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ORIGINAL PAPER

Treatment of cotton fabrics by ionic liquid with PF_6^- anion for enhancing their flame retardancy and water repellency

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Abstract In the present study, we report a new process for modifying cellulosic fabrics by using ionic liquids. To this aim, 1-methylimidazolium chloride propyltriethoxysilane and 1-pyridinium chloride propyltriethoxysilane salts were synthesised. Then, the cotton fabrics were treated with sols containing these salts by the pad-dry-cure process. Finally, the treated fabrics were impregnated in a diluted solution of HPF_6 to perform the metathesis reaction. The morphology and chemical composition of treated and untreated fabrics were analysed by scanning electron microscopy, elemental analysis and infrared spectroscopy. The droplet shape analysis confirmed that the water repellency of the fabrics was significant after surface modification. The flame retardancy was also enhanced by using the PF_6 anion. Thermogravimetric analysis was used to assess the thermal stability of these treated fabrics in air.

Keywords Sol–gel · Ionic liquid · Cotton fabric · Flame retardancy · Water repellency

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Introduction

The ionic liquids (ILs) belong to diverse groups of salts that are liquid below 100 °C. They are typically constituted of a large organic cation and an inorganic polyatomic anion. There is virtually no limit to the number of possible ILs since there are many cations and anions that can be combined (Jiu-Ju et al. 2013). ILs have been the subject of increasing attention because of their unique physicochemical properties such as high thermal stability, high ionic conductivity as well as tremendous solvating capacity (Keskin et al. 2007). Non-volatility and non-flammability are their common characteristics, making them quite relevant materials for many applications. Their range of applications includes electrolytes in batteries, solvents and catalysis in synthesis (Böhm et al. 2014; Ferreira et al. 2014b; Jinmei et al. 2011; Le et al. 2014; Martín et al. 2014). They are also used as matrices for mass spectroscopy and as solvents to synthesise nanomaterials (Brisinski et al. 2014; Pratap et al. 2014; Ruiz et al. 2014; Zhaoxian et al. 2014). In textile industries,

ILs are employed to remove textile dyes from aqueous solutions (Ferreira et al. 2014a; Gao et al. 2013; Hejun et al. 2013; de Menezes et al. 2012) and to impart antifungal properties to linen fabrics (Foksowicz-Flaczyk and Walentowska 2013), and a few patents have addressed the use of ionic liquids as "green" flame retardants for textile fabrics (Xu 2012). ILs may be introduced onto the fibers or fabrics using chemical post-treatment methods, for instance, during the dyeing (Price et al. 2006). In the current study, we have demonstrated that the immobilisation of ionic liquids onto textile matrices can be achieved by the sol–gel process. This synthesis method is currently attracting growing interest for textile functionalisation because of its simplicity and flexibility. As reported in the literature, ILs may play different roles in synthesis procedures. They have been shown to be able to act as chemical additives for drying control, catalysts, structure directing agents, solvents and even precursors for achieving homogeneous gel fibers and adsorbent hybrid materials (de Menezes et al. 2012; Tarkanovskaja et al. 2014). In our case, we have prepared organosilanes based on ILs to enhance flame stability and water-repellent properties of cotton fabrics. For this aim, 1-methylimidazolium chloride propyltriethoxysilane (MCPTS) and pyridinium chloridetriethoxysilane (PCPTS) salts were synthesised and characterised by means of ^{1}H and ^{13}C NMR, mass spectroscopy as well as infrared spectroscopy. Then, we prepared different sols with these salts, which were coated onto cotton fabrics by the pad-dry-cure process (Fig. 1). Afterwards, sol–gel modified textiles were impregnated in a diluted solution of HPF_6 acid to carry out the metathesis reaction to replace the chloride anions with PF_6^- (Fig. 2). Indeed, PF_6^--based ILs are expected to confer better flame stability to cotton fabrics. Thus, in order to assess the final properties of Il-coated cottons, water-repellency and flame-retardancy tests were carried out. Finally, the thermal stability of the sol–gel modified samples was investigated by thermogravimetric analysis.

Materials and methods

Materials

Cotton (CO) woven fabric weighing 168 g m^{-2} was used. The chloropropyltriethoxysilane (CPTS, Mw: 240.79 g mol^{-1}), ethyl alcohol (EtOH, 99 %), HCl (37 %), 1-methylimidazole (99 %), pyridine (99 %) and hexafluorophosphoric acid (HPF_6, 65 %) were purchased from Sigma-Aldrich Co. All the chemicals were analytically pure.

Synthesis of 1-methylimidazolium and pyridinium chloride propyltriethoxysilanes (MCPTS and PCPTS)

The schematic diagram of the synthetic procedure for the MCPTS and PCPTS salts is shown in Scheme 1. One eq 1-methylimidazole or pyridine and 1 eq CPTS were added to a round-bottom flask fitted to a reflux condenser and allowed to react at 100–115 °C for 18 h to obtain 1-methylimidazolium chloride propyltriethoxysilane (MCPTS) and pyridinium chloride

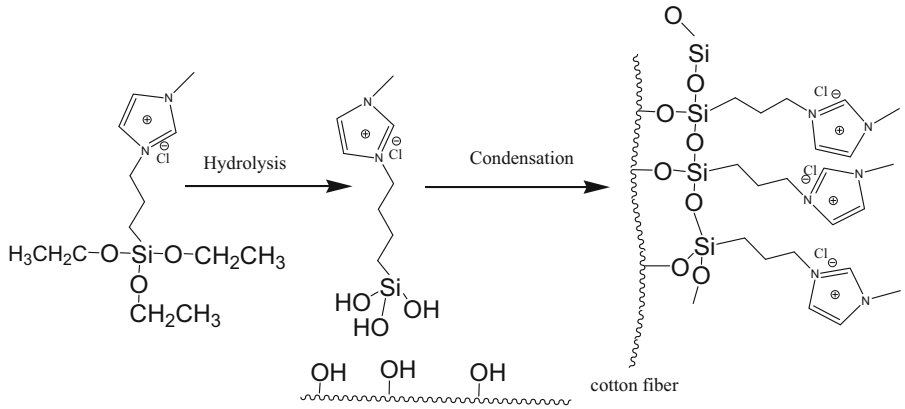


Fig. 1 Hydrolysis and condensation reaction between MCPTS salt and cotton fiber during the sol–gel process

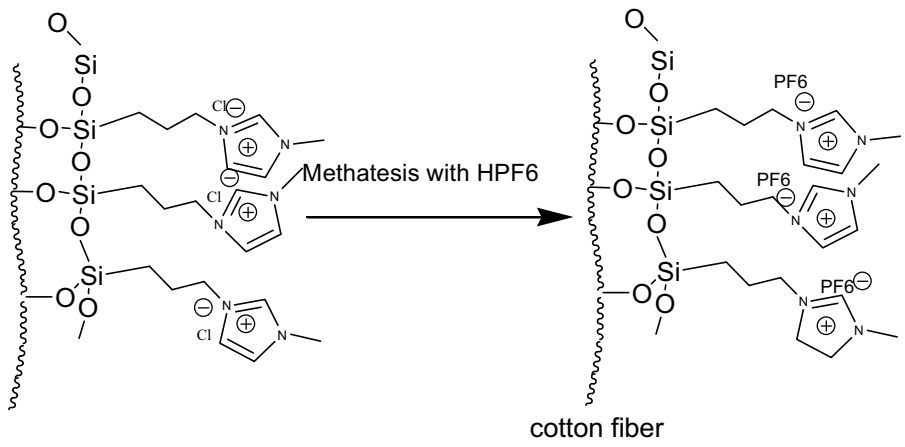
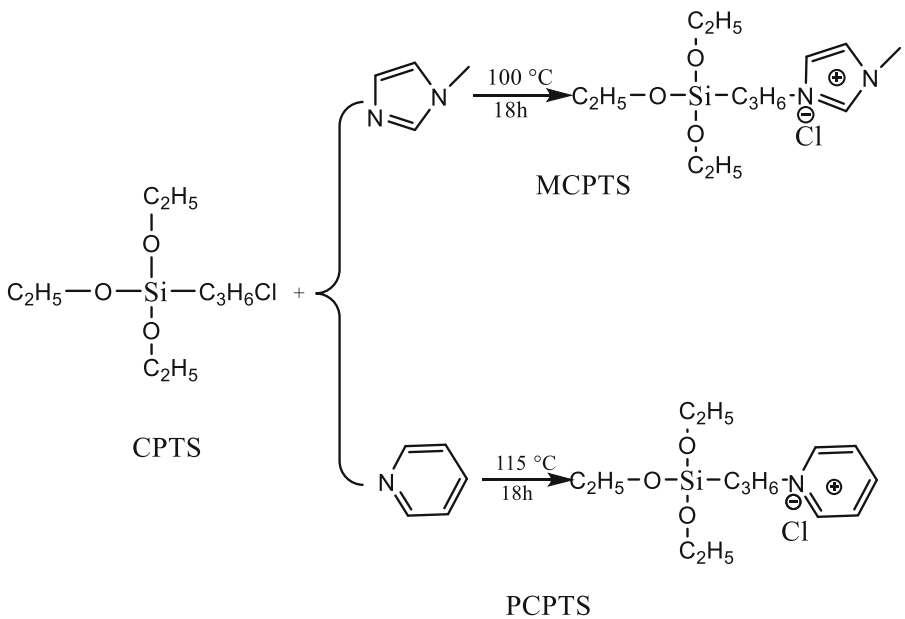


Fig. 2 Metathesis reaction between HPF_6 acid and MCPTS salt grafted on cotton fiber



Scheme 1 Synthesis of MCPTS and PCPTS salts

propyltriethoxysilane (PCPTS) salts, respectively. An orangish viscous liquid was obtained for MCPTS salts and a brownish viscous liquid for PCPTS salts.

MCPTS

FTIR (cm^{-1}) 2973–2888 (C–H), 1570 (C=C stretching of the imidazole ring), 1389 (stretching vibrations of C–N of imidazole ring), 1166 (C–O), 1077 (Si–O) (Mahltig and Bottcher 2003).

^1H NMR (300 MHz, MeOD, δppm) 7.63 (s, 1H, N–CHN),7.06 (s, 1H, NCH=CHN), 6.94 (s, 1H, NCH=CHN), 4.20 (t, 2H, $J = 7.20$ Hz, NCH_2), 3.86 (s, 3H, NCH_3), 3.81(q, 6H, $J = 6.9$ Hz, O–CH_2), 3.31 (t, 9H, $J = 3.3$ Hz, O–CH_2–CH_3), 1.2(quint, 2H, $J = 5.1$ Hz, CH_2–CH_2–CH_2), 0.604 (t, 2H, $J = 9$ Hz, Si–CH_2).

^{13}C (DMSO, 300 MHz, δppm) 147.52, 137.73, 129.86, 114.85, 76.39, 58.58, 52.62, 45.26, 40.53, 40.25, 39.97, 39.70, 39.42, and 12.15.

LC/MSESI: m/z Calculated: 322.15; found: cation (287), ion corresponding to a cluster 2C + Cl (608.89).

PCPTS

FTIR (cm^{-1}) 1630 (C=C), 1385 (C–N), 1166 (C–O), 1077 (Si–O).

^{1}H NMR (300 MHz, MeOD, δppm) 8.14–8.19 (d, 2H), 7.73–7.78 (t, 1H), 7.32–7.37 (d, 2H), 4.66 (t, 3H, NCH_3), 3.73 (q, 6H, $J = 6.9$ Hz, O–CH_2), 3.4 (t, 9H, $J = 7$ Hz, O–CH_2–CH_3), 1.02 (q, 2H, $J = 5.1$ Hz, CH_2–CH_2–CH_2), 0.53 (t, Si–CH_2).

^{13}C (DMSO, 300 MHz, δppm): 62.97, 58.23, 56.37, 48.041, 25.52, 18.94, 18.57, 6.94, 124.38, 128.52, 136.71, 145.94, and 149.89.

LC/MSESI: m/z Calculated: 319, 14; found: cation (284, 18), ion corresponding to a cluster 2C + Cl (602, 85).

Sol–gel treatment of textile

(MCPTS, PCPTS), distilled water, EtOH (99 %) and HCl (37 %) were mixed with a molar ratio (MCPTS, PCPTS)/HCl/EtOH/H_2O of 5/0008/60/55. Then, the mixture was stirred for 3 h at 70 °C until a homogeneous solution was obtained. The textile samples were impregnated in this sol for 24 h and then padded to give 80 % weight pick-up. The dry and cure temperatures were respectively 80 and 120 °C for 1 h. For comparison, the sample without the hybrid coating was cured under the same condition. The coated fabrics were dipped rapidly in a solution of HPF_6 acid (0.66 mol/l), washed with distilled water for several times and dried separately at 80 and 120 °C. The resulting hybrid coatings are named [MCPTS]PF_6 and [PCPTS]PF_6. For comparison, hybrid coatings with a CPTS precursor were prepared by the same procedure. The mechanism of the reaction between ionic liquid functionalised siloxanes and cellulose is the same as the one described in a previous paper (Boukhriss et al. 2015).

FI-IR spectra

The infrared spectra were recorded on a Nicolet iS10 FTIR-ATR spectrophotometer.

Mass spectroscopy

ESI-MS data were obtained on a Quattro II tandem quadripole mass spectrometer (Micromass, Manchester, UK) fitted with electrospray ionisation.

RMN

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance (300 MHz) apparel using TMS as internal reference.

SEM

First, a gold coating was sputtered onto textile samples to make them conductive. The SEM micrographs were recorded using a ZEISS Supra 55VP scanning electron microscope operating under high vacuum at 3 kV and using a secondary electron detector (Everhart-Thornley detector). Qualitative analysis of chemical elements was performed using an Oxford Instruments Aztec Energy Dispersive X-ray Spectroscopy (EDX) system with an X-Max 50 Silicon Drift Detector.

Water-repellency test

The dip test was performed to investigate the water repellency under the customary conditions of the coated textiles. To this aim, the water uptake of the textile under full contact with water was determined. A textile sample of 10 cm × 10 cm was placed in 300 ml of distilled water for 1 min. The water uptake by the textile during placement under water was determined using a balance (Mahltig et al. 2005; Mahltig and Bottcher 2003).

Flame-retardancy test

The flammability test in vertical configuration was carried out by applying a butane flame of 4 cm for 20 s [sccording to the ISO 6940:2004(F) standard] at the bottom of a fabric sample (20 cm × 10 cm). The test was repeated twice for each formulation measuring the burning time, burning surfaces and final residue weight.

Stability to the washing test

The stability of hybrid materials coated onto cotton fabrics was investigated according to the ISO

105-C06:2010 standard. The samples (20 cm × 10 cm) were treated in a 400-ml bath of ECE (European Colour-fastness Establishment) standard detergent with pH = 9.7. The washing was carried out in a standard machine (WashTEC Roaches) at 40 °C for 30 min. The washing procedure was repeated for three cycles.

TG analysis

The thermal stability of the fabrics was evaluated by thermogravimetric (TG) analyses from ambient temperature to 1100 °C with a heating rate of 10 °C/min. A SETARAM SETSYS evolution analyser was used, placing the samples in an open alumina crucible in the presence of air atmosphere.

Result and discussion

Characterisation of cotton fabric

In order to assess the morphology of the coatings deposited on cotton fibers by the sol–gel process, SEM observations were made. The typical morphology of cotton fibers is reported in Fig. 3a; as expected, the surface of untreated cotton fibers exhibits a certain level of irregularity. After treatment with [MCPTS]PF6, slight differences are observed between the untreated and treated sample surfaces, which became smoother (Fig. 3b).

The chemical compositions of untreated and treated fabrics were determined by elemental analysis. Untreated fabrics do not contain the Si, F, P and N elements, while in the sol–gel-treated ones, the presence of these elements was evidenced, as shown in Fig. 4. In the FTIR spectra, gathered in Fig. 5, the vibration band at 835 cm^{-1} indicates the presence of PF_6 on the surface of the cotton fabric and thus confirms that the metathesis reaction was successful. Moreover, the band located at 1083 cm^{-1} is likely due to the vibration of the Si–C bonds in the silica networks.

Water-repellent properties

An untreated CO textile is hydrophilic so that a water droplet placed onto its surface soaks completely through the textile as shown in Fig. 6a. However, after sol–gel treatment with IL-based organosilanes, the surface of the treated fabrics nearly supports the formation of spherical droplets (Fig. 6b). To evaluate the hydrophobic properties of fabric coated with [MCPTS]PF_6 and [PCPTS]PF_6, investigations on coatings were performed using dip tests on CO fabrics. With increasing drying temperature, the amount of water uptake by the textile decreases. After the dip test, the uncoated CO sample exhibits a weight increase of 340 %. Samples sol–gel coated with [MCPTS]PF_6 and dried respectively at 80 and 120 °C lead to a lower water uptake percentage, i.e., 235 and 50 %, respectively (Fig. 7). This behaviour may be induced by the rise of the temperature, which promotes the siloxane network formation and thus the IL adhesion onto the textile. The same trends were observed for cotton treated with [PCPTS]PF_6.

Flame retardancy and thermal stability

Several articles on flame-retardant cellulose have been published. Significant efforts have been made to improve the flame-retardant property of cotton textiles

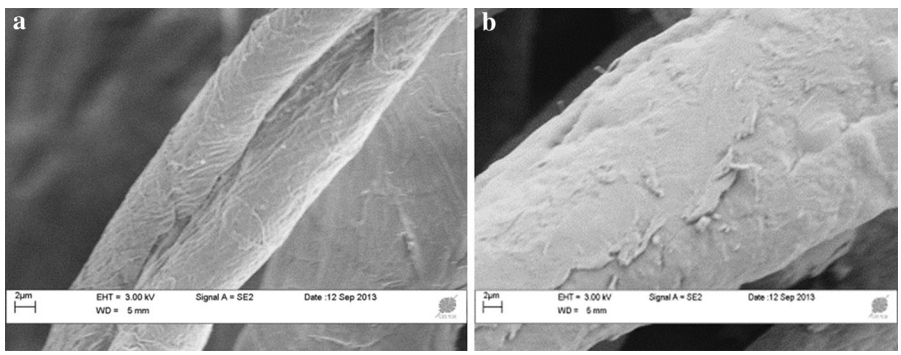


Fig. 3 SEM image of **a** untreated cotton and **b** [MCPTS]PF_6-treated cotton

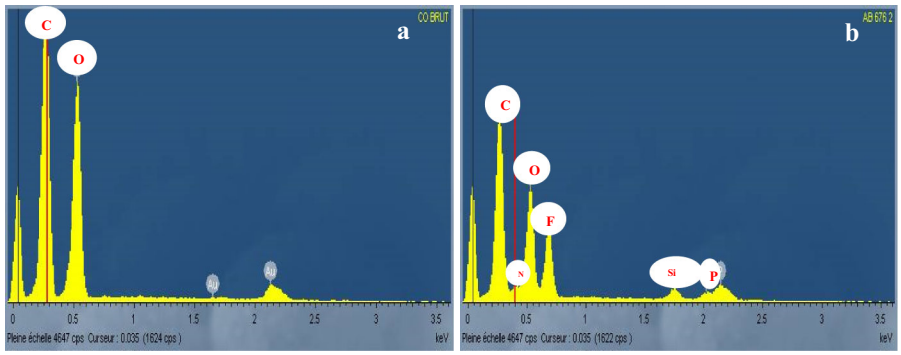


Fig. 4 Elemental analysis of **a** untreated cotton and **b** $[MCPTS]PF_6$-treated cotton

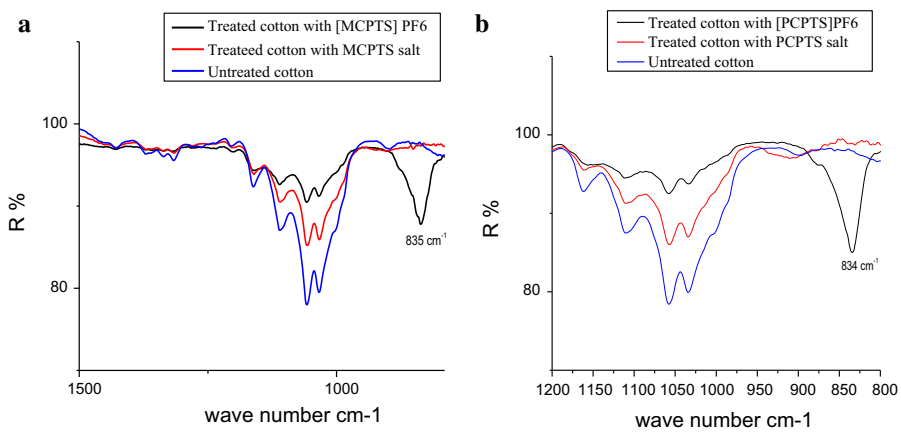


Fig. 5 FTIR spectrum of **a** $[MCPTS]PF_6$ cotton and **b** $[PCPTS]PF_6$ cotton

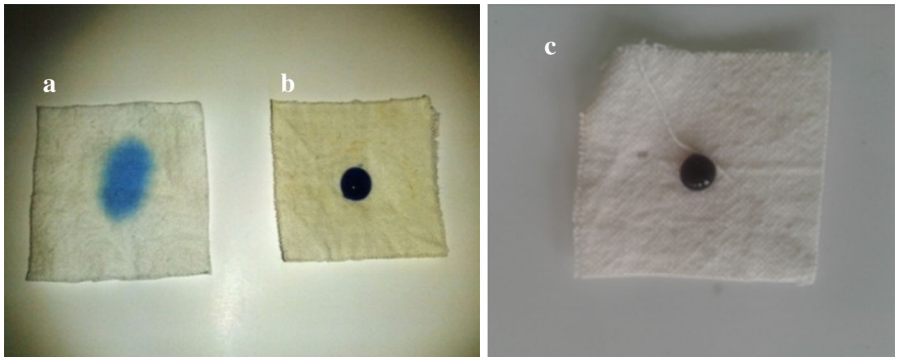


Fig. 6 Water droplet on the surface of **a** untreated fabric, **b** treated fabric with $[MCPTS]PF_6$ and **c** treated fabric with $[PCPTS]PF_6$

using various methods and chemical compounds that can react with the cellulosic fiber or form cross-linked structures on the fiber (Basak et al. 2015; Han et al. 2015; Nguyen et al. 2012; Waly et al. 2012; Yang and Yang 2005; Yang et al. 2012). In this work, as already demonstrated, the sol–gel process was a useful method to enhance the flame retardancy of synthetic and natural textiles. To this aim, metal alkoxides based on silicon, titanium and zirconium have already been used (Alongi et al. 2010, 2012b).

In the present work, ionic liquids combined with a silica precursor showed good resistance to a direct flame. Indeed, as shown in Fig. 8b, d, untreated and treated cotton with CPTS keeps burning for 45 and

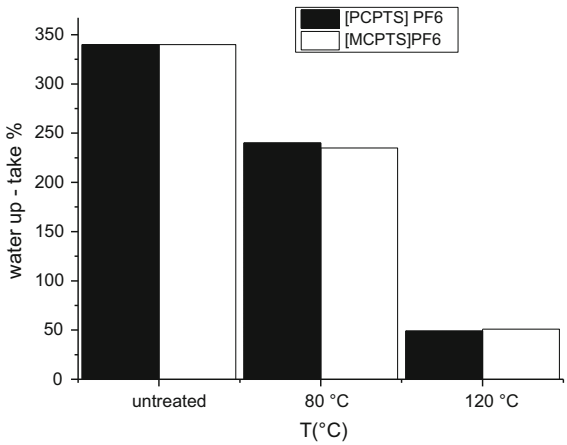


Fig. 7 Comparison of water-repellent properties of untreated samples and cotton fabrics treated by $[PCPTS]PF_6$ and $[MCPTS]PF_6$ heated at 80 and 120 °C

67 s after the removal of the flame, respectively. The final residue after the test is 1 % (in weight) for untreated cotton and 15 % for the one treated with CPTS, and the burned area is 200 cm^2 for both samples. However, cotton fabrics functionalised with $[MCPTS]PF_6$ or $[PCPTS]PF_6$ do not burn. As shown in Fig. 8e, f, treated cotton does not flame during and after the removal of the flame. The weight of the final residue is increased from 1 to 93 %, and the burned area decreased from 200 to 56 cm^2 (see Table 1).

The results obtained with the ionic liquids are much more significant compared to those obtained with the pure silica, as previously reported by Alongi et al. (2012a). A final residue of 48 % was obtained for cotton treated with tetramethylorthosilicate (TMOS) after the application of a flame for 5 s. In our case, a highest final residue of 93 % was obtained after the application of a flame for 20 s. The comparison of these results allows concluding that ionic liquids can be considered as excellent flame retardants for cotton textiles.

To investigate the hybrid coating stability to washing, an ISO 105-C06:2010 standard test was performed. After three washing cycles, the infrared spectrum (Fig. 9) evidenced the departure of PF_6^- anions, whereas the silica bands were still present. This departure of PF_6^- anions may be justified by the weak interaction between these anions and pyridinium or imidazolium cations. The flammability test was carried out for washed samples. The results are gathered in Table 2. It can be noticed that when the PF_6^- anions were removed after three washing cycles, the samples were almost completely burnt.

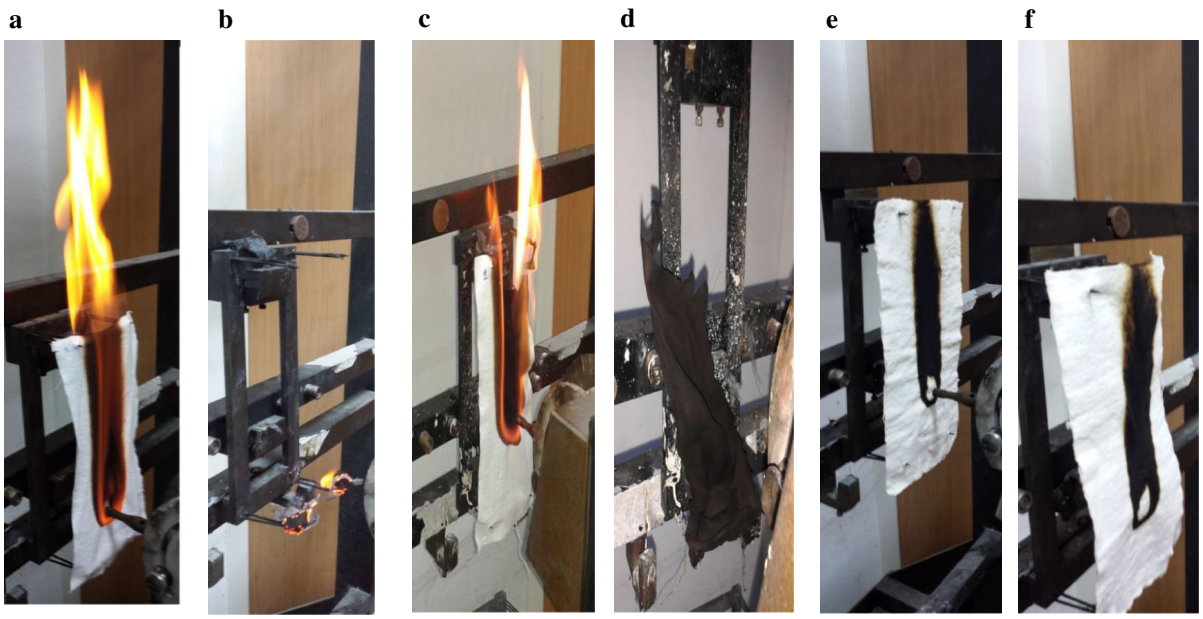


Fig. 8 Fabric residues after the flammability test. **a** Untreated cotton after 20 s, **b** untreated cotton after 45 s, **c** treated cotton with CPTS after 20 s, **d** treated cotton with CPTS after 67 s, **e** $[MCPTS]PF_6$ cotton after 20 s and **f** $[PCPTS]PF_6$ cotton after 20 s

Table 1 Flammability test

Samples	Flame application time (s)	Burned surface (cm^2)	Total burning time (s)	Residue (%)	Residue reported in the literature
Untreated cotton	20	200	45	1	
Untreated cotton	20	200	48	1	
Treated cotton with CPTS	20	200	67	15	
Cotton [MCPTS]PF_6	20	60	Do not burn	92	48 % Alongi et al. (2012a)
Cotton [MCPTS]PF_6	20	56	Do not burn	93	30 % Alongi et al. (2012c)
Cotton [PCPTS]PF_6	20	57	Do not burn	92	
Cotton [PCPTS]PF_6	20	54	Do not burn	92	

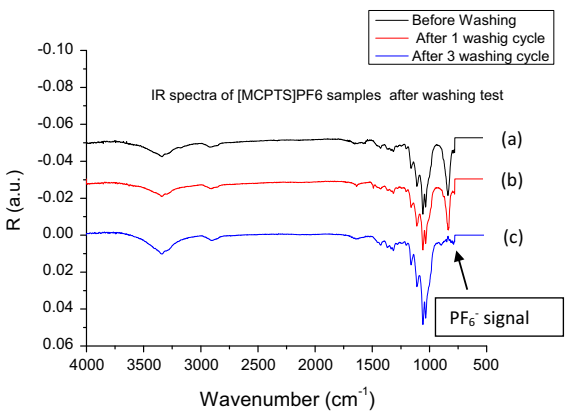


Fig. 9 FTIR spectrum of [MCPTS]PF_6 cotton (*a*) before washing and after (*b*) one and (*c*) three washing cycles

To study the thermal stability of cotton fabrics, thermogravimetric curves of the samples in air are plotted in Fig. 10. For the untreated cellulosic fibers, three steps can be distinguished as previously reported (Price et al. 1997). The first one occurs between 100 and 430 °C and involves two competitive pathways, which yield aliphatic chars and volatile products; the second step, between 430 and 530 °C, corresponds to the conversion of aliphatic chars into aromatics, producing carbon monoxide and carbon dioxide because of the simultaneous carbonisation. During the third and last decomposition step, which ends at 620 °C, the char is oxidised. Figure 9 shows the effect of [MCPTS]PF_6 and [PCPTS]PF_6 coatings on the thermal degradation of cotton fabrics. Based on thermogravimetric curves, there are several distinct thermal degradation behaviours. Treated samples clearly exhibit an improvement of the thermal stability even though they start to be decomposed earlier than the untreated sample. After 430 °C, the pure cotton sample exhibits a lower thermal stability in comparison with sol–gel-treated samples. At 620 °C, the untreated sample was completely decomposed, while the remaining residues (% weight) for cotton fabrics treated with [MCPTS]PF_6 and [PCPTS]PF_6 were respectively 31 and 16 %.

Conclusion

In this article, we have developed a very original methodology to synthesise two onium salts based on methylimidazole and pyridine. These salts were then

Table 2 Flammability test for washed samples after 1 and 3 cycles

Samples	Flame application time (s)	Burned surface (cm^2)	Total burning time (s)	Residue (%)
Cotton [MCPTS]PF_6 after 1 washing cycle	20	68	58	75
Cotton [MCPTS]PF_6 after 3 washing cycles	20	200	72	7
Cotton [PCPTS]PF_6 after 1 washing cycle	20	62	26	70
Cotton [PCPTS]PF_6 after 3 washing cycles	20	200	66	3

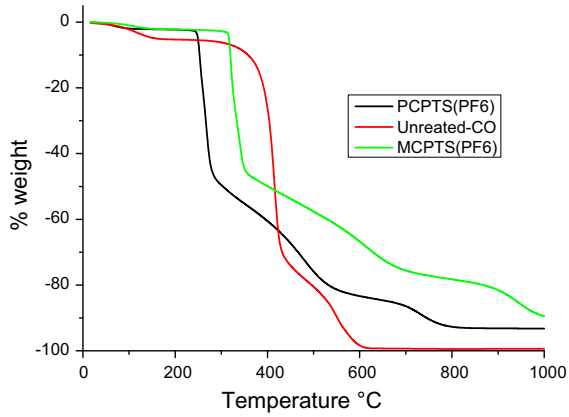


Fig. 10 Thermogravimetric studies of untreated and treated samples with [MCPTS]PF_6 and [PCPTS]PF_6

grafted on cotton fabrics via organosilane-derived compounds. The treated fabrics were subsequently subjected to a metathesis reaction with HPF_6 acid to obtain PF_6^- anions on their surface.

Different characterisations have evidenced that the deposition of ionic liquids onto the textiles by the sol–gel process was effective. The results showed that these fabrics exhibit excellent water-repellent and flame-retardant properties. Indeed, untreated cottons keep burning for 45 s after removal of the flame, unlike those functionalised with [MCPTS]PF_6 and [PCPTS]PF_6, which did not burn. As a result, based on these relevant results, ionic liquids can be considered as excellent flame retardants for cotton textiles. Unfortunately, in order to retain their fire resistance, PF_6^- anions have to be trapped into the cotton fabrics and not removed after the washing test. Future work will be devoted to this task to enhance the stability of PF_6^- anions inside cotton fabrics upon the washing test.

In addition, the thermal study showed that the fabrics coated with hybrid materials based on ionic liquids are more thermally stable compared to the untreated ones.

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