A NOVEL NITROGEN-CONTAINING CARBOXYL-FUNCTIONALIZED ORGANOPHOSPHORUS SYSTEM FOR FLAME RETARDANT FINISHING OF COTTON FABRICS

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Abstract

In this paper, a novel nitrogen-containing carboxyl-functionalized organophosphorus compound was exploited for enhancing the flame retardant properties of cotton fabrics. In particular, 1,2,3,4-butanetetracarboxylic acid and sodium hypophosphite were used as environmentally-friendly binder and catalyst, respectively. Besides, to avoid the formation of insoluble calcium salt during home laundering, the treated samples were recoated employing three sol-gel solutions. Treated and untreated samples were thoroughly characterized to understand the bonding between coatings and substrate, as well as their thermal and fire behaviour. The results obtained from flame and combustion tests revealed that the treated fabrics were able to control the combustion process.

Keywords: N-(Phosphonomethyl)iminodiacetic acid hydrate, flame retardancy, cotton fabric, sol-gel treatment, phosphorous-based finishing

1. INTRODUCTION

Even though the number of fires and fire deaths has been decreased in the last decades, nowadays there are still too many fatalities caused from fires [1]. In particular, most of deaths derives from inhalation of smoke and toxic combustion gases, originated from fires in confined areas. Furthermore, most of these accidents involve textile substrates, whether they are used as nightwear or furnishing [2]. Nowadays, the use of textile substrates is widespread in various areas of everyday life and both synthetic and natural polymers are widely used. Among natural materials, cotton, thanks to its peculiarities (strength, durability, flexibility and air permeability) is the most employed [3]. Unfortunately, its low limiting oxygen index (18%) and combustion temperature (360–425°C) make it highly flammable [4]. To overcome this drawback, in the last years, several treatments have been extensively studied to modify the combustion behaviour of cotton. The majority of these flame retardant treatments can be classified into four distinct groups, as they can be based on the use of halogenated organic, inorganic, organophosphorus, and nitrogen formulations [3,5–8]. The role of these products is to interrupt the self-powered cycle of combustion, reducing the speed of the processes involved, both in gas and condensed phases, through chemical or physical mechanisms. Many of the flame retardant (FR) chemical products currently used generate, during combustion, smokes that are more toxic than those originated by the fire itself. Recent research studies on halogenated compounds have demonstrated their persistence, ability to bioaccumulate, and potential toxicity. In particular, compounds like polybrominated biphenyls, penta and octobromodiphenilethers have been banned, as they could generate corrosive and toxic combustion products (e.g. dioxins and furans) [9]. On the other hand, other consolidated FR finishing (Proban, Pyrovatex) systems turned out to be formaldehyde releasers, which is considered a carcinogenic compound by IARC, responsible for nasopharynx cancer and leukemia [10]. Thus, it is clear that there is an immediate need to replace the above-mentioned chemicals with more eco-compatible ones and, for this reason, different approaches have been investigated in the last years. Phosphorus-based flame retardants seem to be a valid alternative for the above-mentioned FRs, as they act prevalently in condensed phase: they promote the formation of non-volatile polyphosphoric acids that can react with the decomposing polymer, by both dehydration and esterification, enhancing the char formation [11]. The latter acts as a barrier and protects the treated polymer from the attack of radiant heat and oxygen, favouring the combustion extinction. Besides, several studies have shown that the phosphorus-nitrogen combination increases flame resistance in cotton textiles, using a lower phosphorus content than that required when P is employed alone [12]. In this research, a nitrogen- and phosphorous- containing oligomer (PMIDA) was immobilized onto cotton fabrics using 1,2,3,4-butanetetracarboxylic acid as a binder, in the presence of sodium hypophosphite as a catalyst and triethanolamine; the latter was used both for adjusting the pH of the mixture and contributing to phosphorous-nitrogen synergism. When the fabric treated with this polycarboxylic acid is laundered in tap water, the free carboxyl groups on the cotton surface can form insoluble calcium salts, turning out in a leaching of the coating [14]. To overcome this drawback, in a second step, the treated cotton samples were recoated, employing two different hybrid sol-gel solutions, namely 3-aminopropyltriethoxysilane (APTES), or a mixture of tetraethoxysilane (TEOS) and 3-glycidyloxypropyltriethoxysilane (GPTES) precursors. The deposition of the coating onto the substrates was studied by FT-IR spectroscopy, while the thermal and thermo-oxidative behaviour of the treated samples was assessed by Thermogravimetric analysis (TGA), both in nitrogen and air atmospheres.

2. MATERIALS AND METHODS

N-(Phosphonomethyl)iminodiacetic acid hydrate (PMIDA, 97%, MW 227.11), 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hypophosphite (SHP), hydrochloric acid (≥37%), ethanol (≥99.8%), and the sol-gel precursors, namely 3-aminopropyltriethoxysilane (APTES, ≥98%), tetraethoxysilane (TEOS, ≥98%) and 3-glycidoxypropyltriethoxysilane (GPTES, ≥98%), were supplied by Sigma Aldrich (Germany). All chemicals were of analytical reagent grade and were used without further purification. Desized, scoured and bleached plain weave cotton fabric (100%, 331 g/m^2) was supplied by Mascioni SpA (Cuvio, Varese, Italy). The cotton samples were washed in 2% non-ionic detergent at 40 °C for 30 min, then rinsed several times with deionized water, dried and kept into a drier for storage. The cleaned samples were conditioned under standard atmospheric pressure at 65 ± 4% RH and 20 ± 2 °C for at least 24 h prior to all the tests.

The final compound was obtained by mixing 30 g of PMIDA with 10 g of BTCA in the presence of 11.5 g of sodium hypophosphite (SHP). The solution pH was adjusted to 3, by using TEA. To promote the solubilisation of the chemicals, the mixture was heated to 50 °C. Two sol solutions, i.e. APTES and GPTES/TEOS (25:75) were employed as second layers to treated FR cotton fabrics.

Textile fabrics were treated by using a two-stage procedure. In the first step, cotton samples were impregnated with the finishing solutions and afterwards passed through a two-roll laboratory padder (Werner Mathis, Zurich, Switzerland) working with 3 bar nip pressure in order to achieve 70% wet pick-up. After drying at 80 °C for 10 min, textile samples were cured at 170 °C for 2 min. This layer was used as flame retardant coating for the cotton fabrics coded as CO-1. Then, two of these so-treated samples were re-coated with sol solutions, in order to react with the free carbonyl groups onto cellulose surface; thus, FR pre-treated cotton samples were immersed into the APTES sol or into the TEOS/GPTES sol, obtaining the samples coded as CO-2 and CO-3, respectively. Subsequently, the cotton samples were dried and cured in the same conditions used for the first layer.

To investigate the chemical structure of untreated and treated cotton fabrics, Fourier transform infrared spectroscopy (FTIR) was carried out. The spectra were recorded at room temperature in the range from 4000 to 650 cm^{-1} with 64 scans and a resolution of 4 cm^{-1}

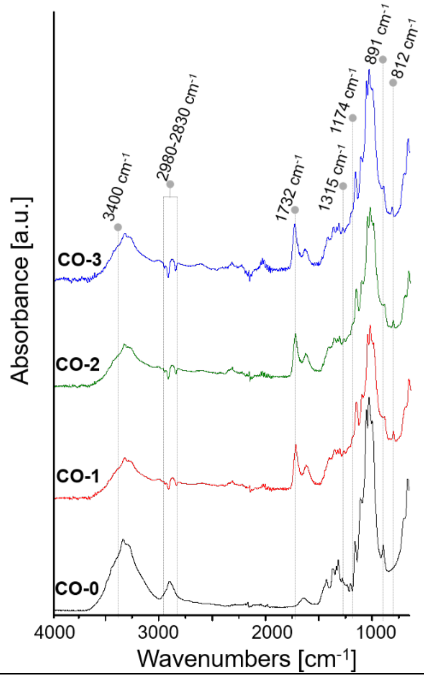
using a Thermo Avatar 370 spectrophotometer, equipped with attenuated total reflection (ATR) accessory and a diamond crystal. The collected spectra were normalized against the 1314 cm^{-1} band, associated with the C-H bending mode of cellulose.

The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses from 50 to 700 °C with a heating rate of 10 °C/min, in nitrogen and in air (gas flow: 60 ml/min for both the atmospheres). To this aim, a TAQ500 thermogravimetric balance was used, placing the samples in open alumina pans. The experimental error was ±0.5% on the weight and ±1°C on the temperature.

3. EXPERIMENTAL RESULTS

3.1 ATR-FTIR spectroscopy

The ATR-FTIR spectra of the treated samples shown in Fig. 1 were carried out in order to compare the structural differences existing between treated fabrics and the untreated counterpart. The frequencies of major absorption bands are reported in Fig.1. CO-0 shows the characteristic spectrum of cellulose with the hydrogen-bonded OH stretching at ca. 3550–3100 cm^{-1}. In particular, the OH infrared absorption bands beyond 3400 cm^{-1} are ascribed to intramolecular hydrogen bonds, whereas those reported to intermolecular hydrogen bonds are visible at wavenumbers below 3400 cm^{-1} [15]. Besides, the stretching vibrations of CH- and CH_2- bonds of methylene and methine cellulose groups are visible at around 2980–2830 cm^{-1}. The peaks at 1315 cm^{-1} and 1159 cm^{-1} are attributed to CH bending and C-O-C asymmetric stretching vibrations, respectively [16]. The infrared absorption spectra of treated samples show a decrease in the intensity of the broad band at 3600–3000 cm^{-1}, compared to the untreated cotton, indicating the presence of the coating on the cotton surface. In CO-2 and CO-3 spectra, the peaks at 1732 cm^{-1} and 1174 cm^{-1}, assigned to the stretching modes of the carbonyl ester bond [17] and to P=O, respectively, confirm the presence of the coatings. Since the carboxyl groups present in BTCA and PMIDA reacted both each other and also with the hydroxyl of cellulose chains, the ester absorption band on the cotton fabric results as the contribution of BTCA-cotton, PMIDA-cotton and BTCA-PMIDA ester linkages. Other characteristics peaks that appear in the treated cotton fabrics and ascribable to -PO_3 moiety can be found in the complex spectral region between 900−1200 cm^{-1} [18]. Though this is a useful “fingerprint” region, the overlap with cellulose absorption bands makes them challenging to provide a full assignment. Finally, the sharp band at 812 cm^{-1} is attributed to the H-P-H wagging modes of sodium hypophosphite.



Band (cm^{-1})	Absoption
3500-3100	ν O-H
2980-2830	ν C-H
1732	ν_{asym} C=O
1315	γ C-H
1174	ν P=O
1159	ν_{asym} C-O-C
891	ν P-O-C
812	γ_W H-P-H

Figure 1. A) FT-IR spectra of untreated and treated cotton fabrics, B) Assignments of FT-IR peaks

3.2 Thermal properties

The thermal and thermo-oxidative stability of the untreated and treated cotton fabrics has been assessed by thermogravimetric analyses performed in nitrogen and air from 50°C to 700°C, as shown in Fig. 2. In nitrogen, the TG curve of untreated cotton sample shows the onset degradation temperature at about 310 °C, together with its maximum mass loss rate at about 360 °C, due to depolymerisation by trans-glycosylation reactions. The treated fabrics show an anticipation in the onset degradation temperature: this finding is attributed to the earlier degradation of the phosphorus-containing compound that catalyses the decomposition of cotton towards the formation of a carbonaceous residue (char). In fact, at the end of the test, the char residue achieves 40%, significantly higher than pure cotton, for which the residue is below 6%. Besides, a decrease in the temperature of maximum weight loss, regardless of the number of deposited layers, can be observed (Fig. 2 B). In air, the thermo-oxidation of cotton samples (pristine and treated) takes place in a similar way: the only difference is for the appearance of a second degradation step at high temperatures (T_{max2}: 460 °C). This phenomenon can be attributed to the oxidation of the char formed during the first step and of all the hydrocarbon species still present [19]. On the other hand, the treated samples start to decompose at around 270 °C and show the maximum mass loss rate at around 320 °C. Also in this case, the finishing is responsible for the decrease of both T_{onset} and T_{max1} as well as for the increase of the final residue that reaches the value of 15%. These findings [20] confirm the protective effect exerted by the formed stable char.

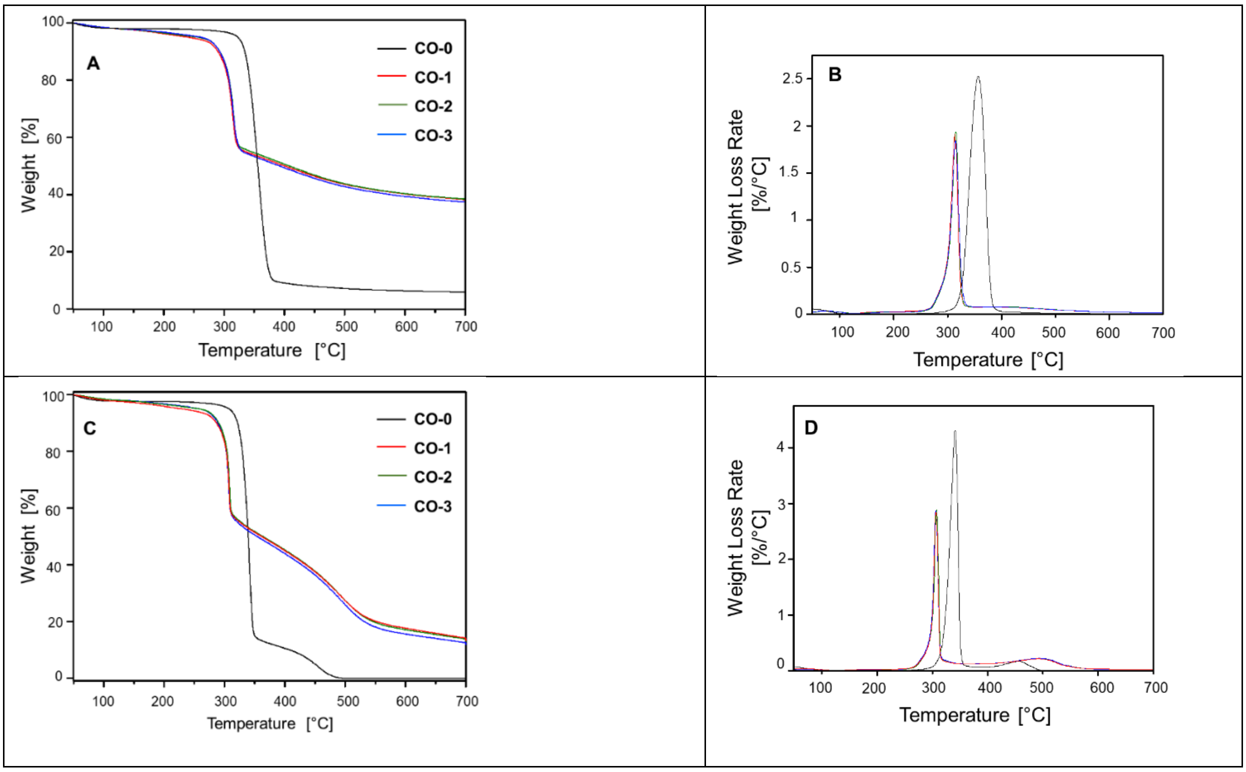


Figure 2. TG and dTG curves in nitrogen (A and B) and air atmospheres (C and D) of treated and untreated fabrics

4. CONCLUSIONS

The global request for less toxic products has increased the demand for fire retardant treatments that should be effective in the protection of textile fabrics, as well as safe for humans. In this work, a finishing that does not contain halogen-based molecules and does not release formaldehyde, is proposed. The FR effectiveness of a nitrogen and phosphorous-containing compound was investigated, mainly in combination with TEA, BTCA and SHP. The structure of untreated and treated fabrics was investigated by Fourier transform infrared spectrometry and their thermal behaviour was assessed by TGA. The obtained data suggest that the proposed flame retardant multilayer coatings are able to control the combustion process increasing the amount of char. Further investigations are underway to design flame retardant coatings with high washing fastness.

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