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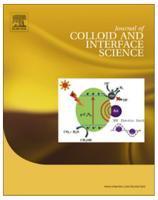

Regular Article

Controlling the melt dripping of polyester fabrics by tuning the ionic strength of polyhedral oligomeric silsesquioxane and sodium montmorillonite coatings assembled through Layer by Layer

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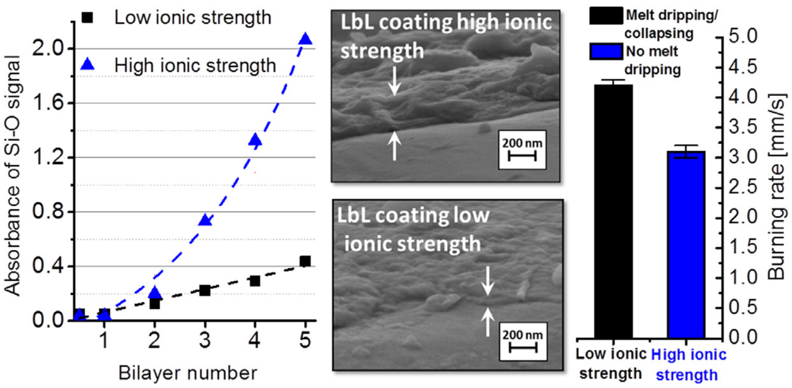
GRAPHICAL ABSTRACT



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ABSTRACT

This work deals with the Layer by Layer (LbL) assembly of hybrid organic/inorganic flame retardant coatings made of Octa-ammonium POSS (polyhedral oligomeric silsesquioxane) and sodium montmorillonite clay on polyester (PET) fabrics. The effects of ionic strength on the achieved flame retardancy properties were investigated. The coating growth as a function of different ionic strengths was evaluated by infrared spectroscopy. 0.10 M NaCl was found able to promote the highest adsorption of each coating species at each deposition step strongly affecting clay stacking as evaluated by X-ray diffraction measurements. The coatings on PET assembled at high ionic strength turned out to be more homogeneous and thicker than the reference one. Thanks to the increased thickness and better surface coverage, the same coatings efficiently suppressed the melt dripping phenomenon and significantly slowed down flame spread rate in horizontal flammability tests with only 2 wt% of coating mass added. Furthermore, the same performances were maintained after 1 h washing at 70 °C. By cone calorimetry, coated fabrics showed a strong reduction in the combustion kinetics by nearly halving the peak of heat release rate. This paper provides an important insight on the viability of tuning deposition of LbL coatings on fabrics employing industrial-like processes by simple modification of ionic strength.

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1. Introduction

Nowadays, synthetic fibers and fabrics, especially polyesters (PET), have become leading materials in textile industry surpassing the production of natural ones [1]. The massive use in application fields such as furniture, clothing industry, automotive amd sport equipment surrounded us with comfortable and cheap yet fast burning and melting materials [2]. The presence of such flammable materials in everyday life increases the risk of fire events in domestic scenarios. In order to prevent this occurrence, the consolidated practice is to improve the fire reaction of polymers by using chemicals known as flame retardants (FRs). FRs are normally employed in polymers either by bulk addition in melt-blending processing or, less frequently, by copolymerization of specifically designed flame retardant monomers.

In past decades, many of the effective solutions for flame retarded materials relied on the chemistry of brominated or halogenated compounds. Unfortunately, due to real or perceived health and environment hazards related to such chemicals, legislators have stimulated the research of safer alternatives. Indeed, some of the traditional FRs have been found to be toxic [3] and persistent in the environment [4], eventually ending up in the food chain [5]. For these reasons, the research has been redirected towards the replacement of traditional chemicals with greener and safer alternatives. Within this context, a possible solution is represented by the so-called surface approach. This latter can be briefly described as a recent trend that aims at the confinement of safe flame retardants on the surface rather than in the bulk of the polymer by exploiting nanotechnology [6,7]. This represents a change in perspective when considering the approach to fire protection and can be strictly related to the key role played by the surface during combustion. Indeed, during combustion, the heat from the flame is transmitted through the surface to the bulk; simultaneously, the bulk material thermally decomposes and produces combustible volatiles that diffuse towards the surface feeding the flame in a self-sustained process [8]. It is therefore clear that the modification of the interface between the condensed matter and the flame may reduce heat and mass transfers hindering the combustion of a polymer [9].

In this scenario the Layer by Layer (LbL) technique turned out to be a valuable tool for the deposition of multi-layered coatings with flame retardant functionalization on fabrics [10], foams [11–14] and films [15,16]. Beside flame retardancy, the LbL has been adopted in other research fields such as sensors [17], biotechnology [18], drug delivery control [19], carrier systems [20], gas barrier [21] and more [22]. The LbL is a relatively simple technique; its fundamentals can be dated back to the 60′s, when Iler published the experimental evidence of layered structures assembled by the alternate deposition of oppositely charged inorganic particles [23]. Later, at the beginning of the 90′s, this basic concept was extended by Decher to the self-assembly of oppositely charged organic polyelectrolytes and the LbL became a general approach for the fabrication of multicomponent films on solid substrate [24,25]. In a brief description, the LbL consists in the stepwise selective adsorption of different interacting species on a substrate. These interactions can be: electrostatic attraction [26], hydrogen bonding [27], ionic-covalent bonding [28] or donor-acceptor coupling [29]. All these interactions allow for the layered self-adsorption of the selected species from dilute suspensions (or solution). Following this route it is possible to obtain complex multi-layered structures with unlimited composition possibilities. Another key-point of the LbL technique, that makes this approach even more attractive, is represented by the possibility of tuning the physical/chemical characteristics of the deposited coating by changing the deposition parameters (*i.e.* time, concentration, pH, ionic strength, temperature) [30]. However, as far as the deposition of flame retardant coatings is concerned, there are only few studies that focus on the effect of the deposition parameters on the achieved fire protection performances. Recently, we showed how pH and molecular weight of the selected polyelectrolytes can influence the burning behavior of LbL treated cotton fabrics [31]. Nevertheless, to the best of our knowledge, there are no studies evaluating the effect of ionic strength on the flame retardancy properties of the deposited LbL coatings. The ionic strength is one of the typical tuning parameter for LbL depositions; indeed, by increasing the ionic strength it is possible to increase the film thickness and also its adhesion to the substrate [32–34]. Thereby, the optimization of ionic strength is attractive for the near-future applications of LbL as thick and highly performing FR coatings could be deposited with a reduced number of deposition steps.

In this paper, we address the deposition of a FR LbL coating consisting of octapropylammonium polyhedral oligomeric silsesquioxane (OAPOSS) and sodium montmorillonite (MMT) on PET fabrics, investigating whether tuning the ionic strength of the LbL process may improve the FR performances of the coating while maintaining a low number of deposition steps. While both OAPOSS and MMT have been previously exploited in surface approach to flame retardancy [35,36], their combination in a LbL assembly has never been attempted before. Moreover, the effects of the LbL deposition parameters on the achieved FR properties on synthetic fabrics have not been studied as heavily as for natural ones. The reasons have to be found in the different burning behavior of the two substrates. Indeed, differently from natural fibers, synthetic thermoplastic fibers can melt and vigorously drip during heating and combustion thus limiting the efficiency of the deposited LbL coating. This behavior poses additional and strong scientific challenges as the deposited coating has to be extremely efficient in order to obtain a substantial FR effect.

First, the coating growth at different ionic strengths has been evaluated by infrared spectroscopy. Then, the best growing conditions, along with the unmodified assembly, have been selected and applied to PET fabric employing a process similar to conventional finishing treatments, as reported in Fig. 1.

The use of such industrially-viable approach is of scientific interest and challenging at the same time. Indeed, while padding is directly relevant to industrial application, the high deformation imparted to the coating during processes might compromise the deposition of the coating to the point of making it impracticable. This is particularly important for LbL assemblies at high ionic strength since in the wet and swollen state the interactions between the components are weaker and thus the coating is more likely to suffer from strong deformations [37].

Treated fabrics have been imaged by Field-Emission Scanning Electron Microscopy (FE-SEM) and probed by FTIR-ATR spectroscopy in order to assess the changes in fabric morphology and surface chemical composition. The thermal and thermo-oxidative stability have been studied by thermogravimetric analyses (TGA) in nitrogen and in air, respectively. The flame retardancy properties have been evaluated by means of reaction to a small flame application (horizontal flame spread tests) and to an impinging heat flux (cone calorimetry). Finally, the best formulation has been selected for a simple washing test in order to obtain preliminary information concerning the durability of the deposited coatings.

2. Experimental

2.1. Materials

The polyester fabric with a *grammage* of 55 g/m^2 was purchased from Fratelli Ballesio S.r.l. (Torino, Italy). The surface was activated