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Green DNA-based flame retardant coatings assembled through Layer by Layer

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ABSTRACT

For the first time, DNA and chitosan are employed using the Layer by Layer technique in order to build green coatings exhibiting efficient flame retardant properties. DNA by its chemical structure can be considered as an intrinsically intumescent compound, since it contains precursor of phosphoric-polyphosphoric acid, a polyhydric char source (deoxyribose) and the nitrogen-containing bases that may release ammonia, acting as a blowing agent. When combined with chitosan, DNA layers promote the char formation of the former, by releasing phosphoric and polyphosphoric acid. Such bioarchitectures show an exponential growth as assessed by infrared spectroscopy and scanning electron microscopy. Very interestingly, these LbL assemblies are capable of i) reaching the self-extinguishment of cotton during horizontal flammability tests, ii) increasing the limit oxygen index up to 24% and iii) reducing the heat release rate by 40% during cone calorimetry tests.

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1. Introduction

In recent years, the Layer by Layer (LbL) technique has arisen as a promising surface modification technique capable of conferring flame retardant (FR) properties to several kinds of substrates [1–4].

This self-assembly technique was firstly presented by Iler in 1966 but saw a practical application only in early 90s [5,6]. In its raw description, the LbL simply consists in an alternate adsorption of chemical species on a chosen substrate exploiting different kinds of interactions, among which electrostatic attraction is the most common [7].

The process through electrostatic attraction is extremely tunable as it is highly affected by such parameters as chemistry of used polyelectrolytes [8], molecular weight [9], temperature [10,11], counterions [12], ionic strength [13], and pH [14]. By the accurate selection of the layer constituents and the deposition parameters it possible to target different FR effects.

The first papers that showed the potential of the LbL assembly in this field were focused on the assembly of hybrid organic–inorganic or totally inorganic coatings with the aim of creating an inorganic barrier on the surface, capable of shielding the substrate from heat and oxygen and thus resulting in an FR effect as demonstrated by Li et al., in 2009 [15]. Subsequently, LbL

assemblies made of silica nanoparticles or zirconium phosphate were able to improve charring when applied to cellulosic textiles or even suppress incandescent melt dripping during flammability tests and reduce both heat and smoke release during combustion when deposited on synthetic fibers [16–19]. Pursuing the LbL development, the coating composition has been designed in order to obtain an intumescent-like behavior during combustion, by simply assuring the simultaneous presence, within the coating, of an acid, a carbon source and a blowing agent that, upon flame application, can develop a blown charred structure protecting the underlying substrate during combustion in a more efficient way with respect to the LbL architectures previously investigated [20–23]. The first intumescent coating made with poly(allylamine) coupled with sodium phosphates was found able to stop the flame in a vertical flame test when applied to cotton [20]. Our research group has firstly employed chitosan (carbon source) coupled with ammonium polyphosphate (acid source and blowing agent) in an intumescent coating successfully deposited on cotton-polyester blends [21–23].

Very recently, the LbL technique has been exploited for depositing coatings with intumescent behavior but having a green composition and derived from renewable sources; to this purpose, chitosan and phytic acid have been used to impart flame retardant properties to cotton [24].

In the present paper we address the LbL assembly of novel and environmentally sustainable FR coatings based on deoxyribonucleic acid (DNA). Indeed, the double helix of DNA represents

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a potential and intrinsically intumescent flame retardant system [25]: the phosphate groups are able to produce phosphoric acid, the deoxyribose units can act as a carbon source and as blowing agents and the nitrogen-containing bases (adenine, guanine, cytosine and thymine) may release ammonia. In addition, thanks to the large scale method recently developed by Wang and coworkers [26], the availability of DNA has become competitive with other chemicals currently employed in the Layer by Layer assembly of FR coatings; it is also worth mentioning that the degree of purity required for FR applications is much lower than that for biological purposes, so that a reduction in raw material costs can be further achieved. Moreover, the Layer by layer approach represents an innovative solution, if compared to conventional dipping, as it allows the possibility of reducing employed materials as well as to fine tune the coating composition.

In order to obtain a high efficient and green FR coating, DNA has been coupled to chitosan that has already proven to be a promising carbon source when used in LbL coatings with intumescent behavior [21–23]. The coating growth has been monitored by FTIR and the FR effect of 5, 10 or 20 bilayers (BL) on cotton has been tested by both flammability (in horizontal configuration) and combustion (cone calorimetry) tests.

2. Experimental

2.1. Materials

Cotton (COT, 200 g/m²) was purchased from Fratelli Ballezio S.r.l. (Torino, Italy).

Prior to deposition, cotton fabrics were washed with water and Marseille soap, ethanol and then diethyl ether. After that, fabrics were dried in an oven at 70 °C for 1 h. Chitosan and DNA powder (from herring sperm) were purchased from Sigma–Aldrich S.r.l. (Milano, Italy); DNA was stored at 4 °C before its application to the fabrics. Chitosan and DNA were used, without any further modification, for preparing 0.5 wt.-% aqueous solutions, using 18.2 MΩ deionized water supplied by a Q20 Millipore system (Milano, Italy). The pH of the Chi solution was adjusted to 3.5 using acetic acid (Sigma–Aldrich), whereas the pH of the water used for preparing the DNA solution was adjusted to 7 using NaOH (Sigma–Aldrich). Single-side-polished (1 0 0) silicon wafers were used for FTIR growth and SEM observations.

2.2. Layer by layer deposition

Si wafer or cotton fabrics were alternately immersed into the positively and the negatively charged solutions; after each adsorption step, the substrates were washed with deionized water. The immersion period for the first couple of layers was set at 5 min; the subsequent layers were obtained after 1 min dipping. The process was repeated until 5, 10 and 20 bi-layers (BL) were built on each specimen type.

2.3. Characterization techniques

The growth of the LbL assembly was monitored using an FT-IR spectrophotometer (32 scans and 4 cm⁻¹ resolution, Perkin Elmer SPECTRUM GX).

Si wafer cross-section and cotton fabrics were imaged using a LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV); an X-ray probe (INCA Energy Oxford, Cu-K α X-ray source, $k = 1.540562$ Å) was used to perform elemental analysis (beam voltage: 20 kV). Cross-sections of the coatings were obtained by fragile fracture of a LbL-treated Si wafer (chosen as a model substrate); referring to 20 BL samples, after the fragile fracture, the LbL

coating detached from the Si wafer, thus making possible its observation as a self-standing film. Untreated and LbL-treated fabric pieces (5 × 5 mm²) were cut and fixed to conductive adhesive tapes and gold-metallized.

Flammability tests in horizontal configuration were carried out by applying a methane flame for 3 s on the short side of the specimens (50 × 150 mm²). These tests were repeated 3 times for each specimen. Total burning time and rate after flame application as well as the final residue were evaluated. LOI (Limiting Oxygen Index) tests were carried out by using a FIRE oxygen index apparatus according to ASTM D2863 standard.

Cone calorimetry (Fire Testing Technology, FTT) was employed to investigate the combustion behavior of square samples (100 × 100 mm²) under 35 kW/m² irradiative heat flux, following the procedure described elsewhere [27]. Time To Ignition (TTI), Heat Release Rate and corresponding peak (pkHRR), Total Heat Release (THR) and final residue were evaluated.

Attenuated Total Reflectance (ATR) spectroscopy of the residues left after combustion tests was performed using a Frontier FT-IR/FIR spectrophotometer, equipped with a Universal ATR Sampling Accessory (diamond crystal, 32 scans and 4 cm⁻¹ resolution).

3. Results and discussion

3.1. Coating growth and characterization

First of all, the pure layer constituents have been evaluated by FT-IR spectroscopy (see Fig. S1). Pure chitosan shows characteristic signals attributable to NH₃⁺ asymmetric and symmetric stretching vibrations (1640 and 1556 cm⁻¹, respectively), N–H in plane deformation and C–N stretching vibration (1556 cm⁻¹), NH₃⁺ rocking (1156 cm⁻¹), CH₂ groups (1411 cm⁻¹) and C–O–C signals ascribed to the glycoside linkage (1090 cm⁻¹) [28]. The DNA spectrum shows the characteristic peaks of the phosphate deoxyribose backbone located at 1228, 1065 and 968 cm⁻¹ and attributable to P=O and PO²⁻, C–O–C and P–O–C groups, respectively. The presence of pyrimidine and purine bases is confirmed by all the signals due to C=C and C=N stretching modes (namely, at 1540, 1478, 1420, and 1376 cm⁻¹), as well as to the strong signal at 1690 cm⁻¹ attributable to the C=O vibration of guanine, cytosine and thymine [29].

As far as the LbL assembly is concerned, the above characteristic peaks of both chitosan and DNA can be distinguished with some wavelength and intensity variations due to the LbL process; Fig. 1 plots the spectra during LbL growth, the evolution of signal at 1065 cm⁻¹ and a typical SEM cross-section of the 20 BL coating.

The strongest peak appears at 1065 cm⁻¹, being such intensity likely the sum of the C–O–C stretching signals of both chitosan and DNA. PO²⁻ stretching vibrations are shifted toward lower wavenumbers, probably due to the presence of NH₃⁺ counterions in the LbL assembly. The presence of chitosan protonated amines may be referred to the shoulder appearing at ca. 1640 cm⁻¹ (Fig. S1).

The absorbance of the signal at 1065 cm⁻¹ as a function of the BL number suggests an overall exponential growth or two regimes of linear growth after 10 BL. Exponential growth has been already reported in the literature and can be ascribed to the initial island-growth of the coating in the first BLs, followed by diffusional growth, for which at least one of the constituting polyelectrolytes diffuses in or out of the film [30,31]. From the direct comparison of the absorbances it seems that signals related to DNA appear to be more intense than those of chitosan; therefore, the coating composition is expected to be DNA-rich. As a consequence of the diffusional growth, the coating thickness strongly increases upon reaching high BL number, as clearly indicated by the 20 BL-based coating cross-section reported in Fig. 1 that averages 2 μm thickness.

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