Chitosan-based Flame-Retardant Systems

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During the last decade, the utilization of chitin, and in particular its deacetylated form, i.e. chitosan, for flame retardant purposes, has represented quite a novel and interesting application, very far from the established uses of this bio-sourced material. In this entry, chitosan is a carbon source that can be successfully exploited, often in combination with intumescent products, in order to provide different polymer systems (namely, bulky materials, fabrics and foams) with high flame retardant (FR) features. Besides, this specific use of chitosan in flame retardance is well suited to a green and sustainable approach.

Keywords: chitin ; chitosan ; flame retardance ; bulky polymers ; fabrics ; textile materials ; foams ; flame spread tests ; cone calorimetry ; multifunctionality

1. Introduction

Polymeric materials, including bulk polymers, textiles and foams, if not inherently flame retarded will easily ignite and vigorously burn when exposed to an irradiative heat flux or to a flame. This behavior represents a dramatic drawback of such materials in all the uses that strictly demand fire-resistance [1][2].

In order to overcome this limitation, from the beginning of the fifth decade of the 19th century onwards, both academics and the industrial world started to design, produce and successfully employ the so-called flame retardants (FRs), i.e., special products designed to limit the propagation of a flame or even to prevent the ignition of the material into which they are incorporated or onto which they are deposited. As nicely described in the literature [3], upon the application of a flame or exposure to an irradiative heat flux, these additives may exploit different mechanisms:

- Char formation: in this case, FRs act in the condensed phase, promoting the formation of a stable carbonaceous residue on the surface (i.e., the so-called char), which acts as a barrier to inhibit gaseous products from di using to the flame, and protects the polymer surface from heat and air [4];
- Intumescence: upon activation, FRs swell together with the degrading material, leading to the formation of a porous foamed structure, which acts as a barrier to heat, air and pyrolysis products [5];
- Reactions in the gas phase: vapor-phase flame retardants are able to interfere with the free radical reactions involved in flame propagation [6];
- Cooling (heat sink mechanism): cooling occurs when the flame retardant decomposes endothermically to cool the pyrolysis zone located at the combustion surface [7];
- Dilution: this may occur in either the condensed or the gas phase. In the former, FRs act to dilute the polymer and reduce the concentration of decomposition-derived flammable gases. In the latter, FRs, upon activation, decompose to inert gases, which dilute the flammable gases.

2. Different Flame Retardant Systems

In this context, different flame retardant systems have been developed. The first and most efficient FRs were halogen-based (mainly brominated and chlorinated) products; though they are still employed, some of them (namely, polychlorinated biphenyls, pentabromodiphenyl or decabromodiphenyl ethers) were recently banned by the USA and the EU, because of their high toxicity for human beings and animals [8]. Then, the research addressed the design of halogen-free flame retardant products, mainly containing phosphorus- or phosphorus/nitrogen compounds [9]. In fact, these types of FRs show good performances in dfferent types of materials (bulky polymers, textiles and foams), and currently represent the best compromise between low environmental impact and e ectiveness.
Quite recently, during the last 10 years, the research carried out in fire retardance has clearly demonstrated that some biomacromolecules and bio-sourced products, with peculiar chemical compositions and structures, can be exploited for the design of “green” and e ective flame retardants for di erent types of materials. In particular, the academic research has

identified some proteins (namely, whey proteins, caseins and hydrophobins), nucleic acids and natural extracts (such as phytic acid, tannins, banana pseudostem sap and pomegranate rind extract, among others) as potential components of flame retardant formulations [10].

3. Derivatives in Flame Retardant

In this context, the possibility of exploiting chitosan and some of its derivatives in flame retardant recipes has been widely assessed; it is well known that chitosan, consisting of β-(1–4)-linked d-glucosamine and N-acetyl-d-glucosamine randomly distributed within the polymer, can be obtained by the partial deacetylation, performed in alkaline conditions, of chitin (i.e., poly(b-(1-4)-N-acetyl-d-glucosamine)), a key polysaccharide and the second most important natural polymer in the world after cellulose, mainly extracted from marine crustaceans, crab and shrimp shells [11]. Besides, in nature, chitin is structured in crystalline microfibrils that give rise to the
structural components in the cell walls of yeast and fungi, as well as in the exoskeleton of arthropods. As a consequence, it shows very good mechanical features. If the deacetylation degree of chitin reaches around 50%, the obtained chitosan can be dissolved into aqueous acidic media, thus converting the insoluble polysaccharide into a polyeletrolyte. This finding is ascribed to the protonation of the amino groups located at the C-2 position of the D-glucosamine repeat unit, and justifies the possible use of chitosan for the buildup of flame retardant Layer-by-Layer coatings on dfiferent types of fabrics.

Apart from the well-known applications (such as in the biomedical and pharmaceutical sectors, for food and nutrition, wastewater treatments and textile finishing, among others), the chemical structure of chitosan suggests the possibility of using it as a carbon and nitrogen source in the design of low environmental impact flame retardant formulations; besides, the presence of such reactive groups as -NH2 and -OH can be successfully exploited in chemically modifying the biomacromolecule, thus introducing phosphorus-containing functionalities. This way, it is possible either to combine chitosan with other additives, in order to design high-performing flame retardants, or to obtain some derivatives that could be directly exploited for the design of e ective flame retardant formulations.

It is worthy of note that chitosan alone, although not intrinsically flame retardant, is a very good carbon source that, if appropriately applied to a polymer substrate (i.e., bulky polymer, textile, foam, wood), can give rise to the formation of a stable protective char. The current state of the art regarding this specific use of chitosan has been recently reviewed [12].

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