

Novel linear polyamidoamine-based intumescent flame retardant coatings for cotton

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Since the middle of the last century, industrial and academic researchers have devoted much effort to the development of safe and effective flame-retardants (FR). As regards cotton, phosphorylated compounds were the predominant FR for several decades [1] despite many of them had been shown to be bioaccumulative [1]. Recently, biomacromolecules including proteins have been proposed as FR [2]. Their high efficiency is due to the intrinsic intumescent character that they exhibit upon heating. This makes them all-in-one safe FR alternatives available. Despite the attractiveness of the “green” and “biosafety” aspects, the industrial exploitation of DNA and proteins as FR is almost unconceivable. In order to fill this gap, the use of a family of synthetic water-soluble biocompatible polymers, namely polyamidoamines (PAAs) [3], bearing in their repeating units the same organic functions present in proteins, as effective and industrially sound FR for cellulosic textiles is here proposed. PAAs are obtained by stepwise polyaddition of prim- or sec-amines to bisacrylamides in water, at room temperature and with no added catalysts. At the end, nothing to be disposed of is left. Hence, PAA preparation is remarkably “green” and easily scalable. Many linear PAAs have high thermal stability coupled with chain structure and side substituents reminding those of proteins [4]. These features suggested that PAAs could act as FR. Eight linear PAAs, some of which deriving from natural α -amino acids, were prepared and were subsequently investigated as phosphorus-free intumescent FR for cotton textiles. The structure of the amine-derived subunits governed their performances. In ignitability tests, amino acid-derived PAAs exposed to direct flame for 10 s did not burn producing carbonaceous porous crusts sheltering the underneath sample still white and intact. Thermogravimetric analyses showed that at ≥ 400 °C all PAAs left in air substantial char residues, higher than those left in nitrogen. This is a peculiar behaviour of PAAs. Furthermore at 450 °C carbonaceous bubble-rich structures were formed clearly indicating the tendency of PAAs to intumesce. Horizontal flame spread tests on cotton stripes impregnated with PAA aqueous solutions showed flame extinguishment at add-ons $\leq 4\%$ and $< 20\%$ for PAAs from amino acids or guanidine-containing monomers, respectively. 2-Methylpiperazine-derived PAAs slowed flame propagation leaving substantial char residues, but did not extinguish flame up to 30% add-on. In vertical flame spread tests, no extinguishment was induced by any PAA at add-ons up to 20%, but all PAA-treated fabrics left significant residues (7-25%) different from untreated cotton. In cone calorimetry tests, all PAAs increased the time to ignition and significantly decreased both the peak of heat release rate and the effective heat of combustion. Furthermore, most PAAs caused a remarkable reduction of carbon monoxide and dioxide release. Morphological characterization of combustion residues by Scanning Electron Microscopy showed bubble-rich structures confirming the intrinsic intumescent character of PAAs.

References

1. R. A. Horrocks, *Polym. Degrad. Stab.* **2011**, *96*, 377.
2. L. Costes, F. Laoutid, S. Brohez, P. Dubois, *Mater. Sci. Eng. Report, R.* **2017**, *117*, 1.
3. P. Ferruti, *J. Polym. Sci, Part A: Polym. Chem.* **2013**, *51*, 2319.
4. F. Danusso, P. Ferruti, *Polymer* **1970**, *11*, 88.