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Polyallylamine–montmorillonite as super flame retardant coating assemblies by layer-by layer deposition on polyamide

Kadir Apaydin [a,b], Abdelghani Laachachi [a,*], Vincent Ball [a], Maude Jimenez [b], Serge Bourbigot [b], Valérie Toniazzo [a], David Ruch [a]

[a] Department for Advanced Materials and Structures, Laboratoire de Technologies Industrielles, Centre de Recherche Public Henri Tudor, 66 rue de Luxembourg, L-4002 Esch-sur-Alzette, Luxembourg

[b] UMET-ISP, UMR 8207, ENSCL, Université Lille Nord de France, BP 90108, 59652 Villeneuve d'Ascq Cedex, France

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ABSTRACT

In this paper, a polyamide-6 (PA6) substrate has been coated with a flame retardant film, made from polyallylamine (PAH) (polycation) and montmorillonite (MMT) (polyanion), elaborated by Layer-by-Layer (LbL) technique. The $(PAH-MMT)_n$ assembly (with n the number of bilayers deposited) exhibits an exponential growth regime. At $n = 20$ bilayers deposition of PAH and MMT, the film reaches a considerable thickness of ~ 5 μm with the alignment of MMT in the direction parallel to the substrate. Scanning Electron Microscopy (SEM) analysis of the cross-section and Atomic Force Microscopy (AFM) analysis display a regular and continuous morphology of the obtained films. Thermogravimetric analysis shows that the presence of $(PAH-MMT)_n$ films at 10 and 20 bilayers enhances the thermal stability of the polyamide substrate. Cone calorimetry evidences excellent reaction to fire of the material since peak of heat release rate (HRR) is decreased by more than 60% in the presence of 20 bilayers of PAH–MMT film in comparison with uncoated PA6. Continuous charred layer was observed during the combustion and the thickness of the coating at the end of the combustion test is twice higher than that of the initial thickness. The presence of this expanded charred layer at the surface acts as protective limiting heat and mass transfer.

1. Introduction

Layer-by-Layer (LbL) deposition technique consists of alternating deposition of polyanions and polycations on a solid substrate leading to the formation of polyelectrolyte multilayer films. This technique was discovered in 1966 by Iler [1] and developed by Decher et al. [2] in the 90's. Nowadays, this popular technique is widely used in various fields such as drug delivery [3,4], anti-reflection [5,6], electrochromic [7–9], oxygen barrier [10–17] and it is only in recent years that this technique has been considered to design flame retardant coatings [15,18–26].

Li et al. [18] have been the first to study the flammability of coatings made from branched polyethylenimine (BPEI) and Laponite clay designed by LbL deposition on cotton fabrics. High-pH BPEI and low-pH clay produced the thickest films (5 nm/bilayer). It was shown by thermogravimetric analysis and vertical flame testing (VFT) that the clay coating delays the degradation of the cotton by providing a sheath like ceramic barrier. In the other work, Li et al. [19] have studied the flame retardant behavior of branched polyethyleneimine (BPEI) (at pH = 7 or 10) – MMT (0.2 or 1wt%) assemblies deposited onto the cotton fabrics. The VFT results showed that the residues from 20 bilayers coated fabrics are heavier, have preserved the fabric structure and provide significant char. Microcombustion calorimeter (MCC) data revealed that all the coated fabrics decrease the total heat release (THR) and heat release capacity (HRC). In this case the BPEI pH 10/1% MMT coatings displayed the best MCC results (HRC decreases by 20%). Then Li et al. [20], also demonstrated that the polyhedral oligomeric silsesquioxanes (POSS) (– or +) coupled to aminopropyl silsesquioxanes oligomer (AP+) improved the fire performance of the cotton fabrics. In this work, several fire methods were used to evaluate the fire performance of this system. VFT results showed that all coatings yield char residue when increasing the number of bilayers. Moreover, MCC data revealed that the maximum reduction of peak of heat release rate (pHRR) (20%) was observed for the $(AP+/POSS-)_{20}$ coatings. Following the pill test, the (AP+/POSS–)

* Corresponding author. Tel.: +352 42 59 91 591; fax: +352 42 59 91 4555.
E-mail address: abdelghani.laachachi@tudor.lu (A. Laachachi).

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and (POSS+/POSS−) at 10 bilayers did not catch fire. Still in order to improve cotton fire retardant properties, Laufer et al. [21] demonstrated that all colloidal silica-polyelectrolyte assemblies tested exhibit a significant amount of char in the VFT test and the MCC results showed that the (PEI/small silica)$_{10}$ coatings were the most efficient samples as they allowed reducing the pHRR by 20%.

Also using the LbL method, Carosio et al. investigated two systems to enhance fire stability of PET substrates [22,23]. The first system based on colloidal silica nanoparticles leads to an increase of the ignition time (TTI) (45%), a decrease of the pHRR (20%) and ables preventing incandescent melt dripping of PET fabric [22]. The second system was based on α-zirconium phosphate combined with three cationic species (polyhedral oligomeric silsesquioxane (POSS+), polydiallyldimethylammonium chloride (PDAC) and cationically modified silica nanoparticles). In this system, the films built with PDAC and SiO_2 increase the ignition time (TTI) and reduce the production of smokes (CO, CO_2). The maximum decrease of the pHRR was observed for POSS based coatings [23]. In the same way, Laufer et al. and Kim et al. have focused their investigations on the improvement of the fire performance of PU substrates [17,24]. Firstly, Kim et al. have made an assembly composed of carbon nanofibers, polyethyleneimine and poly(acrylic acid) to reduce on the one hand the pHRR by around 40% and the THR by 21% and on the other hand to increase the residual mass and the TTI (10%) [24]. Secondly, Laufer et al. have improved the fire stability of PU with (clay–chitosan) based coatings. These coatings have reduced the pHRR by 52% compared to uncoated substrates [17].

More recently several groups of researchers developed, using LBL, an intumescent flame retardant system [15,25–29] which is generally composed of four ingredients: a carbon source, an acid source, a swelling agent and inorganic fillers to reinforce the char layer [30]. The first work dealing with an intumescent flame retardant coating built up by LbL was realized by Li et al. [25]. They demonstrated the effect of (poly(allylamine) (PAAm) − polyphosphate (PSP)) nanocoatings on the fire retardant properties of cotton. The (PAAm–PSP) films at 5, 10 and 20 layer-pairs were tested in VFT and MCC. They showed that these coatings reduce the pHRR, THR, after-flame time, afterglow and increase the char formation as a function of the number of bilayers deposited. Laachachi et al. [15] elaborated an intumescent system including poly(allylamine chloride) (PAH), montmorillonite and PSP. In this work, the (PAH–clay) with and without PSP films were elaborated using classical LbL method with an additional step consisting of diffusing PSP into the multilayer films prepared. The cone calorimeter results displayed an improvement of fire properties of a (polylactic acid) (PLA) based substrate coated with (PAH–MMT)$_n$ assembly. Among all coatings tested, the best fire retardant performance was observed for the films with PSP at 60 BL with a significant decrease of pHRR (37%) and an increase of TTI.

The most recent studies were carried out by Carosio et al. [26], Alongi et al. [27,28], and Laufer et al. [29]. Carosio et al. studied ammonium polyphosphate (APP) coupled with either chitosan or silica to improve the reaction to fire of polyester–cotton blend. They have demonstrated according to cone calorimeter results that the assembly based on Chitosan–APP intumescent films could enhance the pHRR (only for films made from $n = 10$ and 20 BL), the TSR, the amount of residue; the 20 BL films were also able to stop flame spread in the VFT. On the contrary, the films prepared with Silica–APP only improved the ignition time. It is also noteworthy that these coatings tested in VFT show no afterglow after burning [26]. Moreover, Alongi et al. investigated two APP-based coatings. In the first system, they elaborated a Hybrid organic–inorganic coatings containing APP, chitosan and silica to study the flammability and combustion behavior of polyester–cotton blends. The VFT and cone calorimeter results displayed a significant enhancement of the flammability and combustion behavior (suppression of afterglow with a final residue increase) [27]. In the second system, Alongi et al. studied a complex architectures containing APP, poly(diallydimethylammonium chloride) and polyacrylic acid on cotton, polyester and a cotton/polyester blend. The thermogravimetric analysis coupled to isothermal tests showed that these architectures were able to enhance the char formation [28]. Finally, Laufer et al. deposited chitosan (+) and phytic acid (−) assembly on cotton fabric. The microcombustion calorimetry showed that all coated fabric reduce pHRR with the greatest reduction for fabric coated at pH 4. In a VFT test, the fabrics coated with high phytic acid content extinguished the flame contrary to uncoated cotton [29].

In this work we have developed using layer-by-layer technique a flame retardant coating, inspired by Laachachi et al. work [15]. We have shown that it was possible to form a protective layer at the surface of polyamide 6 without using an acid source such as PSP. The thickness, morphology, structure, thermal stability and fire behavior of the 5, 10 and 20 BL assemblies have been examined and discussed in this paper.

2. Materials and methods

2.1. Chemicals and substrates

Poly(allylamine hydrochloride) (PAH) (Sigma Aldrich, M_w = 120 000–200 000 g mol^{-1}) was dissolved at 1 mg mL^{-1} in 50 mM tris(hydroxymethyl) aminomethane (Euromedex, M_w = 121,1 g mol^{-1}) buffer (pH adjusted to 7.5 with hydrochloric acid, Acros Chemicals, 36.5–37%). Sodium montmorillonite (Na^+-MMT) (from Southern Clay Co) was dispersed at 1% (w/v) in water whose pH was adjusted to 10 (±0.1) with a diluted sodium hydroxide solution (Acros Chemicals). This suspension was then sonicated for 1 h in an ultrasonic bath to ensure proper exfoliation of the clay. No sedimentation was observed even after several days of storage in the absence of stirring. All solutions were prepared from doubly distilled water (Millipore Simplicity system, ρ = 18.2 MΩ cm). The Polyamide 6 (PA6) sheets with a thickness of 500 μm and a density of 1.14 g cm^{-3} were purchased from Goodfellow (Cambridge, England) and were used for thermal degradation and fire resistance characterizations. Single-side-polished (1 0 0) silicon wafers (Siltronics Archamps, France) were used for film characterization by SEM, XRD and AFM. All the substrates were cleaned with Hellmanex solution (2%) for 30 min in ultrasonic bath, rinsed with distilled water, diluted HCl (0.1M) and distilled water again and then dried with N_2 before layer-by-layer assembly.

2.2. Layer by layer elaboration

The substrates were immersed alternatively into solutions containing positive (PAH) and negative (MMT) species (Fig. 1). Between each immersion step, the substrates were rinsed with the buffer solution and water solution. The buffer and water rinse steps were aimed to desorb weakly adsorbed PAH and clay, respectively. The adsorption and rinsing step times were set at 1 min. The samples were not blown dry between successive deposition steps. After the number of bilayers (BL) desired, the samples were rinsed in water and put in the oven at 60 °C for 24 h.

2.3. Characterization

X-ray diffraction (XRD) experiments were performed with an INELFRANCE diffractometer. Samples were scanned in the reflection mode using the Cu Kα radiation (λ = 1.5405 Å, starting angle is 3°, step size 0.050° at 3 min^{-1}). The AFM images of the dried