



# Thermal and flame retardant behaviour of cotton fabrics treated with a novel nitrogen-containing carboxyl-functionalized organophosphorus system



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## ABSTRACT

In this paper, a carboxyl-functionalized organophosphorus oligomer was immobilized onto cotton fabrics using 1,2,3,4-butanetetracarboxylic acid as an environmentally-friendly binder, in the presence of sodium hypophosphite, used as a catalyst, and triethanolamine, which contributes to phosphorous-nitrogen synergism. Moreover, with the aim of reducing the formation of insoluble calcium salt during home laundering, due to the free carboxylic acid groups bound to the cotton fabric, the treated samples were recoated employing three sol-gel precursors, namely 3-aminopropyltriethoxysilane, tetraethoxysilane and 3-glycidioxypropyltriethoxysilane. Samples were thoroughly characterized to understand the bonding between coatings and substrate, as well as the related surface morphology. The thermal behaviour was investigated by thermogravimetric analysis, flame and combustion tests. The results revealed that the treated fabrics were able to achieve self-extinction. Comparing to the untreated sample, tearing strength of PMIDA/BTCA/SHP fabric was reduced in both warp and weft directions, while fabrics coated with an additional sol-gel layer were affected more significantly.

## 1. Introduction

Although it has been an important tool throughout human history, fire can generate dramatic consequences if not properly controlled. According to the data from 2016 National Fire Protection Association (NFPA) (Haynes, 2017), the public fire departments in the U.S. responded to 1,342,000 fires that caused 3390 civilian deaths, 14,650 civilian injuries, and an estimated \$10.6 billion loss in direct property. Since a wide range of commonly used materials is flammable, this means that the use of flame retardants can reduce these hazards and significantly contribute to save lives and resources. As the main component of cotton, cellulose is employed for manufacturing apparel, home furnishings and industrial products, even though its low limiting oxygen index (18%) and combustion temperature (360–425 °C) make this material highly flammable (Wakelyn et al., 2006). To overcome this drawback, a chemical modification of the cellulose structure is necessary.

In the last years, several treatments have been extensively studied to modify the combustion characteristics of cotton, in order to meet fire safety regulations and expand the use of cotton in textile applications

that require flame retardancy. 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 (Ghanbari & Salavati-Niasari, 2015; Ghanbari, Salavati-Niasari, & Sabet, 2013; Ghanbari, Salavati-Niasari, & Ghasemi-Kooch, 2014; Jamshidi, Ghanbari, & Salavati-Niasari, 2014; Nguyen, Chang, Condon, & Smith, 2014). Despite their effectiveness, some of these products, like halogen-containing compounds, turned out to be hazardous for human health, due to the use of textile materials that are typically in close contact with skin. The aforementioned disadvantages stimulated the scientific community towards the development of phosphorus-based compounds. Indeed, although all phosphorus compounds cannot be considered generically non-toxic, the development of new phosphorus-based compounds with flame retardant properties has shown that they have lower toxicity profiles as compared to halogen-based counterparts. This finding has been witnessed by several papers (Bruchajzer, Frydrych, & Szymańska, 2015; Grümping, Opel, & Petersen, 2007; Horacek & Grabner, 1996; Salmeia & Gaan, 2015; Salmeia, Gaan, & Malucelli, 2016; van der Veen & de Boer, 2012; Weil, 1978). In the last decades, phosphorus has become the subject of

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several research studies for cotton treatments (Yang & Yang, 2005), as P-containing flame retardants are able to convert into phosphorus-based acids. This promotes the formation of non-volatile polyphosphoric acids that can react with the decomposing polymer, by both dehydration and esterification, enhancing the char formation (Horrocks, 1996). The latter acts as a barrier and protects the treated polymer from the attack of radiant heat and oxygen, favouring the combustion extinction. 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 (Nguyen, Chang, Condon, Uchimiya, & Fortier, 2012) and releasing low amounts of toxic gases. One of the action mechanisms proposed for P-N containing flame retardants involves the Lewis acidity of electrophilic phosphorus, which promotes cellulose dehydration and char formation (Horrocks, 2008a, 2008b). Due to the nucleophilic attack on the phosphate, nitrogen favours the formation of polymeric species containing P-N bonds, characterized by a more polar character than P-O bonds. The enhanced electrophilicity of the phosphorus atom increases its ability to phosphorylate C(6) primary hydroxyl groups of cellulose chains. The actions of organophosphorus retardants are ascribable to: a) nitrogen-synergized phosphorylation of cellulose in the C(6) position to block levoglucosan formation, b) Lewis acid-catalysed dehydration to char, which is not advantageous to levoglucosan formation and c) cellulose cross-linking in order to promote char formation. The hydroxyl groups of the cellulose fibres can react with N-methylol reactive groups included in the structures of organophosphorus compounds in a condensation reaction, resulting in the formation of covalent bonds able to strongly increase the adhesion between finishes and the fibre surface. Among the various phosphorus-based flame retardant agents developed, tetrakis(hydroxymethyl) phosphonium chloride (THPC) and N-methylol dimethylphosphono propionamide (MDPA) have been the most useful halogen-free flame retardants (FRs), employed as cotton fabric flame-retardant finishes. However, these types of FRs have the disadvantage of formaldehyde release, that is considered a carcinogen compound by IARC, responsible for nasopharynx cancer and leukemia (World Health Organization, 2012). Thus, its mutagenic activity makes it imperative to find alternative formaldehyde-free finishes. As binders for organophosphorus FRs, either resins or reactants with at least two carboxylic groups have been studied. Yang et al. investigated the potentiality of 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) as a binder in flame retardant finishing (Wu & Yang, 2003; Yang & Wu, 2003a), while experiments with 1,2,3,4-butanetetracarboxylic acid (BTCA) applied to cotton or cotton blends were carried out (Wu, Yang, & He, 2010; Yang & Wu, 2003b). Unfortunately, as for the aforementioned FRs, DMDHEU tends to release formaldehyde and, consequently, it does not meet sustainable chemistry requirements. Conversely, BTCA, a well-known non-formaldehyde crosslinking reagent containing four carboxylic acid groups, thermally treated in presence of a phosphorus-based catalyst, is able to form effective crosslinks in cotton fabrics, through an esterification mechanism that follows a two steps reaction: first, cyclic anhydrides are formed and hence, during the second step, they react with the hydroxyl groups (–OH) of the cellulosic substrate, giving rise to ester bonds (Huang, Song, Xing, & Dai, 2010). The role of sodium hypophosphite (SHP) is to catalyse the formation of linkages between polycarboxylic acid and cellulose, while cellulose phosphorylation is one of the parallel reactions. Recently, flame retardant properties were achieved by immobilizing phosphorus-based oligomers (Brancatelli, Colleoni, Massafra, & Rosace, 2011) or nanoparticles (Guido et al., 2013) onto the textile surface; in this context, the sol–gel technique has been reported as a promising tool for the preparation of hybrid organic-inorganic nanocomposite coatings (Malucelli, 2016).

The aim of this study is to investigate the flame retardant action of N-(phosphonomethyl) iminodiacetic acid (PMIDA), a molecule bearing two carboxylic groups and one amine group, as a nitrogen-containing carboxyphosphonate, suitable for improving the flame retardancy of

cellulose-based materials. In order to avoid the disadvantage of treating cotton fibres in an excessively strong acidic medium originated by the PMIDA aqueous solutions, triethanolamine (TEA), a tertiary amine containing three polar hydroxyl groups joined by a two-carbon alkyl chain, was used. In addition, this compound may contribute to the phosphorus–nitrogen (P–N) synergistic action in the flame retardancy of cotton fabric. To promote the immobilization of finishes onto cellulose macromolecules, BTCA was used in combination with SHP, that acts as the reaction catalyst. 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 (Yang & Wu, 2003b). To avoid this problem, in a second step, the treated cotton sample was recoated employing two different hybrid sol-gel solutions, namely 3-aminopropyltriethoxysilane (APTES), or a mixture of tetraethoxysilane (TEOS) and 3-glycidyloxypropyltriethoxysilane (GPTES) precursors. In particular, GPTES and APTES were selected because their epoxy and amine functional groups are known to react with carboxylic acids, resulting in the formation of ether or amide bonds, respectively. These second layers act as a barrier that could increase the washing fastness of the treatments. Both hybrid sols, in fact, promote crosslinking during the formation of sol-gel networks exhibiting high flexibility, excellent mechanical properties, no cytotoxic activity (Plutino et al., 2017), and good flame retardant performances (Alongi, Colleoni, Rosace, & Malucelli, 2012). The novelty of this research refers to a critical investigation of the above-mentioned combinations, comparing the obtained results and in particular looking for the best compromise between flame retardancy and washing fastness. To investigate the morphology and the surface composition of fabrics after the proposed treatments and to verify the presence of the deposited layers onto cotton fabrics, Scanning Electron Microscopy (SEM) and FTIR spectroscopy were carried out. Weight percentage changes between treated and untreated samples and between washed and unwashed samples were determined for evaluating the coating durability. The thermal and thermo-oxidative behaviour of the treated samples were assessed by Thermogravimetric analysis (TGA) in nitrogen and in air, respectively. Furthermore, the flame retardancy conferred to the cotton fabrics due to the character of the deposited coatings was tested using both horizontal and vertical flammability tests. These measurements were also repeated after one standardized washing cycle, in order to check the stability and the durability of the finishing. The effectiveness of this novel formaldehyde-free and halogen-free flame-retardant is thoroughly discussed on the basis of the obtained experimental results. With the aim to identify possible weakening as a consequence of the finishing treatments, mechanical tests were finally carried out on treated samples, by measuring their tearing strengths and comparing these values with those of untreated cotton.

## 2. Experimental part

### 2.1. Materials

Desized, scoured and bleached plain weave cotton fabric (100%, 331 g/m<sup>2</sup>) was kindly supplied by Mascioni SpA (Cuvio, Varese, Italy). 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hypophosphite (SHP), N-(Phosphonomethyl)iminodiacetic acid hydrate (PMIDA, 97%, MW 227.11), hydrochloric acid (≥37%), ethanol (≥99.8%), and all the sol-gel precursors, namely 3-aminopropyltriethoxysilane (APTES, ≥98%), tetraethoxysilane (TEOS, ≥98%) and 3-glycidyloxypropyltriethoxysilane (GPTES, ≥98%), were supplied by Sigma Aldrich (Germany). All chemicals were of analytical reagent grade and were used without further purification. 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.

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