

Textiles with reduced flammability – an overview

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Application of flame retardants (FRs) in textiles is crucial to minimize overall fire risk by delaying or suppressing the spread of fire. The use of FRs additives helps to ensure growing demands for reduction of fire hazard caused by highly flammable materials such as textiles and polymers. This paper aims to introduce chemistry and mechanisms as well as review the recent developments in obtaining textiles with reduced flammability (TRF).

Keywords: Flame retardants, Textiles, Reduction of flammability

I. INTRODUCTION

Textiles and more precisely fiber materials are widely used almost everywhere around us. The demand for textiles flame retardant are mainly in work clothing, draperies, upholstery and transportation. Many of this applications require flame retardancy due to human safety since they are crucial in order to reduce overall fire risk by suppressing the spread of fire or by delaying the time of flashover. The concept of FRs is to decrease an item's tendency to burn when subjected to open flame or any other a heat source. It is estimated that escape times can be up to 15 times longer when flame retardants are present.

History of chemical flame retardant textiles starts about 1735 in England where some mineral substances such as borax and vitriol were patented [1]. Borax is still often used for nondurable flame retarding of e.g. tent fabric. In 1821 Gay-Lussac identified ammonium phosphate as highly effective flame retardant and it is still used. During the Second World War a military laboratories studied not only inorganic additives and treatment processes in flame retardancy but also the mechanisms by which combusive processes can be retarded. Much of this work is summarized by Little [2-3]. In the mid-twentieth century a lot of attention has been paid in order to acquire flame retardant cotton garments such as work clothing and sleepwear for children. Nowadays the most common classes of flame retardants are brominated, phosphorus, nitrogen, chlorinated, and inorganic [4].

Latest developments of new flame retardants are mostly motivated by avoidance of environmental and toxicological issues due to legislative changes. Researchers nowadays put a lot of effort in order to replace halogen-based flame retardants which are highly efficient but emit toxic fumes during fire. Moreover they proved to be carcinogenic, bioaccumulative and toxic for animals and humans. Nonetheless phosphorus and halogen-based flame retardants are still the most popular in commercial use. Therefore nowadays appeared growing demand for new flame retardant product options. However these new replacements need to ensure not only a favourable ecological profile but also they have to be of relatively low price and advantageous properties at least comparable to halogen-based systems.

In the basic mechanisms of flame retardancy differ based on the specific flame retardant. In general halogen and halogen antimony systems have a tendency to be flame inhibitors, the phosphorus and boron systems are prone to enhance charring and formation of surface barrier layers while the metal hydroxides tend to be endothermic water-releasing systems.

Combustion mechanism also depends on the material itself. Textiles are manufactured from both natural or synthetic fibers [4-5]. Regarding natural polymers widely used for obtaining the fibers is cellulose. As for the synthetic fibers can be made from polymers such as for example polyesters, polyolefin, polylactide, polyamides or polyacrylonitrile and many others. There are many heat-stable fibers for example such as polyaramides, fluorocarbon, melamine, polyoxazoles, polyimides or polyphenylene sulfides. Fibers can be divided into fire resistant fibers and non-fire resistant fibers according to limiting oxygen index so the combustion performance of various kinds of fibers are shown in Table 1 below.

Table 1 The combustion performance of various kinds of fibers [3].

Classification		Combustion characteristics	Fibers
fire resistant fibers	non-flame fibers	ignition is not possible	polytetrafluoroethylene fiber, metal fiber, carbon fiber, asbestos fiber and glass fiber
	flame retardant fibers	combustible or carbonized with fire, self-extinguishing without fire	aramid fiber, polyvinyl chloride
non-fire resistant fibers	flammable fibers	easy to ignite, but slow burning	polyester, polyamide, vinyl, wool, silk
	inflammable fibers	easy to ignite, and the burning speed is fast	acrylic, polypropylene, viscose, cotton, linen, acetate

The study focused on search for efficient and economic flame retardants that make use of e.g. natural plant extracts or nanotechnology. Not without significance is also seeking environmentally friendly application techniques.

II. FLAME RETARDANCY THEORY AND MECHANISMS

The polymer composition of the textile materials is the most important factor determining their flammability. Understanding the thermal behaviour of polymers alone and in the presence of additives is useful in designing an effective flame retardant system. Subjecting polymers to elevated temperatures may lead to several physical and chemical changes which are related to the physical and chemical structure of the polymer.

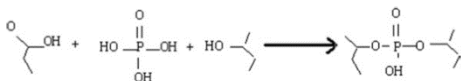
The function of FRs is to interrupt the combustion cycle by chemical and/or physical means during the solid, liquid, or gas phases of burning [4]. Based on that we can distinguish two main modes of action of FRs: the physical and chemical. The physical action is divided into three types: formation of a protective layer; cooling effect and dilution effect. The first action, which is the formation of protective layer should

preferably cut off the heat transport from the heat source and prevent oxygen circulation to the flammable material. Moreover, they should also block the supply of pyrolysis gases to the textile surface. This mechanism can be observed in phosphorus compounds, silicon and boron compounds and inorganic borates [6]. Second one, initiates the endothermic process, which cools the substrate so the ignition temperature is not reached. Flame retardant that behaves in this way, e.g. alumina trihydrate [7]. The third one, create non-flammable decomposition gases and dilute the fuel in both the gas and solid phases so that the flammable gases concentration falls under the ignition limit and thus the textile cannot ignite [7].

As for the second mode of action, the chemical one, we can split it into two phases. First reaction takes place in gas (vapour) phase, the second in solid phase. The exothermic, free-radical mechanism of the combustion process, which takes place in the gas phase, is interrupted by flame retardants and stopped. The system cools down, the supply of flammable gases is reduced and eventually completely suppressed. Polymers under pyrolysis can react with air resulting in chain branching reactions, which advance the combustion. Halogenated flame retardants interfere with this chain reaction by preventing hydroxide and hydrogen free radicals from reacting with oxygen and carbon monoxide. Radicals are captured, therefore disturbing the exothermic oxidative flame chemical processes resulting in the hindrance of combustion [8]. The reactions in the vapour-phase mechanisms are as follows:

- (1) $H\cdot + HX = H_2 + X\cdot$
- (2) $HO\cdot + HX = H_2O + X\cdot$
- (3) $RH + X\cdot = R\cdot + HX$

Flame-retardant chemicals in the solid phase cause a reduction in the amount of gaseous combustibles produced by altering the pyrolytic path. Instead, carbonaceous char, water and carbon dioxide are often produced [8]. The inert insulating material serves to reduce the gases. The char forms a heat- and mass-flow barrier, which serves to protect the fibre. Carbon is stabilized and prevented from turning into combustible gases. Dehydration and cross-linking are two significant processes that play a role in flame retardants, which act by way of the condensed-phase mechanism. Most of these phenomena occur in the case of phosphorus-based FR compounds. These are both recognized to occur in cellulosic and synthetic fibres. These flame retardants can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These form the carbonaceous layer by cycling and cross-linking. The chemical reaction mechanism can be explained as follows [8].



III. TYPES AND CHEMISTRY OF FLAME RETARDANT ADDITIVES

Flame retardant additives used in textiles are generally classified according to their elemental composition [4]. Flame retardant additives are typically made up from compounds containing elements such as: phosphorus (in various organic and inorganic forms); halogens (brominated, chlorinated organics, fluorides of zirconium); silicon (organic or inorganic forms); boron; metals (hydroxides of Al, Mg, Ca, phosphinates of Al, Zn and Ca and Zinc borates, fluorides of zirconium); nitrogen (either alone or together with phosphorus, inorganic or organic); antimony (oxides together with halogens).

Halogen compounds have long been used, usually with a synergist such as antimony trioxide. One of the earliest successful additives that is still used is polycyclic polychlorinated compound made by the Diels-Alder addition

reaction of hexachloro cyclopentadiene with cyclooctadiene-1,5 (a butadiene dimer) [9]. The chlorine atoms resist hydrolysis and dehydrochlorination and as a result the molecule is stable enough to be processed up to about 300°C.

Regarding brominated additives, for a long time, one of the most efficient flame retardant additives was decabromodiphenyl oxide (DBDPO, decabromodiphenyl ether) [9]. This compound is very high melting and insoluble in the polymer, acts as a filler and has negative effects on impact, flexibility, and flow, but it also has some tendency to darken under UV exposure so it was used mostly in uncritical applications. Decabromodiphenyl oxide has been used as a textile flame retardant, particularly by back coating with a binder and usually with antimony oxide as synergist. This system performs well on most fabrics. Unfortunately, the entire family of polybrominated diphenyl ethers has come under environmental criticism as they are bioaccumulative in fat tissue of living organisms.

Melamine additives such as for example melamine cyanurate, allows “halogen-free” marketing as nitrogen-based flame retardant. This compound appears to work by producing enhanced dripping (with nonburning drips) and also by dissociating endothermically to produce non-combustible vapour [9]. In filled polyamides, melamine cyanurate may be found useful in combination with magnesium hydroxide [10].

The best example of fire retardant inorganic hydrate is magnesium hydroxide. This product has a good colour and high CTI, but is difficult to process and is rather stiff [11]. It has been shown [12] that the mode of flame retardant action of Mg(OH)₂ in polyamides is different from the action in polyolefins. Magnesium hydroxide at 60% loading increases the oxygen index of polyamide 6 by 205%, polyamide 66 by 120%, however, polypropylene only by 50%. It is believed that Mg(OH)₂ promotes charring of polyamides by reacting with products of thermal decomposition (probably acids).

Red phosphorus, the thermodynamically stable high-polymer form of phosphorus, is the most effective phosphorus flame retardant [13]. Its use has been held back by problems of colour, handling safety and stability. However, much progress has been made by coating or encapsulating red phosphorus. A lot of the technology of improving red phosphorus has to do with avoiding a slow reaction under the combined action of oxygen and water forming small amounts of toxic and malodorous phosphine gas (PH₃) and corrosive phosphorus acids [9]. In general, phosphine generation during polymer processing can be minimized by use of a stabilized and coated version of red phosphorus. Red phosphorus can be enhanced as a means for achieving a glow wire ignition temperature of greater than 750°C in polyamide by addition of a divalent or trivalent metal phosphate or pyrophosphate, such as calcium pyrophosphate [14] or melamine polyphosphate with a nanoclay [15]. Zinc borate, zinc oxide or iron oxide help to retard the corrosive effect of phosphine and may also enhance the flame retardant action [16]. BASF patent application reveals polyacrylonitrile as an effective synergist for red phosphorus in polyamides such as PA 6 [17].

Polytetrafluoroethylene has been frequently used to retard drip in flame retardant polyamides, and by doing so, it is sometimes possible to go from a UL 94 V2 rating to a V0 rating [9].

In recent years, a lot of studies have been specifically dedicated to the search of environmentally friendly flame retardants that ensure fire performances comparable to those achieved by the conventional fire retardant compounds, which have been usually based as mentioned before, on halogens or their derivatives. Although the halogenated compounds are the most efficient and still widely used FRs, some of them (like pentabromodiphenyl ether, decabromodiphenyl ether and polychlorinated biphenyls) have been clearly shown to be bioaccumulative and possess environmentally toxic features for both animals and humans [18]. In particular referring to cellulosic fabrics, the current attention is focused either on the

production of effective halogen-free substituents for coatings and back-coated textiles or on the use of N-methylolphosphonopropionamide derivatives or hydroxymethyl-phosphonium salts. The latter shows some drawbacks referring to the formaldehyde release during the application of the FR [18].

Despite much effort, no successful coreactant or additive flame retardant has been found for polyamide 6 or 66 textile fiber [9]. A difficulty with additives is that any particulate solid or even melt-blended polymer forming a separate phase will greatly reduce the strength of the melt-spun fibers.

Processing methods for obtaining TRFs

There are two kinds of fire resistant fibers, one is the fiber itself has fire resistant performance, such as PMIA, PPS, PBI, PBO. Another kind is modified fibers, such as flame retardant viscose fibers, flame-retardant PET fibers, flame-retardant PA fibers, flame-retardant PP fibers, flame-retardant PAN fibers.

Obviously, it is possible to increase the fire resistance of the non-resistant fiber through various processes. Flame retardants can be coated on textiles by adsorption and deposition, chemical bonding and adhesive action.

(1) Spraying - flame retardants are sprayed on the textiles by manual or machinery spray.

(2) Dip-padding and immersion - textiles are put in pad fluid formed by flame retardant, crosslinking agent, catalyst, wetting agent and softening agent, after steps of dip-padding, preliminary drying, baking and aftertreatment, textiles absorbs flame retardant.

(3) Coating - the flame retardant is mixed in the resin, the flame retardant is fixated in textiles by the bonding effect of resin.

One of the latest techniques at a lab scale is the combination of phosphorus-based FRs with sol-gel derived oxidic phases, exploiting the joint or synergistic effects [19-21]. For example novel research was conducted among others by J. Alongi et al. [21] where in order to overcome issues encountered by the addition of flame retardant additives during the manufacturing process, the sol-gel process was evaluated to flame retardant flexible polyurethane foam. Various formulations using different catalysts and monomers were prepared and deposited on flexible polyurethane foams by impregnation process. Different sol-gel formulations were tested but a mixture of TEOS and MTES was used as the basis of all formulations. MTES was added to TEOS in order to limit shrinkage and cracks of the coating during drying. However, since MTES is also known to increase gelation time, its amount was kept low. It appears that when a mixture of an appropriate ratio of 3-amino propyl triethoxysilane and diethyl phosphate is prepared in association with tetraethoxysilicate and methyl triethoxysilicate and deposited on flexible polyurethane foam, the coating shows an intumescent behaviour when exposed to a flame. The foam also self-extinguishes after 30 seconds of flame application during UL94 test and a 60% reduction of the peak of heat release rate is obtained under Mass Loss Calorimeter conditions. The stable coating has an intumescent behaviour and builds a 3D silicon network during burning, slows down the release of degradation products and protects the underlying FPUF from burning. The effectiveness of the sol-gel treatment is shown on Figure 1. below.

Another method to increase the fire resistance may be recently reported a covalent deposition method to prepare a zinc oxide film on a cotton surface. Zhang et. al. [22] proves that after grafting with (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane, wetting property of the fabric sample transformed from superhydrophilic to superhydrophobic. Also polystyrene was introduced to enhance the mechanical and chemical stabilities of this superhydrophobic cotton fabric. The results exhibited the outstanding superhydrophobicity,

waterproofing durability and flame retardancy of the cotton fabric after treatment, offering an opportunity to accelerate the large-scale production of superhydrophobic textiles materials for new industrial applications, such as water/organic solvent separation.

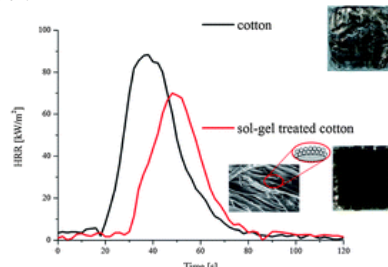


Figure 1. Time variations of Heat Release Rate for bare cotton fabric and for sol-gel treated cotton [21].

IV. THE RECENT TECHNOLOGY FOR APPLICATIONS WITH REDUCED FLAMMABILITY

Nanotechnology is one of the most promising areas including obtaining new fire retardant textiles. Not without significance is also the addition of various nanofillers to many different materials and as a result we are able to obtain nanocomposites with better properties. Thermal and fire decomposition mechanisms of the nanocomposites are totally different from those of the polymer matrix alone. Under the stress of a fire, the presence of nanofillers helps to delay the depolymerisation of the polymer and thus reduce the amount of released heat [23]. This also includes promising research on polyhedral oligomeric silsesquioxanes (POSS) [24-26]. For example, French researchers worked on PET multifilaments containing blends of aluminium phosphinate and different polyhedral oligomeric silsesquioxanes [24]. The textiles were developed via melt spinning process. The chosen POSS were OctaMethyl POSS (OM-POSS) and DodecaPhenyl POSS (DP-POSS) shown on Figure 2. Textiles made by the filled fibers were then produced and investigated. Improved performances of the fibrous materials have been noticed such as a decrease in the dripping effect, in the peak of heat release rate and in the total heat evolved while combustion. Differences on the textiles fire properties were also observed depending on the used POSS nanoparticles with distinct ignition times and char protective properties. Calorimetry results showed that the organic species surrounding POSS nanoparticles remarkably affects the fire behaviour of the material at very low content (1 wt. %). Thus, OctaMethyl POSS presented higher fire performances than DodecaPhenyl POSS with aluminium phosphinates in a fibrous material form.

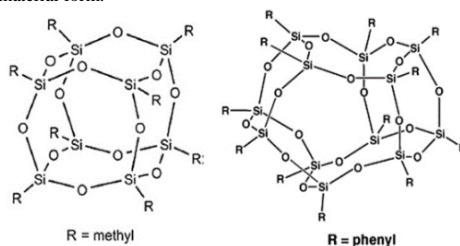


Figure 2. OM-POSS (OctaMethyl POSS) and DP-POSS (DodecaPhenyl POSS) nanoparticles [24].

Improved fire retardant textiles can be also developed thanks to addition of carbon nanotubes or nanofibers which provides the formation of a network of nanoparticles which also allows the molten polymer to viscosity and reduce the gas release [27-28]. Innovative research on this topic was conducted among others by N. Attia et al. [29]. In these studies, halloysite nanotubes (HNTs) have been used as flame retardant filler for textile fabrics for the first time. The electrical and flame retardancy properties were controlled by the preparation method which was a simple and environmentally friendly vapour phase polymerization method. This method was used for the polymerization of polypyrrole layer covering the surface of halloysite nanotubes and textile fabrics which is shown on Figure 3. As a result, the flame retardancy and thermal stability of the new textile nanocomposites were improved. The polypyrrole layer wrapped the surface of inorganic nanotubes and fibers of the fabrics. Moreover, the electrical resistance of the new nanocomposites was reduced to 0.21 k Ω . The flammability properties were significantly reduced, achieving high class flame retardant textile with zero rate of burning compared with 149.3 mm/min for the blank. Thermal stability of the nanocomposites was enhanced reaching up to 50% improvement than for the blank.

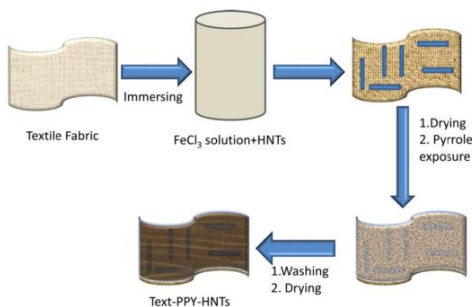


Figure 3. Schematic synthesis of Text-PPY-HNT nanocomposites [30].

The adequate nanofiller may be combined with conventional flame retardants to obtain a synergistic effect for decreasing the amount of these latter in the polymer matrix while achieving the required levels of certain standards [31].

Recently, biomacromolecules such as various kinds of proteins and deoxyribonucleic acid (DNA) have been carefully investigated [18]. They exhibit notable potentials as novel green FRs for selected fabrics such as not only cotton or polyester but also for bulk polymers such as e.g. ethylene vinyl-acetate copolymers and foamed polyurethane substrates. In this context, we started to recognize the full worth of different biomacromolecules (proteins, caseins, hydrophobins, and DNA) to be a valuable unexpected alternative to the conventional flame retardants for textiles. The application of biomacromolecules is considerably easy and could exploit the methods that are already designed and optimized for textile finishing like impregnation or exhaustion or even layer-by-layer depositions, with significant enhancement. However, their greatest advantage is the fact that some of these biomacromolecules are considered to be by-products or even waste from the agro-food industry. Moreover, the excellent mechanical and barrier properties of their coatings, can be engaged in preventing, delaying, or partially inhibiting the thermal degradation of a thin polymer such as a cellulosic fabric, both in inert and oxidative atmosphere.

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