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A new era for flame retardant materials?

**Think proteins and nucleic acids, and
flame proofing might not spring to
mind. But recent research suggests
biomacromolecules may play a part in
the future of textile flame retardation**

The burning of textiles has always been considered a major hazard: indeed, most fibers and fabrics, which play an important role in everyday life (e.g. for transportation, automotive industry, protective garments, the military, furniture upholstery, bed linen and nightwear), are flammable and potentially dangerous materials [1]. As a consequence, chemical species (so-called *flame retardants*) have been developed in order to limit the risk of fire, by inhibiting the fabric ignition or reducing the rate of flame spread. From an “historical” point of view, the use of flame retardants for plastics and textiles has undergone a significant evolution: recently, due to perceived environmental issues related to the use of certain types of high-performing flame retardants, governments have grown concerned, stimulating researchers to design effective, but more environmentally-friendly products. As a result in the last 30 years, most of the high-performing halogen- or formaldehyde-based flame retardants for fabrics have been banned or limited from commercial use, thus favoring the use of phosphorus-containing products.

Meanwhile, different, novel strategies have been designed and are being currently used; in particular, three approaches have shown the most interesting results: (i) the use of nanocomposite synthetic fibers, (ii) the introduction of nanoparticles in traditional back-coatings and (iii) the deposition of (nano)coatings on

the fabric substrates. Up to now, the (nano)coating approach has mainly focused on the use of ceramic protective layers or flame retardant species, either alone or coupled together. Thus, it has embraced different methods, such as nanoparticle adsorption, layer by layer assembly, sol-gel and dual cure processes, and plasma deposition.

Very recently, biomacromolecules such as proteins (whey proteins, caseins, hydrophobins) and deoxyribonucleic acid (DNA) have shown unexpected flame retardant/suppressant features when deposited on cellulosic or synthetic substrates, like cotton, polyester or cotton-polyester blends [2–6]. The use of some of these biomacromolecules (e.g. caseins and whey proteins) as flame retardants, is a significant advantage, since they can be considered as waste or by-products from the cheese and milk industry; on the other hand, despite the current high cost of DNA, its availability has become competitive with those of other chemicals, thanks to the large scale method recently developed, which is based on the extraction and purification of DNA from salmon milt and roe sacs [7].

These biomacromolecules can be applied to fabrics using an impregnation/exhaustion process (that represents a typical finishing process for textiles) or a layer-by-layer method, starting from aqueous solution/suspensions and hence exploiting a significantly green technology.

The mechanism, through which these biomacromolecules are able to confer flame retardancy to fabrics, is still under investigation. However, the flame retardant effectiveness of these green macromolecules seems to be attributable to their chemical composition, as well as to their interaction with the underlying fabrics that, upon heating or exposure to a flame, favors the formation of a stable and protective char (i.e. a carbonaceous residue), which limits the exchange of oxygen and combustible volatile products, hence enhancing the textile flame resistance.

More specifically, caseins and hydrophobins, which contain phosphate groups and disulphide units, respectively, have been assessed as effective flame retardant systems for cellulosic substrates, since these components are capable of influencing the cellulose pyrolysis toward the formation of char. Furthermore, whey proteins have shown their suitability to form protective coatings on cotton, which exhibit great water vapor adsorption that may justify the achieved flame resistance of the treated

fabrics. Compared to proteins, DNA shows unique and peculiar behavior, since it contains the three main ingredients of an intumescent formulation all in one molecule. In particular, intumescence is the result of a combination of charring and foaming at the surface of the burning polymer, which protects the underlying material from the action of the heat or flame. Intumescence is considered the most efficient approach in alternatives to halogen-based flame retardants, as it is able to interrupt the self-sustained combustion of a polymeric material. Due to the phosphate groups, which are able to produce phosphoric acid, the deoxyribose rings acting as a carbon source and blowing agents (upon heating they may dehydrate forming char and releasing water) and the nitrogen-containing bases (guanine, adenine, thymine and cytosine) that may release ammonia, DNA-treated cotton fabrics have even reached outstanding self-extinguishment features.

Despite their significant potential in the flame retardancy field, all of the approaches mentioned above are currently still under

study. At present, one challenging issue on the use of biomacromolecules as flame retardants surrounds the possibility of adjusting this technology to a large scale, which is a key point for assessing its further industrial development. However, the high effectiveness of these bio-treatments, together with their associated environmental and safety issues, indicates a new path for the development of novel flame retardant finishing systems for textiles in the near future.

Further reading

- [1] J. Alongi, et al., Update on Flame Retardant textiles: State of the art, *Environmental Issues and Innovative Solutions*, Shawbury, Smithers Rapra, 2013, pp. 1–348.
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- [3] J. Alongi, et al. *J Mater Chem A* 1 (2013) 4779.
- [4] F. Carosio, et al. *Polymer* 54 (2013) 5148.
- [5] J. Alongi, et al. *Carbohydr Polym* 96 (2013) 296.
- [6] J. Alongi, et al. *Polym Deg Stab* 99 (2014) 111.
- [7] L. Wang, et al. *Chem Mater* 13 (2001) 1273.