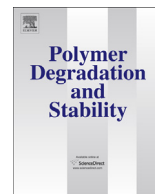




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Current emerging techniques to impart flame retardancy to fabrics: An overview

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ABSTRACT

The present paper is aimed to review the state of the art on the novel and emerging techniques recently developed in the textile field for conferring flame retardant properties to natural and synthetic fibres. In particular, a comprehensive description of the results achieved by depositing (nano)coatings on the fabric surface through nanoparticle adsorption, layer by layer assembly, sol–gel and dual-cure processes, or plasma deposition is presented. Finally, the unexpected and recently achieved results in the use of proteins and nucleic acids are discussed.

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1. Introduction

In the last twenty years, nanotechnology has attracted a great interest from both industrial and academic research, as a consequence of the encouraging and surprising results achieved in many fields by employing nano-sized objects. Referring to fabrics, yarns and fibres, different strategies have been designed and exploited in order to enhance their final properties [1,2]. In particular, in the field of flame retardancy, three approaches have shown the most interesting results: i) the nanostructuring of the synthetic fibres [3], ii) the introduction of nanoparticles in the traditional back-coating [4–8] and iii) the deposition of (nano)coatings [9]. This paper aims to thoroughly review the new perspectives and innovative solutions recently achieved in the textile field based on the deposition of novel coatings able to confer flame retardant features to the fabrics. These issues mainly refer to the use of ceramic protective layers or flame retardant species alone or coupled together. Thus, novel approaches such as nanoparticle adsorption, layer by layer assembly, sol–gel and dual cure processes, and plasma deposition will be deeply discussed. Furthermore, very recently, biomacromolecules such as proteins and deoxyribonucleic acids have exhibited unexpected flame retardant/suppressant behaviour when deposited on cellulosic substrates.

2. (Nano)coatings

Nowadays, significant scientific efforts focus on surface modifications as after-treatments capable of changing or conferring different properties to the investigated textiles. Since such after-treatments should not almost affect the textile substrate properties, thus they have to involve surface modifications and the formation of micro- to nano-sized coatings. As a consequence, the possibility of creating novel coatings suitable to be applied to any type of fibre has to be considered.

These novel coatings, which may exhibit a complete inorganic or hybrid organic–inorganic composition, can be generated by using different approaches [9,10]:

- Nanoparticle adsorption
- Layer by layer assembly
- Sol–gel and dual-cure processes
- Plasma treatments
- Biomacromolecule deposition

2.1. Coatings from nanoparticle adsorption

2.1.1. Synthetic fibres

Nanoparticle adsorption represents the easiest way for pursuing a surface modification employing nanoparticles; it simply consists

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Abbreviation list

APP	ammonium poly(phosphate)
APTES	3-aminopropyl triethoxysilane
BL(s)	bilayer(s)
bTESB	1,4-bis(triethoxysilyl)benzene
bTESE	1,2-bis(triethoxysilyl)ethane
CNa	Cloisite®Na
DEMPHS	diethoxy(methyl)phenylsilane
DNA	deoxyribose nucleic acid
DPTES	diethylphosphatoethyltriethoxysilane
LbL	layer by layer
LOI	limiting oxygen index
MF	N,N,N',N',N'',N''-hexakis-methoxymethyl-[1,3,5] triazine-2,4,6-triamine
PAN	poly(acrylonitrile)

PDAC	poly(diallyldimethylammonium chloride)
PET	polyester
PHRR	peak of heat release rate
PIGP	plasma-induced graft polymerisation
POSS®	polyhedral oligomeric silsesquioxane(s)
QL(s)	quadlayer(s)
SEM	scanning electron microscopy
TBOS	tetrabutylorthosilicate
TEES	triethoxy(ethyl)silane
TEOS	tetraethylorthosilicate
THR	total heat release
TMOS	tetramethylorthosilicate
TSR	total smoke release
TTI	time to ignition
WPI	whey protein isolate
ZrP	α -zirconium phosphate

in the immersion of the fabric into an aqueous suspension of nanoparticles in order to promote their adsorption on the fibre surface as for a usual finishing treatment. Our group has recently demonstrated that it is possible to confer enhanced flame retardancy properties to both synthetic (i.e. polyester) or natural (i.e. cotton) fabrics and their blends through the formation of a nano-sized coating. By this route, an inorganic shield, potentially capable to protect the underlying polymer from heat, oxygen and flame, is deposited on the fibre surface. Indeed, the nano-coating can act as a thermal insulator absorbing the heat and oxygen from the atmosphere and blocking their transfer to the surrounding polymer. At the same time, the coating can entrap the volatile species produced by the substrate that can further fuel the combustion. Hence, the substrate is protected and tends to pyrolyse instead of burning.

In order to measure the fire performances of the treated fabrics, an optimised procedure has been set by using the cone calorimeter [11,12]. Indeed, as is well known, this instrumentation was designed for plastic substrates [13,14], and not for testing thin materials like films or fibres/fabrics.

As far as polyester (PET, density of 171 g/m²) is concerned, the use of hydrotalcite, titania, silica [15] and Cloisite®Na (CNa) [16] has been assessed. The effect of immersion time, pH of the nanoparticle dispersions and surface pre-treatment (by cold oxygen plasma) have been investigated on the final properties of the so-treated fabrics. On the basis of the combustion results assessed by cone calorimeter [15], it is possible to conclude that hydrotalcite is the most promising exploitable nanoparticle under the adopted experimental conditions due to the increase of time to ignition (TTI) values with respect to those of silica and titania at a fixed 60 min immersion time (226 vs. 166 s for hydrotalcite-treated PET and untreated PET, respectively). A further increase of TTI has been observed (up to 290 s) by raising the pH of the suspension to 14.

Once again, the coating acts as a thermal shield for PET exerting a protective role and favouring the char formation instead of volatilisation phenomena.

This study has also highlighted a significant improvement of the nanoparticle adsorption on PET surface when a pre-treatment by cold oxygen plasma was carried out. Thus, selecting different process parameters (namely, power and etching time) plasma surface activation was combined with nanoparticle adsorption [16]. Combustion results (assessed by cone calorimeter) showed that the plasma pre-treatment can increase the density of nanoparticles on the surface and make much stronger their interaction with PET fabric surface. The most performing system (obtained after a cold

oxygen plasma pre-treatment of 180 s at 80 W) gives a TTI of 322 vs. 158 s of untreated PET (Δ TTI = +104%).

2.1.2. Natural fibres

Referring to natural fibres, it has been demonstrated that both hydrotalcite and silica can impart good flame retardancy properties to the cotton fabrics, apart from PET [17]. More specifically, a surface pre-treatment with cold oxygen plasma (200 W for 5 min using a flux of 20 cm³/min) has been combined with the nanoparticle adsorption via simple immersion. The main goal was to assess the role of the immersion time and pre-treatment on nanoparticle uptake on to fibres, and thus on the resulting properties of cotton. The immersion time has been correlated to the nanoparticle type: indeed, the highest silica nanoparticle uptake was reached after 30 min, while hydrotalcite did not evidence significant variations within 30 and 60 min. Scanning electron microscopy (SEM) showed a general pickup rise for both the nanoparticles, which turned out to increase the TTI and decrease the PHRR when used alone or in combination.

These results agree with those published by Horrocks and co-workers [18]: when cotton is previously treated with plasma and subsequently with functionalized clays or a polysiloxane, an inorganic coating that confers reduced flammability is formed. Similar results have been achieved by our group by covalently linking a polyhedral oligomeric silsesquioxane, POSS®, to cotton, using a formaldehyde resin as binder [19]. With a 2 wt.% add-on, TTI increases from 14 (untreated cotton) to 34 s and peak of heat release rate (PHRR) decreases up to 30%.

Nanoparticle adsorption has been exploited also to functionalise cotton fibres with carbon nanotubes [20]. The treated fibres exhibit enhanced mechanical properties, extraordinary flame retardancy, improved UV-blocking and super water repellent properties.

2.2. Coatings from layer by layer (LbL) assembly

Layer by layer assembly can be considered as an evolution of the nanoparticle adsorption process [21]. This process consists in a step-by-step film build-up based on electrostatic interactions; it was introduced in 1991 for polyanion/polycation couples in order to obtain the so-called polyelectrolyte multilayers [22], and subsequently extended to inorganic nanoparticles [23] exploiting different interactions (e.g. covalent bonds, hydrogen bonds, etc.) beside the electrostatic one. The LbL assembly through electrostatic interactions simply requires the alternate immersion of the substrate into an oppositely charged polyelectrolyte (usually water-

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