Development of flame retardant cotton fabric based on ionic liquids via sol-gel technique.

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Abstract. In this study, flame retardant cotton fabrics were developed by the sol-gel method, in order to enhance their flame retardant proprieties. For this aim, seven sols were prepared using tetraethylorthosilicate (TEOS) and different ionic liquids (ILs) consist on pyridinium and Methylimidazolium cations with different anions such as: PF$_6^-$, CH$_3$COO$^-$, and Br$^-$. Those sols were applied separately to the cotton fabrics by a pad-dry-cure process. The flame retardant properties of functionalized cotton fabrics before and after washing were determined by the vertical flame tests according to ISO6940:2004(F) standard. The effects of anions have been thoroughly investigated, aiming at the optimization of the targeted properties. Thermogravimetric and mechanical according to NF EN ISO 13934-1:2013 standard, analyses have been also investigated. The results showed that flame retardancy, thermal stability and mechanical properties of treated fabrics were enhanced by using ionic liquids.

Keywords: Cotton Fabrics, Sol–gel technique, Ionic liquid, Flame retardant

1. Introduction

In the last decades, the sol-gel method has been applied in the treatment of textiles with modified mineral soils. This technique opens up many new opportunities for improving their properties and application for the functionalization of the surface of the fibres. In addition, there are very important applications of sol-gel technologies in textile industry. Indeed, functional silica coatings can be deposited on textile materials and can lead to new textile properties such as: water repellence [1, 2], dyeing[3, 4], antimicrobial properties, self-cleaning properties[5], thermal and flame stability[6].

The application potential of ionic liquids (ILs) has been significantly increased in the 21st century. That is due to their unique physicochemical properties such as high thermal stability, high ionic conductivity and non-flammability that make them ideal solvents for green chemistry and clean synthesis[7].

The areas of application of ILs include electrolyte in batteries, solvents and catalysis in synthesis, solvents to manufacture nano-materials and gas absorption agents. Nowadays, ILs were employed also in textile industries to remove textile dyes from aqueous solution, to impart antifungal properties for linen fabric and few patents addressed the use of ionic liquids as” green” flame retardant for textile fabrics [8].
In the current study, we have showed that the immobilization of ionic liquids onto textile matrices can be achieved by the sol-gel process. For this aim we have prepared 6 organosilanes based ILs to enhance flame retardant properties for cotton fabrics.

2. Materials and methods

2.1. Reagents and materials
The reagents used in this study are: CO fabric weighing 168 g m\(^{-2}\), Tetraethyl orthosilicate (99.999\%), ethyl alcohol (EtOH, 99 \%), HCl (37 \%), 1-methylimidazole (99 \%), pyridine (99 \%), hexafluorophosphoric acid (HPF6, 65 \%), 1-Bromohexane (98\%) and ammonium acetate (\(\geq\)99\%) were purchased from Sigma-Aldrich CO. All the chemicals are analytically pure.

2.1.1. RMN, spectroscopy analysis. 1H NMR and 13C NMR spectra were recorded on Bruker Avance (300 MHz) apparatus using TMS as internal reference.

2.1.2. FT-IR spectra measurements. The infrared spectra were recorded on a Nicolet iS10 FTIR-ATR spectrophotometer.

2.1.3. SEM. First, a gold coating was sputtered onto textile samples to make them conductive. The SEM micrographs were recorded using a Jeol 6060-Low Vacuum scanning electron microscope operating under high vacuum at 5 kV.

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

2.1.5. Stability to the washing test. The stability of hybrid materials coated onto cotton fabrics was investigated according to the ISO105-C06:2010 standard. The samples (10 cm x 20 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 (Rotawash, LAB) at 40 °C for 30 min. The washing procedure was repeated for one cycle.

2.1.6. TG analysis. The thermal stability of the fabrics was evaluated by thermo gravimetric (TG) analyses (in a machine Versatherme HM) from ambient temperature to 900 °C with a heating rate of 20 °C/min in the presence of oxygen.

2.1.7. Mechanical test. The mechanical properties of hybrid materials coated onto cotton fabrics were studied according to the NF EN ISO 13934-1:2013 standard.

2.2. Methods

2.2.1. Synthesis of 3-hexyl-1-methyl-1-H-imidazol-3-ium bromide [Im, Br] and 1-hexylpyridin-1-ium bromide [Py, Br]. The schematic diagram of the synthetic procedure for the [Im, Br] and [Py, Br] salts is shown in ‘figure 1’. One eq 1-methylimidazole or pyridine and 1,1eqBromohexanewere added to a round-bottom flask fitted to a reflux condenser and allowed to react at 115 C for 48 h to obtain 1-methylimidazoliun Bromide [Im Br] and pyridinium Bromide [Py, Br]. An viscous liquid marron was obtained for [Im, Br] salts and a Yellow liquid for[Py, Br] salts[9].
2.2.2. Characterization of 3-hexyl-1-methyl-1-H-imidazol-3-ium bromide [Im, Br].

**FTIR (cm⁻¹):** 2857 -2954 (C–H), 1567 (C=C stretching of the imidazole ring), 1378 (stretching vibrations of C–N of imidazole ring) and 1167 (C–O).

**¹H NMR (300 MHz, CDCl₃, δ ppm):** 8.79(s, 1H), 6.71(s, 2H), 3.15 (t, 2H), 2.85 (s, 3H), 0.86(t, 2H), 0.64(t, 6H), 0.62(t, 3H).

**¹³C (CDCl₃, 300 MHz, δ ppm):** 135.6, 122.87, 121.69, 48.69, 35.61, 29.96, 24.68, 21.49, and 13.

2.2.3. Characterization of 1-hexylpyridin-1-ium bromide [Py, Br].

**FTIR (cm⁻¹):** 2870 -2959 (C–H), 1567 (C=C stretching of the pyridine ring), 1485 (stretching vibrations of C–N of pyridine ring) and 1056 (C–C).

**¹H NMR (300 MHz, CDCl₃, δ ppm):** 9.95-9.93(d,2H), 9.09(t,1H), 8.57 8.53(d,2H), 5.25(t,2H), 2.29(t,2H), 1.29(t,6H), 0.86(t,3H).

**¹³C (CDCl₃, 300 MHz, δ ppm):** 151.51, 150.47, 132.97, 65.42, 37.04, 36.03, 29.71, 26.5, 18.3.

2.2.4. **Synthesis of 3-hexyl-1-methyl-1-H-imidazol-3-ium hexafluorophophate [Im, PF₆⁻] and 1-hexylpyridin-1-ium hexafluorophosphated [Py, PF₆⁻].** The synthetic procedure for the [Im, PF₆⁻] and [Py, PF₆⁻] salts is shown in 'figure 2'. 1 eq of HPF₆ dissolved in 10 mL of Water was added to 1 eq of 3-hexyl-1-methyl-1-imidazol-3-ium bromide [Im, Br] or 1-hexylpyridin-1-ium bromide [Py, Br] and stirred for two hours at room temperature. The organic phase is extracted by decantation and evaporated by rotavap. Finally, the product obtained is purified by washing three times in diethyl ether.

![Figure 1. Synthesis of [Im, Br] and [Py, Br] salts](image1)

![Figure 2. Metathesis reaction of [Im; Br] and [Py; Br] with HPF₆.](image2)
2.2.5. Characterization of 3-hexyl-1-methyl-1-H-imidazol-3-ium hexafluorophosphate [Im, PF6–].

**FTIR (cm–1):** 2857 - 2954 (C–H), 1567 (C=C stretching of the imidazole ring), 1378 (stretching vibrations of C–N of imidazole ring), 1167 (C–O) and 990 (PF6–).

**1H NMR (300 MHz, CDCl3, δ ppm):** 8.61 (s, 1H), 7.37 - 7.32 (d, 2H), 4.14 (t, 2H), 3.91 (s, 3H), 1.86 (t, 2H), 1.82 (t, 6H).

**13C (CDCl3, 300 MHz, δ ppm):** 174.59, 136.22, 123.4, 121.9, 49.29, 35.86, 30.52, 29.61, 25.23, 21.81, 21.71, and 13.37.

2.2.6. Characterization of 1-hexylpyridin-1-ium hexafluorophosphate [Py, PF6–].

**FTIR (cm–1):** 2870 - 2959 (C–H), 1567 (C=C stretching of the pyridine ring), 1485 (stretching vibrations of C–N of pyridine ring), 1056 (C–C) and 835 (PF6–).

**1H NMR (300 MHz, CDCl3, δ ppm):** 8.78 - 8.76 (d, 2H), 8.53 - 8.52 (d, 2H), 7.72 (t, 1H), 4.26 (t, 2H), 2.34 (t, 2H), 1.31 (t, 6H), 0.86 (t, 3H).

**13C (CDCl3, 300 MHz, δ ppm):** 173.81, 145.20, 144.84, 128.15, 61.31, 31.81, 30.74, 25.05, 21.76, 20.96, 13.38.

2.2.7. Synthesis of 3-hexyl-1-methyl-1-H-imidazol-3-ium acetate [Im; OAc] and 1-hexylpyridin-1-ium acetate [Py, OAc]. The synthetic procedure for the [Im; OAc] and [Py; OAc] salts is shown in figure 3.

4 g of ammonium acetate (NH4CH3CO2) is dissolved in 30 mL of acetonitrile. Then, 5 g of 1-Hexylpiridinium bromide was added to the mixture in order to carry out the anion exchange. After 24 hours of stirring at room temperature, we noticed the formation of a white powder (precipitate NH4Br). To remove the latter, a filtration step was necessary. Subsequently, the product obtained after filtration is passed to the rotary evaporator in order to evaporate the solvent (acetonitrile).

**Figure 3.** Metathesis reaction of [Im; Br] and [Py, Br] with NH4CH3CO2

2.2.8. Characterization of 3-hexyl-1-methyl-1-H-imidazol-3-ium acetate [Im; OAc].

**FTIR (cm–1):** 2857 - 2954 (C–H), 1567 (C=C stretching of the imidazole ring), 1378 (stretching vibrations of C–N of imidazole ring), 1167 (C–O) and 1714 (C=O).

**1H NMR (300 MHz, CDCl3, δ ppm):** 9.82 (s, 1H, OH), 8.97 (s, 1H), 7.12 (s, 2H), 3.73 (t, 2H), 3.47 (s, 3H), 1.42 (t, 2H), 0.74 (t, 6H), 0.30 (t, 3H).

**13C (CDCl3, 300 MHz, δ ppm):** 173.81, 145.20, 144.84, 128.15, 61.31, 31.81, 30.74, 25.05, 21.76, 20.96, 13.38.

2.2.9. Characterization of 1-hexylpyridin-1-ium acetate [Py, OAc].

**FTIR (cm–1):** 2870 - 2959 (C–H), 1567 (C=C stretching of the pyridine ring), 1485 (stretching vibrations of C–N of pyridine ring), 1056 (C–C) and 835 (PF6–) and 1713 (C=O).

**1H NMR (300 MHz, CDCl3, δ ppm):** 8.82 - 8.72 (d, 2H), 8.10 (t, 1H), 7.67 - 7.63 (d, 2H), 4.31 (t, 2H), 1.47 (t, 2H), 0.75 (t, 6H), 0.27 (t, 3H).

**13C (CDCl3, 300 MHz, δ ppm):** 173.81, 145.20, 144.84, 128.15, 61.31, 31.81, 30.74, 25.05, 21.76, 20.96, 13.38.
2.3. Sol–gel treatment of textile

In the first step, (TEOS), distilled water, EtOH (99 %) and HCl (37 %) were mixed at (TEOS)/HCl/EtOH/H2O molar ratio of 5/0.008/60/55 (Sol-1). The mixture was stirred for 3 h at 70 °C until a homogeneous solution was obtained. In the second step, ILs with different weight ratio of Ionic liquids: CO (table 1), were added separately to the Sol-1. [10]

| Table 1. Different Sols prepared based on synthesized ILS. |
|-----------------------------------------------------------|
| **ILs precursors** | **Weight ratio (%)** |
| Sol-2- [Im; PF6] | 1-5-10-30 |
| Sol-3- [Im; Br] | 1-5-10-30 |
| Sol-4- [Im; OAc] | 1-5-10-30 |
| Sol-5- [Py; PF6] | 1-5-10-30 |
| Sol-6- [Py; Br] | 1-5-10-30 |
| Sol-7- [Py; OAc] | 1-5-10-30 |

The fabric samples were immersed separately into the sols for 2 min and then dried at 80 °C during 1 h. After that, the coating was cured during 1h at 120 °C.

3. Result and discussion

3.1. Morphology

In order to assess the morphology of the coatings deposited onto textile sample by the sol–gel process, SEM observations have been performed. The typical morphology of CO fibers is reported in ‘figure 4’, as expected, the surface of untreated CO fibers exhibits a certain level of irregularity ‘figure 4(a)’. After treatment with sol-1-, significant differences were observed between the untreated and treated sample surface. Indeed, the treated fibers appear homogeneously covered by continuous thin film consisting in the hybrid network ‘figure 4(b)’.

![Figure 4. SEM magnification of untreated (a) and sol–gel treated (b) CO fabric.](image-url)
3.2. Flame retardancy

As previously reported, ILs have a good thermal stability and flame retardant properties [11, 12, 13]. In the present work, ionic liquids combined with silica precursor showed a good resistance to a direct flame. The flame resistance of CO fabrics treated with different ILs was improved compared to CO treated only with TEOS and untreated one. The important result was obtained for CO treated with ILs based on PF6 anion. Indeed, as illustrated in ‘figure 5’, untreated cotton flames (see table 2 (a) and (b)) and keeps burning rapidly for 82 s after the removal of the flame. The final residue after the test is 1% (weight %). However, cotton functionalized with different ionic liquids does not flame during and after the removal of the flame. The coated CO slowly ignites the flame and keeps burning slowly for 173 s (see table 2 (d)), 111 s, 117 s in case of 30 % [Py, PF6], 30% [Py, Br], 30% [Py, OAC], respectively. The lost of weight for all ILs was about 85%. These results are in good agreement with those reported in the literature based on alkoxides of metals, such as silicon, titanium alkoxides or aluminum[14, 15].

The flame retardancy can be explained by the formation of a silica-based layer which is resistant to propagation and penetration of the flame. In addition, as known in the literature degradation of ILs involves an endothermic reaction[16]. So their addition on a three-dimensional silica network contributes to the slowing down of the flame propagation by the absorption of a quantity of heat.

Figure 5. The Burning time and the lost of weight for coated CO as function of the concentration of ILs.

| Cotton samples | Burning time (s) | Lost of weight (%) |
|----------------|-----------------|--------------------|
| Untreated cotton | 80 | 90 |
| Cotton + TEOS | 60 | 85 |
| (1%) [Im ; PF6] | 70 | 95 |
| (5%) [Im ; PF6] | 80 | 90 |
| (10%) [Im ; PF6] | 90 | 85 |
| (30%) [Im ; PF6] | 100 | 80 |
| (1%) [Py ; OAc] | 85 | 90 |
| (5%) [Py ; OAc] | 95 | 95 |
| (10%) [Py ; OAc] | 100 | 100 |
| (30%) [Py ; OAc] | 105 | 105 |
| (1%) [Im ; Br] | 75 | 80 |
| (5%) [Im ; Br] | 85 | 85 |
| (10%) [Im ; Br] | 90 | 90 |
| (30%) [Im ; Br] | 95 | 95 |
| (1%) [Py ; PF6] | 65 | 70 |
| (5%) [Py ; PF6] | 75 | 75 |
| (10%) [Py ; PF6] | 80 | 80 |
| (30%) [Py ; PF6] | 85 | 85 |

Table 2: Results of Flame retardancy.

(a) Untreated cotton fabric after 10s of flame application. (b) Cotton fabric untreated after 78s of burning time. (c) Cotton fabrics treated with [Py; PF6] after 10s of flame application. (d) Cotton fabrics treated with [Py; PF6] after 173s of burning time.
3.3. Thermal stability
To study the thermal stability of cotton fabrics, thermo gravimetric curves of the samples in air are plotted in ‘figure 6’.

![Thermo gravimetric curves of untreated and treated sample with (30%) [Py, PF6].](image)

**Figure 6.** Thermo gravimetric curves of untreated and treated sample with (30%) [Py, PF6].

In the case of uncoated cotton, degradation has three main stages. The first step starts at 150 °C, and involves two competitive routes which are the release of the volatiles and the carbonization of the aliphatic products. The second step starts at 487 °C which corresponds to the conversion of the carbonized aliphatic products to the aromatics producing mono and carbon dioxide. The third step is completed at 500 °C. And corresponds to the oxidation of the carbonized products[17].

In the case of coated cotton, the degradation has two stages. The first step ends at 250 °C. in which the rate of decomposition is very rapid. During the second and final stages the decomposition rate slowly decreases until dehydration and carbonization of the fibre at 580 °C. Unlike the untreated sample which was decomposed in two stages with a very rapid rate of degradation.
In conclusion, the cotton fabric coated with [Py, PF6] is more thermally stable than the uncoated cotton fabric.

3.4. Stability to the washing test
To investigate the hybrid coating stability to washing, an ISO 105-C06:2010 standard test was performed. For these measurements, only samples prepared from (30%) [Im; PF6] and ((30%) [Py; PF6]), were utilized since they exhibit suitable flame retardancy. Test was carried out for washed samples for 1 cycle.

The results of washing test were reported in ‘figure 7’. For washed samples, the flame-retardant properties decreased compared with the unwashed fabrics. Indeed, the burning time has been reduced from 173 to 122 s and from 163 to 113 for ((30%) [Py; PF6]) and ((30%) [Im; PF6]) respectively, but they still exhibit a higher flame resistance than the untreated fabric (78 s).

![Figure 7. Results of flammability test after one wash cycle.](image)
Untreated cotton

Cotton+TEOS (30%) [Im ; Br]

Cotton+TEOS (30%) [Im ; PF6]

Cotton+TEOS (30%) [Im ; OAc]

Cotton+TEOS (30%) [Py ; Br]

Cotton+TEOS (30%) [Py ; PF6]

Cotton+TEOS (30%) [Py ; OAc]

Figure 8. Breaking strength and elongation rate for treated Cotton fabrics as a function of the concentration of the ionic liquids.

As seen in ‘figure 8’ the application of ionic liquids on cotton fabrics does not affect their mechanical properties. The obtained results evidenced that the sol–gel treatment with onium salts improve slightly the mechanical properties of the CO fabrics. In fact, the breaking strength for Cotton fabrics increase from 301.09N to 352.16 N, 357.25 N and 320.19 N for CO functionalized with 30%[Im ; OAc], (10%[Py ; Br]) and (1%[Im ; Br]) respectively. In conclusion, the sol-gel coatings of the cotton fabrics do not alter their mechanical properties. Such a discrepancy between the mechanical properties may be justified by the fact the hybrid coatings act as cement between the fibers.

4. Conclusion
This work involves the application of ionic liquids on the surface of cotton fabrics by the sol-gel process. The aim is to give the textile material flame retardant properties. After synthesizing 6 onium salts based on 1-Methylimidazole and pyridine we grafted them onto cotton textiles. The results showed that these textiles exhibit very high flame-retardant properties and a better thermal stability compared to the untreated Cotton. The study of the mechanical properties showed that the sol-gel coatings based on the ionic liquids of the cotton textile fabrics did not affect their mechanical properties.

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