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Phosphorus-Silica Sol-Gel Hybrid Coatings for Flame Retardant Cotton Fabrics

Hibridni premazi na podlagi fosforja in silicija, pripravljeni po postopku sol-gel, za dosego ognjevarnih lastnosti bombažnih tkanin

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Abstract

This work investigates the use of organic-inorganic sol-gel coatings based on silica and phosphorous compounds for providing cotton fabrics with flame retardant features. To this aim, diethylphosphatoethyltriethoxysilane precursor was employed for the synthesis of several sols in combination with different chemical additives. Sols were reacted with azo-based compounds and repeatedly applied onto the cellulosic substrate in a multilayer assembly, aiming at assessing the effect of the concurrent presence of Si, P and N on the overall fire behaviour of the fabric. In order to evaluate the flame retardancy of treated cellulosic fabrics, flammability tests were carried out. The obtained results showed that the phosphorus-silica coating is able to promote the formation of a stable char that acts as insulator barrier. Finally, an additive P-N effect of the ceramic oxide coating in terms of increased residue and decreased heat release rate and total burning time was observed in cone calorimetry tests.
Keywords: thermal stability, cellulosic fabric, sol-gel, diethylphosphatoethyltriethoxysilane, hybrid material

Izvleček

V prispevku je raziskana uporaba organsko-anorganskih premazov sol-gel na podlagi silicijevih in fosforjevih spojin, s katerimi bi bombažnim tkaninam zagotovili odpornost proti gorenju. Za ta namen je bil uporabljen prekurzor dietil-fosfatoetil-trietoksisilan za sintezo različnih solov v kombinaciji z različnimi kemičnimi aditivi. Soli, ki so reagirali z azo-spojinami, so bili v več plasteh nanešeni na celulozni substrat z namenom ugotoviti, kako sočasna prisotnost Si, P in N vpliva na obnašanje vlaken v primeru gorenja. Odpornost obdelanih celuloznih vlaken proti gorenju je bila določena s testi gorljivosti. Rezultati testov so pokazali, da je fosfor-silicijev premaz pospešil nastanek stabilnega poogleneleg ostanka, ki deluje kot izolacijska pregrada. Iz rezultatov kalorimetričnih meritev je bil razviden aditivni učinek P-N silicijevega oksidnega premaza v smislu povečanega poogleneleg ostanka, zmanjšane hitrosti sproščanja toplote in skrajšanega celotnega časa gorenja.
Ključne besede: toplotna stabilnost, celulozna tkanina, sol-gel, dietil-fosfatoetil-trietoksisilan, hibridna snov

1 Introduction

In the last years, there has been a considerable interest in the development of flame retardants for cellulosic materials. Generally speaking, fabrics made from natural products, such as cotton and linen easily and vigorously burn with a high combustion rate. In addition to fibres, the flame-spread rate of fabrics is also dependent on the fabric weight (g/m^2) and texture; lightweight and loose fabrics are more prone to catching fire quickly. Among all textile fibres, cotton is the one most commonly used in

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domestic applications (clothes, beddings, furniture, wall-hangings, etc.). Thus, for public safety it is of primary importance to find ways to make this material less flammable, in the most economically and environmentally-friendly way. Various forms of organophosphorus-based flame retardants such as phosphates, phosphoramide, phosphonate and phosphonium salts have been developed and used in flame retardant finishing of cellulosic fabrics for a long time. However, only a few of these products were commercially successful. Current government regulations have raised safety and environmental protection standards on flame retardants, which led to a renewed interest on the development of environmentally-friendly structures. Flame retardant for cottons are usually produced by exploiting a chemical treatment performed during the textile finishing process, which, depending on their chemical process, generates flame retardant properties having varying degrees of durability to various laundering processes. Flame retardants [1] may be (i) simple salts (e.g. ammonium phosphates, polyphosphate and bromide borate–boric acid mixtures) providing non-durable finishes due to their water-solubility; (ii) functional finishes (e.g. organophosphorus and nitrogen-containing monomers such as alkylphosphonamide derivatives, or polycondensates such as tetrakis(hydroxylmethyl)phosphonium salt) which contain reactive groups which may chemically react with surface functionalities to confer more-durable flame retardancy, or (iii) back-coatings, which usually comprise a resin-bonded antimony-bromine flame retardant system. A sol-gel represents a versatile synthetic route based on a two-step reaction (hydrolysis and condensation), starting from (semi) metal alkoxides (e.g. tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide), which leads to the formation of completely hybrid inorganic or organic-inorganic coatings at room temperature [2]. These coatings are capable to protect the polymer surface by creating a physical barrier, thus improving some specific properties, such as for example water or oil repellence and wear resistance [2]. As far as textile applications are considered, usually the sol-gel technique has been proposed for conferring new functional properties to fabrics, such as antimicrobial or UV radiation protection [3], dye fastness [4], anti-wrinkle finish [5] and hydrophobicity [6]. With the goal of improving flame resistance of fabrics, in the last years, textile finishing by sol-gel method has been systematically studied [7–13]. The treatment of textile materials with hydrolysed metal alkoxide solutions is an excellent tool to convey new properties to polymer surfaces, particularly if organic components, like phosphorous-based chemicals, are incorporated into the formulation [9]. Consequently, developed studies were focused on the investigation of the synergistic effects among silica, nitrogen and phosphorus on the thermal behaviour of treated fabrics [14]. Previous results demonstrated that sol–gel processes could be exploited as fireproof treatments with lower environmental impact for textile fabrics as compared with common flame retardant processes [9]. In this composition, the hybrid organic-inorganic materials (HOIMs) [8, 9, 14] show the properties of both the phases. Therefore, the thermal stability at high temperatures, proper of inorganic constituents, can be combined with the flame retardancy provided by organic phosphorus-based compounds. To this aim, in the present work, diethylphosphatoethyltriethoxysilane (DPTS) has been used in a novel multistep process consisting of 1–6 consecutive depositions in order to form architectures differing for the number of layers. In the first step, a FT-IR study of xerogels applied on glass slides was carried out in order to investigate the chemical structure of the produced thin films. Then, Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and thermogravimetric analyses (TGA) in inert and oxidative atmospheres were carried out in order to assess the chemical, morphological and thermal properties of the untreated and sol-gel treated fabrics. Finally, the flammability of untreated and treated fabrics was assessed according to the ASTM D1230 standard. The results showed a substantial enhancement of the char-forming properties and flame retardancy for the fabrics modified with the oxidic thin films.

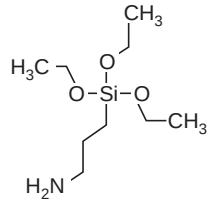
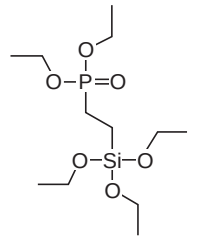
2 Materials and methods

2.1 Materials

Scoured and bleached 100% plain-woven cotton fabric (240 g/m^2) was used. The sol-gel precursor (DPTS) was purchased from Gelest and used as received; 3-aminopropyltriethoxysilane (APTES, purity grade 95%), 1-hydroxyethane 1,1-diphosphonic acid (P; 60% aqueous solution), melamine (M,

99%), urea (U, 99%), dibutyl tindiacetate (DBTA, condensation catalyst), hydrochloric acid, sodium hydroxide and ethanol were purchased from Sigma-Aldrich. N,N,N′,N′,N″,N″-hexakis-methoxymethyl-[1,3,5] triazine-2,4,6-triamine (MF) in aqueous solution (50 w/v%) was a commercial product supplied by Europizzi S.p.A. (Italy). All the chemicals were used without any further purification. The names, codes and chemical structures of the sol-gel precursors employed in the present work are reported in Table 1.

Table 1: Code, name and chemical structure of the used sol-gel precursors

Code	Name	Chemical formula
APTES	3-Aminopropyl triethoxysilane	
DPTS	Diethylphospha-toethyltrie-thoxysilane	

2.2 Functional finishing of cotton fabric

Each sol was stirred for 4 h at room temperature prior to the application. 0.0125 mol of APTES and 0.0125 mol of DPTS were hydrolysed, separately, with 0.0002 mol of HCl (0.1 N) in 45.07 mL of deionized water under vigorous stirring for 10 h at room temperature to obtain the silica sols. Three different solutions containing the MF were prepared by adding 0.002 mol, 0.004 mol and 0.006 mol of MF (MF30, MF60, MF90 respectively) in deionized water up to 50 mL of total volume. For the DPTS-APTES05, DPTS-APTES1 and DPTS-APTES2 sols, the molar ratios of APTES (0.06, 0.12 and 0.25 M) and DPTS (0.25 M) were 1 : 4, 1 : 2 and 2 : 2, respectively. DPTS sols (0.25 M) containing MF were prepared by adding 0.0125 mol of DPTS in three different solutions with, respectively, 0.002 mol, 0.004 mol and 0.006 mol of resin (DPTS-MF1, DPTS-MF2, DPTS-MF3 respectively). The different sols were applied to the cotton samples by a pad-cure-method, using a Werner Mathis padder. After having been dried at 80°C for 2 h, the fabrics were cured at 150°C for 2 min in a laboratory oven.

2.3 Characterization

Thermogravimetric analyses were carried out on a TA Instruments Q500 thermobalance, operating under nitrogen and air atmosphere using an alumina pan containing samples of approximately 10 mg (± 0.5). The runs were performed over a temperature range between 50 and 800°C at 10°C/min heating rate and 60 mL/min flow. The burning behaviour of the samples was studied using the Flammability Tester Model 7633E by United States Testing Company, Inc., according to the ASTM D1230 standard. In these tests the sample is mounted in a frame and horizontally held in a cabinet, with a tilting angle of 45°. A standardized flame is applied to the surface from the bottom; the ignition time was set at 5 s. Five samples for each textile fabric were processed in order to get reproducible data; burning time, burning rate and the final residue were measured.

3 Results and discussion

Sol–gel processes have been exploited for assessing the effects derived from the concurrent presence of silica, phosphorus and nitrogen on cotton thermal and fire stability. To this aim, a specific combination of diethylphosphatoethyltriethoxysilane, with P and N donors (1,1-diphosphonic acid, N,N,N‘,N‘,N“,N“-hexakis-methoxymethyl-[1,3,5]triazine-2,4,6-triamine, respectively and urea) was chosen and exploited for preparing hybrid phosphorus doped silica films. Since infrared absorption bands characteristics of the hybrid thin film applied onto the fabric surface are covered by the strong vibrational peaks of the cellulosic substrate, xerogels have been applied and annealed on glass slides and textile samples in order to perform FT-IR characterizations. The frequencies of major absorption bands are shown in Table 2.

Table 2: Main vibration modes ascribable to DPTS in xerogel thin films on glass slides and on cotton fabrics

Frequencies [cm^{-1}]		Vibrational modes
On glass substrate	On fabric substrate	
2800–3000	2800–3000	νs,as (CH)
1368	1370	ω (CH_2)
1393	1392	δs (CH_3)
1445	no detectable	δas (CH_3)
1480	no detectable	δs (CH_2)
1413	1414	δ (Si–CH_2)
778	783	ν (P–O)
1235	1210–1223	ν (P=O)
1020	1020–1027	ν (Si–O–Si)
724	no detectable	δ (Si–O–Si)

The Si–O–Si asymmetrical stretching absorption band at 1020–1027 cm^{-1} confirms the presence of the SiOx phase on the treated cotton fabric. However, the hybrid xerogel applied onto textile fabric shows few changes in the absorption bands when compared with the treated glass substrate due to the interactions between silica and cellulose. The ν (P=O) absorption band, located at 1235 cm^{-1} in the FT-IR spectrum of the xerogel, is shifted towards low frequencies in the spectra of the treated fabrics by about 10–25 cm^{-1}. This finding could indicate the involvement of the phosphoryl group in the formation of hydrogen bonds.

SEM observations have been performed in order to establish the morphology of the hybrid finishing deposited on cotton fibres through sol-gel processes. As expected, the surface of raw cotton fibres shows a certain level of heterogeneity and irregularity, which disappear when the fibres are sol-gel treated. Indeed, their surface becomes smooth and flawless. All the treated fibres appear homogeneously covered by the coating, irrespective of the kind of treatment [18]. The composition of the films was determined by EDX analysis. For the treated cotton fabric surfaces, depending on the nature of coating, silicon, nitrogen and phosphorus were the only detected elements in addition to fabric reference, confirming the occurred deposition of the hybrid coatings under investigation.

The thermal and thermo-oxidative stability of the sol-gel treated samples have been evaluated by thermogravimetric analysis and compared with that of the untreated cotton fabrics. As reported in the literature, cotton shows a peculiar thermal degradation in nitrogen and air atmospheres [15, 18]. Usually, cotton pyrolyses in nitrogen according to two alternative pathways: (i) the decomposition of glycosyl units to char at lower temperature (namely, dehydration) and (ii) the depolymerisation of such units to volatile products containing levoglucosan at higher temperature. If cotton is treated with only

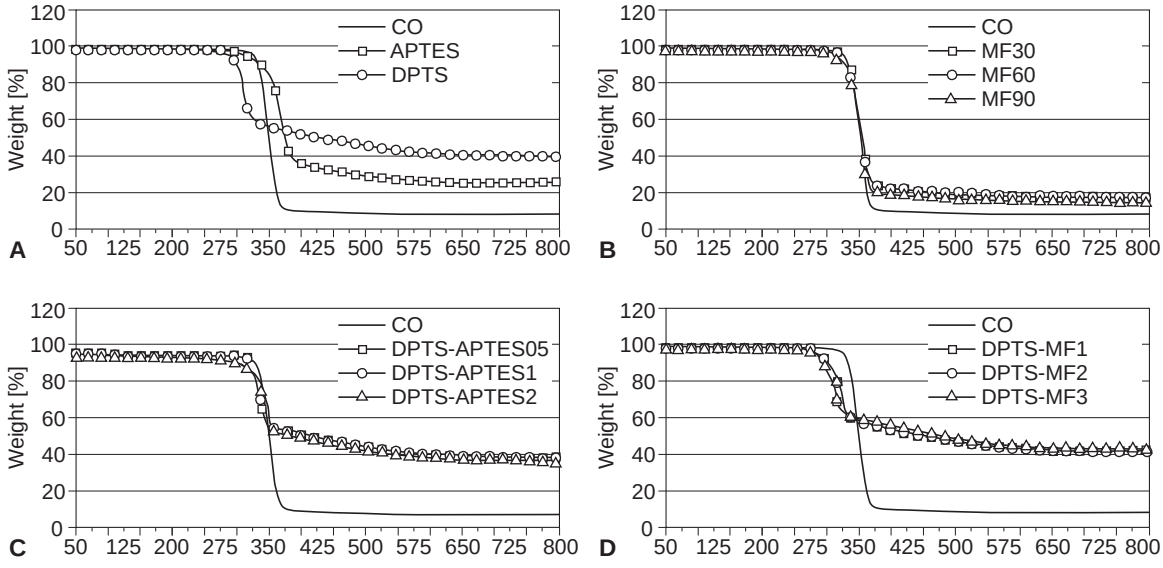


Figure 1: TG curves of pure and treated cotton fabrics in nitrogen: Weight/% vs Temperature/°C

APTES or DPTS (Figure 1A), its thermal stability increases, as indicated by the shift of Tmax values toward higher temperatures and by the final residue at 750°C. By combining APTES and DPTS in different molar ratios (Figure 1C), it is possible to observe a joint effect involving the sol–gel derived silica, P and N elements present in the hybrid film (Figure 1). The concurrent presence of Si, P and N turns out to further hinder the formation of volatile products during the first step of cellulose degradation and, at the same time, to favour the formation of the char. In order to further investigate the behaviour of the hybrid coatings containing Si, P and N species, MF was used at different concentrations and combined with DPTS as an alternative to APTES. When cotton was treated with MF only (Figure 1B), the mechanism and kinetics, through which the fabric degraded, did not change in a remarkable way, with the exception of the final residue at 750°C. Similar results were found when a combination of MF and DPTS was employed (Figure 1D). In spite of a significant anticipation of the degradation as compared with the untreated cotton, these hybrid films are able to protect the cellulose from degradation, as already observed with DPTS-APTES-based formulations. At 750°C they show very high residues (41%) with respect to cotton (8%).

For the investigated systems, two decomposition peaks of cotton in air are observable in between 340 and 470°C. With the exception of a slight anticipation in the Tonset for the APTES-based formulation, the first degradation peak (Tmax1) turns out to be affected by the presence of each single species. On the contrary, in presence of both APTES and DPTS, regardless of the used molar ratio, the degradation profile of cotton strongly changes: indeed, the formation of a thermally stable char is favoured, thus the second step disappears. This behaviour can be attributed to the thermal insulation exerted by the formed silica, which promotes cotton dehydration towards the char formation, instead of the formation of volatile combustible products. An increased thermal stability of cotton in air was achieved for all the compositions under study. These results are very important since cotton flame retardancy could increase as a consequence of its increased thermal stability in air (Table 3). The collected results prove that the films deposited on cotton fibres play a protective role against the thermal decomposition of cotton, favouring the char formation.

Table 3: TGA data of untreated and treated cotton fabrics in air

Sample	Residue at 360°C [%]	Residue at 750°C [%]
Untreated cotton	14	2
DPTS	53	23
APTES	41	8
DPTS-APTES05	56	27
DPTS-APTES1	57	22
DPTS-APTES2	60	21
MF30	39	3
MF60	37	5
MF90	31	4
DPTS-MF1	60	20
DPTS-MF2	60	29
DPTS-MF3	60	33

The presence of the coating induces the anticipation of the cotton decomposition and of the maximum weight loss, but favours the formation of a thermally stable char that evolves at high temperatures and leaves a residue significantly higher with respect to that of pure cotton. Furthermore, the residue increases as the number of applied layers increases. By combining DPTS and APTES in different molar ratios, it is possible to observe a joint effect amongst the sol–gel derived silica and P and N elements present in the hybrid film.

The flammability data (Table 4) show that the treatments starting from DPTS sols are able to significantly reduce the total burning time of cotton (in spite of a slight increase of the burning rate) and to protect the treated fabric from the flame, favouring the char formation.

The flammability data show that the formulations containing APTES or MF acting as reactive agents with DPTS are able to further reduce the total burning time and rate of cotton and protect the treated fabric from flame, as they favour the char formation instead of the production of volatile species that could promote a further combustion.

The most important result is the achievement of high residues at the end of the test in comparison with the untreated cotton or the cotton separately treated with APTES, DPTS or MF. Finally, in the DP combination, the deposited coating is able to protect

the fabric, leaving a very coherent and consistent final residue at the end of the test (40%), aligning the flammability parameters with cotton.

Table 4: Collected data of untreated and treated fabrics by flammability tests

Sample	Total burning time [s]	Burning rate [mm/s]	Residue [%]
Untreated cotton	33	10	–
DPTS	35	6	37
APTES	24	7	33
DPTS-APTES05	21	10	60
DPTS-APTES1	20	9	48
DPTS-APTES2	24	8	53
MF30	150	10	27
MF60	51	12	19
MF90	28	8	20
DPTS-MF1	17	10	79
DPTS-MF2	19	8	68
DPTS-MF3	23	7	66

Table 5: Flammability data

Samples	Total burning time [s]	Residue [%]
Untreated cotton	36	–
O_D	24	25
O_P	23	10
O_M	25	2.0
O_U	36	2.0
D_P	38	40
D_M	15	24
D_U	25	22

Finally, the cotton fabrics treated with phosphorus-doped silica coatings have been further doped with phosphorus or nitrogen agents, aiming to assess the eventual synergisms or additive effects that can be derived from the combination of thermal insulating effect of the silica coatings with the well-known flame retardant character of species such as a bisphosphonate (1-hydroxyethane 1,1-diphosphonic acid, P), melamine (M) or urea (U). Both samples treated with only DPTS (O_D) and only bisphosphonate (O_P) are able to act in the condensed phase during the combustion of cellulose, favouring its dehydration and thus the formation of a coherent and thermally stable residue at the end of the test (25 and 10% for O_D and O_P, respectively) (Table 5).
In the DPTS-bisphosphonate combination (D_P), the deposited coating is able to protect the cotton, leaving a very coherent and consistent final residue at the end of the test (40%), aligning the flammability parameters with cotton. On the contrary, the other two formulations (i.e. D_M and D_U samples) are not able to ameliorate the performances of O_D. Indeed, no variations of flammability have been found in presence of urea, while melamine is only able to strongly reduce the total burning time, but also to significantly increase the burning rate.

4 Conclusion

This work has clearly shown that hybrid phosphorus-doped silica architectures obtained by sol-gel technique can be successfully applied on cotton fabrics to enhance their thermal stability and flame retardancy. The deposition of hybrid silica network promotes a significant increase of the residues at high temperature and is responsible for a strong anticipation of cellulose decomposition. The presence of phosphorous additive in the silica matrix favours the char formation, as shown by thermogravimetry and flammability test. Indeed, the acidic species, released during the decomposition of the bisphosphonate (at ca. 260°C), catalyse the cellulose dehydration, favouring the appearance of the carbonaceous residue. In addition, the hybrid phosphorus silica coating, acting as a thermal insulator, further helps in the formation of an aromatic char resistant to the flame propagation.

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