A Novel Boron-nitrogen Intumescent Flame Retardant Coating on Cotton with Improved Washing Durability

Shuk Ying Chan[a], Liping Si[a], Ka I Lee[a], Pui Fai Ng[a], Lei Chen[a], Bin Yu[a], Yuan Hu[b], Richard K.K. Yuen[c], John H. Xin[a] and Bin Fei[a]

[a] *Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

[b] *State Key Lab of Fire Science, University of Science & Technology of China, Hefei, China*

[c] *Department of Architecture and Civil Engineering, City University of Hong Kong, Kowloon, Hong Kong, China*

Bin Fei, Corresponding author: E-mail: tcfeib@polyu.edu.hk ; Tel.: +852 2766 4795

Abstract

A series of boron-nitrogen polymers (PEIPAs) were synthesized to provide a green alternative for flame retardant finishing on cotton fabrics. An organic boron compound, phenylboronic acid (PA) was successfully bonded to the branched polyethylenimine (PEI), which was confirmed by ^{1}H NMR and FTIR analysis. Thermogravimetric analysis showed that the polymer with molar ratio 1:1 of ethylenimine (EI):PA, (PEIPA 1:1), presented the optimal thermal-oxidative stability. PEIPA 1:1 was easily applied on cotton fabrics through a simple dipping method with high uptake in acetone medium. The fabric with 33.8 wt% add-on got self-extinguishing ability. SEM analysis on the char morphology of the treated fabrics revealed the fire protection by the coating through intumescent flame retardant mechanism. TGIR analysis showed the coated fabric has significant reduction in the flammable volatiles production. Further improvement of the coating washing durability was achieved by a novel formaldehyde-free cross-linking treatment. The new washing stable coating achieved LOI values 29.6% and 23.2% before and after repeated launderings respectively with 30 wt% add-on. Cone calorimetry analysis showed that the total heat releases of PEIPA 1:1 treated sample and cross-linked sample (PEIPA 3:1/NeoFR treated) were decreased by 30.3% and 45.5% respectively. Smoke analysis revealed that the treated fabrics have significant decrease in CO_2/CO ratio, indicating an effective flame inhibition in gas phase. The novel coatings, simple to synthesize and easy to apply with low waste, are suitable alternative to toxic halogenated flame retardants for cellulosic products.

Keywords *Flame retardant, Cotton, Boronic acid, Intumescent char, Volatiles reduction, Durability*

Introduction

Recent statistics from the National Fire Protection Association present that there was a 20% decrease in the number of fires in the United States from 2000-2015. However, there is no obvious change in the number of structure fires in 2015, and home fires (which is part of structure fires) caused 78% of all fire deaths (Haynes 2016). Therefore, decreasing the fire risk of home could be the best direction to reduce the number of fire incidents and fire death in the future. Textile products, like upholsteries, bedding and clothing, which are the flammable materials at everyone's home, should be modified to improve the fire retardancy. Since cotton is a very common material for home textiles, these burnable products represent a big threat to human life as the source of fire disasters. The best way to improve the flame retardancy (FR) of cotton is most likely by the treatment with flame retardants (Wilkie and Morgan 2010). Traditional flame retardants containing halogens, notably chlorine and bromine, are gradually phased out due to their generation of toxic and corrosive gases during thermal degradation (Kilinc and Textile Institute (Manchester England) 2013; Lu and Hamerton 2002; Martin et al. 2006b; Mosurkal et al. 2011; Papaspyrides and Kiliaris 2014; Wiacek et al. 2015). Current market of textile flame retardants is dominated by compounds containing phosphorus and nitrogen elements that act synergistically (Horrocks and Price 2001; Tai et al. 2012). Pyrovatex® CP and Proban® CC are commercial durable organophosphorus-based flame retardants for cotton fabrics over 60 years (Kilinc and Textile Institute (Manchester England) 2013; Pan and Sun 2011). However, formaldehyde is released during treatment and service life of the products, which is harmful to human health (Liu et al. 2012; Pan and Sun 2011; Zhou et al. 2014). Other than fire and heat attack, smoke and toxic gases emitted during burning are also the deadly factors for human, since most fatality (over 85%) in fire resulted from the inhalation of toxic smoke/gases (Lv et al. 2013). Therefore, research on developing green and safe flame retardants is still necessary.

Since the 1980s, researchers have been concentrating on the investigation of more effective, environmentally friendly, halogen-free, formaldehyde-free, washing-durable, as well as scalable flame retardant finishing for cellulosic substrates (Alongi and Malucelli 2015). New discoveries, like some phosphorus and/or nitrogen rich bio-macromolecules (e.g. DNA), are proved as effective flame retardants on cotton (Alongi et al. 2013; Alongi et al. 2014; Carosio et al. 2013). However, problems like low washing durability, and the high cost of materials are limiting the application for commercial use. Another type of green flame retardant, i.e. nano-particles (such as polyelectrolytes and clays), are the more promising FR materials on cotton. For example, Haile and the co-workers (2016) developed a thin film on polyester-cotton fabric, which could withstand 5 laundering cycles through a modified layer-by-layer assembly process under special condition. The fabric coated with 18 wt% insoluble polyelectrolyte complexes exhibited a 30% reduction in total heat release in the cone calorimeter test. Another coating technologies, such as sol-gel and dual-cure processes, also achieved a good washing durability on cotton by the formation of covalent bonds between the nano-coating and cellulose. However, possibility for industrialization is still in doubt (Alongi et al. 2014). Based on the more demanding requirements on the flame retardant treatment on cotton, we designed a novel halogen-free and formaldehyde-free flame retardant system, which is more scalable for mass production and durable to washing. A green synergistic pair was selected for more effective flame retardant effect. Simple application process, e.g. using traditional pad-dry-cure equipment, was adopted.

Boron and nitrogen compounds might be much greener than halogen chemicals, because they produce environmentally safer byproducts during combustion (Horacek and Grabner 1996; Lu and Hamerton 2002; Mosurkal et al. 2011; Wiacek et al. 2015; Yang et al. 2012) . Boron compounds have two modes of flame retardant actions. Physically, borates degrade thermally to form impenetrable glassy coatings. The glasslike coatings on surface are barriers against the basic elements of fire, thus preventing further propagation of combustion (Martín et al. 2006; Wang et al. 2008) . Chemically, they promote char formation in the burning process through the reaction of boric acid with alcohol moieties (Abdalla et al. 2003; Martín et al. 2006). On the other hand, boron compounds have been reported as the exceptional smoke inhibitors (LeVan and Tran 1990). While for the nitrogen compounds, they act as a gas diluent or blowing agent by producing non-flammable gases, like ammonia, to reduce the concentration of flammable volatiles and oxygen next to the substrate surface. Hence, the substrate's heat decomposition rate could be reduced (Horacek and Grabner 1996; Lu and Hamerton 2002; Xie et al. 2013; Zhou et al. 2014). In addition, nitrogen compounds are also suitable for recycling (Lu and Hamerton 2002).

Xie et al. (2013) have reported the excellent synergistic effect of boron and nitrogen compounds, where boric acid and 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) demonstrated the LOI value of the treated cotton fabric increased to 27.5%. Some reports have focused on the syntheses and FR performances of boron-containing phenol–formaldehyde resins and a few boron-modified polymers (Martin et al. 2006; Xu and Jing 2010). However, in the present stage, these borate polymers are unstable in aqueous media, because they are easy to hydrolyze and detach from the polymer frameworks. Herein, we propose a new boron polymer to enhance the boron-based flame retardant stability in washing. When it is incorporated into typical textile fibers, satisfying flame retardancy, volatiles inhibition and improved washing stability could be achieved.

Phenylboronic acid (PA) could be a good candidate for flame retardant synthesis: Its benzene group is favorable for char formation due to lower hydrogen content and higher unsaturation of hydrocarbon (Kilinc and Textile Institute (Manchester England) 2013; Wilkie and Morgan 2010); And its B-C bond is stable against wet conditions. Polyethylenimine (PEI) was chosen as the nitrogen source (Nedel'ko et al. 1975). In this research, several phenylboronic-grafted PEIs (PEIPAs) were synthesized by a simple one-step method, with varying mole ratios between ethylenimine (EI) and phenylboronic acid (PA). The contributions of nitrogen and boronic acid were analyzed by comparing the FR properties of these new polymers. Thermogravimetric analysis (TGA) was performed to study the thermal decomposition behavior of different PEIPA polymers. The optimal PEIPA was applied on cotton fabric by simple dipping method, and tested by standard vertical flame test to show its flame retardancy efficiency. Thermogravimetric Fourier-Transform-Infrared Spectroscopy (TGIR) analysis was employed to evaluate the volatile inhibition property of the coating. On the other hand, a formaldehyde-free crosslinking treatment between PEIPA 3:1 and NeoFR (which is a cross-linker synthesized by us before), was done to improve the laundering stability of the FR coating (Yang et al. 2012b). Limiting oxygen index (LOI) test was used to assess the change of flame retardancy of the treated cotton fabrics before and after repeated launderings. Finally, cone calorimetry was employed to further assess the flame retardancy and smoke production property of the FR treated fabrics.

Experimental

Materials

Branched polyethylenimine with MW. 1200 (PEI) was purchased from the International Laboratory; 4-Bromophenylboronic acid (BPA) from the Alfa Aesar; Ethyl acetate and tetrahydrofuran (THF) from the Duksan Pure Chemicals Co.; Triethylamine (TEA) and deuterated dimethyl sulfoxide (DMSO-d6) from the Sigma-Aldrich; Desized, scoured and bleached plain weave pure cotton fabric (weighting: 110g/m2, density: 83x163/inch) from Nan Kee Goods-Piece. All the chemicals were used without further treatment while cotton fabric was further scoured with water and then tumble dried.

Synthesis of PEIPA polymers

0.01 mole of PEI (43 g/mol), 0.01 mole of BPA (200.83 g/mol), 0.01 mole of TEA (101.19 g/mol), and 50 ml of THF were introduced into a 100 ml 3-Neck Schlenk Flask. Nitrogen gas was supplied to prevent oxidation reaction during synthesis. A rubber stopper with a narrow hole was placed at one of the flask neck for releasing the gas pressure inside the flask. The mixture was kept at 60 ^{o}C in oil bath with constant stirring at 400 rpm for 24 hours. The resulting mixture was filtrated to remove any precipitates. Then the remaining solution was dried by vacuum evaporator at 50 ^{o}C to remove the THF. The dried sample was washed by 10 ml of ethyl acetate to remove unreacted raw materials. In order to find out the optimum boron and nitrogen composition, four different PEIPA polymers were prepared by varying the mole ratio between PEI and BPA, i.e., 1:1, 2:1, 4:1 and 8:1. PEIPA polymers were white to slightly yellow powder based on the EI:PA ratio. If the ratio of EI:PA is larger than 4:1, the product was a viscous opaque paste. Then, the PEIPA polymers were analysed by ^{1}H NMR and FTIR (ATR) spectroscopy.

> PEIPA 1:1. ^{1}H NMR spectrum of PEIPA 1:1 (500MHz, DMSO-d6): 7.70-7.50 (dd, J= 82.5, 8, 4H, H-Ar of PA); 7.41(s, 4H, H-Ar of PA); 3.42 (br s, 2H, NH of PEI or OH of solvent); 2.48-2.477 (d, J=1.5, 4H, CH2 of PEI)
>
> FTIR (ATR)/cm^{-1}: 2844 (C-H, aliphatic carbon chain), 1583 (C-C, aromatic ring), 1330 (B-O, from the boronic acid), 1271-1246 (C-N, aromatic amine).

Flame Retardant Finishing on Cotton Fabrics

Acetone was chosen as the solvent to prepare PEIPA 1:1 solution for cotton treatment, as the polymer is more soluble in organic solvents than water. For the finishing procedure, at first, known concentrations of PEIPA 1:1 solutions were prepared. While for the fabric samples, they were cut into size 30 x 7.6 cm^{2} following the ASTM D6413-08 standard. Secondly, the solution was poured into a suitable container in fume cupboard. Thirdly, the cotton fabric was dipped into the solution immediately. As the dipped fabric dried in air quickly just after dipping, the dipping procedure was immediately repeated. Based on repeated trials, 10 ml of PEIPA 1:1 solution was absorbed by the fabric sample after 3 times of dipping. Finally, the treated fabric was dried at 60 °C for 30 minutes to remove acetone completely.

The weight % (wt%) add-on of sample was calculated by the following equation:

$$wt\% = \left[\left(W_1 - W_0\right)/W_0\right]x100\%$$

Where W_1 is the weight of treated sample after pad-dry, and W_0 is the initial weight of sample.

PEIPA 3:1/NeoFR Crosslinking Treatment on the Cotton Fabric

NeoFR, which was developed by our group previously, could form water insoluble network with PEI. Therefore, NeoFR could act as a crosslinking agent with PEIPA polymers. PEIPA 3:1 was selected because more free amine groups were available to react with the vinyl group of NeoFR. There were two steps to apply the crosslinkable FR coating on the fabric. Step 1: Application of NeoFR. Known concentration of NeoFR solution was prepared by dissolving the calculated amount of NeoFR in 100ml of deionized water. Then the fabric was immersed into the solution for 1 minute. After that, the wetted fabric was padded by the laboratory Wringer/padder from FANYUAN Instrument (HF) Co., LTD. Until desired amount of wet add-on was achieved, the fabric was dried inside the oven at 65 °C for 30 minutes. Step 2: Application of PEIPA 3:1. The procedure of applying PEIPA 3:1 was the same as the method for applying PEIPA 1:1 coating on the sample.

Characterization and measurements

Chemical structures of different PEIPA polymers were characterized by attenuated total reflectance (ATR) type Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer FTIR spectrum 100) with scanning at mid-infrared region ranging from 4000 to 650 cm^{-1}.

Proton nuclear magnetic resonance (^1H NMR) spectroscopy (Varian Unity Inova 500 NB NMR Spectrometer) was applied for chemical structure analysis at room temperature at 500 MHz with 64 scans. Before the ^1H NMR measurement, 5 mg of sample was put into a NMR tube and 0.4 ml of deuterated dimethyl sulfoxide (DMSO-d6) was added as solvent.

Thermal-oxidative stabilities of the samples were investigated through thermogravimetric analysis (TGA) in air, from room temperature to 700 °C, with heating rate 5 °C min^{-1}, on Mettler Toledo TGA-1. Weight of each sample was about 8-10 mg.

Flammability of the cotton fabrics (300 mm x 76 mm) was evaluated by the vertical burning test following the ASTM D 6413-08 standard. The time durations of after-flame (flame burning time after withdrawal of burner flame) as well as after-glow (the time of flameless combustion after the flame gone) were recorded. If the sample self-extinguished, char length would be measured with a tearing force 100 g.

Surface morphology of char residues was observed through ESCAN VEGA3 scanning electron microscopy (SEM). Before SEM analysis, the fabric samples were pretreated by HITACHI E-1010 ion sputter for 90 seconds.

Washing fastness to laundering test was done by following the AATCC TM 61-2013 standard. Test 2A was chosen. The sample was washed with AATCC 1993 standard washing powder and 59 steel balls inside the AATCC Standard Instrumental ATLAS launder-ometer at 49 °C.

The LOI values of the samples (50 mm x 140 mm) were found by following the ASTM D2863-13 standard. The test was conducted inside the ZR-1 intelligent oxygen index analyzer with oxygen and nitrogen gases supply at 0.2 MPa under room temperature.

TGIR instrument, TGA Q5000 V3.13 Build 261, was employed. Temperature for measurement was from 25 to 800 ^oC. Heating rate was 20 ^oC/min. Scanning range was from 4000 to 450 cm^{-1}. Sample weight was about 10 mg.

Cone calorimetry test was conducted through the cone calorimeter from the Fire Testing Technology (FTT, UK) under heat flux 35 kW/m^2. Sample size was prepared with 100 mm x 100 mm following the ASTM E 1354 standard. Each sample was tested in double layers. Data such as time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), total smoke release (TSR), carbon monoxide (CO) and carbon dioxide (CO_2) yields were recorded.

Results and Discussion

Characterization

The scheme of chemical reaction between PEI and BPA is shown in Fig. 1(a). The amine groups of PEI attacked the carbon centre of benzene that bonded with bromine (Br) in BPA. The by-product was removed by the acid acceptor, triethylamine (TEA). Chemical structure of PEIPA 1:1 was analysed by identifying the peaks of functional groups. Considering the FTIR spectra in Fig. 1(b), the PEIPA 1:1 spectrum has important peaks at 2983-2804 cm^{-1} (aliphatic –CH stretching vibration), 1583 cm^{-1} (C-C stretching vibration in aromatic ring) (Stuart 2004) and 1330 cm^{-1} (B-O bond vibration) (Romanos et al. 2013; Wiacek et al. 2015). These characteristic peaks of PEIPA 1:1 also present in the PEI and BPA spectra. The absence of secondary amine vibration peak (3277 cm^{-1} N-H) in PEIPA 1:1 spectrum indicates the reaction happening at the amine groups of PEI (Lambert 2011; Stuart 2004). Moreover, a new peak at 1271-1246 cm^{-1}, which is relating to C-N stretching in aromatic amine (Stuart 2004), further confirms the link of phenylboronic acid (PA) onto the PEI polymer chain at the amine sites. Therefore, PEIPA 1:1 has the PEI polymer backbone and the PA side groups.

^1H NMR spectra of PEIPA 1:1 and their starting materials are shown in Fig. 1(c). Signals at 7.7-7.4 ppm are assigned to the aromatic protons of the PA (Abdalla et al. 2003; Martín et al. 2006; Peng et al. 2010) while the signal at 2.48 ppm is assigned to the –CH groups of PEI (Peng et al. 2010). On the other hand, signal at 8.2 ppm, which is also assigned to the aromatic protons, disappeared and a new peak at around 7.4 ppm appeared. It is due to the reaction between PEI and BPA, where the more electron withdrawing group in BPA, i.e. Br, was substituted by the more electron donating group NH-R in PEI. The shielding effect on the aromatic protons that next to the reaction site was increased after reaction. Therefore, a new aromatic proton peak shifted to the right, i.e. 7.4 ppm. Moreover, signal at 2.96 ppm, which is assigned to the amine protons of PEI, shifted to a more upfield region (3.4 ppm) and fused with the solvent peak. It is due to the electron withdrawing ability of benzene ring that made the nearby amine protons less shielded by the electron cloud. These changes in peak positions provide strong evidence to indicate the site where reaction proceeded.

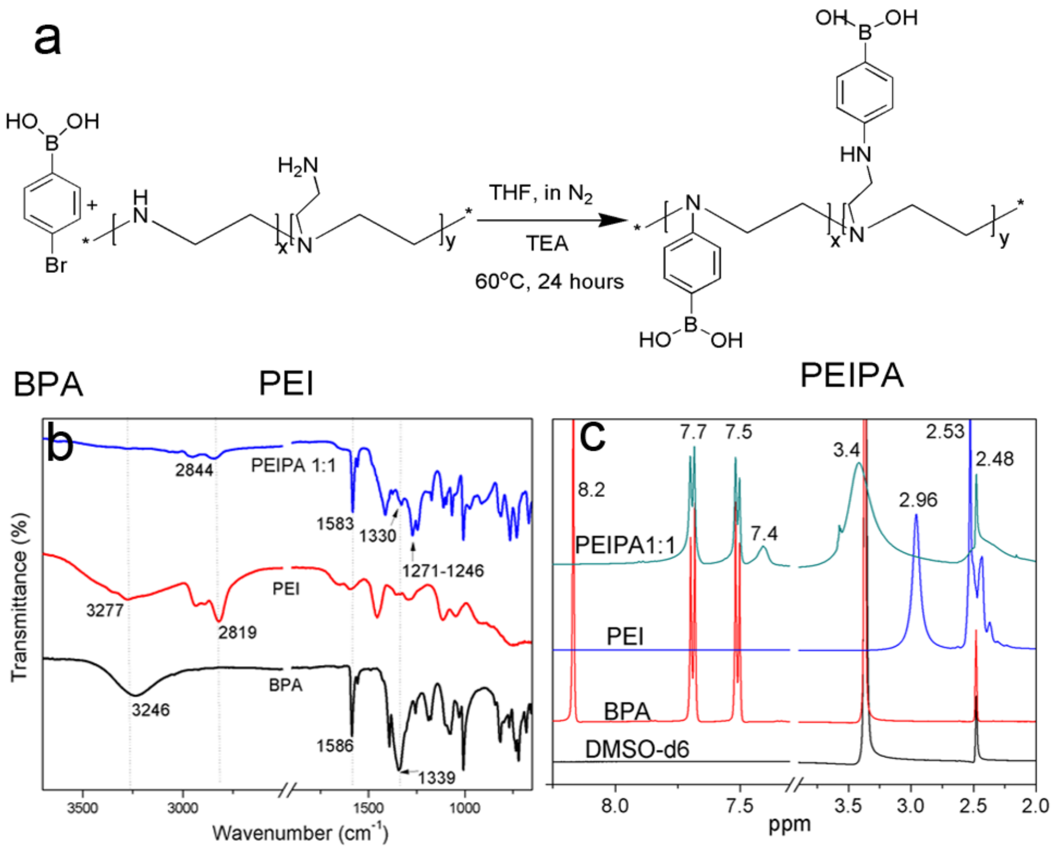

Fig. 1 (a) Chemical reaction between BPA and PEI; (b) FTIR spectra and (c) ^{1}H NMR spectra of PEIPA 1:1, PEI and BPA

Thermal oxidative stability and flammability of PEIPA polymers

Four different PEIPA polymers, PEIPA 1:1/2:1/4:1/8:1, were synthesized by varying the mole ratio between EI and PA to study the effects of the two main effective elements, boron and nitrogen, on the resistance of the thermal-oxidative decomposition. The contribution of nitrogen in promoting the oxidative heat stability of the PEIPA polymers could be studied when the amount of nitrogen increased in the PEIPA polymers. Fig. 2(a) shows the weight loss of different PEIPA polymers against temperatures and 2(b) shows the rate of weight loss as a function of temperature. Table 1 summarizes the data of the $T_{10\%}$ and T_{max}, which are defined as the temperatures for the first 10% weight loss and the fastest weight loss respectively.

As shown in Fig. 2(a) and Table 1, PEI and BPA have $T_{10\%}$ at 225 and 290 ^{o}C respectively, while PEIPA polymers started to decompose in a lower temperature range (i.e. 182 -72 ^{o}C). PEI almost decomposed completely after 370 ^{o}C and left 0.47% char at 700 ^{o}C. BPA is thermally more stable than PEI as it left 6.52% char at 700 ^{o}C. All PEIPA polymers (except PEIPA 8:1) have higher char yields (>10%) at 700 ^{o}C than their raw materials. Based on the onset decomposition temperatures ($T_{10\%}$), PEIPA polymers are less thermally stable as they decomposed easier at lower temperature than their raw materials. However, all PEIPA polymers show remarkable decrease in peak decomposition rate in Fig. 2(b), and almost left more char finally. It is believed that, PEIPA is a “catalytic-type” flame retardant in which thermal decomposition is initiated at low temperature and results in more char via catalytic effect in following decomposition (Martín et al. 2006). These chars act as physical barrier and reduce the decomposition rate at higher temperatures.

On the other hand, PEIPA samples with higher PEI ratio (i.e. higher nitrogen content) have lower maximum decomposition rate while samples with higher PA content (i.e. higher amount of boron) have higher $T_{10\%}$, T_{max} and char yields. Such results imply that, PA (boron) acts as charring agent (Shen 2014) through the formation of borate esters/salts for further dehydration (Abdalla et al. 2003). The boron containing char is thermally more stable, so the samples with higher PA content lose less weight after 500 °C (see Fig 2a). From the TG and DTG analysis, the optimal EI:PA ratio was identified as 1:1, since it produced the highest amount of stable char at 700 °C.

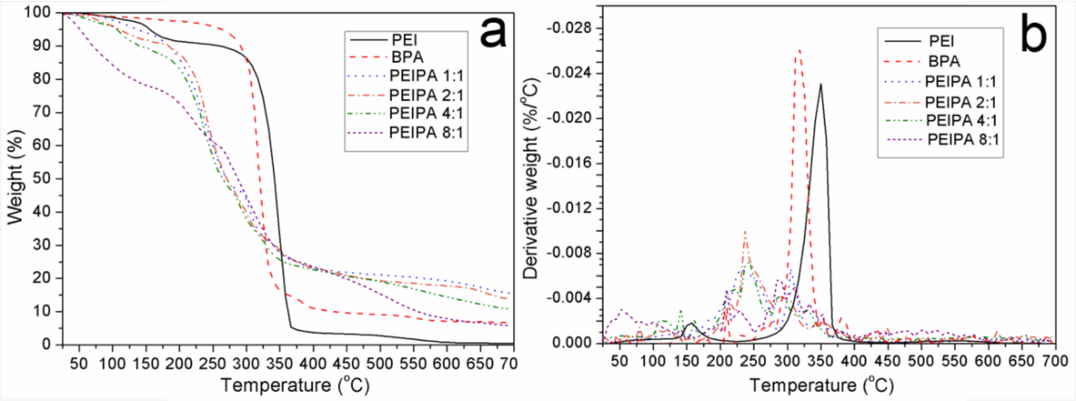

Fig. 2 (a)TG curves and (b) DTG curves of PEI, BPA and PEIPA polymers under air atmosphere

Table 1 TGA data of PEI, BPA and PEIPA polymers under air atmosphere

Sample	$T_{10\%}$ (°C)	T_{max} (°C)	Residue at 700 °C (%)
PEI	225	350	0.47
BPA	290	320	6.52
PEIPA 1:1	182	230	15.59
PEIPA 2:1	168	235	13.67
PEIPA 4:1	134	240	10.79
PEIPA 8:1	72	290	5.77

The flammability of PEIPA 1:1 polymer was evaluated under the supply of gas flame. The whole process was recorded in Fig. 3(a). At the beginning, PEIPA 1:1 melted and released some smoke in contact with gas flame. Later, the discrete powders were melted together and expanded to form some bubbles. Further supply of flame caused the formation of a black shell on the substrate surface. Finally, the protective black shell was stable under continuous supply of flame, and the substrate under the black cover was kept in molten state. PEIPA 1:1 was non-flammable during the whole process, and carbonized rather than volatilized under continuous heating. Furthermore, the PEIPA 1:1 showed an intumescent character (Alongi et al. 2015) during the flaming process. Fig. 3(b) shows the schematic illustration of the anti-flaming mechanism of PEIPA1:1. When the polymer was heated, some nitrogen containing gases and other gases were released to dilute the oxygen concentration around the substrate surface; then impenetrable carbonized barrier was formed to isolate the oxygen and the evolved gases to hinder oxidative reaction. Therefore, combustion was successfully prevented. This behaviour of PEIPA 1:1 is in accordance with its TG result.

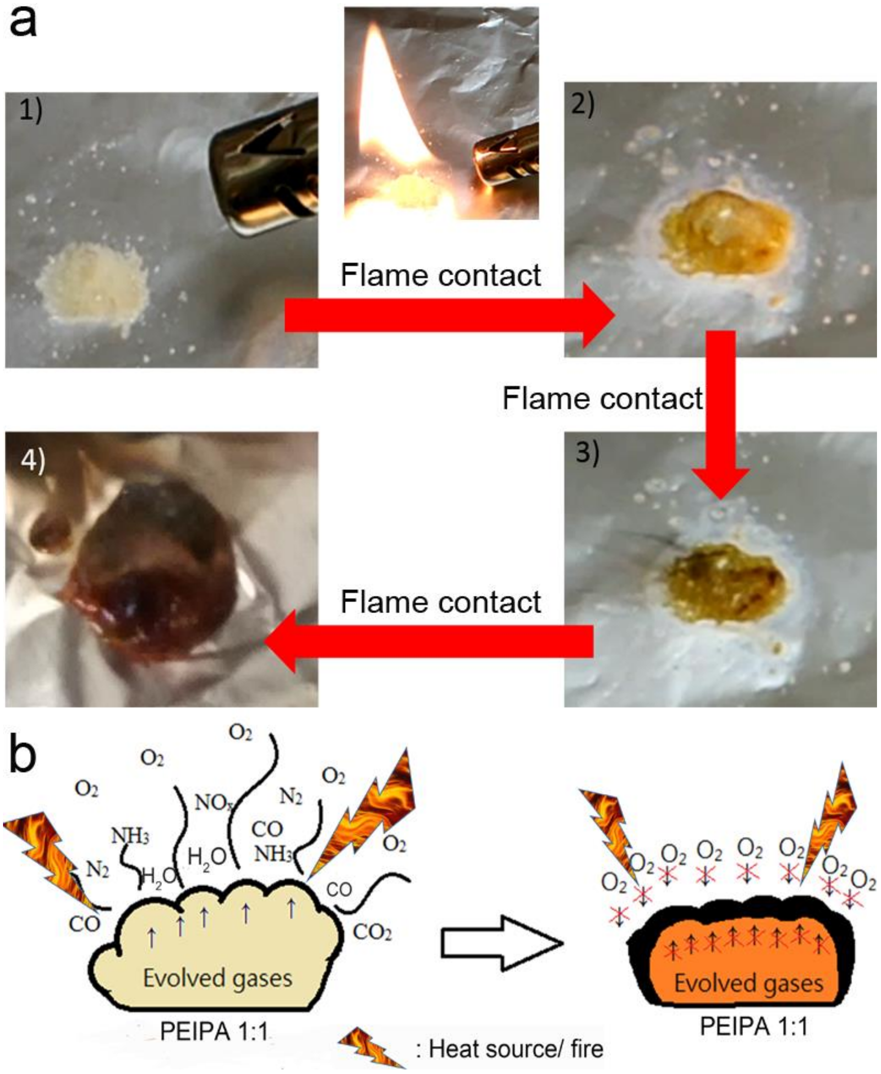

Fig. 3 (a) Digital photos showing the behaviour of PEIPA 1:1 toward direct burning by gas flame; (b) schematic illustration showing the dilution and protective barrier effects for anti-flaming property of PEIPA 1:1

Flammability of PEIPA 1:1 treated cotton fabric

All samples were burned directly with Bunsen burner flame for 12 seconds in vertical direction at the bottom of the fabric samples. The residues after burning test were shown in Fig. 4. From Fig. 4(a), control fabric was burned vigorously and almost completely, leaving very little amount of ashes at the equipment boundary. Samples that have 16.7 wt% and 23.8 wt% add-ons were also burned over by flame but left more char and burned less vigorous than the control. Moreover, they had 8 seconds after-flame time, meaning that when the supply of burner flame was stopped, the fire on the fabrics could be sustained by the fuel and energy, i.e. the flammable volatiles derived from the decomposition of cellulose, and the heat released through oxidation reaction (Kilinc and Textile Institute (Manchester England) 2013; Wilkie and Morgan 2010). Such char produced was not able to prevent releasing of volatiles and heat. Only the sample with 33.4 wt% add-on self-extinguished within 5 seconds without after-flame and left 10 cm char. The direct flame could not ignite the charred area anymore. The char formed could provide great heat shielding effect as well as a very good barrier to volatiles. Therefore, the sample could not burn continuously.

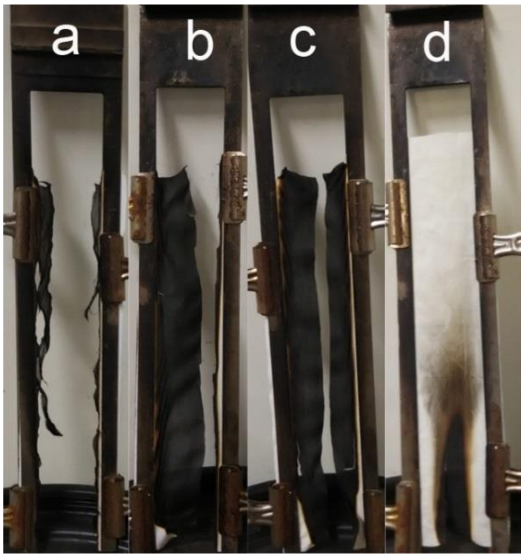

Fig. 4 Digital photos showing the residues of samples (a) control cotton, and treated cotton fabrics with (b)16.7 wt%, (c)23.8 wt% and (d)33.4 wt% add-ons of PEIPA 1:1 after vertical burning test

Evolved volatiles analysis

TGIR technique is a powerful tool to study the volatilized products of a sample during thermal degradation in a dynamical base. Fig. 5(a) shows the absorbance of pyrolysis products of cotton and PEIPA 1:1 treated cotton versus time. The maximum decomposition (also gas releasing) peaks of the treated sample shifted to lower temperature, i.e. from 395 to 375 ^{o}C. Such phenonmen reveals that PEIPA 1:1 could catalyze the thermal decomposition of cotton. Moreover, the total absorbance of the evolved volatiles of FR treated fabric has 24% reduction (based on the integrated area) when compared with pure cotton. It is due to the high quality char derived from PEIPA 1:1.

Fig. 5(b) shows the FTIR spectra of the evolved products from the pure cotton and treated cotton at their top evolution rate (i.e. at 395 and 375 ^{o}C respectively). Some pyrolysis products can be identified by the characteristic FTIR signals of functional groups. The identified gaseous products include: water (3566 cm^{-1}), hydrocarbons (2798 cm^{-1}), CO_2 (2354 cm^{-1}), carbonyl compounds (1746 cm^{-1}), aromatic compounds (1510 cm^{-1}), aliphatic ethers (1104 cm^{-1}), and ammonia (934 cm^{-1}) (Chen et al. 2016; Chen et al. 2013; Jimenez et al. 2015; Mu et al. 2015; Pan et al. 2015; Tai et al. 2012; Wang et al. 2016). All samples had similar FTIR pattern to each other. However, their peak intensities were significantly different. The flammable volatiles, such as hydrocarbons, carbonyl compounds, and aliphatic ethers were greatly reduced after FR treatment. On the other hand, no characteristic peak of boron was found in the FTIR spectrum. So boron remained in the condensed phase during thermal decompostion.

Fig. 5(c) and (d) show the 3D TGIR spectra of cotton and FR treated cotton respectively. The changes of the volatiles' composition across the temperatures can be easily traced in the 3D graphs. In Fig 5.(c), the prominent peaks representing the flammable volaitles, i.e. hydrocarbon, carbonyl compounds, aromatic compounds, and aliphatic ethers, existed aross a relatively wide temperature range, i.e., from 355 to 415 ^{o}C. The treated cotton in Fig. 5(d) produced the same volatiles at a narrower temperature range, i.e., from 375 to 385 ^{o}C. Moreover, the treated sample presented lower intensity of signals. Furthermore, Fig. 6 (a-f) reveal more details about the absorbance of specific gases evolved from the thermal decomposition of cotton and treated cotton versus time. The peak intensities of non-flammable gases, like H_2O and CO_2, were greatly increased after FR treatment. The flammable volatiles, like hydrocarbons, carbonyl compounds and aliphatic ethers, were significantly reduced. On the other hand, the peak intensity of the less flammable aromatic compounds was increased after treatment (Fig. 6e) may be due to the decomposition of the phenylboronic acid group in PEIPA 1:1 polymer. During the thermal degradation of cotton, flammable volatiles were continuously produced after the peak decomposition temperature. After treatment with PEIPA 1:1, flammable volatiles were greatly inhibited, and more non-flammable gases (e.g. H_2O and CO_2) were released for cooling and dilution effects.

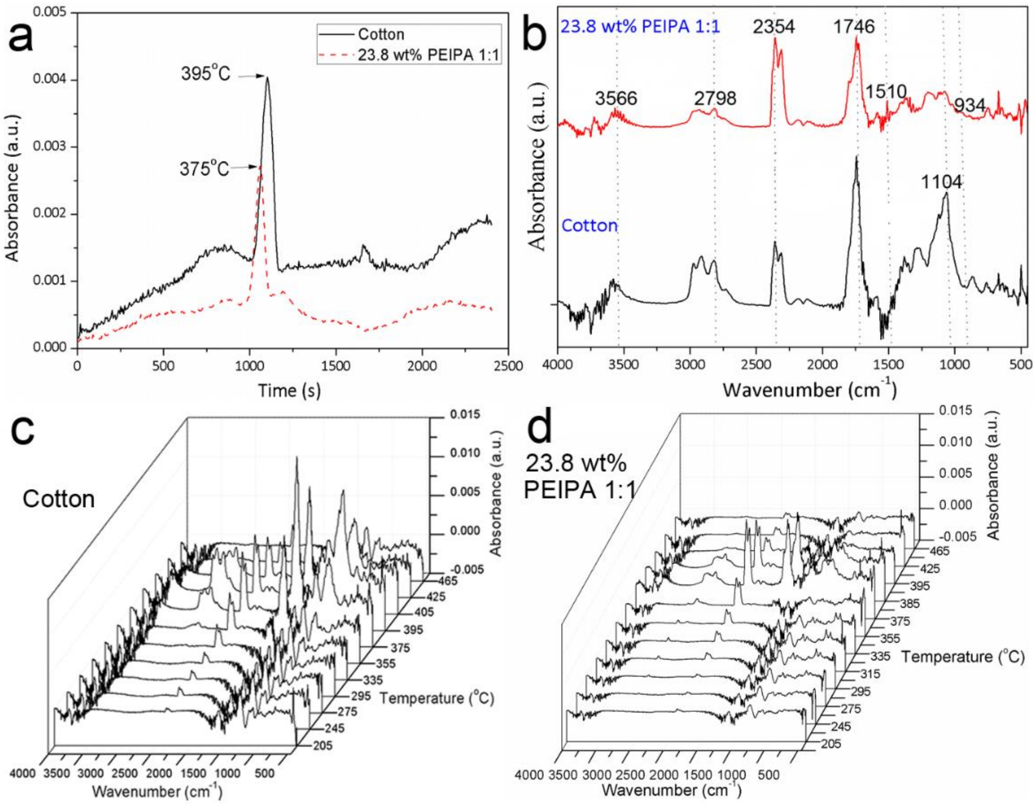

Fig. 5 (a) Absorbance (versus time) and (b) FTIR spectra (at maximum decomposition rate) of pyrolysis volatiles of pure cotton and PEIPA 1:1 treated cotton; 3D TG-IR spectra of (c) pure cotton and (d) PEIPA 1:1 treated cotton

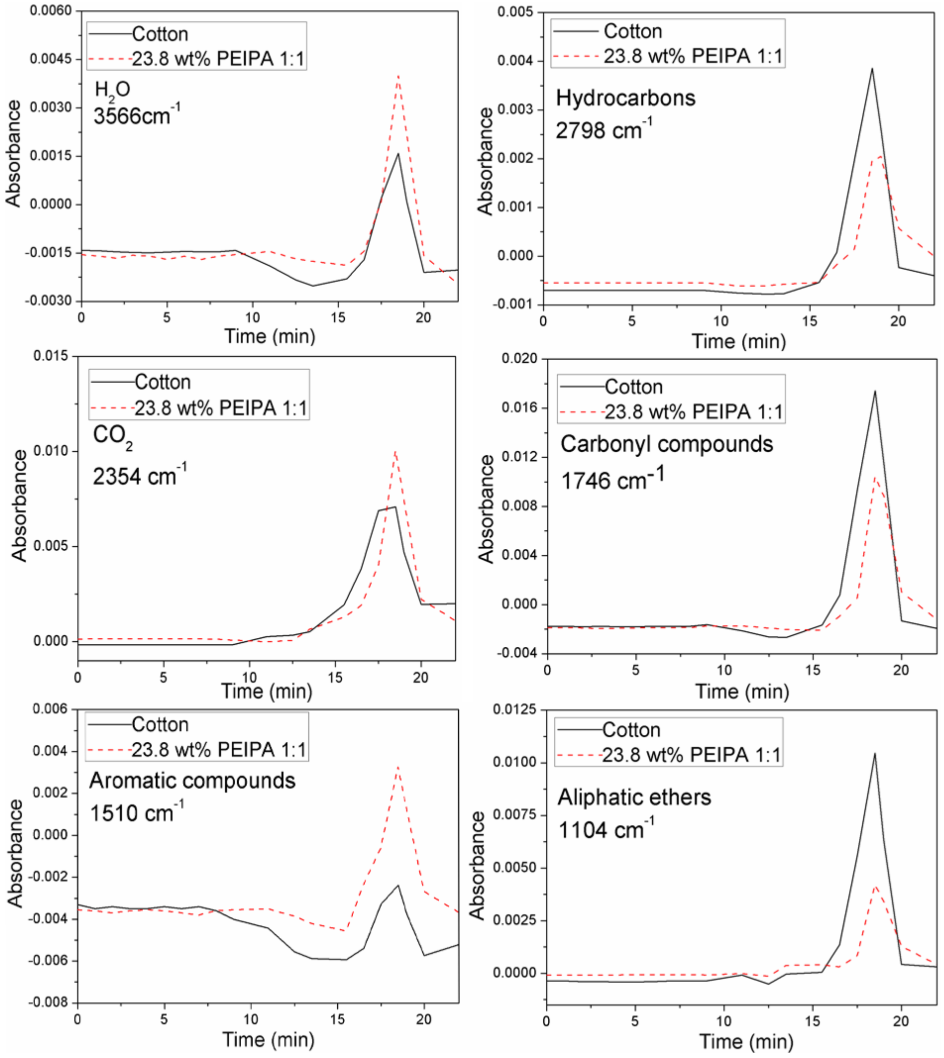

Fig. 6 Absorbance of a) H_2O, b) hydrocarbons, c) CO_2, d) carbonyl compounds, e) aromatic compounds, and f) aliphatic compounds of cotton and PEIPA 1:1 treated cotton versus time

PEIPA/NeoFR crosslinking treatment and washing durability of treated cotton

According to our previous research (Yang et al. 2012), our novel flame retardant can be crosslinked and made durable against washing. The insoluble FR network was formed through the reaction between the amine groups of PEI and the vinyl groups in the NeoFR compound. Since our PEIPA 3:1 flame retardant has more free amine groups than PEIPA 1:1, we combined it with NeoFR to form a network structure on cotton fibers. The reaction mechanism between the PEIPA 3:1 and NeoFR is illustrated in Fig. 7(a) and (b).

Washing durability of the flame-retardant coatings on the cotton fabrics was assessed through the measurement of the changes in flammability before and after repeated launderings, by LOI value. LOI refers to the minimum oxygen concentration for continual candle-like downward combustion. Mostly, the higher the LOI value, the higher the flame retardancy of a substrate. Any changes in flammability of the samples can be shown quantitatively. Table 2 shows the LOI values of the control, PEIPA 1:1 treated, and PEIPA 3:1/NeoFR treated cottons before and after 5 launderings accordingly. Pure cotton has LOI 18.2%, which means it is very flammable under normal condition. The cotton with 33.8 wt% PEIPA 1:1 has LOI 24.8%, representing a 36.3% increase in LOI value and a significant improvement in flame retardancy. On the other hand, cotton treated by the new cross-linking FR system (PEIPA 3:1/NeoFR) with 30 wt% add-on has LOI 29.6%, representing a 62.6% increase to the control. Since the cross-linked coating results in higher LOI with less add-on than the pure PEIPA coating, the NeoFR is recognized as FR synergist for the PEIPA 3:1. The remarkable increases in LOI values may be due to the enhanced char yields (as shown in the TG results in Table 2). The char acted as an effective thermal insulating barrier to hinder transfer of heat and fuel and stop combustion. However, after repeated washing, the LOI value of PEIPA treated cotton dropped dramatically to 18.4%, which is close to that of pure cotton. Therefore, the PEIPA coating is not a wash-durable FR treatment for cotton. On the other hand, cotton with the cross-linked FR coating has LOI value 23.2% after 5 launderings. Though the flame retardancy of the fabric decreased, a significant effect was still retained on the cotton (higher than the control by 27.4%). All in all, the new cross-linking system successfully improved the washing durability of the PEIPA coating on cotton.

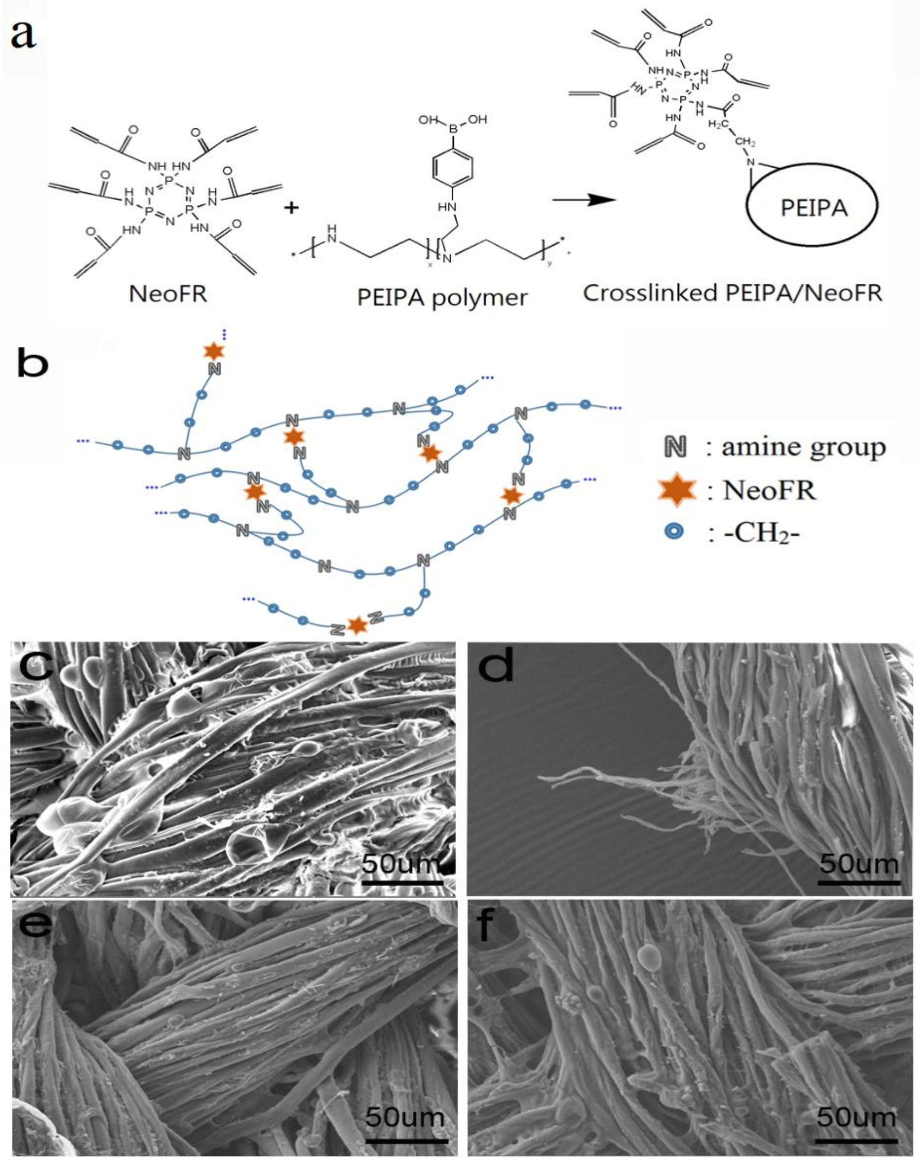

Fig. 7 (a) Chemical reaction between PEIPA 3:1 and NeoFR; (b) schematic illustration showing the crosslinked network of PEIPA 3:1/NeoFR; SEM images showing the char morphology of PEIPA treated cotton (c)without and (d) with launderings; as well as PEIPA 3:1/NeoFR treated cotton (e) without and (f) with launderings

Table 2 TGA data and LOI values of control, PEIPA treated and PEIPA3:1/NeoFR treated cotton fabrics

Sample	$T_{10\%}$ (^oC)	T_{max} (^oC)	Residue at 500 ^oC (%)	LOI (%)	LOI after 5 launderings (%)
Control	320	333	0	18.2	/
PEIPA 1:1 treated cotton	216	326	16.2	24.8	18.4

PEIPA 3:1/NeoFR treated cotton	243	298	30.7	29.6	23.2

The char residues after LOI test were observed under SEM. Fig. 7 (c) and (d) show the char surface morphologies of PEIPA treated cotton before and after launderings respectively. Many bubbles were observed on the PEIPA treated cotton without washing, which was the characteristic feature of intumescent-type flame retardant. The fibre shape of cotton was still ribbon-like and intact. After 5 launderings, the fabric residue became significantly thinner in fiber diameter, without any bubbles. Therefore, PEIPA treatment on cotton fabric is not washing durable. The char morphologies of PEIPA 3:1/NeoFR coated cotton before and after launderings are shown in the Fig. 7(e) and (f) respectively. No obvious difference can be found in these residues. Intumescent bubbles and intact fibers were observed in both of the chars, demonstrating a significantly improved washing stability. Hence, a reliable FR system was achieved for cotton finishing, based on crosslinking components and intumescent FR mechanism.

Thermal stability and cone calorimetric analysis of the FR-treated cottons

The oxidative thermal stability of PEIPA 3:1/NeoFR treated cotton was compared with the PEIPA treated cotton. Details about the initial decomposition temperature ($T_{10\%}$), maximum decomposition temperature (T_{max}), and the amount of char residue at 500 °C were summarized in Table 2. All treated cottons have lower $T_{10\%}$ and T_{max} than the control, meaning that the coatings changed the decomposition behaviour of cellulose for more char formation (lower temperature favours char forming pathway) (Demirbas 2009). PEIPA 3:1/NeoFR treated cotton has almost a double amount of char (30.7%) than the PEIPA treated cotton (16.2%) at 500 °C, notably by the synergistic effect caused by the P-N containing NeoFR (which exhibits FR effects in condensed and gas phase) (Schartel 2010). Under the same temperature, pure cotton was completely pyrolyzed. Since higher thermal stability was observed in PEIPA 3:1/NeoFR treated cotton, this coating is recognized as a more effective flame retardant system.

Cone calorimetry analysis became an essential technique for studying the flammability of different materials. HRR is the most important data for flammability assessment, indicating the size of fire and the rate of fire growth (Zhang et al. 2012). Moreover, cone calorimetry provides smoke and gas analysis, which is also very useful to predict the fire toxicity of a material. Pure cotton, 33.4 wt% PEIPA 1:1 treated and 15 wt% PEIPA 3:1/15 wt% NeoFR treated cottons were tested under heat flux 35 kW/m^2. The details about the fire behaviours of the samples are listed in Table 3. From the table, FR treated cotton has shorter TTI due to the catalytic effect of the flame retardant. PEIPA 1:1 treated sample (TTI: 5s) started to burn earlier than the PEIPA 3:1/NeoFR treated sample (TTI: 8s), because the PEIPA 1:1 coating on cotton has lower onset decomposition temperature ($T_{10\%}$, in Table 2). Fig. 8 shows the HRR curves of the samples. Both samples showed a sharp peak and then a levelling off. The PHRR of the PEIPA 1:1 treated cotton was 172 kW/m^2 and the THR was 2.3 MJ/m^2, which were 33.3% and 30.3% lower than the pure cotton (258 kW/m^2 and 3.3 MJ/m^2) respectively. While PEIPA 3:1/NeoFR treated cotton has 129 kW/m^2 and 1.8 MJ/m^2, which were 50% and 45.5% lower than that of cotton respectively. The significant decreases in the PHRR and THR was due to the formation of protective char. As shown in Fig. 9(a), the control cotton was almost completely pyrolyzed. While in Fig. 9(b) and (c), the FR treated cottons left larger amount of char with intact fabric structure. Hence, the improvement of char formation leaded to the reduction in flammable volatiles and penetration. Therefore, less fuel and heat were fed back to the combustion zone, reduced the severity of pyrolysis. PEIPA 3:1/NeoFR presented stronger flame retardancy than the PEIPA 1:1 due to the addition of phosphorus-nitrogen containing compound for further enhanced char formation. All in all, this cone test result agrees with the above TG results.

Regarding the smoke production during cone combustion, Table 3 reveals significant increase in total smoke release (TSR) from FR treated cottons. PEIPA 1:1 treated cotton has about 2.6 times higher amount of smoke than the control (2.6 m^2/m^2), while PEIPA 3:1/NeoFR treated cotton has 9.2 times higher. PEIPA 3:1/NeoFR treated cotton released the most smoke due to the addition of P-N containing cross-linker (NeoFR) that has heterocyclic structure and gas phase function. Phosphorous species inhibited the burning of volatiles and allow them to gather into smoke particles in air (Lu et al. 2002). CO yields of the PEIPA 1:1 treated and PEIPA3:1/NeoFR treated cottons were 149 ppm and 160 ppm respectively, obviously higher than the pure cotton (71 ppm) mainly due to the incomplete combustion under char barrier. The CO_2/CO ratio indicates the combustion efficiency by revealing the degree of conversion from partial oxidization product (CO) to full oxidization product (CO_2) (Jia et al. 2017). The FR treated cottons presented about 81.2% decrease in CO_2/CO ratio when compared with the cotton, indicating the FR significant reduction in combustion efficiency by both FR treatments.

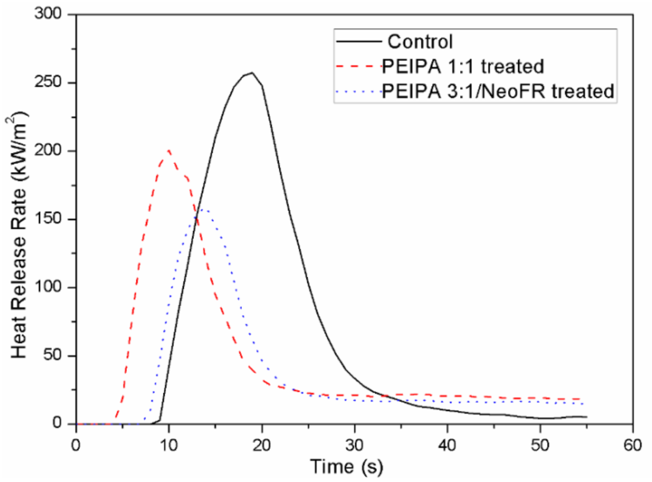

Fig. 8 Heat release rate curves of control cotton and FR treated cottons

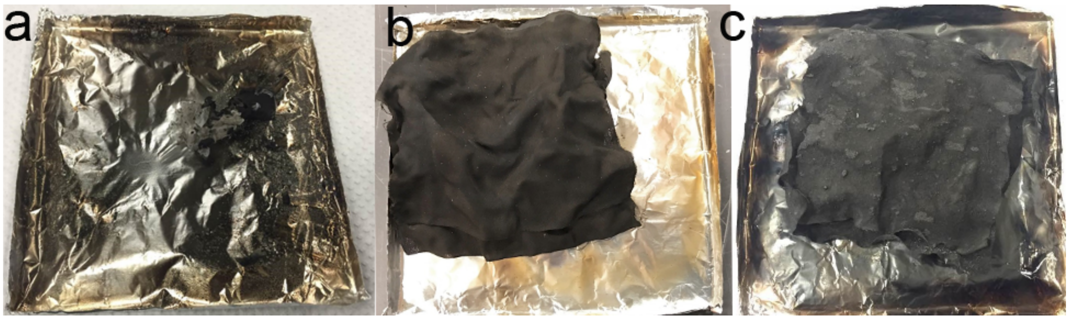

Fig. 9 Char residues of (a) cotton, (b) PEIPA 1:1 treated cotton and (c) PEIPA 3:1/NeoFR treated cotton after cone calorimetry test

Table 3 Data in cone calorimetry test showing the burning and smoke production behaviours of cotton and FR treated cottons

Sample	TTI (s)	Peak HRR (kW/m^2)	THR (MJ/m^2)	TSR (m^2/m^2)	[CO] (ppm)	Yield ratio CO_2/CO
Cotton	9	258	3.3	2.6	71	37.7
PEIPA 1:1 treated	5	172	2.3	6.7	149	7.2
PEIPA 3:1/NeoFR treated	8	129	1.8	23.8	160	7.0

P.S. fatal CO concentration to human in 30 minutes, C_f value: 4 x 10^3 (Naval Engineering Standard 713, 1985)

Conclusion

The novel boron-nitrogen polymers, PEIPAs, were successfully synthesized. PEIPA 1:1 has the optimal thermal stability, which can improve the flame retardancy of cotton significantly by enhancing the char formation. The cotton with 33.4 wt% of PEIPA 1:1 has self-extinguishing property in standard vertical flammability test, a LOI value up to 24.8%, and a THR decreased by 33.3%. Intumescent char was observed under, revealing the intumescent FR mechanism of PEIPA

1:1. TGIR results revealed less production of flammable volatiles from the PEIPA 1:1 treated cotton. To sum up, PEIPA 1:1 achieved good flame retardancy through multiple actions, including (1) Accelerating the cotton decomposition at low temperature to promote char formation; (2) Reducing flammable volatiles and flammability by char formation; (3) Reducing heat release by the barrier effect of intumescent char. Further improvement on its washing durability was achieved by using NeoFR as the cross-linker to form insoluble network which also resulted in improvement in anti-flammability. The combined FR system (PEIPA 3:1/NeoFR) realized high LOI 29.6% and a THR reduced by 45.5%, although the release of smoke and CO production was increased. The quick self-extinguishing and the non-smouldering properties also facilitate people to escape from the fire scene. The PEIPA polymers and the PEIPA 3:1/NeoFR coating system would be be suitable semi-durable alternative to toxic halogenated flame retardants on cellulosic products, especially for household textiles that do not require frequent washing.

Acknowledgements

We thank the funding support of GRF project 15208015 and PolyU G-UA1Z.

References

Abdalla MO, Ludwick A, Mitchell T (2003) Boron-modified phenolic resins for high performance applications. Polymer 44:7353-7359. doi:10.1016/j.polymer.2003.09.019

Alongi J, Carletto RA, Di Blasio A, Cuttica F, Carosio F, Bosco F, Malucelli G (2013) Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics. Carbohydr Polym 96:296-304. doi:10.1016/j.carbpol.2013.03.066

Alongi J, Carosio F, Malucelli G (2014) Current emerging techniques to impart flame retardancy to fabrics: An overview. Polym Degrad Stab 106:138-149. doi:10.1016/j.polymdegradstab.2013.07.012

Alongi J, Han Z, Bourbigot S (2015) Intumescence: Tradition versus novelty. A comprehensive review. Prog Polym Sci 51:28-73. doi:org/10.1016/j.progpolymsci.2015.04.010

Alongi J, Malucelli G (2015) Cotton flame retardancy: state of the art and future perspectives. Rsc Advances 5:24239-24263. doi:10.1039/C5RA01176K

Carosio F, Di Blasio A, Alongi J, Malucelli G (2013) Green DNA-based flame retardant coatings assembled through Layer by Layer. Polymer 54:5148-5153. doi:10.1016/j.polymer.2013.07.029

Chen S, Li X, Li Y, Sun J (2015) Intumescent Flame-Retardant and Self-Healing Superhydrophobic Coatings on Cotton Fabric. ACS Nano 9:4070-4076. doi:10.1021/acsnano.5b00121

Chen X, Ma C, Jiao C (2016) Enhancement of flame-retardant performance of thermoplastic polyurethane with the incorporation of aluminum hypophosphite and iron-graphene. Polym Degrad Stab 129:275-285. doi:10.1016/j.polymdegradstab.2016.04.017

Chen XL, Huo LL, Jiao CM, Li SX (2013) TG-FTIR characterization of volatile compounds from flame retardant polyurethane foams materials. J Anal Appl Pyrol 100:186-191. doi:10.1016/j.jaap.2012.12.017

Demirbas A (2009) Pyrolysis Mechanisms of Biomass Materials. Energ Sources Part A 31:1186-1193. doi:10.1080/15567030801952268

Fei B, Yang Z, Shao S, Wan S, Xin JH (2010) Enhanced fluorescence and thermal sensitivity of polyethylenimine modified by Michael addition. Polymer 51:1845-1852. doi:10.1016/j.polymer.2010.02.017

Haile M, Leistner M, Sarwar O, Toler CM, Henderson R, Grunlan JC (2016) A wash-durable polyelectrolyte complex that extinguishes flames on polyester-cotton fabric. RSC Adv 6:33998-34004. doi:10.1039/C6RA03637F

Haynes HJG (2016) Fire loss in the United States during 2015. National Fire Protection Association

Horacek H, Grabner R (1996) Advantages of flame retardants based on nitrogen compounds. Polym Degrad Stab 54:205-215. doi:10.1016/S0141-3910(96)00045-6

Horrocks AR, Price D (2001) Fire retardant materials. Woodhead Pub., Boca Raton, Fla., Cambridge

Jia Y, Hu Y, Zheng D, Zhang G, Zhang F, Liang Y (2017) Synthesis and evaluation of an efficient, durable, and environmentally friendly flame retardant for cotton. Cellulose 24:1159-1170. doi:10.1007/s10570-016-1163-z

Jimenez M, Lesaffre N, Bellayer S, Dupretz R, Vandenbossche M, Duquesne S, Bourbigot S (2015) Novel flame retardant flexible polyurethane foam: plasma induced graft-polymerization of phosphonates. Rsc Adv 5:63853-63865. doi:10.1039/c5ra08289g

Kilinc FS, Textile Institute (Manchester England) (2013) Handbook of fire resistant textiles. Woodhead Publishing series in textiles no 140. Oxford, Philadelphia, Pa.

Lambert JB (2011) Organic structural spectroscopy. 2nd edn. Prentice Hall/Pearson. Upper Saddle River, N.J.

LeVan SL, Tran HC (1990) The role of boron in flame-retardant treatments. In the Proceedings of First International Conference on Wood Protection with Diffusible Preservatives 47355:39-41

Lindholm J, Brink A, Hupa M (2009) Cone Calorimeter—A Tool for Measuring Heat Release Rate. Åbo Akademi Process Chemistry Centre, Finland

Liu W, Chen L, Wang Y-Z (2012) A novel phosphorus-containing flame retardant for the formaldehyde-free treatment of cotton fabrics. Polym Degrada Stab 97:2487-2491. doi:10.1016/j.polymdegradstab.2012.07.016

Lu SY, Hamerton I (2002) Recent developments in the chemistry of halogen-free flame retardant polymers. Progin Polym Sci 27:1661-1712. doi:10.1016/S0079-6700(02)00018-7

Lv Q, Huang J-Q, Chen M-J, Zhao J, Tan Y, Chen L, Wang Y-Z (2013) An Effective Flame Retardant and Smoke Suppression Oligomer for Epoxy Resin. Ind Eng Chem Res 52:9397-9404. doi:10.1021/ie400911r

Martín C, Hunt BJ, Ebdon JR, Ronda JC, Cádiz V (2006) Synthesis, crosslinking and flame retardance of polymers of boron-containing difunctional styrenic monomers. React Funct Polym 66:1047-1054. doi:10.1016/j.reactfunctpolym.2006.01.013

Martin C, Ronda JC, Cadiz V (2006) Boron-containing novolac resins as flame retardant materials. Polym Degrad Stab 91:747-754. doi:10.1016/j.polymdegradstab.2005.05.025

Mosurkal R, Kirby R, Muller WS, Soares JW, Kumar J (2011) Simple green synthesis of polyborosiloxanes as environmentally-safe, non-halogenated flame retardant polymers. Green Chem 13:659-665. doi:10.1039/c0gc00376j

Mu XW, Yuan BH, Hu WZ, Qiu SL, Song L, Hu Y (2015) Flame retardant and anti-dripping properties of polylactic acid/poly(bis(phenoxy)phosphazene)/expandable graphite composite and its flame retardant mechanism. Rsc Adv 5:76068-76078. doi:10.1039/c5ra12701g

Nedel'ko VV, Korsunskii BL, Dubovitskii FI, Gromova GL (1975) The thermal degradation of branched polyethylenimine. Polymer Science USSR 17:1697-1703 doi:10.1016/0032-3950(75)90172-0

Pan N, Sun G (2011) Functional textiles for improved performance, protection and health. Woodhead Publishing, Oxford, Cambridge, Philadelphia, New Delhi

Pan Y, Zhan J, Pan HF, Wang W, Ge H, Song L, Hu Y (2015) A novel and effective method to fabricate flame retardant and smoke suppressed flexible polyurethane foam. Rsc Adv 5:67878-67885. doi:10.1039/c5ra09553k

Papaspyrides CD, Kiliaris P (2014) Chapter 1- Polymers on Fires. In: Polymer green flame retardants. Elsevier, Amsterdam, pp 1-43.

Peng Q, Chen F, Zhong Z, Zhuo R (2010) Enhanced gene transfection capability of polyethylenimine by incorporating boronic acid groups. Chem Commun 46:5888-5890. doi:10.1039/C0CC00877J

Romanos J et al. (2013) Infrared study of boron-carbon chemical bonds in boron-doped activated carbon. Carbon 54:208-214. doi:10.1016/j.carbon.2012.11.031

Schartel B (2010) Phosphorus-based Flame Retardancy Mechanisms—Old Hat or a Starting Point for Future Development? Materials 3:4710-4745. doi:10.3390/ma3104710

Shen KK (2014) Chapter 11 - Review of Recent Advances on the Use of Boron-based Flame Retardants. In: Polym Green Flame Retardants. Elsevier, Amsterdam, pp 367-388. doi:10.1016/B978-0-444-53808-6.00011-1

Stuart B (2004) Infrared spectroscopy : fundamentals and applications. John Wiley & Sons, Ltd., Chichester

Tai QL, Song L, Feng H, Tao YJ, Yuen RKK, Hu Y (2012) Investigation of a combination of novel polyphosphoramide and boron-containing compounds on the thermal and flame-retardant properties of polystyrene. J Poly Res 19:9763. doi:10.1007/s10965-011-9763-7

Wang DC, Chang GW, Chen Y (2008) Preparation and thermal stability of boron-containing phenolic resin/clay nanocomposites. Polym Degrad Stab 93:125-133. doi:10.1016/j.polymdegradstab.2007.10.021

Wang W et al. (2016) Fabrication of LDH nanosheets on beta-FeOOH rods and applications for improving the fire safety of epoxy resin. Compos Part a-Appl Sci Manuf 80:259-269. doi:10.1016/j.compositesa.2015.10.031

Wiacek M, Wesolek D, Rojewski S, Bujnowicz K, Schab-Balcerzak E (2015) Boronated (co)polystyrene: monomer reactivity ratios, thermal behavior and flammability. Polym Adv Technol 26:49-56. doi:10.1002/pat.3418

Wilkie CA, Morgan AB (2010) Fire retardancy of polymeric materials. 2nd edn. CRC Press, Boca Raton

Xie KL, Gao AQ, Zhang YS (2013) Flame retardant finishing of cotton fabric based on synergistic compounds containing boron and nitrogen. Carbohydr Polym 98:706-710. doi:10.1016/j.carbpol.2013.06.014

Xu PJ, Jing XL (2010) Pyrolysis of Hyperbranched Polyborate Modified Phenolic Resin. Polym Eng Sci 50:1382-1388. doi:10.1002/pen.21675

Yang Z, Fei B, Wang X, Xin JH (2012) A novel halogen-free and formaldehyde-free flame retardant for cotton fabrics. Fire Mater 36:31-39. doi:10.1002/fam.1082

Yang ZY, Wang XW, Lei DP, Fei B, Xin JH (2012) A durable flame retardant for cellulosic fabrics. Polym Degrad Stab 97:2467-2472. doi:10.1016/j.polymdegradstab.2012.05.023

Zhang R, Xiao X, Tai Q, Huang H, Hu Y (2012) Modification of lignin and its application as char agent in intumescent flame-retardant poly(lactic acid). Poly Eng Sci 52:2620-2626. doi:10.1002/pen.23214

Zhou XD, Chen K, Yi H (2014) Synthesis and application of a formaldehyde-free flame retardant for bamboo viscose fabric. Tex Res J 84:1515-1527. doi:10.1177/0040517514525877

Naval Engineering Standard 713, Issue 3, Determination of the toxicity index of the products of combustion from small specimens of materials, March 1985.