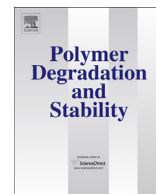




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Layer by layer assembly of flame retardant thin films on closed cell PET foams: Efficiency of ammonium polyphosphate versus DNA

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ABSTRACT

The present work aims to investigate the layer by layer deposition of flame retardant thin coatings on closed cell polyethylene terephthalate foams. To this aim, two coating architectures have been selected in order to evaluate the efficiency of ammonium polyphosphate (APP) versus the freshly proved flame retardant deoxyribonucleic acid (DNA). Both the selected architectures were able to homogeneously coat the external surface of the foams; APP-based coatings yielded average thicknesses around 450 nm while DNA based counterparts reached 340 nm. Flammability and cone calorimetry tests clearly demonstrated the superior performances of APP-based coatings. Indeed, only these latter were capable of suppressing the melt dripping behavior typical of PET and reducing the heat release rate peak by 25%.

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1. Introduction

In recent years, the Layer by Layer (LbL) assembly has been proven to be a powerful technique for the nanoscale controlled deposition of multifunctional coatings [1]. Such multi-functionality arises from the nearly unlimited choices of reagents and parameters controlling the deposition, as well as the simplicity of this multi-step deposition technique. Indeed, the LbL assembly is based on a very simple concept, i.e. the alternate adsorption of chemical species on a substrate due to particular interactions (e.g. electrostatic, hydrogen bonding, etc...) occurring in between the selected reagents [2,3]. Up to now, the most exploited interaction is represented by the electrostatic attraction that occurs between positively and negatively charged solutions/suspensions of polyelectrolytes or nanoparticles. In this widely studied version of the process, water is normally used as solvent for the depositions baths, the concentrations of which are normally below 1 wt.-%. All these aspects, that make the LbL a green deposition technique, certainly contribute to the increasing interest received up to now by the scientific community. Among the recent applications, the LbL has been adopted for the deposition of protecting coatings targeting flame retardancy [4,5]. Even in this challenging research field, the effectiveness of this technique has been proven on several

substrates. When applied to cotton, the first studied substrate, the deposited LbL coatings were able to confer self-extinguishment behavior to the fabric, as well as to strongly affect the combustion rates [6–8]. On synthetic fibers like polyesters, LbL nanoparticle-based architectures achieved the suppression of the melt dripping phenomenon during flammability tests, meanwhile increasing time to ignition and reducing of smoke production during cone calorimetry tests [9,10]. Recently, LbL coatings have been deposited on open cell polyurethane foams with promising results. More specifically, the first attempt has been made with carbon nanofibers-based coatings that proved to significantly lower the heat release rate during combustion [11]. Subsequently, sodium montmorillonite has been widely exploited in combination with one or two polyelectrolytes for the deposition of inorganic thermal barrier coatings capable of influencing the combustion rates of the treated PU foams [12,13]. Assemblies without nanoparticles have also been deposited; as an example, chitosan in combination with polyvinyl sulfonic acid has been found to greatly reduce the heat release rate peak during cone calorimetry tests due to the formation of an organic charred shield made of chitosan, in combination with a smoke diluting effect exerted by the polyvinyl sulfonic acid [14]. Furthermore, our research group has recently developed a LbL architecture with enhanced char forming characteristic [15]. The coating, made of chitosan, polyacrylic acid and polyphosphoric acid, was capable of achieving self-extinguishment in flammability tests, reducing the heat release rate when tested by cone calorimetry under different heat fluxes (namely, 35, 50 and 75 kW/m²) and

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withstanding the penetration of a propane/butane flame torch. Along with textiles, PU foams represent an ideal substrate for the LbL deposition: indeed, its open cell nature gives rise to a high surface to bulk ratio; this practically means that there is plenty of surface available for the LbL deposition with respect to the overall amount of material that needs protection.

From this point of view, and in the field of foamed materials, closed cell foams represents a challenging substrate since only the external surface is available for the deposition; as a consequence, to the best of our knowledge, the LbL assembly on these substrates has never been attempted. Thus, the present work is devoted to the investigation of the layer by layer assembly of flame retardant coatings for the surface protection of closed cell polyethylene terephthalate (PET) foams. The development of extruded PET foamed products has been prompted, during years, by the favorable cost/performance characteristics, good mechanical properties, high temperature stability and recyclability issues. The current applications of extruded foamed PET are expanding and involve thermoformable thin sheets for food packaging, foamed panels for building/construction, furniture and/or transportation as well as composite sandwich structures [16].

PET foams have been treated with a layer by layer intumescent coating characterized by a four layer repetitive unit (quad-layer) consisting of poly(diallyldimethylammonium chloride) (PDAC)/polyacrylic acid (PAA)/poly(diallyldimethylammonium chloride)/ammonium polyphosphate (APP). In the coating structure, PDAC and PAA serve as carbon source, while APP can provide both acid and blowing agents [17,18]. Subsequently, APP has been replaced with deoxyribonucleic acid in order to evaluate the contribution of this newly discovered flame retardant within the proposed architecture. The DNA structure by itself has some similarities with APP, as it can be thought of as both a source of acid (phosphates) and a blowing agent (nitrogen-containing bases); however, the presence of the deoxyribose back-bone adds the carbon source to the molecule structure, thus making the DNA an all in one intumescent system. The flame retardant features of DNA have been already assessed by employing this macromolecule in textile impregnation processes, layer by layer assembly and surface coatings [19–23].

The coating growth and morphology on PET foams have been characterized by infrared spectroscopy and scanning electron microscopy, respectively. The flame retardant properties have been evaluated by means of flammability and cone calorimetry tests.

2. Materials and methods

2.1. Materials

Closed cell polyethylene terephthalate foams with a density of 120 kg/m³ and a thickness of 10 mm were kindly supplied by BC Foams (Torino, Italy).

Poly(diallyldimethylammonium chloride) (100000 Mw, 20 wt.-% in water), poly(acrylic acid) (Mw, 35 wt.-% in water), branched polyethylene imine (10000 Mw) and DNA powder (from herring sperm) were purchased from Sigma Aldrich (Milwaukee, WI). Ammonium polyphosphate (PHOS-CHEK[®] P30) was purchased from ICL Performance Products, Inc.

All the reagents have been used without any further purification for preparing 1 wt.-% water solutions, using ultra-pure 18.2 MΩ deionized water supplied by a Q20 Millipore system (Milano, Italy).

2.2. Layer by layer deposition

PET foams (or Si wafers) were alternately dipped in the solution of negatively charged poly(acrylic acid), APP or DNA and positively

charged (PDAC) in order to deposit a LbL coating with a four layer repetitive unit (quad-layer, QL), as schematized in Fig. 1.

The dipping time of the first deposition cycle was set to 5 min and reduced to 1 min for the subsequent cycles. In between each adsorption step, the foams have been washed with ultrapure water. The process was repeated till 2 or 4 QL were deposited for each coating formulation. In the followings, APP containing architectures will be labeled as APP-based while those containing DNA will be labeled as DNA-based.

In parallel, the same LbL dipping process was also performed on Si wafers (previously activated by 10 min dipping into 0.1 wt.-% BPEI solution), chosen as a model substrate, which were suitable for the morphological characterization (FT-IR and scanning electron microscopy, SEM).

2.3. Characterization techniques

The growth of the LbL assembly was monitored using a FT-IR spectrophotometry (32 scans and 4 cm⁻¹ resolution, employing a Frontier FT-IR/FIR spectrophotometer).

The morphology of Si wafer cross-sections, untreated and LbL-treated PET foams has been studied using a LEO-1450VP Scanning Electron Microscope (imaging beam voltage: 5 kV); an X-ray probe (INCA Energy Oxford, Cu-K α X-ray source, $k = 1.540562 \text{ \AA}$) was used to perform elemental analysis. Cross-sections of the coatings were obtained by fragile fracture of the LbL-treated Si wafer or LbL-treated PET foams; PET foam pieces (5 × 5 mm²) for SEM investigations, were cut using a doctor blade, fixed to conductive adhesive tapes and gold-metallized.

The flammability of prepared samples has been tested in horizontal configuration, tilting the fabric specimen at 45° with respect to the vertical plane; the sample (50 × 150 × 10 mm³), held in position by a metallic clamp, was ignited from its short side by a 40 mm methane flame (two flame applications of 10 s each). In order to assess the incandescent melt dripping phenomenon, a dry cotton wad was placed 30 cm beneath the sample. Each test was repeated 3 times for each formulation in order to ensure reproducibility; during the test, parameters such as burning time, burning rate, final residue and melt dripping were registered.

The combustion behavior of square samples (50 × 50 × 10 mm³) was investigated by cone calorimetry (Fire Testing Technology, FTT) under a heat flux of 35 kW/m² in horizontal configuration. Time To Ignition (TTI), peak of Heat Release Rate (pkHRR), Total Heat Release (THR), CO and CO₂ production peaks (pkCO and pkCO₂), Total Smoke Release (TSR) and final residue were evaluated.

3. Results and discussion

3.1. Coating growth and morphology of LbL-treated PET foams

The coating growth and thickness on Si wafer have been assessed with infrared spectroscopy and SEM observations, respectively. Fig. 2 plots the collected spectra during LbL growth and a typical SEM cross-section of the 4 QL coating for both APP- and DNA-based architectures.

As far as the spectra of the assemblies containing APP are concerned, it is possible to detect the main characteristic signals of the adopted coating constituents. In detail, the strongest signal is found at 1720 cm⁻¹ and it is ascribed to the C=O stretching vibration of PAA; the typical signals of PDAC can be found at 1564 and 1400 cm⁻¹ and are due to C–N and OH stretching vibrations [24,25]. The signal at 1474 cm⁻¹ can be attributed to CH₂ groups present in both PAA and PDAC. Finally, APP signals linked to NH₄⁺ and P=O groups can be found at 1450 and 1260 cm⁻¹, respectively [26]. All the above-mentioned IR signals increase by increasing the

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