $X'$  and  $Y'$  ( $X' + Y'$ ) is the ED which can be 0–6 and 0–12 for simultaneous and separate mechanisms, respectively.  $T$  and  $T'$  are phosphate residues, and  $T''$  is the borate thereof in the separate mechanism.

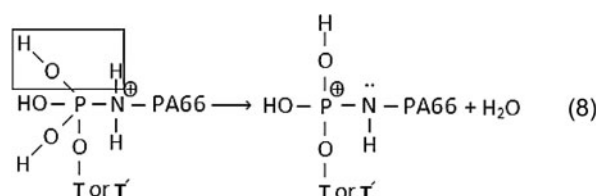
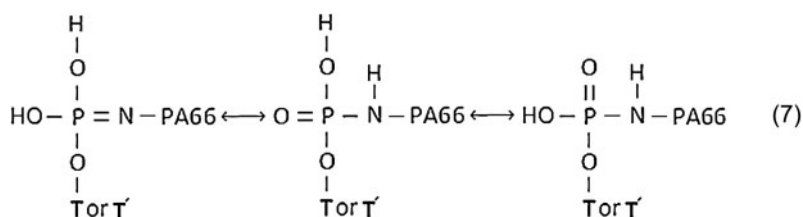
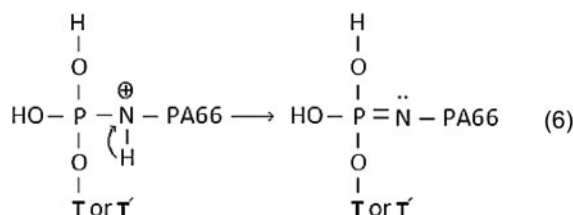
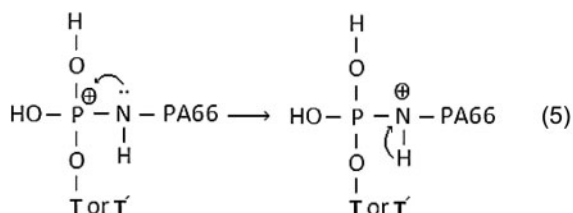
It is assumed that a bond between the ester mixture and PA66 can be formed by attaching the phosphate group to the polymeric backbone via an electrophilic reaction. Scheme 3 illustrates the possible addition reaction between the phosphate residue and the  $\text{H}^+$

through which one further  $-\text{OH}$  group attaches to phosphorus atom. The resultant intermediate leaves  $\text{P}$  with a positive charge. If a reaction intermediate does not continue the reaction pathway, then it would lose  $\text{H}^+$  and revert to the  $\text{P}=\text{O}$  form (Scheme 7). The same mechanism is possible for each of the Schemes 4 and 5, where the structures represent reaction intermediates illustrating transfer of electrons and leaving the positive charge on nitrogen. The final structure in Scheme 6 has a double bond to nitrogen with two further  $-\text{OH}$  groups and an ester group shown by  $\text{O}-\text{T}$ ; however, the actual structure is probably best considered as a resonance hybrid of  $\text{O}=\text{P}-\text{NH}$  and  $\text{HO}-\text{P}=\text{N}$  contributors, shown in Scheme 7.  $\text{O}$  in  $\text{P}=\text{O}$  can be either of the two  $-\text{OH}$  groups shown in the product structure in Scheme 6. The double-headed arrows in Scheme 7 imply equilibrium.



The suggested mechanism of bond formation between PhA–BA esters and PA66 is shown in Schemes 4–6 and 8, where Scheme 8 is the intermediate stage between Schemes 4 and 5.





## Experimental

### Materials

PhA 85%·w/w was obtained from Chem Supply Company, Australia; PA66 yarn was purchased from Invista Company, America; Mannitol 98%, BA powder 98%, and formic acid (FA) 99% were obtained from Ajax Finechem Pty Ltd, New Zealand. Triton X100 was supplied by Sigma-Aldrich. All the materials were used without further purification.

### Preparation of ester mixtures

To obtain different ED values, two different molar ratios, 0.5 or 1, were chosen for each ingredient (PhA,

BA, and mannitol) as shown in Table 1. All the seven mixtures in separate 500-mL beakers were stirred at –300 rpm and 75°C on a hot plate stirrer until clear solutions were obtained. To gain higher ED values, water was removed (both that were present and produced during reaction) from the solutions using a Gallenkamp vacuum oven at –500 mbar and 130°C.

### Calculation of ED values

Equation (1) was implemented to calculate ED values (20).

$$\text{ED} = \frac{\text{IW} - [\text{FW} + \text{TWW}]}{18 \times \text{NMM}} \quad (1)$$

where IW is the initial formulation weight (g); FW is the final formulation weight (g); TWW is the total water weight (g), which is the summation of water

content present in PhA 85%·w/w and the weight of water added to the initial mixture (60%·w/w); NMM stands for number of mannitol moles in the initial mixture; and 18 refers to water molar mass.

### Film preparation

Two hermetically sealed containers were filled with a mixture comprising 50/50%·w/w of ester of the highest ED and 13%·w/w of PA66–FA solution. Both containers were stirred for 30 minutes but at different temperatures (110°C and 25°C). These procedures are referred as Hot method and Cold method in this paper, respectively (Figure 1).

Three 2 mm-thick film samples, two from Hot method and one from Cold method, were prepared by applying the slurries on three glass plates using a Type SV-MATIS laboratory coating machine.

The Cold-film glass plate was placed under the laboratory hood and left to dry at the room temperature, 25°C, for 24 h to produce a dry Cold-film (Cold sample). One of the Hot-film glass plates was placed in the vacuum oven at –300 mbar and 130°C for 30 minutes to produce a dry Hot-Oven film (Hot-Oven sample). The second Hot-film glass plate was placed

Table 1. Mixed ester solutions with different molar ratios of PhA:BA:mannitol (water: 60% w/w).

Ester mixture	E1	E2	E3	E4	E5	E6	E7
PhA:BA:mannitol	1:1:1	1:1:0.5	1:0.5:1	0.5:1:1	1:0.5:0.5	0.5:1:0.5	0.5:0.5:1

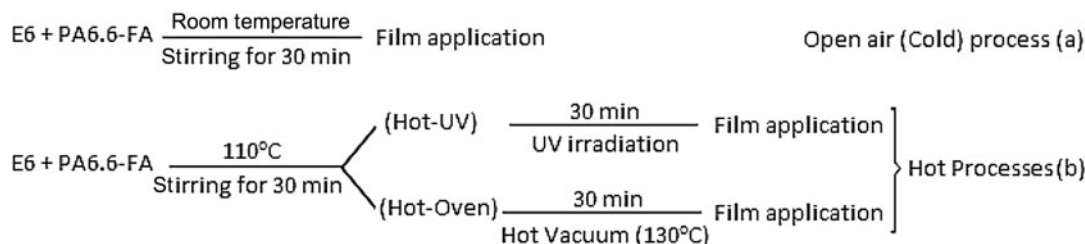


Figure 1. (a) Cold- and (b) Hot-film production methods.

in an ultraviolet (UV) light box equipped with two SW-8 UV tubes at a lamp-sample distance of 10 cm and left to cure for 30 minutes at the room temperature to produce a dry Hot-UV film (Hot-UV sample). All film samples were placed under the laboratory hood for 24 h and desiccated at the room temperature for 24 h.

Each film sample was shredded into small pieces and washed with 2 g/L nonionic surfactant in water solution at 60°C for 30 minutes, then thoroughly rinsed with cold water, left to air dry, and desiccated for 4 days.

### Thermal analysis

Thermogravimetry (TGA) experiments were carried out using a PerkinElmer TGA 7 thermogravimetric analyzer to measure weight loss and remaining char ratio. The TGA temperature range was set between 40°C and 850°C for esters and between 40°C and 750°C for washed film samples. The heating rate was 20 K/min under the nitrogen purge and each sample weighed between 7 mg and 9 mg.

### Fourier transform infrared spectroscopy (FTIR) analysis

To identify new bonds between the PhA-BA esters and the PA66, FTIR analysis was performed using a PerkinElmer spectrum 400 FT-IR/FT-NIR spectrometer ranging between 650  $\text{cm}^{-1}$  and 2000  $\text{cm}^{-1}$ .

## Results and discussion

### Theorized correlation between ED and thermal behavior

Remaining char level after the first major decomposition, 700°C, was considered as a char level index for all esters. This index can be referred to as the major

factor in flame retardancy since char acts like a shielding barrier against the heat and retards the fire to spread over the substrate (17). As shown in Figure 2, E6 had the highest remaining char ratio, 58.42% w/w, and hence, the most potential flame-retardant effect compared with other esters in this paper.

Table 2 shows ED values. Figure 3 illustrates the linear correlation between the ED and the level of remaining char after the first decomposition, 700°C.

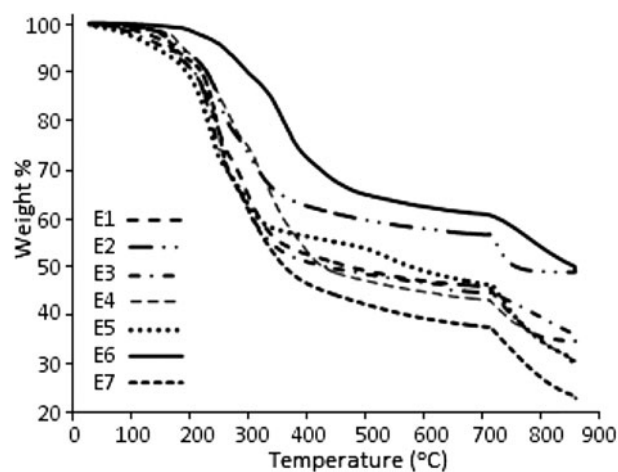


Figure 2. TGA thermograms for PhA and BA ester mixtures.

Table 2. ED values of prepared esters.

Ester mixture	E1	E2	E3	E4	E5	E6	E7
ED	2.03	4.57	0.63	2.52	2.22	5.12	0.57

### TGA analysis for films

Resulting TGA graphs for PA66 and washed film samples, AW, are shown in Figure 4. The highest

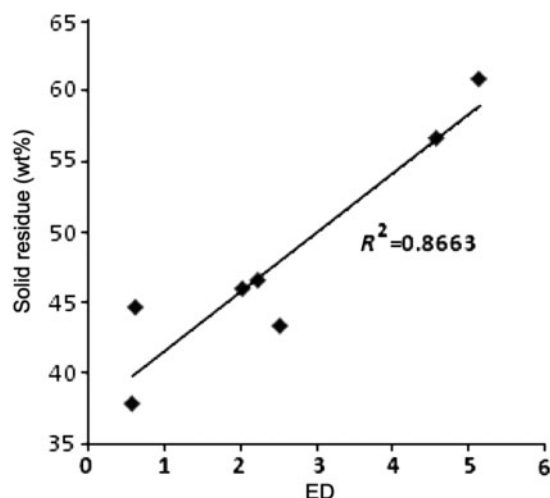


Figure 3. ED value vs. solid residue after the first decomposition at 700°C for all ester mixtures.

charring level among washed films belonged to Hot-UV, 25.67%·w/w (Table 3).

Table 3 indicates that the treated films remained a high level of char ratio after washing. The increased amounts of char residue compared with PA6.6 for Cold-AW, Hot-Oven-AW and Hot-UV-AW samples were 17.73, 17.98 and 21.66 wt%, respectively. Suggested Hot-UV process for producing PA66-ester films was found more effective in elevating char formation compared to the previous works done by Yang et.al and Yang, which resulted in 16%·w/w at 600°C and 17%·w/w at 500°C, respectively (10, 18).

### FTIR analysis

The FTIR spectra of PA66, E6, and unwashed film samples are shown in Figure 5. The main absorption bands in phosphates appear between 1000  $\text{cm}^{-1}$  and 1111  $\text{cm}^{-1}$ . Peaks at 930  $\text{cm}^{-1}$  and 1081  $\text{cm}^{-1}$  associate

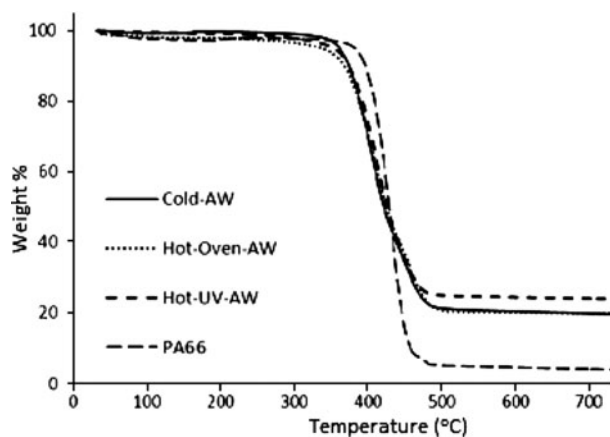


Figure 4. TGA thermograms of washed treated films.

Table 3. Remaining char wt% for PA66, E6, and washed treated films after the first decomposition.

Samples	PA66	E6	Cold (AW)	Hot-Oven (AW)	Hot-UV (AW)
Remaining char wt%	4.01	58.42	21.74	21.99	25.67

with P–O–R (in phosphate form) and P–O stretching bonds, respectively. On the other hand, B–O stretching bond should appear at around 1400  $\text{cm}^{-1}$  for free BA and around 1150  $\text{cm}^{-1}$  for borates. However, bonds can shift from one point to another due to the presence of other materials in a combination. For unwashed film samples (Cold, Hot-Oven, and Hot-UV) shown in Figure 5, the bands around 930  $\text{cm}^{-1}$ , 1020  $\text{cm}^{-1}$ , 1080  $\text{cm}^{-1}$ , 1301  $\text{cm}^{-1}$ , and 1451  $\text{cm}^{-1}$  associate with P–O–R in phosphate form, B–O–H in plane bending, P–O stretching, P=O stretching, and B–O stretching in BA form, respectively (21–24).

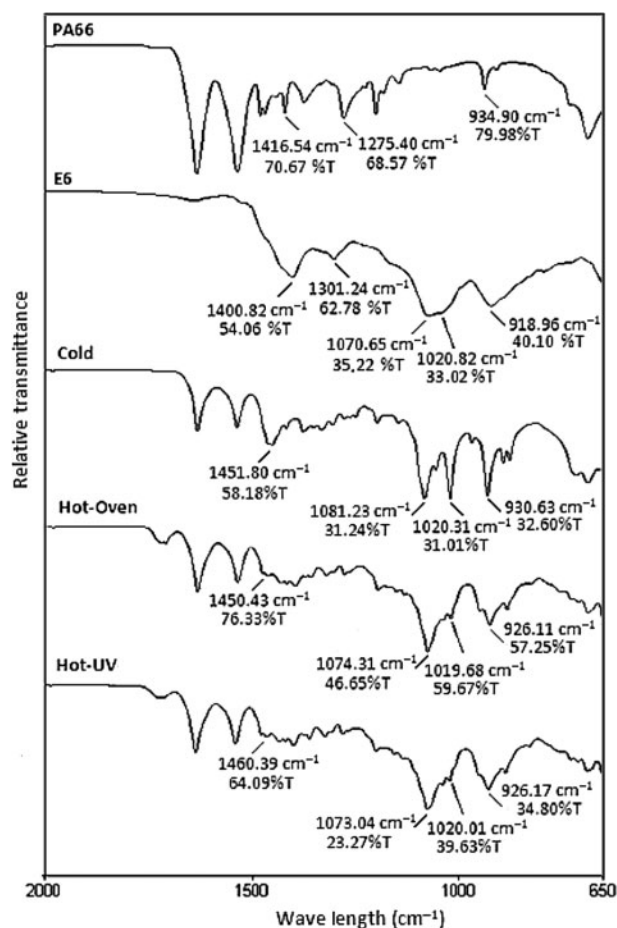


Figure 5. FTIR spectra of E6 and unwashed treated films.



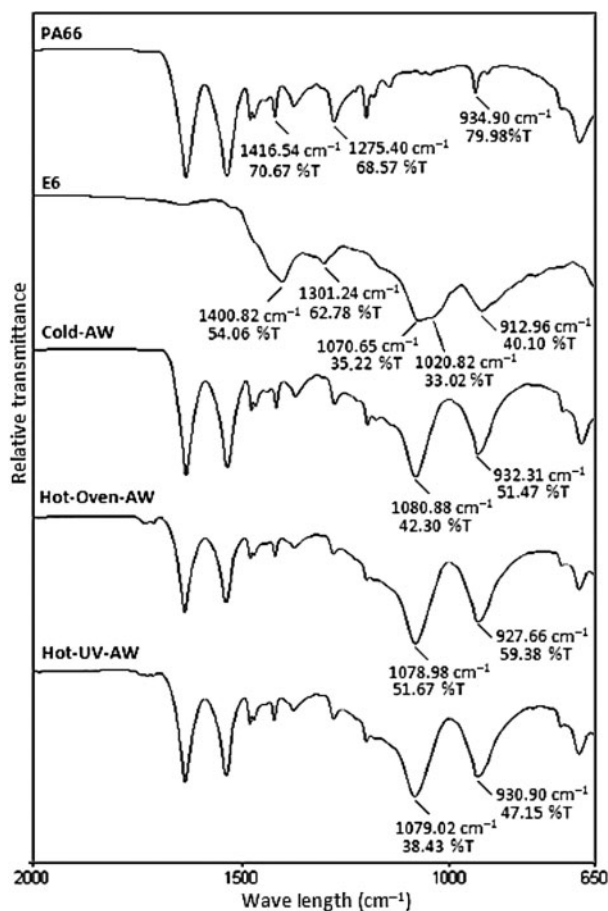


Figure 6. FTIR spectra of E6 and washed treated films.

The disappearance of bands at  $1020\text{ cm}^{-1}$ ,  $1301\text{ cm}^{-1}$ , and  $1451\text{ cm}^{-1}$  from FTIR spectra of washed samples (Figure 6) suggests the separate esterification mechanism, as illustrated in Scheme 2. The presence of P–O–R bands at  $930\text{ cm}^{-1}$  as well as  $1080\text{ cm}^{-1}$  associating with P–O vibrations confirms the successful ionic grafting of the phosphate group to PA66. However, the lack of bands at  $1020\text{ cm}^{-1}$  and  $1451\text{ cm}^{-1}$  after wash indicated the incapability of borate for strong bonding with PA66. Thus, the films would be more effective in flame-retardant applications where tough washing is not required so that borate will remain in the film.

In Figure 6, the washed Hot-UV sample showed the highest peak intensity at the bands  $930\text{ cm}^{-1}$  and  $1079\text{ cm}^{-1}$  compared with washed Cold and Hot-Oven samples. This suggests the effectiveness of UV irradiation grafting toward making stronger bonds between phosphorus and PA66, since a higher peak intensity evidences stronger bonds (24).

## Conclusion

A mutual relationship between ED and level of char formation, as a major parameter of flame resistance,

was observed for the mixture of PhA and BA esters. When the molar ratio of PhA:BA:mannitol was 0.5:1:0.5, the ED was the highest, 5.12. The ester produced with this ratio showed a high level of char formation and underwent an ionic reaction with PA66 for flame-retardant PA66 films. The existence of new bonds after washing was confirmed by FTIR analysis for all the prepared films. Initial esterification reaction was found to take place via a separate esterification mechanism shown in Scheme 2. Lack of borate bonds in the FTIR spectra of washed samples proves the incapability of BA ester to form B–O bonds with PA66. The highest remaining char ratio, 25.67% w/w, resulted from UV irradiation method compared with other ones. Given the successful char elevation after grafting the mentioned ester to PA66, the spinning of the prepared dope via the suggested method can be investigated for textile applications. Production and evaluation of physiomechanical properties of such fibrous materials are future objectives.

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