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Flammability and combustion properties of ammonium polyphosphate-/poly(acrylic acid)- based layer by layer architectures deposited on cotton, polyester and their blends

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ABSTRACT

Layer by layer architectures consisting of four layer repetitive unit (QL) based on poly(diallydimethylammonium chloride)/poly(acrylic acid)/poly(diallydimethylammonium chloride)/ammonium polyphosphate have been deposited on cotton, polyester and their blends in order to promote the formation of an aromatic and stable carbonaceous structure (*char*) during combustion. The LbL-treated fabrics have been subjected to flammability (reaction to flame application) and combustion (reaction to different external heat fluxes) tests. The coatings were able to remarkably enhance the char formation of each substrate just after 1QL deposition; furthermore, 5 and 10QL assemblies have favoured the formation of intumescent-like structures with further improvement of the final residue. As a consequence, the treated fabrics have shown a strong reduction of the flammability (afterglow and incandescent melt dripping suppression) and combustion (reduced heat released). Infrared spectroscopy has pointed out the aromatic nature of the residues left after the combustion.

1. Introduction

In recent years, the Layer by Layer technique has been arisen as a new standard for surface modification and nanostructuration in several research fields [1].

This self-assembly technique has been discovered by Iler in 1966 and reinvented by the group of Decher in early 90s [2,3]. It simply consists in an alternate adsorption of positively and negatively charged species on the selected substrate [4,5]; by accurately selecting the layer constituents and the deposition parameters it is possible to target a wide range of application fields where surface interaction or surface tailoring play a key role, such as oxygen barrier [6] or conductive thin films [7], biomedical applications [8] and flame retardancy [9].

During the last years, the application of the LbL technique in the flame retardancy research field witnessed an increased number of published papers. The first papers showed the potential of the LbL and focused on the LbL assembly of hybrid organic-inorganic or totally inorganic coatings with the former made, as an example, of polyelectrolytes such as branched polyethylene imine coupled to silicate nanoplatelets and the latter made of oppositely charged silica nanoparticles [10–12]. When applied to cotton, such coatings were able to modify the flammability of the cellulosic substrate, yielding increased charred residue after combustion and preventing afterglow phenomena; a similar effect on the charring properties of the substrate was observed on synthetic fabrics along with the suppression of incandescent melt dripping during flammability tests and the reduction of both heat and smoke release during combustion.

Then the technique was extended to other substrates, such as foams [13] and rigid plastics [14,15], and, mostly important, the coating composition and fire proofing action were directed towards the intumescence field [16]. Indeed, the latest papers deal with coatings with intumescent-like compositions where the simultaneous presence of an acid, a carbon source and a blowing agent can develop, during combustion, a blown charred structure capable of protecting the substrate and hence favouring the char formation in a more efficient way with respect to the previous studies [17–19].

Most of the above mentioned papers were focused on substrates (such as fabric or foams) characterized by a high surface to bulk ratio; among the different types of fabrics, cotton has been widely exploited for both its surface and combustion properties. Indeed, cotton fibre hydrophilicity and surface roughness can certainly promote and favour the formation of a homogenous coating during the LbL assembly, while the char forming nature of the cellulose can improve the coating physical stability during combustion [20–22].

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This latter represents a crucial point: if sustained, the LbL coating is capable of protecting the underlying substrate favouring the formation of a thermally stable carbonaceous residue and reducing, at the same time, the release of volatile products. This mutual assistance favours the cellulose dehydration, instead of its depolymerisation, thus leading to the formation of thermally stable aromatic structures, with an overall flame retardant effect [23].

Completely synthetic fibres normally show different burning behaviour if compared to cotton; indeed, upon exposure to an external heat flux, synthetic fibres first melt and then undergo the degradation processes that lead to the formation of combustible volatile gasses. The melting process that takes place before combustion is of crucial importance if a functional coating is deposited on the fabric: as far as the coating is meant to have only a shielding effect toward heat and oxygen, then its efficiency may be partially or totally reduced if the above melting process compromises the integrity of the shield. On the other hand, if the coating is designed not only for exhibiting a shielding effect but also for releasing active species, this latter function can be preserved regardless to the coating physical stability and integrity. As a consequence, synthetic fibres result more difficult to protect from combustion.

The seeking for a universal coating capable of protecting both synthetic and natural fibres represents a challenging and interesting topic; our research group has recently developed a LbL architecture, with both shielding and release of active species effects, capable of greatly enhance the char formation of cotton, polyester and their blends when subjected to heat treatment at high temperatures (namely 300, 400 and 500 °C) [24]. Because of the obtained promising results, in this study we present a detailed investigation on the performances of such architectures during combustion; more specifically, LbL-treated fabrics have been tested in terms of both reaction to a flame application (in horizontal and vertical configuration) and exposure to different heat fluxes (namely 25, 35 and 50 kW/m^2). The resulting charred residues have been collected, analysed and correlated with the observed fire behaviour.

2. Experimental part

2.1. Materials

Cotton (COT, 220 g/m^2), polyester (PET, 170 g/m^2) and a COT-PET blend (28% PET, 340 g/m^2) were kindly supplied by Antecuir SA (Alicante, Spain).

Ammonium polyphosphate (APP), poly(diallydimethylammonium chloride) and polyacrylic acid were purchased from Sigma Aldrich (Milwaukee, WI). All these products were used as received for preparing 1wt.-% suspensions, using 14.6 μS deionized water supplied by a Q20 Millipore system (Milano, Italy).

2.2. Layer by layer deposition

Fabric substrates were alternately immersed into the positively – poly(diallydimethylammonium chloride) – and the negatively – poly(acrylic acid) and APP - charged suspension following the procedure described in Ref. [24]. Table 1 collects the mass gains, evaluated by weighting the fabrics before and after the LbL treatment, as a function of the deposited quad-layer (QL) number.

Table 1
Mass gains for the different fabrics as a function of the QL number.

Quad-layer number	COT [%]	COT-PET [%]	PET [%]
1QL	7	10	3
5QL	20	21	13
10QL	30	38	36

2.3. Characterization techniques

The surface morphology of the collected residues was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV); an X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, $k = 1.540562$ Å) was used to perform elemental analysis (beam voltage: 20 kV). Fabric pieces (5 × 5 mm^2) were cut and fixed to conductive adhesive tapes and gold-metallized.

The flammability of prepared samples has been tested both in horizontal and vertical configuration; as far as the former is considered, the sample (50 × 150 mm^2) was clamped with a metal frame and ignited from its short side by a 20 mm methane flame tilted by 45° (flame application time: 5 s). Flammability test in vertical configuration was carried out by applying a 20 mm methane flame for 5 s at the bottom of a fabric specimen (50 × 150 mm^2) held in position by a metallic frame. In both configurations some dry cotton wad was placed 30 cm beneath the fabric in order to assess the formation of incandescent melt dripping (mostly for PET fabric). Each test was repeated 4 times for each formulation in order to ensure reproducibility; during the test, burning time, afterglow time, final residue and formation of incandescent droplets of molten polymer was registered.

Cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behaviour of square samples (100 × 100 mm^2) under different irradiative heat flows of 25, 35 and 50 kW/m^2 in horizontal configuration, following the procedure described elsewhere [25]. Time To Ignition (TTI), Heat Release Rate and corresponding peak (pkHRR), Total Heat Release (THR), CO_2 and CO average production and their ratio (CO_2/CO), Total Smoke Release (TSR) and final residue were evaluated.

Since the treated fabrics showed an increased weight with respect to the reference due to the presence of the LbL coating, the pkHRR, THR and TSR values were referred to the initial mass of each specimen. For each sample, the experiments were repeated four times in order to ensure reproducible and significant data. The experimental error was evaluated as standard deviation (σ).

The chemical structure of the residues left by the LbL-treated fabrics after the combustion test was evaluated by Attenuated Total Reflectance (ATR) spectroscopy. ATR spectra were recorded at room temperature (32 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal.

Table 2
Flammability data in horizontal configuration.

Sample	Burning speed [mm/s]	Burning time [s]	Afterglow time [s]	Residue [%]
COT	1.2	159	14	0
COT 1QL	1.1	165	–	9
COT 5QL	–	9	–	94
COT 10QL	–	3	–	98
COT-PET	0.8	210	35	0
COT-PET 1QL	0.7	270	–	12
COT-PET 5QL	–	14	–	96
COT-PET 10QL	–	6	–	97

	Burning time [s]	Melt dripping	Residue [%]
PET	78	Yes	42
PET 1QL	8	Yes	98
PET 5QL	8	–	95
PET 10QL	7	–	94