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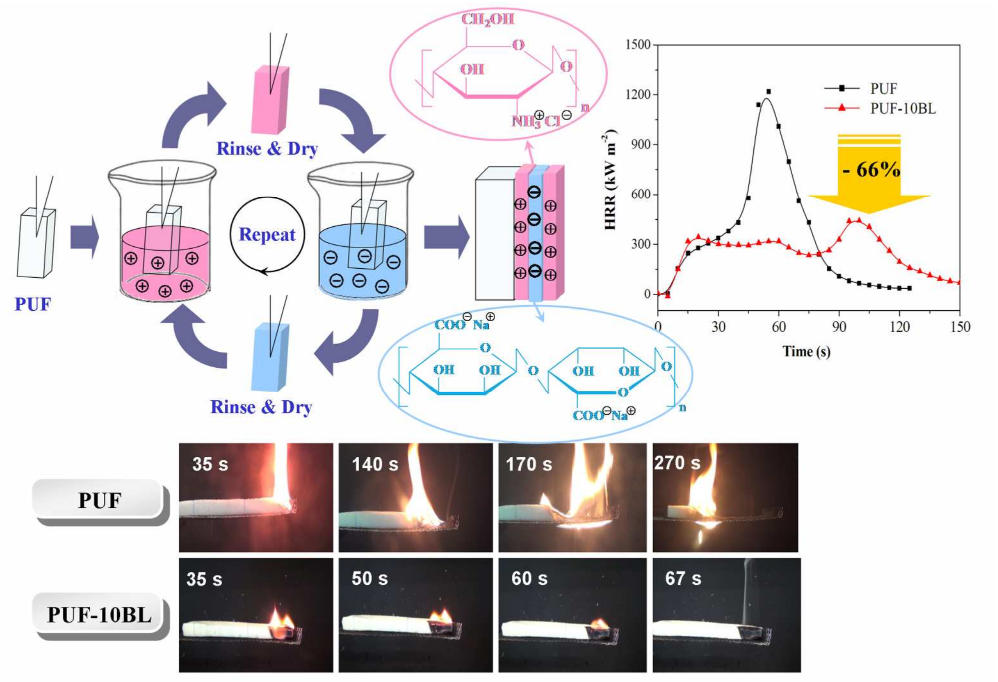

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ARTICLE TYPE

An Eco-friendly Way to Fire Retardant Flexible Polyurethane Foam: Layer-by-Layer Assembly of Fully Bio-based Substance

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The objective of the present study is to develop fully renewable and environmentally benign techniques for improving the fire safety of flexible polyurethane foams (PUFs). Multilayered coating made from cationic chitosan (CS) and anionic alginate (AL) was deposited on PUFs through layer-by-layer assembly. This coating system exhibits a slight influence on the thermal stability of PUF, but significantly improves the char formation during combustion. Cone calorimeter reveals that 10 CS-AL bilayers (only 5.7% of the foam's weight) leads to a 66% and 11% reduction in peak heat release rate and total heat release, respectively, compared with those of the uncoated control. The notable decreased fire hazards of PUF are attributed to that the CS-AL coatings are beneficial to forming an insulating protective layer on the surface of burning materials that inhibits the oxygen and heat permeation and slows down the flammable gases into vapor phase, and thereby improves the flame resistance. This water-based, environmentally benign natural coating will stimulate further efforts in improving fire safety for a variety of polymer substrates.

1. Introduction

The fire statistics in the past several years illustrate that at least 2565 of the fires fatalities occurred in homes and buildings in 2007 in seventeen EU Member States (including UK);[1] just in the UK (2010-2011), 36000 fires occurred in civilian homes and there were 212 fire deaths in accidental dwelling fires.[2] Ignition of soft furnishings (mattresses, upholstered furniture) is one of the most common fire reasons accounting for the residential home fires and high amount of fire civilian fatalities. Polyurethane foams (PUF) are widely used in modern homes decorated with upholstered furniture. However, these foams, which are not treated by fire retardants, are easily ignitable and highly flammable. In order to prevent the loss of life and property, more and more countries and regions have issued various mandatory upholstered furniture fire safety regulations.

In the past few decades, various flame retardant additives have been incorporated into PUFs to increase the foam ignition temperature and reduce the rate of flame spread. Halogenated flame retardants are widely used to improve the fire resistance of FPUF, such as tris(2-chloroethyl) phosphate (TCEP), tris(1, 3-dichloroisopropyl) phosphate (TDCPP) and tris(1-chloro-2-propyl) phosphate (TCPP).[3] Although these halogenated compounds possess high efficiency in lowering heat release rate, the potential toxicity and environmental problems emerge from PUF's storage, transportation and combustion.[4,5] Therefore, this type of flame retardant is gradually replaced by halogen-free flame retardants. Organophosphorus compounds are considered as suitable alternatives to halogenated flame retardants. Phosphonates,[6] phosphates[7] and phosphinates[8] have been reported as effective flame retardant additives for PUFs. Very recently, layer-by-layer deposition of polyelectrolytes on polymeric foams as flame retardant coatings has been developed. Laufer *et al.*[9] developed a effective flame retardant nanocoating comprised of positively charged chitosan (CH) and anionic poly(vinyl sulfonic acid sodium salt) (PVS) on flexible polyurethane foam; however, the application of sulphur-containing compounds might result in some acidic gases. Li *et al.*[10] prepared clay-based multilayer nanocoating on polyurethane foams, but the flame retardant efficiency is not very notable: a 4.8% increase in the substrate mass only led to a 30% reduction in peak heat release rate.

The incorporation of the flame retardants aforementioned has the benefits of improving fire resistant properties and reducing the fire hazard in terms of fire spread and heat release, but might also increase the toxicity of the fire emissions or introduce other risks due to the chemicals themselves. Therefore, developing environmentally friendly, renewable and bio-based techniques will be the best solution to flame retardant polymeric foams for soft furnishings.

In this work, two fully renewable and environmentally benign polyelectrolytes, cationic chitosan (CS) and anionic alginate (AL), was deposited on PUFs through layer-by-layer (L-b-L) assembly. The morphological features, thermal stability and fire suppression of the coated and un-coated PUFs were investigated. The mechanism of the enhanced fire safety of the coated PUFs was proposed. It is anticipated that this multilayered coatings made from natural polyelectrolytes will provide a green solution to reduce the fire hazards of polymeric foams.

2. Experimental

2.1. Materials

Chitosan (M_v 60-120 kDa, 75-85% deacetylated), sodium alginate, poly(acrylic acid) solution (MW 100 kDa), hydrochloric acid and sodium hydroxide were purchase from Sigma-Aldrich and used as received. Polyurethane foam without flame-retardant additives was prepared in our laboratory by mixing FlexFoam-iT® V part A and B (Smooth-on Inc., USA) thoroughly with the weight ratio of 105:100 and then cut for the flammability experiments. Deionized water is used for all experiments unless otherwise stated.

2.2. Layer-by-layer deposition of chitosan and alginate on PU foams

Firstly, cationic polyelectrolyte solutions were prepared by adjusting the pH of deionized water to 2 using HCl and then introducing 0.5 wt % chitosan. Anionic polyelectrolyte solutions were prepared by adding 2.0 wt % of alginate to deionized water. Both the solutions were vigorously stirred for 24 h until the polyelectrolyte was completely dissolved, and their pH was adjusted to 6 prior to deposition. Subsequently, PU foams were immersed into a 1 wt % poly(acrylic acid) solution for 30 s as a primer layer to improve adhesion. Samples were then alternately immersed into the cationic and anionic polyelectrolyte solutions. Initial immersions were 5 min each, while following immersions were for 1 min. After each immersion, foams were rinsed with deionized water and then squeezed by hand to expel liquid as an alternative to the traditional drying step. This procedure is shown schematically in Fig. 1. Finally, when the desired number of bilayers was deposited, foams were dried at 80 °C in an oven for 12 h before testing.

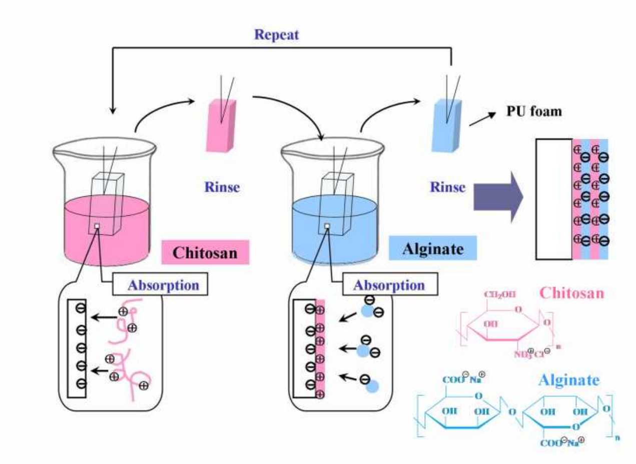

Fig. 1. Schematic illustration of layer-by-layer assembly of CS and AL on PUF.

2.3. Characterization

The thickness of the coating on the silicon wafer was measured by M-2000DI discrete wavelength ellipsometer (Microphotonics, J. A. Woollam Co.) with the HeNe laser (632.8 nm). Mass increments were measured in each bilayer with a commercial microbalance apparatus (ES 125SM, Swiss). The porosity of un-coated and coated PU foams was determined using a liquid displacement method similar to that reported by Guan et al.[11] Surface morphology of un-coated and coated foam samples before and after burning was observed with a scanning electron microscopy (EVO MA15, Zeiss, Germany). All the samples were coated with a conductive layer of gold prior to SEM observation. The horizontal burning characteristics of the foam samples were measured according to ISO 9772-2001. Each specimen, of dimensions 150 mm × 50 mm × 13 mm, was exposed to direct flame from a methane Bunsen burner in a burning chamber (Fire Testing Technology, UK). At least five parallels were tested to obtain average values. The flammability of the foam samples was also characterized using dual cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Samples with the size of 100 mm × 100 mm × 20 mm were mounted into aluminum foil only (no frame and grid) and irradiated horizontally at a heat flux of 35 kW m^{-2}. Measurement was done in triplicate and the average data were reported. Thermogravimetric analysis of the foam samples were carried out with Q50 thermal analyzer (TA Instruments, USA) from 30 to 650 °C at a heating rate of 20 °C min^{-1} in nitrogen atmosphere. The thermogravimetric analysis/infrared spectrometry was performed using the Q50 thermal analyzer which was coupled with the iS50 FT-IR spectrophotometer (Nicolet Instruments, USA) through a stainless steel transfer pipe. The pipe and gas cell were kept at 300 and 250 °C, respectively, to avoid the condensation of the volatile products.

3. Results and discussion

CS/AL bilayers were deposited on silicon wafers for thickness measurement. The thickness of this bilayer sequence grows linearly as a function of the number of bilayers deposited (inset of Fig. 2). This successfully grown CS-AL coating was next deposited onto PU foams in varying numbers of bilayers. The mass increased versus the number of bilayers plots for the coated PU foams is shown in Fig. 2. It is found that sequential deposition of cationic CS and anionic AL on the PU foams also confirms the linear growth trend. The mass increased for PUF-5BL and PUF-10BL is 2.6% and 5.7%, respectively.

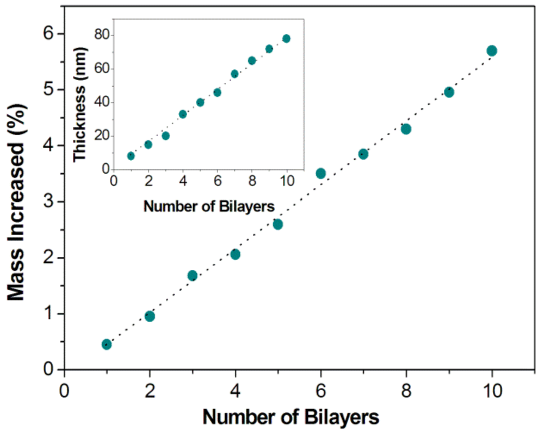

Fig. 2. Mass as a function of the number of bilayers deposited, and the film thickness as a function of deposited BLs (inset).

Scanning electron microscopy was used to observe the morphology of the uncoated and coated PUF samples. The natural porous structure and smooth surface feature of the PUF can be seen in Fig. 3 (top row). The coating of 5 bilayers does not obscure the cellular structure of the foam, but at higher magnification (middle row of images in Fig. 3) the rougher surface can be clearly seen. This roughness suggests that the polyelectrolytes are successfully deposited on the surface of the foams to form those bridges. With 10 bilayers of CS-AL (bottom row of images in Fig. 3), it is difficult to see the original cellular structure of the foam, a thickly depositing coating filled the holes of the foams. The porosity measurement also confirms this morphological feature (Table 1), and the porosity is reduced after coating CS-AL bilayers. This coating serves as a shield to protect underlying foam from heat penetration and thermal damage.

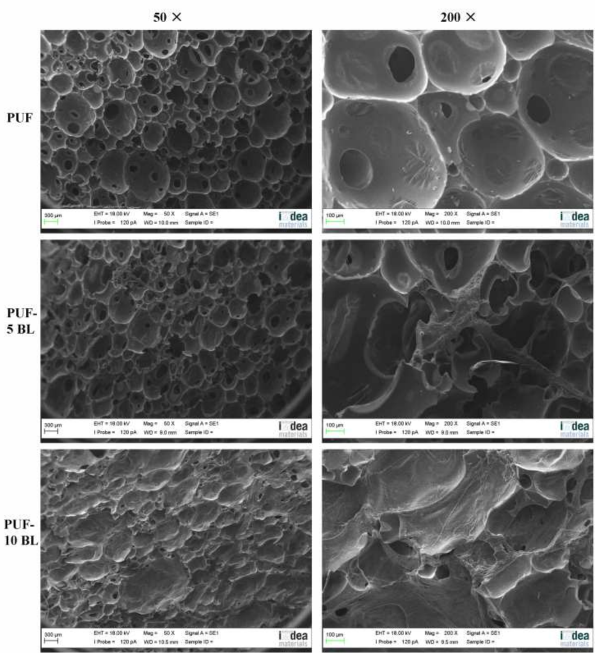

Fig. 3. SEM images of PUF, PUF-5BL and PUF-10BL at different magnification.

The flame retardant properties of the treated PUFs are evaluated by horizontal flame tests, and the results are summarized in Table 1. In horizontal configuration, un-coated PUF vigorously and completely burn (burning rate: 26.6 mm min^{-1}). After PUF is coated by CS and AL, the sample starts to burn very slowly and the burning rate is reduced to 10.4 and 8.4 mm min^{-1} for PUF-5BL and PUF-10BL, respectively. Additionally, the presence of CS-AL coating inhibits the dripping of PUF (see Figure S1 in Supporting Information).

Table 1. Horizontal burning test results for uncoated and coated PU foams

Sample	Porosity (%)	Extinguishing time (s)	Dripping	Burning Rate (mm min^{-1})
PUF	65	280 ± 11	Yes	26.6 ± 0.7
PUF-5BL	43	105 ± 5	No	10.4 ± 0.3
PUF-10BL	28	67 ± 3	No	8.4 ± 0.4

Fig. 4 gives the heat release rate (HRR) curves of the control and coated PU foams. A typical curve with two peaks is observed for the control sample. The first peak is attributed to the initial “collapse” stage of foam combustion.[12] Subsequent generation of a quickly released flammable gases leads to the second, larger PHRR. Depositing 5 bilayers of CS-AL significantly decreases PUF flammability. Increasing the number of bilayers further diminishes the fire risk. A significant suppression in fire hazards of PUF-10BL is observed, with the reduction in PHRR and THR of 66% and 12% respectively, compared to the uncoated control. The reduction in THR suggests CS-AL coatings are binding up some PUFs to participate in the carbonization process and thus reduce the fuel into the vapor phase.

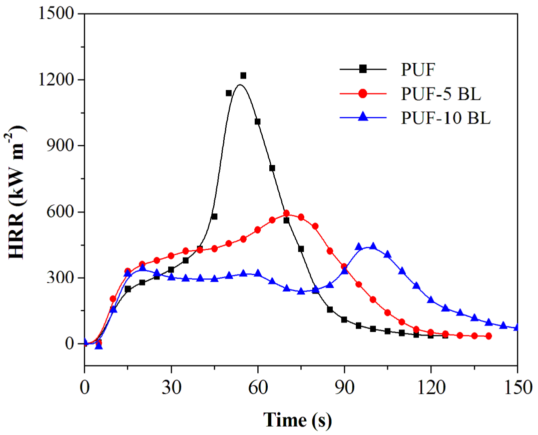

Fig. 4. Heat release rate curves of PUF, PUF-5BL and PUF-10BL under the heat flux of 35 kW m^{-2}.

Some important parameters obtained from the cone calorimeter tests, such as the time to ignition (TTI), the peak heat release rate (PHRR), the total heat release (THR), the total smoke production (TSP), average effective heat of combustion (av-EHC) and the fire growth rate index (FIGRA), are also summarized in Table 2. From Table 2, it can be found that incorporation of CS-AL has a slight improvement on the TTI of the coated PU foams, which is probably attributed to that the presence of coatings delays the release of flammable decomposition gaseous products. With regard to the total smoke production, the coated PU foams show lower TSP compared to the control one. The reduction of toxic smoke will be beneficial for fire rescue when an accident occurs. The fire growth rate index (FIGRA), as an indicative of the burning propensity of a material, has been calculated by the ratio of PHRR and time to PHRR. The FIGRA value of the control sample is 22.2 kW m^{-2} s^{-1}, whereas that for PUF-5BL and PUF-10BL is 8.5 and 4.4 kW m^{-2} s^{-1}, respectively. The dramatically reduced FIGRA value of PUF-10BL means the suppressed fire spread and possible ignition of the material.[9]

Table 1. Horizontal burning test results for uncoated and coated PU foams

Sample	TTI (s)	PHRR (kW m^{-2}) [%Reduction]	THR (MJ m^{-2}) [%Reduction]	TSP (m^{-2}) [%Reduction]	av-EHC (MJ kg^{-1}) [%Reduction]	FIGRA (kW m^{-2} s^{-1}) [%Reduction]
PUF	5 ± 1	1219 ± 32 [-]	43.3 ± 0.3 [-]	6.68 ± 0.11 [-]	29.45 ± 0.25 [-]	22.2 [-]
PUF-5BL	6 ± 1	593 ± 17 [51]	41.2 ± 0.8 [5]	6.45 ± 0.21 [3]	25.93 ± 0.18 [12]	8.5 [62]
PUF-10BL	8 ± 1	416 ± 13 [66]	38.3 ± 0.5 [12]	6.25 ± 0.18 [6]	24.74 ± 0.13 [16]	4.4 [80]

Note: [% change] is the percent reduction in a given parameter for flame-retardant PUF relative to un-coated one

Thermogravimetric analysis was conducted to evaluate the thermal degradation behaviors of the uncoated and coated PU foams. Fig. 5 presents the TG/DTG profiles for the uncoated and coated PUFs as a function of temperature at the heating rate of 20 °C min^{-1}. The thermal degradation process of PUF mainly consists of two stages. The first stage in the temperature range of 200-360 °C is related to the urethane/urea bond depolymerization (approximately 44% mass loss); while the second stage in the temperature range of 360-450 °C can be attributed to the decomposition products from polyol (approximately 50% mass loss). In the case of PUF-5BL and PUF-10BL, the thermal degradation process also shows the similar two-stage behavior as the control one. However, the presence of CS-AL coatings increases the char yield significantly compared to the control sample. Furthermore, from DTG profiles, it can be seen that the maximum mass loss rate of PUF-5BL and PUF-10BL is much lower than that of the control sample. This behavior is in accordance with the condensed-phase flame retardant mechanism: the CS-AL coatings could form an insulating protective layer that inhibits the heat permeation and slows down the mass loss rate, and thereby improves the flame resistance.[13]

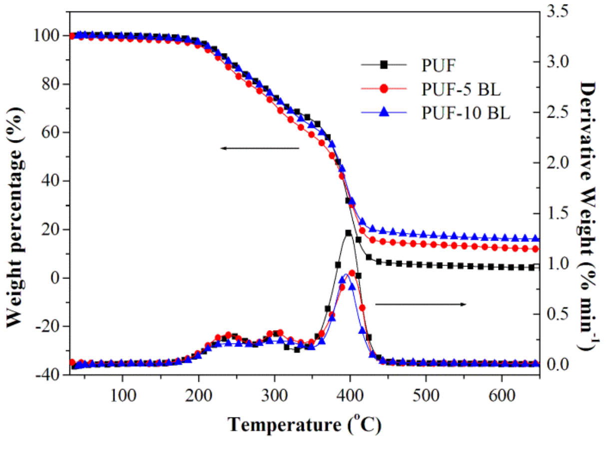

Fig. 5. TG and DTG profiles of PUF, PUF-5BL and PUF-10BL under nitrogen atmosphere.

To investigate the influence of CS-AL coatings on the evolved gaseous products of PUF, the volatile components of PUF and PUF-10BL are investigated by TG-FTIR technique. The 3D diagrams of PUF and PUF-10BL are presented in Fig. 6. It can be observed that the absorption characteristic peaks mainly appear in the regions of 3400-3700, 2800-3100, 2250-2400, 1650-1800, and 1000-1250 cm^{-1}.

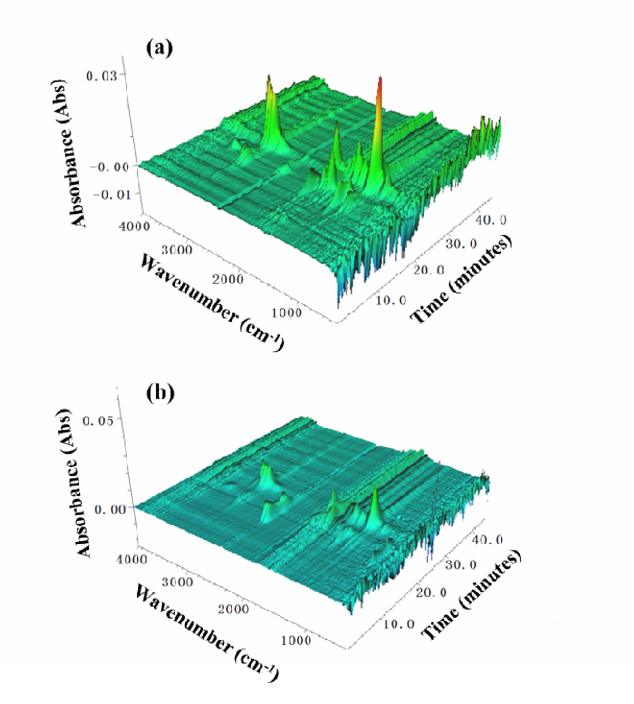

Fig. 6. The 3D diagrams of the gaseous volatiles during decomposition process of (a) PUF and (b) PUF-10BL.

In order to provide a clear comparison, FTIR spectra of pyrolysis products of PUF and PUF-10BL at maximum decomposition rates are depicted in Fig. 7. The FTIR spectrum of PUF-10BL is similar to that of PUF, indicating that the deposition of CS-AL coatings does not alter the thermal decomposition process of PUF significantly. Some of the gaseous pyrolysis products of the PUF are unambiguously identified by the characteristic FTIR signals: the bands at 3450-3600 cm^{-1} are ascribed to the vibration absorption of hydroxide groups, indicating the release of water vapor;[14] the bands at 2876-2982 cm^{-1} are assigned to the aliphatic C-H bonding arising from various alkanes;[15] the sharp band at 1740 cm^{-1} is owing to the absorbance of stretching vibration of C=O group;[16] the strong absorption band at 1108 cm^{-1} is due to the stretching vibration of C-O-C bond from ethers.[17]

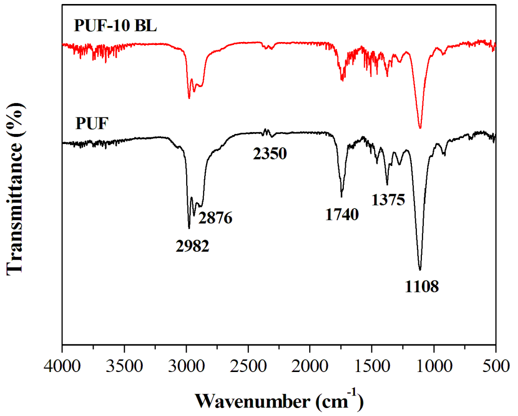

Fig. 7. FTIR spectra of pyrolysis gaseous products emitted from PUF and PUF-10BL at maximum evolution rate.

To further understand the mechanism of the improved fire safety by CS-AL coatings, the absorbance of the selected gas products for PUF and PUF-10BL versus temperature is revealed in Fig. 8. It can be clearly seen that the maximum absorbance intensity of the pyrolysis products for PUF-10BL is much lower than that for PUF. The reduced amount of the alkane, carbonyl and ether compounds means less "fuel" to be fed back to the flame, and thereby the reduced heat release rate and total heat release are observed in cone calorimeter measurement. Additionally, the reduced amount of these organic volatiles further leads to the inhibition of smoke, since the organic volatiles are the major source of smoke particles.[15]

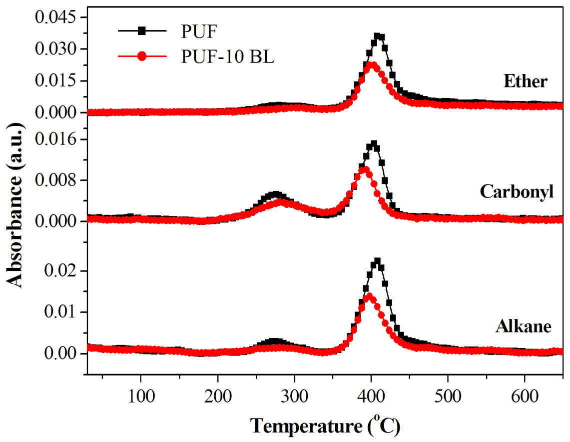

Fig. 8. Intensity of characteristic peaks for pyrolysis products of PUF and PUF-10BL.

SEM images of the postburn samples after cone calorimeter are shown in Fig. 9. As can be observed, PUF exhibits a loose and porous residue after burning, and there is evidence of its high flammability. These holes and gaps serve as sites where heat and oxygen could easily penetrate through the surface of foams and thermally damage the internal parts. PUF-5BL also shows a loose and porous residue but some compact sections are also formed. By contrast, PUF-10BL displays an absolutely different residue from the former samples, a continual and compact residue. This residue provides a protective shield to slow down heat and mass transfers between the flame and the underlying materials,[18] corresponding well with cone calorimeter and DTG results.

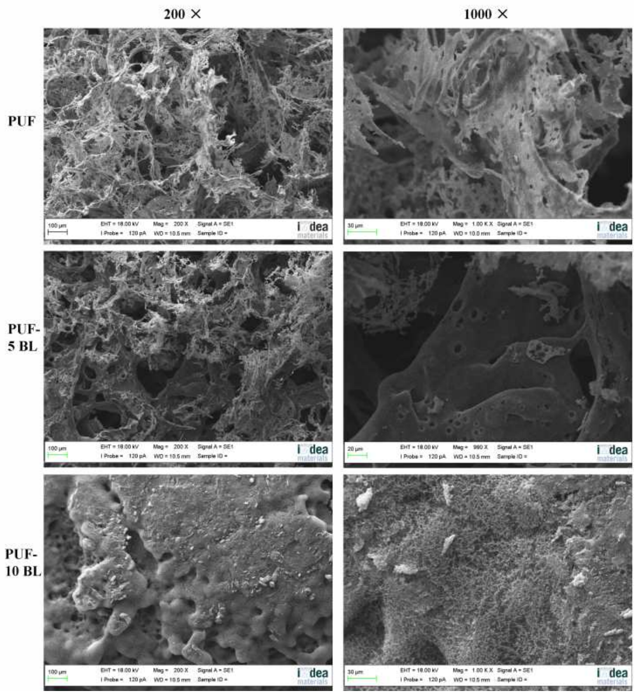

Fig. 9. SEM images of PUF, PUF-5BL and PUF-10BL after cone calorimeter testing.

In summary, the possible mechanism of the improved fire safety of PUF is proposed as follows: both chitosan and alginate are carbohydrate polymers that promote PUF to form a carbonaceous insulating layer;[19-21] the increased char yield means more PUFs participating in the carbonization process and less fuels into the vapor phase; moreover, the char layer could protect the underlying materials from thermally damage by heat.

4. Conclusion

In conclusions, chitosan-alginate coatings were successfully deposited onto PUF by the layer-by-layer assembly. The incorporation of chitosan-alginate did not alter the thermal stability of PUF significantly, but improved the char yield dramatically. The fire safety of PUF was notably improved in terms of reduced burning rate, PHRR, and FIGRA. The enhanced char yield by the presence of chitosan and alginate was responsible for the reduced fire hazards of PUF: more PUFs participated into the carbonization process, less fuel went into the vapor phase and meanwhile the underlying materials were shielded from heat. It is believed that the fully renewable and environmentally benign polymer coatings described herein will provide a safe and efficient solution for improving fire safety of polymeric foams.

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