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Layer-by-layer assembly of efficient flame retardant coatings based on high aspect ratio graphene oxide and chitosan capable of preventing ignition of PU foam

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ABSTRACT

The layer-by-layer (LbL) technique is adopted for the construction of multilayers encompassing chitosan and graphene oxide (GO) platelets capable of improving the flame retardant properties open cell PU foams. The LbL assembly follows a linear growth regime as evaluated by infrared spectroscopy and yields a multilayer structure where GO platelets are embedded within a chitosan continuous matrix. 3 and 6 bi-layers (BL) can efficiently coat the complex 3D structure of the foam and substantially improve its flame retardant properties. 3BL only add 10% to the original mass and can suppress the melt dripping during flammability and reduce both the peak of heat release rate by 54% and the total smoke released by 59% in forced combustion tests. Unprecedented among other LbL assemblies employed for FR purposes, the deposition 6BL is capable of slowing down the release of combustible volatile to the limits of non-ignitability thus preventing ignition in half of the specimens during cone calorimetry tests. This has been ascribed to the formation of a protective coating where the thermally stable char produced by chitosan serves as a continuous matrix embedding GO platelets, which control volatile release while mechanically sustaining the PU foam structure.

1. Introduction

In recent years, the layer-by-layer (LbL) technique has been exploited as one of the most useful surface modification tool able to create functional coating on several substrates [1]. The principles behind LbL were reported for the first time by Iler [2] in 1966, but the first practical applications are documented only thirty years later by the group of Decher [3]. The most used LbL approach is the one that relies on electrostatic interaction occurring during the alternate adsorption of polyanion and polycation on the selected substrate, but many variants based on different interactions (*e.g.* hydrogen bonding) can be employed [4]. The process is quite simple and tunable as it is affected by several parameters like the nature of the employed polyelectrolyte [4], temperature [5], pH [6], the ionic strength [7] and the presence of counterions [8]. By modulating these parameters it is possible to build coatings with controlled thickness (in the 10–1000 nm range) [5,6,9] and introduce functionalization which can influence the surface chemistry of the substrate and change, for example, its wettability [10] or macromolecule anchoring properties [11].

In this way, the LbL has been used in a variety of applications ranging from drug delivery [12], gas barrier [13–15] to sensors [16–18]. Recently, this technique has been employed to build-up coatings oriented towards the fire safety and fire protection fields, proving that it is possible to impart flame retardant (FR) properties by the proper selection of the component of the multi-layers assembly and the deposition parameters [19–21]. This has been proven to be an efficient approach as polymer flammability is a typical surface property [22]. Indeed, during combustion, the heat radiated from the flame is transmitted through the surface to the bulk of the material. This triggers the thermal degradation of the polymer with the production of combustible volatiles that diffuse through the superficial layer reaching the gas phase and feeding the flame. It is then apparent that by modifying the exchange between the condensed matter and the flame it is possible to control the burning behaviour of a polymer and obtain a FR effect. In addition, recent European regulations have driven the FR research towards environmentally safe alternatives [23]. Indeed, some of the best performing FR additives have been found to be persistent in the environment, ending up in the food chain. This is leading to

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limitations in use or complete removal of the chemicals which hazard has been proven [24]. In this context, LbL has been presented as a good candidate for satisfying the need for innovative and green FR because, compared with traditional treatments, it has several advantages. The process is carried out in ambient conditions, uses water as solvents and very low concentrations (normally below 1%wt. in water) and the employed solutions can be recycled after use. The application of LbL in the FR field is documented since 2006 [25]. Through years the composition of the LbL coatings has been directed towards different FR actions. Initially, inorganic or hybrid organic-inorganic coatings containing nanoparticles were employed as thermal shields capable of creating, during combustion, an inorganic barrier that protects the substrate and favour the char formation [26,27]. Lately the coatings have been designed to mimic intumescent systems by incorporating an acidic source, a carbon source and a blowing agent within the assembly [28–30].

FR LbL coatings with hybrid flame retardant mechanism have been deposited on different substrates but the main focus has been on fabrics and open cell poly(urethane) (PU) foams [31]. PU foams represent an important substrate to protect as they are one of the first items to be ignited in fires, quickly leading to flashover events [32]. Different coating compositions have been proposed in order to reduce the fire threat of PU foams. Sodium montmorillonite (MMT) has been employed with chitosan in order to deposit environmental-friendly coatings [21] or in hybrid intumescent compositions with polyphosphates [33]. Both of these systems were able to suppress the melt dripping phenomenon typical of PU foams and achieve a consistent reduction in heat release rates (up to 50%) during cone calorimetry tests in horizontal configuration. The exploitation of lamellar shape nanoparticles has been demonstrated to confer the best FR properties especially when high aspect ratio platelets were employed [34].

However, the majority of the published papers on PU foam protection deals with the use of inorganic nanoparticles like sodium montmorillonite and vermiculite, while limited attention has been directed towards the use of graphene related materials (GRM). This class of materials showed promising FR results when employed in bulk thermoplastic or thermoset polymer nanocomposites [35,36]. GRM can be successfully exploited in water based LbL assemblies by employing partially oxidised graphene sheets normally referred as graphene oxide (GO) [37]. From a chemical point of view, GO is negatively charged in water due to the presence of oxygenated functionalization obtained by exposing graphene to strong oxidizers, typically sulphuric acid and potassium permanganate [38]. In this manner, it is possible to prepare stable GO suspensions in water or polar organic solvents. A previously reported study employed low concentration GO suspensions for the production of FR LbL coatings where the main constituents were chitosan and alginate, demonstrating the potential of GO in conferring FR characteristics to PU foams [39].

In the present paper, we address the LbL assembly of an efficient FR coating comprising chitosan (CHIT) and Graphene Oxide (GO) for the protection of open cell PU foams. Large GO nanoplatelets (50 ± 4 μm) are the main constituents of the assembly. The main aim is the production of an efficient LbL coating capable of delivering strong FR performances with a reduced number of deposition cycles and the obtainment of a deeper insight on the thermal degradation of this GO-based coating.

Chitosan is a biopolymer and is found in nature only in some fungi but it is easily synthesized by the thermochemical deacetylation of chitin [40,41], which is largely available in nature. The reduction of acetylated units in chitosan ensure the presence of free amino groups that, in acidic conditions, allow its employment as a cationic polyelectrolyte [42]. Within the coating compositions CHIT represents the continuous matrix that holds together GO platelets in a so-defined brick and mortar structure. Upon the application of a flame or radiative heat flux, CHIT may evolve towards the formation of thermally stable aromatic structures that, along with the presence of high aspect ratio GO, will produce a protective coating capable of protecting the PU foam. The LbL growth of this CHIT/GO assembly was monitored with FT-IR spectroscopy and the morphology of the deposited coatings on PU foams was characterized by scanning electron microscopy (SEM). Flammability and forced combustion behaviour of untreated and LbL-treated foams have been investigated by horizontal flammability testing and cone calorimetry, respectively. A novel approach was applied to investigate the evolution of the coating during combustion by means of infrared and Raman spectroscopies as well as by electron microscopy.

2. Experimental section

2.1. Materials

Polyurethane foam (PU) with a density of 24 g/dm^3 and thickness of 15 mm was purchased from the local warehouse. PU foam was washed with deionized water and dried in oven at the temperature of 80 °C prior to the LbL deposition. Chitosan (CHIT, 75–85% deacetylated), acetic acid, polyacrylic acid (PAA, solution average Mw ~100,000, 35 wt.-% in H_2O) and branched poly(-ethylene imine) (BPEI, Mw ~25,000 by Laser Scattering, Mn ~10,000 by Gel Permeation Chromatography, as reported in the material datasheet) used in this work were purchased from Sigma-Aldrich (Milano, Italy). Graphene oxide (GO) as 1% wt suspension in water was supplied by AVANZARE Innovacion Tecnologica (Navarrete -La Rioja, Spain). The detailed description of GO suspension preparation along with Transmission Electron Micrographs (TEM) are reported in the Supplementary material file (Fig. S1). Solutions and suspensions employed in this work were prepared using ultrapure water having a resistance of 18.2 MΩ, supplied by a Q20 Millipore system (Milano, Italy). Single side polished (100) silicon wafers were used for monitoring LbL growth.

2.2. Layer-by-layer deposition

CHIT solution (0.25% wt.) was prepared by adding ultrapure water to the chitosan powder and adjusting pH to 4 with acetic acid. The resulting light yellow solution was kept under magnetic stirring for one night. The GO suspension (1%wt) was diluted with ultrapure water to 0.5% wt. and kept under magnetic stirring for 4 h. PAA 1% wt. solution was obtained by diluting the original PAA solution with ultrapure water. BPEI was employed at 0.1% wt.

Si wafer was employed as model substrate in order to monitor the LbL growth by FT-IR spectroscopy. The surface of Si wafers was activated by 10 min dipping in the BPEI followed by 10 min in the PAA solution. After these two steps the Si wafer was alternately dipped in the CHIT and GO solution/suspension. The dipping time was set to 10 min for the first bi-layer (BL, *i.e.* one CHIT/GO pair) and then reduced to 1 min for subsequent layers. After each deposition step, the Si wafer was washed by static dipping in ultrapure water for 1 min and subsequently dried using dust- and oil-filtered compressed air prior to FTIR analysis. IR spectra were collected after each deposition step, up to 10 BL.

PU foams were first immerged in the PAA solution for 10 min in order to activate the surface and create a negatively charged surface. After this activation step, PU foams were alternatively immerged into the positively (CHIT) and negatively (GO) charged baths and washed with ultrapure water after each deposition. During the deposition and washing steps the PU foams were squeezed several times in order to let the solution/suspension or washing water penetrate inside the foam structure. The dipping