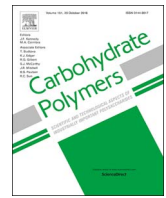




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Construction of flame retardant coating on polyamide 6.6 via UV grafting of phosphorylated chitosan and sol–gel process of organo-silane

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ABSTRACT

Phosphorylated chitosan (PCS) was synthesized and grafted onto the surface of polyamide 6.6 (PA 6.6) fabrics via UV-induced grafting polymerization in order to improve the flame retardant properties. Subsequently, PCS grafted PA 6.6 fabrics were modified by (3-aminopropyl) triethoxysilane (APTES) through sol-gel process in order to form a cross-linking coating. The results obtained from the vertical burning test indicated that only the PCS grafted and simultaneously sol-gel treated fabrics could stop the melt dripping. A maximum reduction (30%) in the peak heat release rate was achieved for the PA6.6-PCS-4W-SG fabric sample. The optimal flame retardant effect was achieved for the PA6.6 fabrics treated by PCS and APTES simultaneously, which was attributed to the joint effect of thermal shielding exerted by the silica and char-forming effect derived from PCS.

1. Introduction

Growing concern over toxicity and environmental issues caused by various flame-retardant treatments on textiles has created a demand to use “green” materials (Laufer, Kirkland, Morgan, & Grunlan, 2012). Chitosan (CS) is an amino polysaccharide obtained from the shells of crustaceans (e.g., lobsters and shrimp) (El-Tahlawy & Hudson, 2006), one of the most plentiful green materials, which is renewable and highly biocompatible (Silva et al., 2005). CS has been acquired wide applications such as a flame retardant additive, because its structure contains multi-hydroxyl groups that can boost the charring during the combustion process (Alongi, Poskovic, Frache, & Trotta, 2010; Don, Hsu, & Chiu, 2001). It is reported that CS plays an active role in intumescent flame retardant system where it serves as a char-former, and also as a blowing agent during degradation (Carosio, Alongi, & Malucelli, 2012; Zeng, Qin, Wang, & Li, 2011).

Phosphorylated chitosan (PCS) is a derivative from CS that contains phosphorus acid moieties. Due to the unique structure, PCS is expected to be used as char former and acid agent simultaneously that shows higher efficiency on fire resistance (Chen, Hu, Jiao, & Song, 2007). Previously, Hu et al. prepared a chitosan-based flame retardant material containing phosphorus and acrylate structure and then incorporated into epoxy matrix through UV curing (Hu, Song, Pan, Hu, & Gong, 2012). They further developed a chitosan based flame retardant combining phosphorus and nickel, which was able to improve the flame retardant properties of PVA matrix (Hu, Song, Pan, & Hu, 2012).

Although phosphorus-based compounds are widely used flame

retardants for polymeric materials, they usually cause deteriorated thermal stability of polymer matrix. It is found that the silicon-containing compounds can produce the silicon-carbide or silicon dioxide after degradation, which can shield char residue from further decomposition at high temperature. During combustion, phosphorus primarily works for char formation, while silicon offers an enrichment of the thermal stability of the char. So, the co-incorporation of phosphorus and silicon elements may successfully deliver these two factors in flame retardant mechanism in an effective way (Alongi, Colleoni, Rosace, & Malucelli, 2014; Wang et al., 2013; Wu, Liu, & Chiu, 2002). Moreover, it is also found that coexistence of silica, phosphorus, and nitrogen can increase both the thermal and thermo-oxidative stability and flame retardant properties of textiles (Alongi et al., 2012).

Polyamide 6.6 (PA 6.6), also known as nylon 6.6, is a thermoplastic textile material used in many fields including apparels and industrial textiles due to its excellent properties like good mechanical behavior, low cost, resistant to shrinkage and pleasant aesthetics. However, it is highly flammable accompanying with severe dripping problems, which limit its use in wide range applications (Apaydin et al., 2015; Liu et al., 2010). Coating treatment of PA 6.6 fabrics is one of the most common ways to improve its flame retardancy. But the hydrophobicity and relatively low surface energy of polyamide fibers make it difficult to conduct coating treatment. In order to solve this problem, surface modifications or partial degradation of such fibers through UV irradiation might create additional reactive functional groups on material surface, which facilitate the way of more effective grafting or adherence of coatings in imparting flame retardant or some other functional

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properties (Wintzer, Walther, & Leuthaeusser, 2015). Previously, Liu et al. used acrylamide as a flame retardant for PA 6.6 fabric through photo grafting, and the modified PA 6.6 fabric showed enhanced thermal stability and suppressed melt dripping (Liu et al., 2011). Microwave induced grafting polymerization of some other monomers like 2-hydroxyethyl methacrylate (HEMA) and allylthiourea in enhancing flame retardant properties of PA 6.6 fabric were also reported recently (Zhang et al., 2014; Zhao et al., 2014). In our previous work, we used chitosan in an intumescent system along with alginate and phytic acid to impart flame retardant properties to PA6.6, which was able to stop melt dripping of PA6.6 and improve the char yield (Kundu et al., 2017).

In this work, a chitosan-based flame retardant named as PCS was synthesized and applied it into PA6.6 through UV-induced graft polymerization. Then, (3-aminopropyl) triethoxysilane (APTES) precursor was hydrolyzed to prepare a silica modified sol, which was expected to further enhance the thermal and flame retardant properties of PA 6.6 fabrics. The structure of synthesized flame retardant was well characterized and subsequently, the morphological information, flame retardant properties and thermal stability of the treated fabrics were studied. In addition, influences of surface modification of PA 6.6 fabrics through UV irradiation on the thermal and flame retardant properties were also discussed.

2. Experimental

2.1. Materials

Chitosan (viscosity 50–800 mPa s, degree of deacetylation 80–95%), (3-aminopropyl)triethoxysilane (APTES), phosphorus pentoxide, methanesulfonic acid were provided by Sinopharm Chemical Reagent Co., Ltd. Diethyl ether, acetone, methanol, ethanol and HCl were purchased from Shanghai Chemical Reagents Company. Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173), used as a photo initiator, was purchased from Aladdin Industrial Corporation. PA 6.6 woven fabrics with the density of 100 g/m² were obtained from Yangzhou City Jiaxing Weaving Industry Co. Ltd. The fabric swatches were previously scoured and subsequently modified with UV irradiation, and finally air-dried at room temperature.

2.2. Preparation of PCS-grafted PA 6.6 fabrics

Phosphorylated chitosan (PCS) was synthesized according to a

previously reported method (Nishi et al., 1986; Zhao et al., 2012), as shown in Scheme 1a. Briefly, chitosan powder (8.0 g, 43 mmol) was firstly mixed with methanesulfonic acid (64.0 mL) in a three-necked flask. Then phosphorus pentoxide (7.2 g, 50.4 mmol) was added gradually into the above mixture. The mixture was mechanically stirred at 0–5 °C for 2 h and then poured into ether for precipitation. The precipitate was filtered and the filter cake was washed with acetone (20 mL, three times), methanol (20 mL, three times) and ether (20 mL, three times). Thereafter, the product was dried in vacuum at 60 °C for 24 h and named as phosphorylated chitosan (PCS).

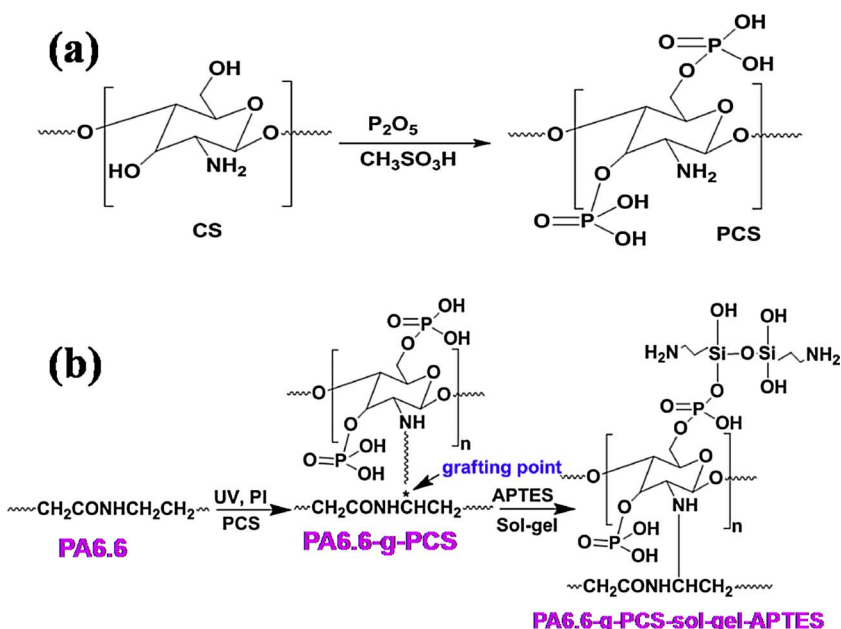
The resulting PCS was dissolved in 2% (v/v) glacial acetic acid aqueous solution with PCS concentration of 2 wt.% (PA 6.6-2W) and 4 wt.% (PA 6.6-4W) under magnetic stirring. 2-Hydroxy-2-methyl-phenylpropane-1-one (Darocur 1173) was used at 4 wt.% with respect to PCS. Thereafter, the fabric samples were impregnated into the PCS solution at 80 °C for 1 h. Samples were dried for 10 min at 80 °C and then single-sided exposed to UV light source at air atmosphere. Subsequently, each sample was washed once in a textile linitester to remove non-bonded FRs, then dried at room temperature and finally, the fabric was dried in an oven at 80 °C for 1 h.

2.3. Sol-gel treatment on PCS grafted PA6.6 fabrics by organo-silane

APTES (20.14 mL, 0.06 mol) was pre-hydrolyzed with HCl (37.5%) (16 mL, 0.2 mol) and ethanol (10 mL) in reflux conditions for 24 h. Next, this pre-hydrolyzed solution was diluted with water to a final volume of 100 mL and then the pH was adjusted to 5 using 1 N sodium hydroxide. Afterwards, the sol was stirred for 4 h at room temperature. Then, the PCS-grafted fabrics were impregnated with the sol solutions for 2 h and subsequently, padded with an 80% weight pick-up. Then, the fabric samples were dried and cured at 80 °C and 120 °C for 1 h, respectively. Finally, the fabric samples were washed for 1 h in distilled water at 60 °C to eliminate the un-reacted precursor. The preparation procedure of treated PA 6.6 fabrics is shown in Scheme 1b. The information about the sample formulations are summarized in Table S1. Weighing measurements were used to monitor the amount of the flame retardant coated on the fabrics. Dry weight pickup (add on) is determined as follows:

$$\text{dry weight pick up(\%)} = \frac{W_1 - W}{W} * 100\% \quad (1)$$

Where, W and W₁ are the weight of the un-grafted PA 66 fabric sample



Scheme 1. (a) Synthetic route of PCS; (b) Schematic illustration of UV grafting and sol-gel treatment of PA 6.6 fabrics.

and W_1 is the weight of the grafted PA 6.6 fabric sample. The information about the sample formulations are summarized in Table S1.

2.4. Instruments and characterization

Nicolet 6700 FT-IR spectrophotometer was employed to characterize the FR monomer using thin KBr disk method. The transmission mode was used and the wavenumber range was set from 4000 to 500 cm^{-1} .

The ^{31}P NMR measurement was conducted on an Avance 300 spectrometer (Bruker Biospin, Switzerland) at room temperature using D_2O as the solvent with a frequency of 162 MHz.

ICP-OES was conducted on the ICAP 6300 DUO (Thermo Fisher Scientific Inc., Waltham, MA, USA) with argon plasma at the wavelength of 178.284 nm and used to determine the content of phosphorus.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed using a Thermo Nicolet Avatar 6700 FTIR equipped with an attenuated total reflectance device.

The PA 6.6 fabric samples were first sputter-coated with a conductive layer, and then its morphological structures were observed by JSM-6700F scanning electron microscopy (SEM, JEOL, Japan).

Combustion property was investigated on a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660-1 standard. All the fabric samples for this test (100 mm x 100 mm) were horizontally irradiated under the heat flux of 35 kW/m^2 and an air flow of 24 L/s.

LOI tests were measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 150 mm x 58 mm.

Vertical burning tests were performed according to ASTM D6413-08 using a vertical burning tester (CZF-3, Nanjing Jiangning Analytical Instrument Company, China). The samples (300 mm x 76 mm), held 19 mm over the Bunsen burner, were first exposed to the flame for a period of 12 s and then rapidly removed.

Thermogravimetric analysis (TGA) was carried out on a TGA Q5000 IR thermogravimetric analyzer (TA Instruments) using a heating rate of 20 $^\circ\text{C}/\text{min}$ under air atmosphere.

3. Results and discussion

3.1. Chemical structure characterizations of PCS

The FTIR spectra of CS and PCS were shown in Fig. S1a. For CS, the characteristic peak at 1600 cm^{-1} was attributed to N–H group and the broad peak at 3435 cm^{-1} was assigned to the –OH group. The peaks at 2875 and 1383 cm^{-1} were due to –CH– stretching and –CH₃ symmetric deformation, respectively. For PCS, due to phosphorylation, a new peak was observed at 1333 cm^{-1} , which was attributed to the asymmetric stretching of P=O. The other new peaks at 1045 and 484 cm^{-1} could be ascribed to the P–O structure, such as P–O–C and P–OH. Moreover, the absorption band at 1600 cm^{-1} was shifted to 1631 cm^{-1} , which might be due to the transformation of amino groups to phosphorylamide groups (Wang, Ma, Wang, & He, 2001). The ^{31}P NMR spectrum of PCS was shown in Fig. S1b. The peak at around 2 ppm indicated that phosphorylation occurred on C-6 hydroxyl groups of chitosan. In addition, the presence of a shoulder peak at 3.3 ppm meant that the hydroxyl groups on C-3 of chitosan took part in the reaction partially (Wang et al., 2001). Furthermore, ICP-OES analysis revealed that the phosphorus content of the synthesized PCS was 16.7 wt.%.

3.2. Morphology

The morphological features of the fabric samples before and after the PCS-grafting and sol-gel treatment were observed by SEM, as shown in Fig. 1. The polyamide fabric is constituted by a thick network of fibers. The fiber from the control sample has a relatively flat and

smooth surface (Fig. 1a) compared to the fiber from PCS grafted fabric samples (Fig. 1b). After the grafting process, the surface roughness of the grafted fabric samples (Fig. 1b, e) slightly increased. The results also revealed that there are no signs of cracks on the fibers caused by UV irradiation and the space between the fibers remained free, which guaranteed the breathability of the fabric (Guan, Gao, Feng, & Shen, 2000). However, after the sol-gel treatment, the surface roughness of the fibers from the treated fabric samples further increased, demonstrated by the formation of a continuous thin film consisting of the hybrid network (Fig. 1c, f).

3.3. ATR-FTIR analysis

ATR-FTIR spectra of the PA 6.6 fabric samples are shown in Fig. S2. The grafting of PCS on the surface of PA 6.6 fabrics was confirmed by the appearance of C–N absorption peak at around 1171 and 1173 cm^{-1} . Compared to the control sample (Fig. S2a and Fig. S2d), PA 6.6-PCS-4W (Fig. S2b) and PA 6.6-UV-PCS-4W (Fig. S2e) showed additional peaks around 1200 cm^{-1} and 920–931 cm^{-1} , which can be attributed to the characteristic peaks of (P=O) and (P–O–C) bonding, which also confirmed the presence of PCS on to the PA 6.6 fabrics (Chao et al., 2015). After sol-gel treatment, some new characteristic peaks at around 1005–1016 cm^{-1} and 1132–1140 cm^{-1} were observed which could be assigned to asymmetric stretching of Si–O–P bond for PA6.6-PCS-4W-SG (Fig. S2c) and PA6.6-UV-PCS-4W-SG (Fig. S2f) (Massiot, Centeno, Carrizosa, & Odriozola, 2001).

3.4. XPS analysis

X-ray photoelectron spectroscopy was used to examine the surfaces of PA6.6 fabrics. Fig. 2a shows XPS spectra of virgin PA6.6, PCS grafted and sol-gel treated PA6.6 fabrics. For PCS grafted fabric, a new peak at 133.68 eV (P_{2p}) was detected relative to the control one, indicating the presence of PCS on the fabric surface. For the sol-gel treated fabric sample, two new peaks at 133.26 eV (P_{2p}) and 102.20 eV (Si_{2p}) were found which confirmed that the grafting process and the sol-gel treatment were carried out successfully. Moreover, changes in relative intensity of the surface elements for the treated fabric samples, in terms of atomic percentage (Table S2), was also observed after the grafting and sol-gel treatment compared to the pure one. In the O_{1s} narrow scan spectrum (Fig. 2b), the curve was deconvoluted into three sub-peaks: 531.5 eV for P=O species, 531.9 eV for P–OH species and 533.1 eV for C–O–C/P–O–C species (Bai et al., 2014; Rupper, Gaan, Salimova, & Heuberger, 2010). Moreover, after the sol-gel treatment, an additional peak at 534.1 eV for Si–O–P species (Almeida, Vasconcelos, Gonçalves, & Santos, 1998) was found (Fig. 2c).

3.5. Flame retardant properties of the PA6.6 fabrics

LOI values of the fabric samples are listed in Table 1. The LOI values of PCS grafted fabric samples are slightly higher than that of control fabric samples, whereas no significant changes were observed for the sol-gel treated fabric samples. PA 6.6-PCS-4W and PA 6.6-UV-PCS-4W fabric samples showed the highest LOI value of 24.0% and 24.3%, respectively. The vertical burning (UL-94) test results are also listed in Table 1. It can be seen that the PCS grafted fabrics with higher FR content showed higher damaged length compared to the control fabric samples, and the melting tendency was not stopped as well. The sol-gel treated fabric samples were completely consumed during the test; however, the melting tendency was reduced significantly. The positive effect of sol-gel treatment on anti-dripping properties of PA 6.6 fabric was due to the “scaffolding effect” caused by deposited silica moieties. It was assumed that the PCS decomposed ahead of PA 6.6 fabric, resulting in the formation of char residue and APTES protected the char from further decomposition to support the molten. During the combustion, the char layer inhibited the transmission of heat, energy, and

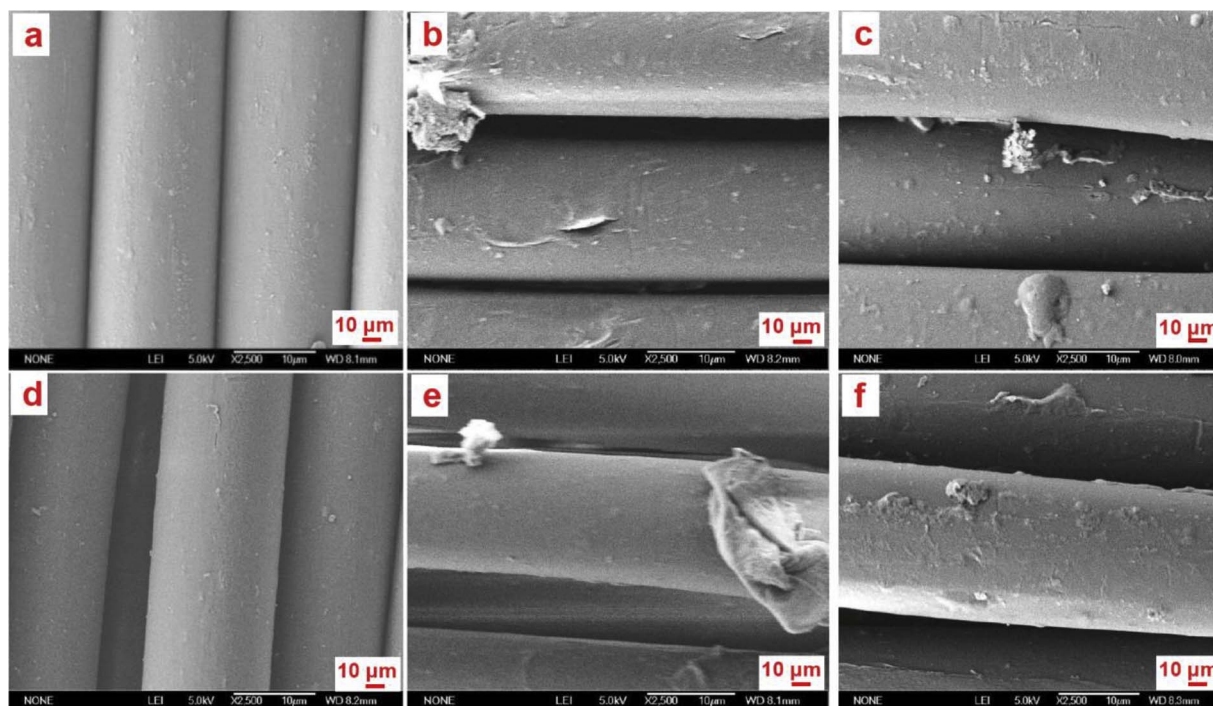


Fig. 1. SEM micrographs of PA6.6-Control (a), PA6.6-PCS-4W (b), PA6.6-PCS-4W-SG (c) PA6.6-UV-Control (d), PA6.6-UV-PCS-4W (e) and PA6.6-UV-PCS-4W-SG (f) fabric samples.

O₂ between flame and molten PA6.6 fabric and retarded the decomposition of the melting PA 6.6. Thus, both flame retardant properties and melt dripping resistance were improved for the sol-gel treated samples.

The flammability performance and smoke suppression of the treated

PA6.6 fabric samples were evaluated using cone calorimetry and the corresponding data are summarized in Table 2. It can be found that the pHRR values of the treated PA6.6 fabrics were reduced compared to that of the control one. The PA 6.6-PCS-4W-SG sample revealed a maximum reduction by about 30% in pHRR. The catalytic effect of

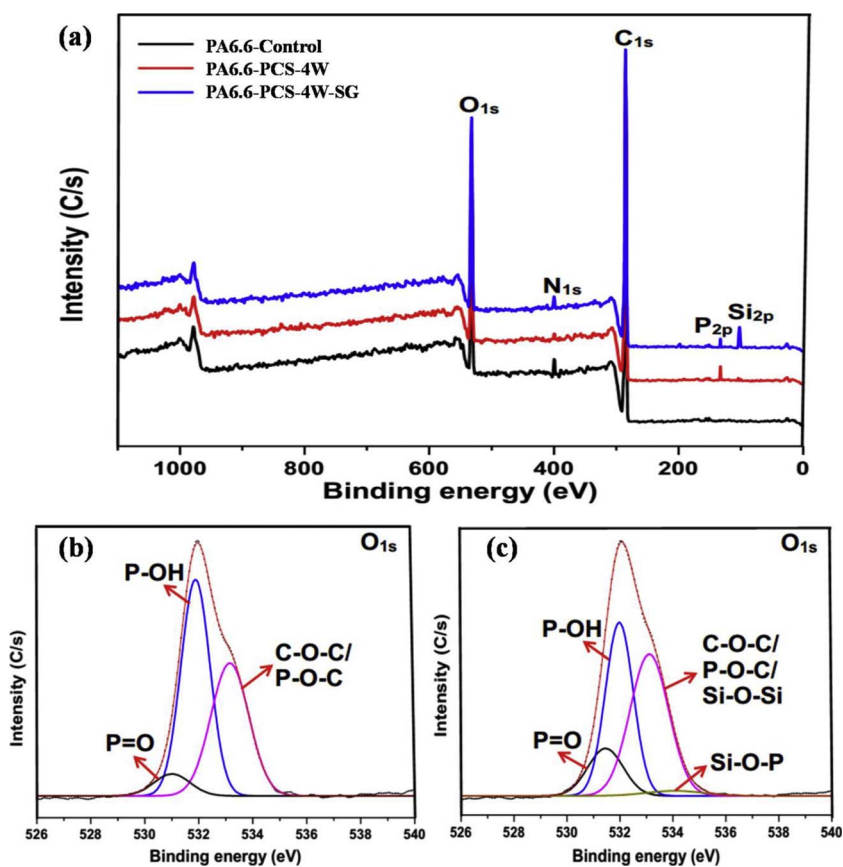


Fig. 2. (a) XPS spectra of virgin PA6.6, PCS grafted and sol-gel treated PA6.6 fabrics; High-energy-resolution XPS spectra of O_{1s} of PA6.6-PCS-4W (b) and PA6.6-PCS-4W-SG (c) fabrics.

Table 1
LOI and Vertical flame test data of control and grafted PA6.6 fabric samples.

sample	LOI (%)	After flame time (s)	After glow time (s)	Char length (cm)	Dripping	Cotton ignition	UL-94 Rating
PA6.6-Control	19.5	11	0	10	yes	yes	NR
PA 6.6-PCS-2W	22.3	21	0	19	yes	yes	NR
PA 6.6-PCS-4W	24.0	26	0	23	yes	yes	NR
PA 6.6-PCS-4W-SG	20.5	53	0	30	no	no	UL-94-V1
PA-6.6-UV-Control	20.0	4	0	12	yes	yes	NR
PA 6.6-UV-PCS-2W	23.0	29	0	21	yes	no	UL-94-V2
PA 6.6-UV-PCS-4W	24.3	19	0	30	yes	no	UL-94-V2
PA6.6-UV-PCS-4W-SG	21.0	51	0	30	no	no	UL-94-V1

Table 2
Cone calorimetry data of PA6.6 fabric samples.

Sample	TTI (s)	pHRR (kW/m ²)	pSPR (m ² /s)	% Reduction in pHRR
PA6.6-Control	30	249	0.033	–
PA 6.6-PCS-2W	18	216	0.047	13
PA 6.6-PCS-4W	16	221	0.060	11
PA 6.6-PCS-4W-SG	15	175	0.029	30
PA-6.6-UV-Control	26	256	0.035	–
PA 6.6-UV-PCS-2W	17	228	0.063	11
PA 6.6-UV-PCS-4W	15	235	0.058	8
PA6.6-UV-PCS-4W-SG	16	185	0.031	28

phosphorus species from PCS accelerated the char formation, which provided a thermal-insulating barrier to slow down the release rate of heat. The TTI values in Table 2 indicated the earlier ignition for the treated fabric samples. Generally, the phosphorus-containing additives showed earlier decomposition ahead of PA 6.6 matrix. The presence of PCS played multiple roles in suppressing the flammability of PA 6.6: (1) a blowing agent which led to the swelling of the char layer formed; and (2) an acid source during the degradation to catalyze the polyamide fabric itself in char formation (Li et al., 2011). However, the UV irradiated fabric samples showed comparatively less effective in pHRR reduction which could be attributed to the higher hydrocarbon contribution from amino and carboxylic acid groups due to surface modification of PA6.6 fabric samples (Gaan, Rupper, & Salimova, 2009).

The combustion of organic polymeric materials often generates a lot of smoke, which prevents fire victims from early escaping. Obviously, the smoke production rate (SPR) is an important parameter for assessing the fire safety of materials. From the collected data, it can be seen that the PCS grafted fabric samples released higher amount of smoke compared to the control fabric, due to the incomplete combustion in the presence of PCS. However, sol-gel treated fabric samples exhibited more significant reduction in the SPR. The formation of Si-O-Si network in char structure improved the thermal stability and the quality of char layer in condensed phase, which was more effective in smoke suppression (Qian, Wei, Jiang, Zhao, & Yu, 2011). So, both the PA 6.6-PCS-4W-SG and the PA 6.6-UV-PCS-4W-SG displayed the lowest pHRR and pSPR values.

3.6. Thermal properties

Fig. 3 shows the TGA and DTG curves of pure PA6.6, PCS grafted and sol-gel treated fabric samples in air atmosphere and the corresponding TGA and DTG data are summarized in Table S3. The control PA 6.6 fabric samples (scoured and UV treated) exhibited two apparent degradation steps under air atmosphere. The first mass loss step was assigned to the main chain breakdown, releasing water, NH₃, CO₂, hydrocarbon fragments and CO, and the second step was attributed to the thermo-oxidative degradation of the char residues (Siat, Bourbigot, & Le Bras, 1997). The T_{5%} (defined as the temperature corresponding to 5% mass loss) of the PA 6.6 fabric samples grafted with 2 and 4 wt.%

of PCS shifted to lower temperatures in comparison to the control sample, confirming the earlier degradation of the organic phosphonate group of PCS. The earlier degradation triggered the formation of char layer which prevented the rapid heat release rate and fire spread, which was beneficial to fire protection rather than defects (Wang et al., 2017). For the control PA 6.6 fabrics, the amount of residual char at 700 °C was 3.3%. The final residue of PCS grafted fabric samples was comparable to that of control PA6.6, suggesting that the char was not thermally stable at high temperatures under air atmosphere. When PCS-grafted fabric samples were treated by sol-gel process with APTES, the char yield at 700 °C was increased to 4.7% and 5.4% for PA 6.6-PCS-4W-SG and PA 6.6-UV-PCS-4W-SG, respectively. Because the hybrid coating was able to thermally protect the fabrics, favoring the char formation instead of thermal degradation of the char. Herein, it was noted that the phosphorus species acted as a char-promoter and simultaneously contributed to the thermal shielding effect of silica for PCS grafted and sol-gel treated fabric samples compared to the only PCS grafted fabric samples (Alongi et al., 2014). So, the coating converted to an efficient thermal insulator, favoring the formation of thermally stable char and thus the best performances was obtained in the combination of silicon moieties with phosphorus.

From the DTG curves (Fig. 3b), it can be seen that the control PA6.6 fabric samples degraded in two steps at around 460 and 586 °C, respectively. It is well known that the thermo-oxidative degradation of virgin polyamide leads to three principal reactions: (i) formation of N-acylamides, (ii) formation of N-formamides (due to C1–C2 bond scission) and (iii) oxidative dealkylation that yields carbonyl compounds (Guido et al., 2013). In contrast to virgin PA6.6, the T_{max}s of PCS treated PA6.6 samples shifted to lower temperature, due to the catalytic effect of PCS on the decomposition of PA6.6 matrix. However, for sol-gel treated fabric samples, the T_{max} occurred at higher temperature compared to the control sample, owing to the improved thermal stability of treated fabrics with silicon moieties. Also, it can be observed that the maximum mass loss rate of the treated PA6.6 fabrics was decreased in contrast to the control sample. This finding agrees well with the improved char yield, which serves as a physical barrier to retard the mass loss rate.

3.7. Analysis of char residues

The char formation ability of the virgin and treated PA6.6 was directly observed through burned fabrics, as shown in Fig. 4. After burning, the untreated polyamide fibers changes from a fibrous state to a molten state (Fig. 4a). The PCS grafted sample showed a shrunken charred fabric with a faintly black residue (Fig. 4b), which was not enough to prevent the fabric from further degradation. In contrast to the former two samples, an expanded carbonaceous char was formed for PA6.6-PCS-4W-SG after burning (Fig. 4c), which exhibited a compact and entire char. Generally, the degradation of silicon species led to the formation of a ceramic layer consisted of SiO₂ that strengthened the thermal oxidative resistance of the char. Such a char layer acted as a thermal barrier to protect the substrate from flame attack.

In order to further gain insight into the flame retardant mechanism,

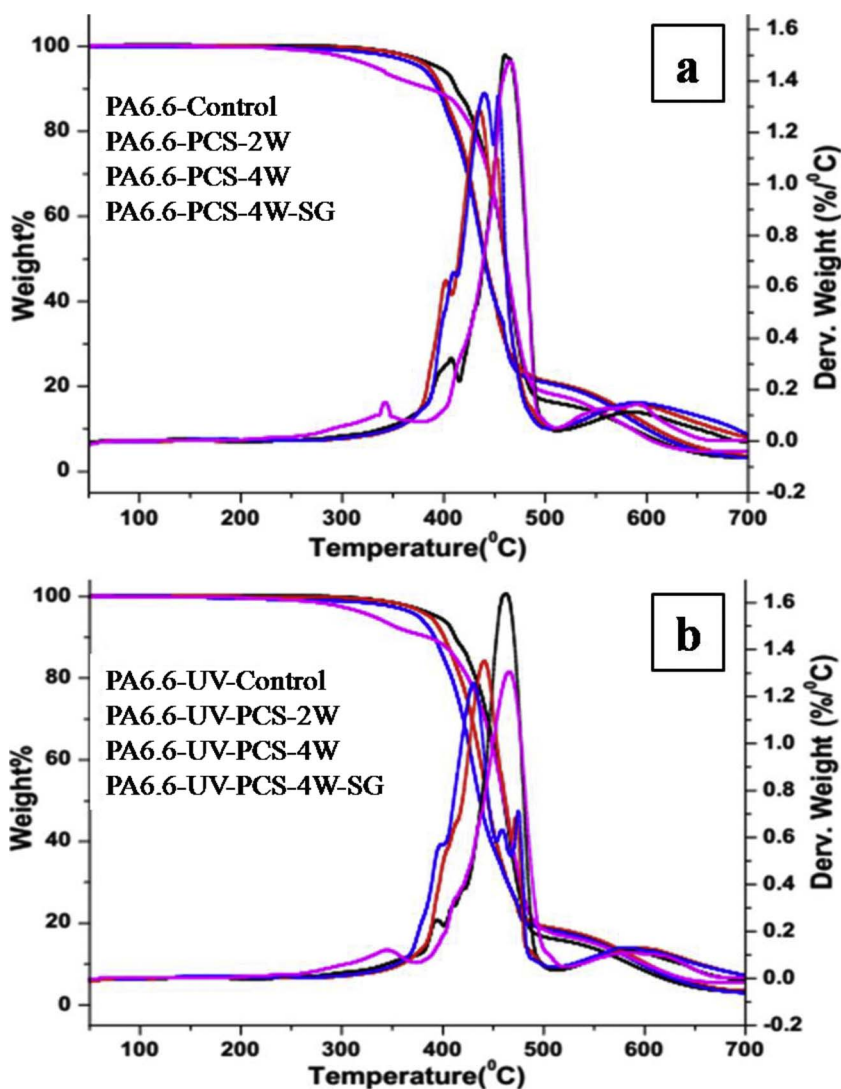


Fig. 3. TGA and DTG curves of PA6.6 fabric samples (a) without UV treatment and (b) with UV treatment under air atmosphere.

the treated fabric samples were fully carbonized in a muffle furnace at 500 °C for 15 mins, and the carbonized char residues were analyzed by FTIR spectroscopy, as shown in Fig. 5. It can be clearly seen that virgin PA6.6 displayed some characteristic peaks: 3080 cm^{-1} for carboxylic acid group, 2920 cm^{-1} for C–H stretching mode, and 1540 cm^{-1} for –CONH–. After burning, these characteristic peaks almost disappeared in the char residues of virgin PA6.6 and treated PA6.6. Instead, an absorption band at around 1580–1600 cm^{-1} was observed, indicating the generation of aromatic structures during the carbonization process of PA6.6 (Costa, Avataneo, Bracco, & Brunella, 2002). For the char

residue of PCS grafted PA6.6 fabrics, two new peaks at 864 cm^{-1} (the asymmetric stretching vibration of P–O–P band) (Costa, Avataneo, Bracco, & Brunella, 2002) and 1178 cm^{-1} (asymmetric stretching of P=O) (Zhu & Shi, 2003) appeared, indicating the formation of poly-phosphoric acid (PPA). Moreover, the char residue of the sol-gel treated fabric displayed a peak at 1045 cm^{-1} , corresponding to the Si–O–Si stretching mode. This phenomenon confirmed the presence of the inorganic SiO₂ in the charred residues (Brancatelli, Colleoni, Massafra, & Rosace, 2011). The FTIR results suggested that the char residue was mainly consisted of complexes with aromatic structure bridged with P–



Fig. 4. Digital images of PA6.6 fabric samples (a. PA6.6 Control, b. PA6.6-PCS-4W, and c. PA6.6-PCS-4W-SG) after burning.

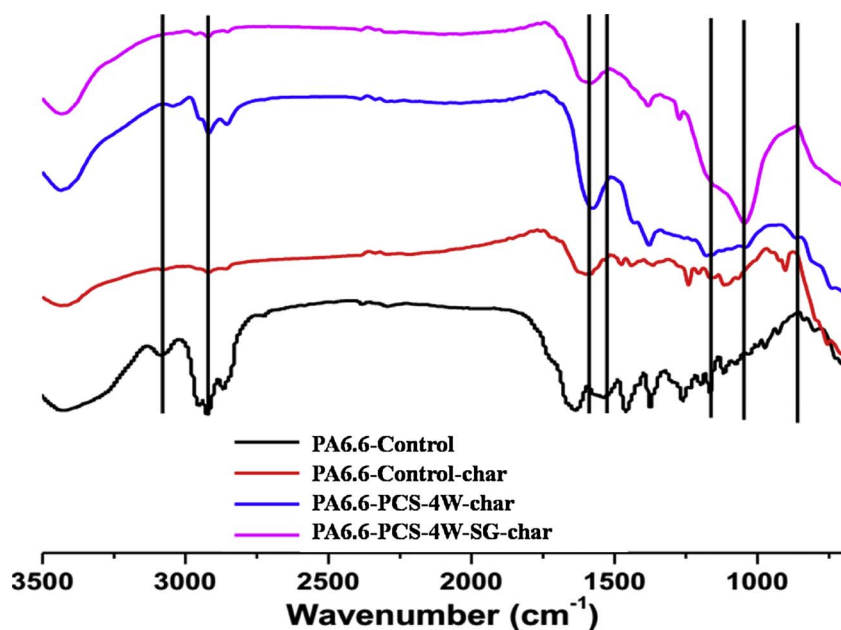


Fig. 5. FTIR spectra of virgin PA6.6 and char residues of virgin and treated PA6.6 fabric samples.

O-P structure and/or ceramic layer of SiO_2 . The char residue with such structure served as an effective thermal-insulating barrier towards protecting the underlying polymer material, which rationalized the improved flame retardant properties for the treated fabric samples.

4. Conclusions

In conclusion, an organic-inorganic hybrid coating derived from chitosan and APTES was deposited on PA6.6 fabrics through UV grafting and sol-gel method in order to enhance the fire retardant performance of the fabrics. The LOI values of PCS grafted fabric samples are slightly higher than that of control fabric samples, whereas no significant changes were observed for the sol-gel treated fabric samples. In the UL-94 vertical burning test, the presence of PCS cannot stop the melting tendency of the treated fabrics, while the sol-gel treated fabric samples displayed significantly suppressed melting tendency and achieved V-1 rating. The combination of PCS and organo-silane treatment also showed best effect in lowering peak heat release rate (pHRR) and smoke production rate in cone calorimetry tests. The PA 6.6-PCS-4W-SG sample revealed a maximum reduction by about 30% in pHRR. The improved flame retardant properties of PCS and organo-silane treated PA 6.6 fabrics were attributed to the increased char yield and enhanced char quality, as evidenced by TGA results. The phosphorus species from PCS catalyzed the char formation upon ignition, and the degradation of silane converted to silica that strengthened the thermo-oxidative stability of the char. FTIR results proved that the char residue was composed of complexes with aromatic structure bridged with P-O-P structure and/or ceramic layer of SiO_2 , which was thermally stable to serve as an effective thermal-insulating barrier towards protecting the underlying polymer material from further burning. This study demonstrates that the combination of UV grafting and sol-gel method provides an effective and environmentally friendly solution to fire retardant treatments of polyamide 6.6 fabrics.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2017.11.069>.

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