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Flame retardant cotton fibers produced using novel synthesized halogen-free phosphoramide nanoparticles

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ABSTRACT

Flame retardant cotton fibers were successfully produced using five new nanosized phosphoramide compounds synthesized by ultrasonic method. The ^{1}H NMR spectra of compounds **1**–**3** illustrate $^3J(\mathrm{H,H})_{\mathrm{cis}}$ and $^3J(\mathrm{H,H})_{\mathrm{trans}}$ corresponding to the splittings of cis and trans protons present in the $CH{=}CH_2$ bond. Comparing the char lengths of cotton fibers treated with phosphoramides **1**–**5** indicates that the samples with greater degree of grafting (DG) provide smaller char lengths so that the least and the greatest char lengths are observed for the treated fibers with phosphoramides **1** and **5**, respectively. The very close DG and char lengths of compounds **1** and **2** can be described based on their chemical structures containing 4-nitroaniline and 4-chloro-3-trifluoromethyl aniline groups that both can release electrons through their resonance effects to their corresponding P—N bonds and enhance the P—N system synergistic effect. The TGA/DSC analyses on the treated fibers revealed that the maximum weight losses at 800 °C are occurred within the range 43.52% (for fiber treated with **1**) to 56.37 (for fiber treated with **5**) which are all smaller than that of the raw fiber (56.83%). The in vitro antibacterial activity experiments on phosphoramides **1**–**5** displayed the greatest and the least antibacterial activities for compounds **2** and **4**, respectively. Furthermore, when these phosphoramides are applied on the cotton fibers, they also demonstrate the above order for the antibacterial activities.

1. Introduction

Cotton is one of the most important natural fibers employed in the textile industries. However, it is also one of the most flammable fibers with low limiting oxygen index (LOI = 18.4%) and onset of pyrolysis at 350 °C. Improvement of thermal stability of cellulose based textiles is still a challenging issue. Numerous investigations have been conducted in finding innovatory solutions for conferring enhanced and durable flame retardant cotton fibers both at the academic and the industrial levels to achieve the performances of the major industrial target compounds known as Proban® and Pyrovatex® (Alongi et al., 2013a; Weil & Levchik, 2008; Xie, Gao, & Zhang, 2013). To overcome the thermal instability of cotton, surface treatment either with durable (e.g. monomers containing phosphorus and nitrogen along with reactive moiety) or with non-durable (usually inorganic salts containing ammonium, urea, phosphate and poly phosphates) flame retardants are performed (Edwards, El-Shafei, Hauser, & Malshe, 2012; Horrocks, 2011). Indeed, the flame retardants (FRs) are chemicals added to materials both to prevent combustion and to delay the spread of fire after ignition. FRs may have different compositions so that they may contain halogens (bromine and chlorine), phosphorus, nitrogen, metals, minerals based on aluminum and magnesium, or they may be based on borax, antimony trioxide, molybdenum, or the FR may be a nanocomposite.

The most used FRs for rendering cotton fabrics flame retardant were halogen-containing compounds. However, it was established that the halogen-based compounds are not environmentally friendly because they generate toxic gases, which can be endocrine disruptive (Legler & Brouwer, 2003; Rahman, Langford, Scrimshaw, & Lester, 2001), and may cause liver, thyroid, and neuro developmental toxicity. Also, it was demonstrated that they result in liver cancer in laboratory rats and mice (US EPA, 2012). In addition, it was evidenced that they persist in the environment and accumulate in living organisms (Legler & Brouwer, 2003; Rahman et al., 2001; US EPA, 2012). Therefore, the production of the halogenated FRs were

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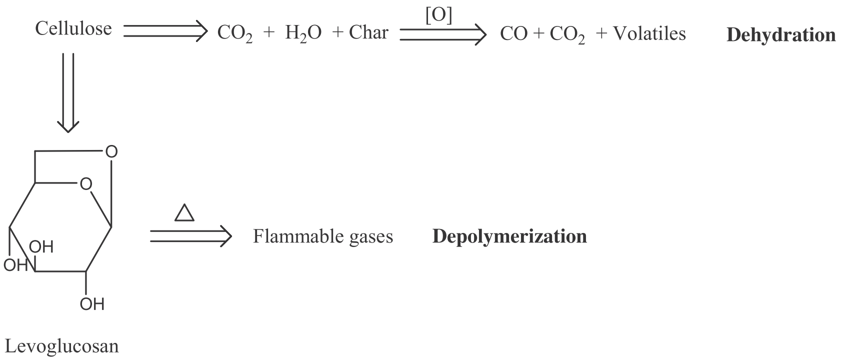

Scheme 1. The proposed mechanisms for the burning/pyrolysis products of cellulose fibers.

banned especially the two major classes including polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in EU and USA (Legler & Brouwer, 2003; US EPA, 2012).

After the ban on some brominated flame retardants (BFRs), phosphorus flame retardants (PFRs), which were responsible for 20% of the flame retardant (FR) consumption in 2006 in Europe, were replaced as alternatives for BFRs (Andrae, 2007). PFRs can be divided in three main groups, inorganic, organic and halogen containing PFRs. Most of the PFRs have a mechanism of action in the solid phase of burning materials (char formation) while some may also be active in the gas phase. Some PFRs are reactive that are chemically bound to a polymer, whereas others are additives and mixed into the polymer.

Most of the treatments applied in order to confer a flame retardant behavior to many types of fabrics involved a pad-dry process containing familiar organophosphorus compounds particularly those containing P—N bonds (Abou-Okeil, El-Sawy, & Abdel-Mohdy, 2013; Alongi, Colleoni, Rosace, & Malucelli, 2013b; Maki et al., 2000; Wei et al., 2011). These compounds are the most commonly used as flame retardants due to their ability to promote char formation. Many approaches have been developed to deposit a phosphorus-based flame retardant onto cellulose fiber such as the pad/dry/cure technique, graft copolymerization to cellulose, or in situ polymerization of monomer which can form three dimensional network in or on fibers (Horrocks, 1983; Tsafack & Levalois-Grutzmacher, 2006). The char residue acts as a barrier to protect the fabric from attack of oxygen and radiant heat of fire and it can also reduce smoke emission (Duquesne et al., 2004; Granzow, 1978; Green, 2000; Price et al., 2000; Wang, Cheng, Tu, Wang, & Chen, 2006).

The phosphorous–nitrogen (P—N) containing flame retardants have been widely studied (Hebeish, Waly, & Abou-Okeil, 1999). Such systems attracted much attention because of their appropriate thermal stability, low toxicity, and superior performance, due to the synergistic effect of P—N (Lewin, 1999; Pandya & Bhagwat, 1981). The P—N synergism is not a common phenomenon and depends on the nitrogen containing compound and polymer nature (Levchik, 2006). Some theories have been presented for the P—N synergism (Cullis, Hirschler, & Tao, 1991; Gaan, Sun, Hutches, & Engelhard, 2008) and elucidated that P—N compounds reduce the formation of flammable volatiles and catalyze char formation.

Current industrial flame retardant finishing treatments for cotton fabrics exploit the phosphorus–nitrogen synergism (Proban-Rhodia, Pyrovatex). It was shown that upon cellulose pyrolysis at high temperatures, phosphorus compounds can phosphorylate the C(6) of the glucose monomer, avoiding the source of fuel formation as levoglucosan and promoting the dehydration process that is a competitive route to depolymerization (Scheme 1) (Broido, Evett, & Hodges, 1975). In the P—N compounds, the FRs may be converted into phosphorus acid amides that also catalyze the dehydration and carbonization of cellulose thereby the amounts of combustible gases at reduced temperatures are decreasing and the formation of a carbonaceous replica of the original textile fiber is improved. It was illustrated that the most effective FRs are those which cause the transformation of the flammable polymer to a carbonaceous char (Davies, Horrocks, & Miraftab, 2000). The charred residue not only reduces the creation of flammable volatiles but also leads in a flame/heat barrier between the ignition source and the fabric inner layers (Horrocks, Kandola, Davies, Zhang, & Padbury, 2005). The enhancement in char formation is feasible both by conventional intumescents and by increasing thermal barrier properties through nanoparticles (White, 2004).

Functional coating methods are considered as alternative flexible ways to conventional finishing techniques because they are independent of fabric type and necessitate low amounts of additives as well as allow incorporation/combination of different functionalities (Gulrajani & Gupta, 2011). These methods include layer by layer (LBL) assembly, immobilization of enzymes, nano coating and using plasma for deposition of functional molecules. The layer by layer (LBL) assembly was developed to fabricate thin composite films on solid surfaces by sequential adsorption of oppositely charged polycations and polyanions to build a series of polyelectrolyte multilayer films on the substrate (Dvoracek, Sukhonosova, Benedik, & Grunlan, 2009; Everett, Jan, Sue, & Grunlan, 2007; Jang, Rawson, & Grunlan, 2008). Both free and immobilized enzymes can be used to treat the fibers but immobilized enzymes are permanently attached to the textiles. Therefore, the free enzyme is lost after its first use but the immobilized enzyme continues to catalyze the anticipated reactions repeatedly (Banerjee, Pangule, & Kane, 2011; Tasso et al., 2009). The nano coatings based on zinc, silver and titanium dioxide nanoparticles have extensively been applied on the fabrics to produce anti UV, antimicrobial and self cleaning textiles (Kathirvelu, D'Souza, & Dhurai, 2009). Usually, pad/dry/cure, thermal, radiation or chemical methods have been utilized to fix these nanoparticles on textiles. It was found that nano coating through LBL is a chemically mild alternative to other processes in order to produce ultrathin, transmissive and stable coatings. Plasma can also be applied on textiles for surface activation, to perform polymerization on the surface or for deposition of compounds containing different functionalities. In the plasma enhanced chemical vapor deposition (PECV) technique, the plasma functionalizes the substrate surface before chemical vapor deposition (Alongi, Tata, & Frache, 2011). In a recent work, LBL assembly of branched polyethylenimine and Laponite clay was examined and it was shown that these clay-based assemblies endow flame-resistant behavior to cotton fabric by creating a protective sheath ($\sim$10 μm diameter) around each individual microfiber (Li, Schulz, & Grunlan, 2009).

In this work, using ultrasonic method, nanoparticles of five novel phosphoramides were synthesized and characterized by