Study of flame-retardant finishing of cellulose fibres: Organic–inorganic hybrid versus conventional organophosphonate

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ABSTRACT

The aim of this study was to introduce a non-formaldehyde inorganic–organic hybrid sol–gel flame-retardant precursor (SiOP) containing phosphorous, nitrogen, and silicon and to compare its functional properties with those of the conventional formaldehyde-containing organic flame-retardant agent, organophosphonate (OP). SiOP was used at concentrations of 2%, 4%, and 8%, and OP was used at a concentration of 200 g/dm^3. Both agents were applied to 100% cotton (CO) woven fabric by the pad-dry-cure method under the appropriate conditions. The presence of the SiOP and OP coatings on the CO fabric was confirmed by scanning electron microscopy, energy dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy. The results of the vertical tests of flammability and the thermogravimetric analyses showed that the presence of the SiOP coating changed the thermal degradation pathway of the CO fabric and resulted in an increase in the thermo-oxidative stability of the cellulose fibres. The thermo-oxidative stability was enhanced by the addition of higher amount of dry solids. At comparable dry solids contents, OP preserved significantly greater flame retardancy and thermo-oxidative stability than did SiOP. These results indicated that the SiOP precursor could not act as an effective alternative to the OP agent in the flame-retardant protection of CO fabric.

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1. Introduction

Low thermal stability, easy ignition, and rapid combustion of cellulose fibres represent their weaknesses and limitations in the production of high-performance fire-protective textile products [1]. Thermal degradation of cellulose in air starts with cellulose pyrolysis at 300–400 °C through two competitive reactions: dehydration, which creates aliphatic char, and depolymerization, which creates levoglucosan. Whereas cross-linked char acts as a thermally insulating barrier at the surface, which protects the underlying cellulosic material from heat, levoglucosan decomposes and creates highly flammable, low-molecular-weight products that are further oxidized during exothermic combustion to support the pyrolysis process of cellulose. At higher temperatures (up to 800 °C), aliphatic char is converted to an aromatic form and oxidized to produce CH_4, H_2O, CO and CO_2 [1–3].

To provide flame retardancy to cellulose fibres, several different inorganic and organic flame retardants have been synthesized and applied as one-component agents or as mixtures [4,5]. The most effective flame retardancy can be achieved by the beneficial effects of the synergistic action of specific combinations of elements, especially phosphorus and nitrogen. Several organophosphorus compounds are widely used to create durable, highly effective flame-retardant coatings on cellulose fibres. The mode of flame-retardant action of organophosphorus is complex; it includes the formation of phosphoric acid at lower temperatures, which has a catalytic effect on cellulose dehydration and char formation at the expense of cellulose depolymerization and the formation of levoglucosan and flammable volatiles [6–8]. These effects shift the starting decomposition temperature to lower values. In addition, a polyphosphoric acid formed at high temperatures inside the fibres and on their surface promotes cellulose dehydration and the formation of char stabilized by crosslinking reactions [9]. Polyphosphoric acid also forms a viscous coating that protects the underlying cellulosic material and sub-surfaces from the heat of burning [7].

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The flame-retardant synergistic action of nitrogen in combination with phosphorus is attributed to the ability of nitrogen to enhance the catalytic effects of phosphorus toward promoting char formation by cellulose dehydration and by blocking levoglucosan formation [2]. Organophosphorus compounds that include N-methylol reactive groups in their structures can react with the hydroxyl groups of the cellulose fibres in a condensation reaction, which results in the formation covalent bonds that strongly increase the adhesion between the flame retardant and the fibre surface. Despite the high resistance of covalent bonds toward hydrolysis during multiple launderings, a methylolated melamine resin, such as trimethylolmelamine, is usually used as a co-reactant in the presence of a phosphoric acid catalyst to increase the number of covalent bonds to the cellulose fibres and to enhance the flame-retardant performance via nitrogen–phosphorus synergism [10–12]. Regarding the phosphorus–nitrogen synergistic action, Gaan et al. proposed the formation of a protective polymeric P–N–O coating on the surface of the char that acts as a barrier to heat and flammable gasses [13].

However, because the reactive N-methylol group is created by the reaction of formaldehyde with an amino group present in the structure of the organophosphorus compound, this flame retardant is classified as a formaldehyde-containing agent [14,15], which limits its use from an ecological point of view because formaldehyde is a known human carcinogen [16]. In addition, the presence of phosphoric acid diminishes the breaking strength of the cotton fabric [5,10].

As an alternative to the use of formaldehyde-containing organophosphorus compounds, sol–gel technology has enabled new ecologically friendly chemical modifications of fibres that provide flame retardancy and thermal stability. For this purpose, sol–gel technology usually involves the application of non-phosphorus containing silicon alkoxide-based precursors in combination with different phosphorous-based compounds [17–21] and phosphorus-functionalised silane organic–inorganic hybrids [22–31]. These sol–gel precursors include reactive alkoxide groups that are easily converted into silanol groups via a hydrolysis reaction; in a subsequent polycondensation reaction, the silanol groups produce a three-dimensional polysiloxane network in which the organic flame-retardant groups are incorporated as an integral part of the network architecture [32]. The synergistic action of phosphorus and silicon or phosphorus, nitrogen, and silicon is preserved according to the structure of the functional organic group. Furthermore, the silanol groups of the precursors can also react with the fibre surfaces to form hydrogen and covalent bonds. These covalent bonds are formed between the precursor silanol groups and the hydroxyl groups of the fibres in a condensation reaction and strongly increase the adhesion of the polymer film to the fibre surface as well as the degree of polymer network orientation.

This study aimed to investigate the functional properties of halogen-free and formaldehyde-free flame-retardant coatings on cotton fabric. These coatings were created via a contemporary inorganic–organic hybrid sol–gel precursor (SiOP) with phosphorus–nitrogen–silicon synergism, which was synthesized in our laboratories according to the method reported in the literature [31].

For comparison, the conventional and commercially widely used organic flame-retardant agent organophosphonate (OP) was used. The important objective of this research was to determine the strengths and weaknesses of both coatings and to determine whether the SiOP precursor can function as an effective alternative to the OP agent in the flame-retardant finishing of cellulose fibres.

2. Experimental

2.1. Materials

Scoured, bleached, and mercerized cotton woven fabric (plane weave, with a weight of 119 g/m^2) made by Tekstina d.d., Ajdovščina (Slovenia) was used for this research. An organo-functionalized trialkoxysilane sol–gel precursor (SiOP) with phosphorous and nitrogen elements present in the organic portion was synthesized in our laboratories according to the method reported in the literature [31]. The conventional flame-retardant agent organophosphonate (OP, Apyrol CEP, Bezema, Switzerland) was used. The chemical structures of the precursor SiOP and the agent OP are shown in Fig. 1.

2.2. Application method

SiOP was prepared in ethanol at concentrations of 2%, 4%, and 8%. Hydrolysis was performed by the addition of acidified water (0.1 M HCl) to the SiOP solutions. The OP was prepared in deionized water at a concentration of 200 g/dm^3 in combination with 10 g/dm^3 H_3PO_4 as a catalyst. In both cases ethanol or water were used as solvents. Both agents were applied to the cotton samples by the pad-dry-cure method, which included full immersion at 20 °C, wet pick-up of 100 ± 1% at 20 °C, drying at 120 °C, and curing at 150 °C for 5 min. After the agents were applied, the samples were left for 14 days under standard atmospheric conditions (65 ± 2% relative humidity and 20 ± 1 °C) to allow complete network formation of the applied finishes. The sample and coating codes are presented in Table 1.

To determine the total quantity of dry solids added, A, the untreated and coated cotton samples were dried until a constant mass was achieved, and their masses were determined by weighing. The value of A was calculated as follows:

$$A = \frac{w_2 - w_1}{w_1} \times 100 [\%] \tag{1}$$

where w_1 and w_2 are the weights of the untreated and coated cotton samples, respectively.

2.3. Characterization techniques

2.3.1. Scanning electron microscopy and energy dispersive X-ray spectroscopy

The surface morphology of the fabric samples was observed by a JEOL JSM 6060 LV scanning electron microscope (SEM) operating with a primary electron beam of 10 kV accelerating voltage and a
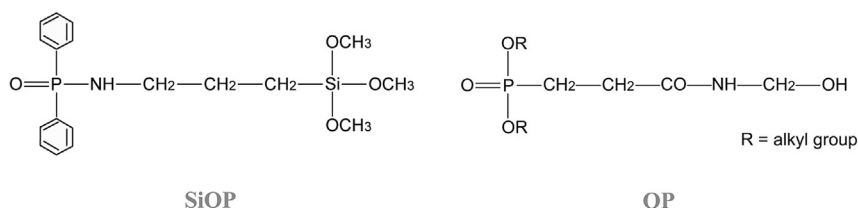

Fig. 1. Structures of the flame retardant precursor SiOP and agent OP.