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Thermal behaviour and flame retardancy of monoethanolamine-doped sol-gel coatings of cotton fabric

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ABSTRACT

Recent studies have shown that the combustion behaviour of cellulose-based materials can be strongly affected by the presence of a protective phosphorus-rich silica coating obtained with a promising sol-gel approach. Thus, in the present work, monoethanolamine (MEA) was used in combination with diethylphosphatoethyltriethoxysilane sol-gel precursor (DPTES) to investigate both the ability of MEA to neutralize the acidic conditions of DPTES sol before cotton fabric treatment and the fire resistant properties of the obtained coating (COT-A). Moreover, to study the influence of an inorganic–organic silica matrix on the durability of the proposed flame retardant finishing, the DPTES-MEA sol was mixed with tetraethoxysilane (TEOS) and 3-glycidoxypropyltriethoxysilane (GPTES) precursors, to produce hybrid coatings on cotton fibres (COT-B). Scanning Electron Microscope (SEM) and Attenuated Total Reflection-Infrared (ATR-IR) spectroscopy were used to characterize the surface morphology, as well as the chemical structure of the treated and untreated fabrics. Furthermore, thermogravimetric Analysis (TGA), Microscale Combustion Calorimeter (MCC), and Limiting Oxygen Index (LOI) were performed on the treated cotton fabrics with a promising outcome. The results showed that DPTES-MEA sol is able to enhance the thermal and thermo-oxidative stability of cotton, exploiting the joint effect of thermal shielding (exerted by the silica phases) and char-forming (exerted both by the phosphoric acid source present in the alkoxysilane precursor and by the nitrogen content in MEA). Both proposed sol-gel treatments allow the cotton samples to achieve a LOI value of 29, classifying them as self-extinguishing materials.

1. Introduction

Even though the use of synthetic fibres has grown dramatically during the last years, cotton as a cellulose based natural fibrous polymer material is still one of the most important materials in the textile industry. This is due to its excellent intrinsic characteristics including comfort, biodegradation, hygroscopic, regeneration and softness properties. Among the natural textile fibres, cotton is one of the most important materials used to produce apparel, home furnishings and workwear but, due to its low Limiting Oxygen Index (LOI) and combustion temperature (360–425 °C), this biopolymer is inflammable. Consequently, it is necessary to develop successful flame-retardant systems to prevent its fire hazards. In the last years several flame retardant finishings have been developed to comply with fire safety regulations and extend the use of cotton in textile applications requiring flame resistance. In particular, a lot of effort has been undertaken to develop flame retardant finishes containing phosphorus and nitrogen instead of halogen-containing flame retardant, as the latter releases smoke and harmful substances during combustion [1,2]. According to flame retardancy mechanism, compounds that contain phosphorous are transformed into phosphoric acid during thermal degradation or combustion. Consequently, the formed non-volatile polyphosphoric acid is able to react with the decomposing macromolecule by esterification and dehydration promoting char residue formation [3,4]. Acting as a barrier, the char residue protects the underlying polymer from attack by oxygen and radiant heat, thus extinguishing the fire. Advantages, such as the low release of toxic gases during combustion, can be observed using nitrogen-containing phosphorus based flame retardant compounds [5]. In fact, through the formation of a phosphorous-nitrogen intermediate, the presence of nitrogen in molecules such as dicyandiamide, melamine and urea [6] can accelerate cellulose phosphorylation, synergizing the flame retardant action of phosphorus [7]. Recently the sol-gel technique has been

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reported to be an encouraging and versatile approach to create transparent films on the fabric surface at room temperature. Particularly, great attention has been dedicated to the development of textile samples showing antimicrobial, antimosquito or ultraviolet radiation protection [8–10], dye fastness [11], anti-wrinkle finishing [12], hydrophobicity [13], biomolecule immobilization [14], self-cleaning properties [15] and sensing characteristics [16,17]. Moreover, sol-gel technique has been shown to be able to produce a thermal shielding effect on the polymer surface, improving the flame retardancy of treated fabrics [18,19].

As recently investigated [20–22], hybrid organic-inorganic finishes, containing both P and Si elements, can be used for textile finishing able to increase char residue during combustion and to improve thermal shield properties, due to the phosphoric-acid source and the inorganic network, respectively. To this aim, diethylphosphatoethyl-triethoxysilane (DPTES) has been employed as a precursor to synthesize hybrid organic-inorganic phosphorus-silicon coatings to enhance cotton flame retardancy. In the last years different aspects such as the use of a multi-step sol-gel process [23,24], the presence of a condensation catalyst [24], the role of the precursor pre-hydrolysis [25] and the synergism occurring when other phosphorus or nitrogen- sources are employed [22,26–28] have been investigated by the authors. In some cases it has been established that a synergistic effect between phosphorus and silica occurred in the realized cotton fabric finishing. In all proposed formulations the aqueous solutions obtained by DPTES precursor showed strongly acidic values. Consequently, to avoid the disadvantage of affecting cotton fibres in an excessively strong acidic range, the mixtures were partially neutralized with sodium hydroxide to obtain a slightly acidic solution with low acid-catalyzed depolymerization of cellulose polymer. As well as other species containing available electron pairs, ethanolamines are useful in pH adjustment. Indeed, in acidic environment, they are able to accept proton onto their basic amino group, thus acting as Brønsted-Lowry bases. Particularly monoethanolamine (MEA), a small-molecular weight nitrogen-containing buffering agent, is a commonly used alkanolamine to remove sour gases (e.g. H_2S and CO_2) from natural gas during refining in the so-called "sweetening process" [29]. The present work aims to study the effect of MEA in the sol-gel preparation of DPTES flame retardant treatment for cotton fabrics. The selected molecule, composed of a polar hydroxyl group and a polar amino group joined by a two carbon alkyl chain, has been used for two reasons: first because it replaces sodium hydroxide to neutralize DPTES acidity, and second because it contributes to the nitrogen content required for additive effect with phosphorus in the flame retardant mechanism of cellulosic fabric.

Considering that, at the best of our knowledge, no studies on this dual purpose have been reported so far, we decided to study the effect of MEA on the thermal behaviour of DPTES treated cotton fabrics. Moreover, to investigate the influence of an organic-inorganic silica matrix on the durability of the proposed flame retardant finishing, the DPTES-MEA sol was then mixed with a solution of 3-glycidoxypropyltriethoxysilane (GPTES) and tetraethoxysilane (TEOS), with the aim of achieving washing fastness silica coatings on the cotton fibres. The feasibility of increasing durability of sol–gel matrix onto textile fabrics using GPTES has already been demonstrated in previous studies [8,30]. Scanning electron microscopy (SEM) and infrared (IR) spectroscopy have been exploited to investigate the surface morphology and chemical structure of thin film derived from DPTES-based xerogels applied on cotton fabrics. Thermal stability of the treated samples were then evaluated using thermogravimetric analyses (TGA) and microscale combustion calorimeter (MCC). Finally, to investigate the relationship between degradation behaviour and flame retardancy of cotton samples, the degree of flame retardancy was determined by Limiting Oxygen Index (LOI), never measured in previous investigations on DPTES finishing.

2. Material and methods

2.1. Materials

Cotton fabric (scoured and bleached plain-weave, 100% cotton, 240 g/m^2) was used as substrate. The sol-gel precursors were purchased from Gelest (DPTES, 95%) and Sigma Aldrich (TEOS, 98%; GPTES, 97%) and used as received. Hydrochloric acid (HCl, 37.5%), ethanol absolute and monoethanolamine (MEA, 99%) were supplied by Sigma-Aldrich and used without any further purification. The untreated and treated cotton samples were conditioned under 65 ± 4% R. H. at 20 ± 2 °C, before all the experiments.

2.2. Nanosol preparation and application process

20.14 ml (0.06 mol) of silane precursor (DPTES) were hydrolysed with 16 ml (0.2 mol) of HCl (37.5%), in the presence of 5 ml of ethanol for 10 h under vigorous mechanical stirring and reflux conditions. Finally, distilled water was added to a total volume of 100 ml and the pH was adjusted to 5 by adding pure monoethanolamine dropwise and mixing with a magnetic stirrer. The obtained sol (Sol-A) showed a DPTES:MEA molar ratios equal to 1:3.5; according to this stoichiometry, the resultant P:N atomic ratio was set at 1:3.5 for DPTES-MEA sols.

The formulation with TEOS/GPTES (Sol-B) was produced according to a similar procedure. Initially, the DPTES solution was prepared, as previously described, mixing under mechanical stirring 20.14 ml of DPTES (60 mmol), 16 ml of HCl (37.5%) and 5 ml of ethanol. Then into the sol was added one-third of the monoethanolamine, 4.18 ml of GPTES and 3.12 ml of TEOS. The so obtained solution was stirred for 3 h to complete the hydrolysis of both precursors. Finally, the rest of MEA and water was added to reaching a volume of 100 ml and a pH value of 5. The cotton samples (25 cm x 35 cm) were wetted with the hybrid sols and then were passed through a two-roll laboratory padding machine at nip pressure of 1.5 bar with about 80–90% of wet pick-up. After drying at 80 °C for 10 min, the fabric sample was re-coated with the same sol solution, to form a second layer and then was again subjected to drying and, finally, to thermal curing at 170 °C in a laboratory oven for 4 min. The cotton fabrics treated with Sol-A and Sol-B were coded as COT-A and COT-B, respectively. After one washing cycle the same samples were coded as COT-A W and COT-B W. The amount (A, wt% owf) of coatings on the treated samples was determined using Mettler balance (10^{-4} g) as following:

$$A = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the weight of the sample before and after the padding and thermal treatment, respectively. For each sample, an average value was determined on the basis of the three measured data, with the standard deviation always lower than ±2%. The calculated add-on% on treated samples was 18.2% and 19.0% for COT-A and COT-B, respectively. The add-on values calculated on treated samples after one washing cycle were 6.9% and 8.4% for COT-A and COT-B, respectively.

2.3. Characterization techniques

Thermo Avatar 370 spectrometer, equipped with an attenuated total reflection (ATR) accessory using a diamond crystal, was used to acquire FT-IR spectra. Three replicate spectra were acquired at a resolution of 4 cm^{-1} and 128 scans for each sample over a fre-

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