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Intumescent flame retardant properties of graft co-polymerized vinyl monomers onto cotton fabric

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Abstract. In this paper, an intumescent flame retardant treatment, obtained by a combination of vinylphosphonic acid (VPA) and methacrylamide (MAA), was applied to cotton fabrics. In order to improve the cross-linking degree onto cellulose polymers, potassium persulfate was used as initiator of a radical polymerization technique. The application on cotton was carried out by padding, followed by drying and a curing treatment. The treated samples were characterized by SEM, TGA and FTIR-ATR analyses and tested in terms of flammability and washing fastness. The thermal and fire behavior of the treated fabrics was thoroughly investigated. The results clearly showed that the VPA/MAA coating was able to exert a protective action, giving rise to the formation of a stable char on the surface of textile fibers upon heating, hence improving the flame retardant performance of cotton. Horizontal flame spread tests confirmed that the coated fabrics achieved self-extinction, and the residues well preserved the original weave structure and fiber morphology; at variance, the uncoated fabric left only ashes. A remarkable weight loss was observed only after the first washing cycle, then the samples did not show any significant weight loss, hence confirming the durability of the self-extinguishing treatment, even after five laundering cycles.

1. Introduction

Recently, textile materials have increased their field of use beyond traditional application. In particular, compared to other materials, the strongest potential for cellulose products is originated from the combination of their low cost, biodegradability and high specific strength. These advantages allow cotton, the most used among the cellulosic fibres, to be easily manipulated and adapted to a wide range of end-use requirements, hence undergoing a remarkable growth in the textile industry for technical applications [1]. Unfortunately, when ignited, cotton fibers burn easily and the flame spreads quickly, causing several problems such as loss of material properties, production of smoke and gases during thermal decomposition, which could affect both human life and equipment [2]. Due to the role played in everyday life, the burning of cellulose-based fabrics has always been considered a major hazard. They are largely used in clothing, furniture upholstery, bed linen, as well as in transportation, automotive industry and protective garments. Consequently, flame retardant finishes for cotton fabrics have attracted much interest in research studies due to their capability to reduce risks derived from flame exposure. Furthemore, thermal stability improvement of cotton fabric has been a major challenge for extending its use to a wide number of applications. The pyrolysis of cellulose is a chain degradation initiated by a heterolytic bond scission of glucose producing levoglucosan. The lability of the C-6 hydroxyl group in the cellulose repeating unit is crucial to depolymerization. So far, several fire retardant additives, such as phosphorus-based compounds, have been used to treat cotton textiles,

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and in some formulation, their efficiency could be further enhanced by addition of some nitrogen-containing additives, giving rise to the synergistic phosphorus–nitrogen action [3].

The most important approach to flame retardant finishes was set in the well-known "Golden period" of fire retardants [4], between 1950 and 1980, after the success of those developed during the Second World War. Afterwards, little research has been developed up to 2000 due to the environmental issues that some flame-retardants were showing. Currently, government regulations have raised safety and environmental protection standards on flame retardants, hence determining a renewed interest on the development of environmentally friendly structures. Furthermore, many voluntary standards, often without coordination, highlighted the lack of adequate control in the release of toxic chemicals during textile processes. Consequently, in recent years, several research papers were focused on the development of environmentally friendly chemicals for flame retardant treatments of textile fabrics, in order to replace formaldehyde- and halogen-based compounds. In fact, formaldehyde, which is commonly used in several flame retardant compounds, is toxic and therefore undesirable for textile finishing. Moreover, halogenated flame retardants are environmentally persistent and, during combustion, they can generate toxic gases that threaten both air and water ecosystems. Finally, health implications and environmental claims associated also with antimony trioxide (SbO_3) suggest the development of new flame retardant antimony-free.

In the last years, novel approach in the field of textile fabrics flame retardancy has attracted a great interest from both industrial and academic research [5]. Among the tested technologies, sol-gel appears to exhibit particularly interesting results and, for this reason, it has been exploited in the textile field for conferring multifunctional properties [6], anti-wrinkle finishing [7], antimicrobial or UV radiation protection [8], biomolecule immobilization [9], dye fastness [10], hydrophobicity [11], photocatalytic properties [12] and sensor characteristics [13, 14]. In the last years, sol-gel architectures were found to be capable of protecting the polymer surface by exerting a thermal shielding effect, thus improving the flame retardancy of the treated fabrics [15,16]. These results are based on the synergistic effect generated by the simultaneous presence of phosphorous and nitrogen in the finishing system [17]: the former ~~one~~ acts on the dehydration of the polymer chain forming a protective layer (char), while the latter is able to dilute the oxygen concentration thanks to the release of non-toxic gases. In this work, aiming at providing flame retardant properties to cotton fabrics, a novel approach based on graft-copolymerization of vinyl monomers, containing P and N, onto cotton fabrics was thoroughly investigated. The grafting reaction was carried out in the presence of potassium persulfate (KPS) used as radical-initiator. The basic mechanism starts from the creation of free radical sites on both the used vinyl monomers and on cellulosic chains, in order to obtain a permanent combination of VPA and MAA with the textile substrate.

ATR FT-IR spectroscopy and weight percentage changes between treated and untreated samples have been used to investigate the surface composition and the coating durability. Thermal stability, flammability and combustion behavior of the treated and untreated cotton fabrics have been assessed by using thermogravimetric analyses and horizontal flame tests, respectively.

2. Experimental part

2.1. Materials and methods

Scoured and bleached 100% plain-weave cotton fabric (mass per unit area of 237 g/m^2) was kindly supplied by Mascioni Spa, Varese, Italy. Textile samples were washed in 2% non-ionic detergent at 40°C for 20 min, before any treatments. Methacrylamide (98%) (MA), Vinylphosphonic acid (97%) (VPA) and potassium persulfate (KPS) were purchased from Sigma-Aldrich and used without further purification. VPA and MA were chosen as phosphorus and nitrogen sources, respectively. The graft co-polymerization was performed under nitrogen atmosphere by dissolving VPA in water. Then, after heating at 60°C, MAA (VPA/MAA = 1:1 molar ratio) was slowly added to the solution.

Graft co-polymerization reactions took place after the addition of KPS initiator; in order to limit any premature gelation [5], the final solution was applied on cotton fabrics within 10 min at 60°C.

Scoured and bleached 100% plain waive cotton fabric was treated with the VPA/MAA/KPS solution by a pad-cure process, using a Werner Mathis lab device with 2 bar nip pressure.

The treated fabric samples were then dried (20 min at 60°C) and cured (3 min at 165°C). To evaluate the coating durability, treated samples were washed in standard conditions (EN ISO 6330:2000). The total dry solids add-on (A, wt.%) on cotton sample and the weight loss of the coating after washing cycles (WLW, wt. %), were calculated using a Mettler balance (accuracy: 10^{-4} g) according to Eq.1 and Eq.2, respectively:

$$A = \frac{W_T - W_{UT}}{W_{UT}} \times 100 \quad (1)$$

$$WLW = \frac{W_{TW} - W_T}{W_T} \times 100 \quad (2)$$

where W_{UT} and W_T are the dry weights of the cotton samples before and after the pad-cure treatment respectively, while W_{TW} is the dry weight of the cotton sample after washing cycles.

Textile fabrics, before and after the washing cycles, were weighted five times with the standard deviation always lower than 2%. The final dry add-on of the treated sample was 67.4%, while its weight losses after 1 and 5 washing cycles were 34.2 and 34.6% respectively.

3. Results and discussion

Due to the grafting process induced on cotton fabrics, covalent bonds are formed between monomers and polymer, hence providing new functionalities to the treated fabric with high durability [18,19]. The presence of the coating was checked by FT-IR spectroscopy through the identification of the absorption bands of characteristic moieties of the two vinyl monomers (Figure 1).

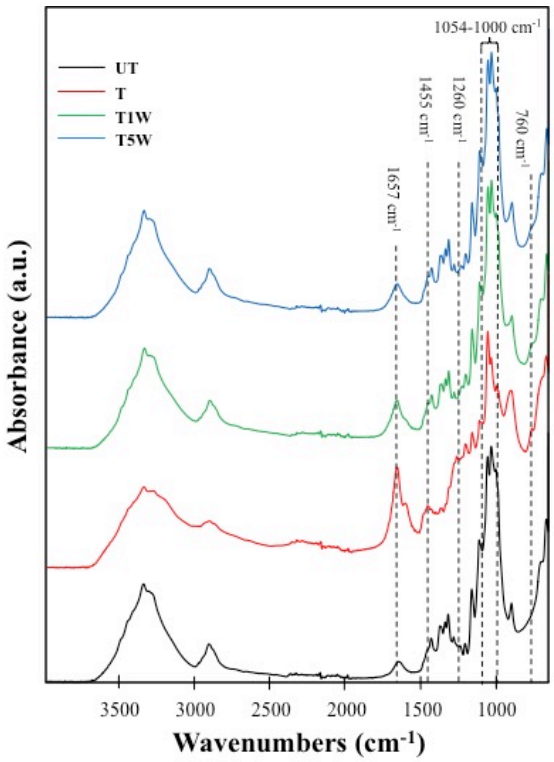


Figure 1. Normalized FT-IR spectra of untreated (UT) and treated (T) samples, also after 1 (T1W) and 5 washing cycles (T5W).

With respect to the reference fabric, the infrared absorption bands of the treated sample in the ranges 3500–3000 cm^{-1} and 3000–2800 cm^{-1}, characteristic of hydrogen bonded O-H stretching and C-H stretching of cellulose, respectively, decrease in the intensity due to the presence of the vinyl based film on the surface of the treated cotton fabric. Furthermore, the disappearance of the characteristic absorption band assigned to C=C at 1614 cm^{-1} and 1646 cm^{-1} for vinyl groups of VPA and MAA, respectively, confirms the graft co-polymerization of both vinyl monomers onto cotton fabric.

The presence of MAA is further confirmed by the appearance of absorption bands characteristic of the amide group and assigned to C=O stretching (1657 cm^{-1}) and NH_2 bending (1599 cm^{-1}). In addition, the FT-IR band at 1402 cm^{-1} is ascribed to the C-N stretching, while the signal at 760 cm^{-1} is assigned to the N-H out-of-plane bonding. Furthermore, the peaks at 1260 cm^{-1} and 1455 cm^{-1} are attributable to P=O stretching and CH out-of-plane bending, respectively.

The thermal and thermo-oxidative stability of the pure and treated cotton fabrics has been assessed by thermogravimetric analyses performed in nitrogen and air, respectively. Table 1 collects the obtained data for the different materials investigated.

Table 1. TG data of CO_UT, CO_T, CO_T1W in nitrogen atmosphere.

Sample	$T_{onset10\%}$ (°C)	T_{max1} (°C)	R@ T_{max1} (%)	T_{max2} (°C)	R@ T_{max2} (%)	R@ 700°C (%)
UT	336	362	50.3	-	-	8.3
T	253	317	72.5	411	56.7	43.4
T1W	278	326	63.2	419	44.3	34.3

The presence of the intumescent coating significantly anticipates the cellulose decomposition: in particular, regardless of the possible washing cycle applied to the treated fabrics, $T_{onset10\%}$ and T_{max1} values decrease, while, at the same time, the residues found at T_{max1} are within 63 and 72%, respectively. This finding can be attributed to the presence of vinylphosphonic acid that, upon activation, favors the cellulose decomposition towards dehydration, hence limiting the production of volatile species and giving rise to the formation of a protective and quite stable char, as indicated by the high residues found at T_{max1} by comparing the values listed in Table 1.

The protection feature was also confirmed by cone calorimetry tests that also highlighted the washing fastness of the coating. Table 2 lists the obtained data, in terms of Time To Ignition, Total Heat Release, peak of Heat Release Rate and final residue. Under a 35 kW/m^2 heat flux, cotton burns vigorously in 160 s, while the coated fabric does not ignite at all. The sample undergoes thermal-oxidation, leaving a 31 wt.% final residue, which can be attributed to the extent of the pyrolysis process, instead of combustion.

According to these results, horizontal flame spread tests showed for the treated samples, either before or after washing, self-extinguishing properties (Table 3).

Table 2. Combustion data from cone calorimetry tests.

Code	TTI (s)	pkHRR (kW/m^2)	THR (MJ/m^2)	Residue (%)
UT	26	175	5.2	0
T		NO IGNITION		31
T1W		NO IGNITION		13
T5W		NO IGNITION		12

All the treated and washed fabric samples were subjected to horizontal flame spread tests, according to UL94 HB standard.

The results showed a substantial enhancement of char-forming properties and flame retardancy for the treated fabrics. These latter, either before or after the washing cycles, achieve self-extinction few seconds after the flame application. It is worth noticing that even 5 washing cycles did not change the flammability behavior of the treated fabrics, which were self-extinguishing similarly to those subjected to one washing cycle only.

Table 3. Flammability behaviour and data of UT, T, T1W and T5W.

Data	**UT**	**T**	**T1W**	**T1W**
Total burning time (s)	149	5	7	7
Char length (mm)	100	4	5	5
Residue (%)	0	99	99	99
Self-extinction	NO	YES	YES	YES

The weight loss calculation and the presence of absorption bands related to the deposited coating were also evaluated after one and five washing cycles, in order to confirm the washing fastness of the applied coating.

It is worthy to note that the treated fabrics, despite a significant decrease of the final residue (13 vs. 31 wt.%, before and after washing, respectively), still do not ignite even after the washing cycles: this finding further confirms the durability and protection exerted by the treatment.

4. Conclusions

In this research work, in order to allow a durable chemical modification of cotton surface, a combination of vinylphosphonic acid and methacrylamide was grafted onto textile samples, in presence of KPS as radical initiator. The obtained coating was able to enhance the thermal stability of cotton, confirming the intumescent effect promoted by VAA and MAA, as phosphoric acid and nitrogen sources, respectively.

The modified textile achieved self-extinction in horizontal flame spread tests; this behavior was maintained at least up to five washing cycles. Therefore, this new halogen-free flame retardant finishing, durable and effective at least up to five washing cycle, may represent a potential alternative to the commercially available treatments for cellulose-based polymers.

Acknowledgments

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