# Chapter 6
# Flame Retardant/Resistant Based Nanocomposites in Textile

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**Abstract** Due to the increasing consideration in nanotechnology during the past decade, numerous studies were undertaken in improving the flame retardancy properties of natural, artificial and synthetic fibers as well as fabrics by applying nanocomposite approach. This chapter considers key issues concerning traditional and novel approaches or processes to develop nanocomposites coating, nano-coatings on textile as well as the incorporation of nanoparticles into fibers. The incorporation of nanocomposite to form flame retardant coatings onto the surface of textiles or to functionalize fibers by melt spinning which can be subsequently woven or knitted are mainly related for application fields required high performance such as automotive, protective clothing, etc.

## 6.1 Introduction

Textiles and wider fibrous materials are materials that exhibit depending on technologies (weaving, knitting, nonwovens, breading) extremely varied forms and are used as such or combined with other materials for a variety of applications that are limited not only to the basic function of dressing. Fibrous materials are present all around us: they are multifunctional materials with textile protection against all kinds of

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aggression; textile coverings may be flame retardant (FR), cutting and stab resistant, and bullet proof. There are smart textiles integrating sensors or becoming themselves sensors with electro conductive fabrics, there are also cosmetic textile with refreshing textile or slimming textiles. Fibrous materials are the base of composite materials; they are the reinforced composite materials present in the automotive, aerospace, and all other composite applications. Textile are also fishing nets, geotextiles, stretched structures or insulating material for buildings, any kind of filter based on nonwovens, textile is used in medical applications like human implants such as artificial arteries. Apart protective clothing, heat and fire resistant textiles are needed in areas where fire protection is essential namely transport and housing with furniture, bedding, seat cover, interior (floor and wall covering), structural composite materials, filters, insulation acoustic and thermal panels …. The key element of textile is fiber. At the beginning natural and then artificial, from the second half of the 20th century with the development of polymers, are now synthetic fibers which have world's largest production. More recently, synthetic fibers called high performance are widely used for technical textiles. There are many heat-stable fibers (polyaramids, fluorocarbon, melamine, polybenzimidazoles, polyimides, polyoxazoles, polyphenylene sulfides …) that are inherently fire resistant. However, for various reasons (economic, ease of implementation, conservation of secondary functionality …), the fire behavior improvement of common fibers remains a major challenge. The nanomaterials strategy is one of several principles for improving the burning behavior of textiles.

The development of nanostructured structure textile to improve performances and/or new functions has gained considerable attention for several years, especially to textile applications polymer matrix. The main benefit is the increasing of the strength of the materials by adding of exfoliated clays, nanoparticles and carbon nanotubes. Nevertheless the application of nanotechnology in textile field allows producing multifunctional substrates such as antibacterial, superhydrophobic and also fire retardant. In order to obtain materials with the desired performance, two principle ways can be considered to bring the properties, e.g. melt spinning and fiber surface finishing treatments.

Before detailing the various principles of nanostructured textiles and their fire behavior, it is necessary firstly to recall the classic flame retardants for plastics and textiles and secondly to present the specifics of the fire behavior of textile material. Textile including nanomaterials can be divided into two main groups, in which the nanostructured materials refer to condensed bulk materials and nanophase/nanoparticle materials are usually dispersive nanoparticles [1]. Nanomaterials usually used in textile field such as textile structures, finishes and coating are mainly nanofibers, polymer nanocomposites, and/or nanostructured surfaces. Textile requires effective flame retardancy properties with a minimal environmental impact, since these structures are often washed and flame retardant additives of coating can leach out into the environment [2, 3].

## 6.2 Flame Retardant for Plastic

The chemical nature of flame-retardant additives for plastic is highly varied and the action of these compounds is not only optimized for a particular polymer chemistry but also to prevent flammability effects such as flame spread, smoke release, dripping… Thus, the choice of the additives should take in account the chemical nature of the plastic and the end-use application.

World-wide 1.8 billion kilo of fire retardant additives are used annually [4]:

- 700 million kilo of halogenated fire retardants;
- 200 million kilo of organophosphorous fire retardants;
- 750 million kilo of aluminium hydroxide fire retardants;
- 150 million kilo of other fire retardants.

Halogenated fire retardants are still used on a very large scale, mainly because they have the least effect on the mechanical properties of the materials and are cost-effective. In many cases replacements of halogenated flame retardants have already been found. Some progresses were especially made in the field of phosphorous-nitrogen and metal hydroxide compounds. New compounds are developed and synergistic formulations are found that boost the performance. However, the mechanical properties of materials after FR addition ares till worse than the ones using halogenated flame retardants.

### 6.2.1 Mode of Actions

Flame retardant additives may have a mode of action in gas phase to extinguish the flame by radical inhibition or dilution, that leading to the decrease of the flame temperature or to reduce the availability of flammable gases and oxygen; and/or in condensed phase, in the vicinity of the flame to perturb the thermal degradation of the substrate by dehydration and char formation. Therefore, according to the chemical nature and the stage of the combustion process acting, the action modes can be classified into five categories, i.e. gas dilution involving the use of additives which decompose into non-flammable gases and lead to reduction of both fuel and oxygen levels; thermal quenching in which flame retardants reduce the rate of burning by endothermic decomposition; protective coating when the additives induce the formation of a barrier or a thermal shield; physical dilution with the incorporation of an inert and non-flammable component; and chemical interaction, when the flame retardant additive decomposes into radical species in competition with the burning process. The flame retardant compounds can be classified either according to their chemical structure or their mode of action to provide fire resistance. Flame-retardant materials are a major business for the chemical industry and can be found practically everywhere in modern society. However, many additives have detrimental effects on the environment and human health and thus should be limited in use.

## 6.2.2  Halogen-Containing Flame Retardants

The halogen-containing flame retardants, used in most of cases in combination with metal compounds, show a chemical action in gas phase, even if the condensed phase reactions with the polymer could be involved. These compounds are based on chlorine and bromine to react with flammable gases to significantly reduce the combustion rate by radical transfer. Thus, during the first step of the reaction, the halogen compounds interrupt the chain reaction of combustion by the release of halogen hydracids which transform the highly reactive radicals, $OH^•$ and $H^•$ by less reactive radicals. Thus, the effectiveness of halogen compounds depends mainly on the ease of release the halogen and on the nature of the group containing the halogen. To achieve good levels of flame retardancy, high concentrations, 40 wt% for chloride and 20 wt% for bromide, are required [5]. Therefore to reduce the halogen concentration and to enhance significantly flame retardant properties, several metal compounds such as metal oxide, could be used as synergists. Amongst these synergistic agents, antimony trioxide plays the role of an inhibitor in the gas phase, others common synergists are phosphorus, nitrogen, zinc and tin-containing compounds. Nevertheless, these compounds are less and less used since they release during their degradation toxic gases and corrosives as dioxins, benzofurans, HCl and HBr and they also present some environmental health hazards. Thus, some compounds such as brominated flame retardants have in effect been banned via the RoHS directive (2002/95/EC), but this does not imply that all other flame retardants are free from health and environmental concerns.

## 6.2.3  Inorganic Compounds

Amongst the four mains families of flame retardant chemicals, metal hydroxide compounds offer an attractive alternative to halogenated formulations lying in their low toxicity, corrosion properties and emission of smoke during processing and burning. Thus, these compounds decompose endothermically and release water, which reduce the heat and temperature from the substrate. Typical metal hydroxide flame retardants are aluminium trihydroxide, magnesium carbonate, magnesium hydroxide, zinc borate and calcium borate. Furthermore, as cited by Chen and Wang [6], $Al(OH)_3$ and $Mg(OH)_2$ are the most important metal hydroxides used as flame retardants in polymer materials and the effects of these compounds were found similar in the improvement of flame-retardant properties, even if $Al(OH)_3$ was superior by the cone calorimetric test. Besides, the nano-scale $Mg(OH)_2$ have better flame retardancy than micro-sized.

Inorganic compounds, as hydrates of aluminium and magnesium based on endothermic additives are used to slow down the rate of pyrolysis. They have rather low prices, low toxicities but high loading content is required to provide

the fire performances of interest [7–10], and therefore it results in the decrease of the mechanical properties of the polymer. This class of compounds acts simultaneously in gas and condensed phase, when their endothermic decomposition induces in one part the water release to cool down the system and to dilute fuels in the flame zone and in other part the forming a metal oxide barrier. Aluminium and magnesium hydroxide, which decompose thermally in the temperature range of 180–240 and 330–360 °C, respectively [11], are widely used as halogen free alternative to brominated flame retardants, as well as inorganic phosphorus. This inorganic group, containing also boron salts, inorganic antimony, tin, zinc and red phosphorus, represent around 50 % by volume of the global flame retardant production.

### 6.2.4  Charring and Intumescent Systems

Among the flame retardants for polymers, intumescent flame retardant (IFR) has been very carefully studied in recent years, since they represent an environmental friendly alternative to the traditional halogen-containing compounds. Even if intumescent systems have existed since the 1940s in paint industry, they have only appeared in the textile field market for about 30 years. Furthermore, IFR presents many advantages compared to halogen-containing flame retardants, such as less toxicity, less acidic fumes during the burning process [12]. Flame retarding textile substrate by intumescence process has been known for several years and is essentially a special case of a condensed phase mechanism [13–19]. Intumescent systems interrupt the self-sustained combustion of the polymer at the thermal degradation with evolution of gaseous fuels. And thus, the intumescence process results from a combination of charring and foaming of the surface, limiting heat and mass transfer between the gas and the condensed phases and the flame and the substrate [15]. Furthermore, the layer inhibits the evolution of volatile fuels via an entrapment process, which limits the oxygen diffusion to the polymer bulk [13]. Intumescent formulations contain three kind of active additives [20, 21], i.e. an acid source or precursor for catalytic acidic species which can be an acid (phosphoric, sulphuric, boric), ammonium salts (phosphates or polyphosphate, sulfates, halides), a phosphate of amine or amide (urea, melamine phosphate, …) or an organophosphorus compound as tricresyl phosphate, alkyl phosphate or haloalkyl phosphate; a carbonic or polyhydric source such as starch, dextrin, sorbitol, pentaerythritol or methylol melamine; and a blowing or spumific agent like urea, urea-formaldehyde resin, dicyandiamide, melamine or polyamide. The carbonic source additive is not necessary when the treated material has an intrinsic charring behavior as for example most of polyamides, polyurethanes and carbohydrate polymers (cellulose). Contrary to these polymers having intrinsic charring behavior, the presence of charring agent in IFR system is required for polyolefin as PP which is the most studied. The most widely reported IFR for replacing halogen-containing agent is phosphorus-nitrogen containing compounds. Thus, the IFR formulations

for PP include generally these kinds of system, i.e. ammonium polyphosphate—melamine-pentaerythritol [22]; ammonium polyphosphate—triazine compound, mixture of melamine phosphate with pentaerythritol [23] or their reaction products and these derivative compounds [24, 25] in addition with a charring polymer [26, 27]. However, these conventional intumescent flame retardant agents need to be improved and especially by the addition of synergistic agent such as zeolithe [28–30], montmorillonite [31, 32] or sepiolite [29], silicotungstic acid [33], metal oxide [34–37], silica or alumina [38], or in working condition to adjust the relative ratio of each component [39]. Furthermore, the high loading content of IFR additive leads to a decrease in the mechanical properties of the polymer, and most of the time these compounds being highly polar induce the problem of water leaching. Several authors reported the possibility to decrease the polarity and therefore to improve the compatibility with polypropylene by using reactive extrusion to synthesize melamine salt of pentaerythritol phosphate [40, 41].

Unfortunately, conventional IFR systems have presented some drawbacks. Acid sources and charring agents are globally hydrophilic chemicals. They have some problems such as moisture sensitivity and poor compatibility in polymer matrix in particularly in non-polar polymer like PP. Migration phenomenon could occur during the processing, the application or the ageing of the material. Thus, exudation and high water solubility are encountered problems, which lead to the loss of FR properties [15]. Moreover conventional IFR systems show efficiency only from 20 wt% loading. The minimum loading of IFR systems and the poor compatibility of their components induce homogeneity problems; create damage of the surface quality and decrease of mechanical properties for the final material. Finally, the necessity to have the three components of IFR system is not convenient for the industrial implement of final PP materials. These drawbacks make impossible the introduction of conventional IFR systems in the core of PP fiber by melt spinning process. Indeed, it is well-known that moreover the high level of fillers is incompatible and induces some problems during the drawing step. Thereby, the coating process still needs a possible way to apply IFR formulation on PP fabrics. However the loss of handle is one of disadvantage of this process without to solve problems of IFR systems.

The concept of microencapsulation is a way to solve the different drawbacks of conventional IFR systems. Microencapsulation is a process of enveloping microscopic amounts of matter (solid particles, droplets of liquids or gas bubbles) in a thin film of polymer which forms a solid wall (microcapsule) or inside a polymeric matrix (microsphere). These structures allow the isolation of the encapsulated substance from the immediate surroundings and thus protect it from any degrading factors such as water. Also the microencapsulation processes allow encapsulating acid source of IFR system and protects it from any degrading factors such as moisture. The polymeric membrane of microcapsule permits also to improve the compatibility of acid source in the materials and thus to keep FR and mechanical properties. Moreover, the polymeric matrix or membrane of microcapsules should be appropriately chosen in order to have the chemical characteristics of charring agent and/or blowing agent (polyurethane, aminoplast resin,

isocyanurate). Also, the combination of the encapsulated acid source and the microcapsule membrane with charring and/or blowing properties form an intrinsic IFR formulation. The concept to have "all in one system" makes easier the IFR incorporation system into polymeric matrix.

### 6.2.5 Nanocomposites

A material is considered as nanocomposite if nanofillers in the polymer matrix are uniformly dispersed in preserving its nanometric size (without agglomerate). Obtaining a real nanocomposite is not so easy despite the improvements of effective implementation technologies. The desired properties of the material are obtained only if the polymer matrix contains uniformly fillers remained nanoscale [42–52]. The properties of nanocomposite material are governed mainly by the dominance of the interfacial structure. Thus thermal and fire decomposition mechanisms of the nanocomposite are totally different from those of the polymer matrix alone. Under the stress of a fire, the presence of nanofillers generally used to delay the depolymerisation of the polymer and thus reduce the amount of released heat [48, 49]. Nanofillers most studied to improve the fire behavior of almost all conventional polymers are clays (natural or synthetic), carbon nanotubes and nanofibers. In the case of clay, it appears that the viscosity of the molten polymer is larger and the pyrolysis of the polymer is hindered by the formation of a clay-rich layer which acts as a barrier to fuel [53, 54]. With carbon nanotubes or nanofibers, there is the formation of a network of nanoparticles which also allows the molten polymer to viscosity and reduce the gas release [55, 56]. The nanofiller may be associated 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 [48, 49].

## 6.3  Flame Retardancy of Textile

The fire behavior of a fabric largely depends on the chemical nature of the fibers that compose it. Also the same major flame retardant products for polymeric materials in general are found in textiles. However, textile materials have several characteristics. Regarding their fire behavior, textiles generally exhibit large specific surface and ease of access to atmospheric oxygen which causes a faster ignition compared to a full plastic material. Their physical characteristics (surface area and linear aspect of fiber/yarn) and their specifications (washability), application techniques of fire retardant products for textile materials are very diverse and differ from plastic materials. This part shows the outline of the burning behavior of textiles [57, 58] and their products fire retardant [2, 3, 57] that have already the subject of many reviews.

### 6.3.1 Burning Behavior and Fire Hazard of Textile

The burning behavior of fibers is influenced by thermal transition temperatures and thermodynamics parameters. Table 6.1 lists the commonly available fibers with their ignition temperature and the behavior when approaching a flame.

It is recognized that fiber is flammable if its ignition temperature is low and its flame is hot. This is particularly true for cellulose fibers and some synthetic fibers like acrylic. LOI (Limiting Oxygen Index) of common fibers is also given in the Table 6.1. LOI is the minimum concentration of oxygen in order to insure the combustion of the matter. Knowing that the concentration of oxygen in air is 20.8 %, the fibers with a LOI less than or equal to 21 % ignite easily and burn quickly. From 26 %, the fibers have typically flame retardant behavior and textiles from these fibers pass most of the fire tests. It should be noted that the cellulose fibers, wool and nylon are naturally charring contrary to polypropylene and polyester. This difference in thermal degradation was key strategies to improve the fire performance of these fibers. For the former, fire retardant products have the primary role to emphasize the char formation to reduce the release of fuel. For the latter, the flame inhibitor products (action in phase) were selected: their action is coordinated to the fact that these fibers by melting flee the fire that does not spread to the rest textile. Textiles without fire retardant treatment have several specific risks with respect to the fire, especially if the fabric is in direct contact with humans (clothing, furniture). As indicated in Table 6.1, of these dangers, we

**Table 6.1** Ignition temperature, limiting oxygen index and flammability of commonly used fibers [57, 58]

| Fiber | Ignit. temp. (°C) | LOI (%) | Flammability |
| --- | --- | --- | --- |
| Wool | 600 | 25 | Supports combustion with difficulty |
| Cotton | 350 | 18.4 | Burns readily with char formation and afterglow |
| Viscose | 420 | 18.9 | Burns readily with char formation and afterglow |
| Nylon 6 | 450 | 20–21.5 | Melts, supports combustion with difficulty |
| Nylon 6.6 | 530 | 20–21.5 | Melts, does not readily support combustion |
| Polyester | 480 | 20–21 | Burns readily with melting and soot |
| Acrylic | >250 | 18.2 | Burns readily with melting and sputtering |
| Polypropylene | 550 | 18.6 | Burns slowly |
| Modacrylic | 690 | 29–30 | Melts, burns very slowly |
| Polyvinyl chloride | 450 | 37–39 | Does not support combustion |
| p-aramid (e.g. Kevlar) | >550 | 29 | Self-extinguishing |
| Polybenzimidazole (PBI) | >450 | 40–42 | Incombustible |

**Table 6.2** Smoke emission from fabrics made from different fibers or blends [57]

| Sample | Decrease in visibility (%) | Optical density |
|---|---|---|
| Acrylic | 97 | 1.5 |
| Cotton | 4 | 0.02 |
| Cotton, flame-resist treated | 98 | 1.7 |
| Rayon | 4 | 0.02 |
| Wool | 18 | 0.09 |
| Nylon | 6 | 0.03 |
| Polyester | 28 | 0.14 |
| 65 % polyester—35 % cotton | 99 | 2.00 |
| 55 % polyester—45 % wool | 98 | 1.70 |
| Polyvinyl chloride | 34 | 0.18 |

should note the risk of falling melt matter inflamed or not causing direct burns and also the spread of fire. This is the case of textiles base only conventional flammable synthetic fibers.

Like all types of materials, the burning behavior of textiles depends on many external factors (nature, duration and placement of ignition, material orientation, ventilation …). Apart from the nature of the fibers used, some physical characteristics of the textile also play a role in fire behavior. Thus, a fabric with a low surface density (open structure) increases the burning rate [59]. Other parameters as effect of yarn geometry and fabric structure have an influence less obvious on flame behavior.

The leading cause of death in a fire is smoke on the one hand by its opacity generating panic and disorientation and secondly by its toxicity [60]. Table 6.2 provides an indication of the amount of smoke released by fabrics made of different fibers or blends. Aliphatic polymers are those which release less smoke the same when they have heteroatoms (cotton, nylon, wool). Furthermore, the quantities of smoke released by fabrics from fiber blends are very difficult to predict. Indeed both polyester/wool and polyester/cotton blends release a much greater amount of smoke than the fibers alone. Finally, the presence of fire retardant in a material usually leads to a larger amount of smoke either by inhibition of the oxidation reaction generating incomplete combustion (fire retardant agent acting in the gas phase such as those based on halogen) or by reduction of the heat flux that the flaming combustion turns at time into smoldering.

### 6.3.2  Flammability Testing of Textiles

The fire standards for textiles are extremely numerous, not only because each country has its own regulation, but also because the textile fire standards are moreover available by sectors and end-use applications (curtains, nightwear, protective

clothing, furnishing, bedding, aircraft seats, railway seat…). Most common textile flammability tests are currently based on ease of ignition and/or burning rate behavior which permit to compare easily fabrics and composites in varying geometries. These fire tests use as a source of ignition "small" flame, and among these the most emblematic tests is the vertical test or equivalent (ISO 6940). Specific tests to the final application (bedding, furniture) refer to sources of ignition (match and cigarette) present in the actual conditions of use of textiles. However, it is widely accepted that in actual fire conditions, the most critical feature in propensity to fire spread is the heat released rate of the material. Only textiles used in building materials, aircraft and transport interiors and seating are required to have minimal levels of heat release rate (HRR, peak of heat release rate PHRR), which is measured mainly by cone calorimeter [61].

### 6.3.3 Flame Retarding Systems for Textile

Flame retarding systems for textiles are divided into three main groups: (i) Nonreactive systems; (ii) Reactive system; (iii) Inherently FR fiber. For the first two groups, the FR system is applied to the textile substrate (woven, knitted, nonwoven). Currently available commercial FR reactive and nonreactive treatments are listed in Table 6.3. In the case of nonreactive systems, there is no chemical reaction between the FR agent and the fiber. Several processes are within this category. With conventional finishes by padding, by spraying or by exhaustion from bath, the FR agent is deposited on the surface of fabrics (cohesion by Van der Waals forces). The durability of the treatment is often improved either with insolubilisation of FR agent or with the addition of a binder (resin). There is also for specific applications (furniture, transport, technical textiles), the deposition of a coating or back-coating (mainly acrylics, silicone or polyurethane) containing FR agent on the fabric. In reactive systems, the processes need advanced requirements (e.g. ammonia gas cure unit). The FR treatment is obtained with chemical reactions from FR agent; either FR agent and fiber react together with covalent link (graft copolymerization of FR with fiber) or there is in situ polymerization of FR compounds on the surface of the fiber. The reactive treatments are intended to be durable, i.e. that the fire retardant properties are retained beyond 50 washes. In the third group, we find man-made inherently FR fibers which may be derived from various techniques. The FR agent could be directly incorporating in fiber during spinning process. Otherwise the fiber could be produced by copolymerization of FR compounds with fiber-forming monomers. The last case concerns advanced spinning processes with thermostable aromatic polymers (Polyarmids, e.g.: Nomex, Kevlar, Twaron; Poly(aramid-arimid), e.g.: Kermel; Novoloid, e.g.: Kynol; Polybenzimidazole, e.g.: PBI; Carbonized acrylics, e.g.: Panox). The Table 6.4 gives the currently inherently FR man-made fibers (except thermostable aromatic fibers).

**Table 6.3**  Principal examples of currently available FR treatments for textiles [3]

| Substrate textile fiber(s) | Generic formula | Comments |
|---|---|---|
| Cellulose (cotton, viscose and cotton-rich blends) | | |
| *Non-durable* | Ammonium phosphates and mixtures with other salts; ammonium polyphosphate; organic N- and P-containing compounds; bore derivatives (Borax) | Available as proprietary formulations; semi-durability may be developed by post-curing to achieve cellulose phosphorylation or by addition of resins |
| *Durable* | Tetrakis (hydroxymethyl) phosphonium salt (THPX) adduct condensates N-methylol and N,N′-dimethyloldialkylp hosphonopropionamides and derivatives | Typified by the ammonia-cured Proban® (Solvay) Exemplified by Pyrovatex® (Huntsman) its variations and equivalents. Requires presence of cross-linking resins |
| Back-coatings (application to most textile substrates) | Halogen-organic antimony III oxide (ATO) formulations Intumescent-based systems | Durability is determined by resin choice |
| Wool durable to dry cleaning | Zirconium and titanium hexafluoride complexes Tetrabromophthalic anhydride (TBPA) | Typified by Zirpro® |
| Polyester: durable | Cyclic organophosphonate | Amgard CT (Rhodia) applied by thermofixation |
| Polyamide: durable | N- and S-containing polycondensates typically based on thiourea-formaldehyde formulations | Find application in technical fabrics |
| Acrylics and multifiber blends and composites (e.g. furnishing fabrics) | Back-coatings based on halogen-ATO formulations | The only commercial alternatives to using modacrylic fibers, e.g. Kanecaron |

**Table 6.4**  Inherently FR man-made fibers currently in use [3]

| Fiber | Additive or comonomer | Comments |
|---|---|---|
| Viscose rayon | Cyclodithiophosphoric-anhydre additive | Developed in the 1970s now available as Exolit 5060 PK (Clariant) Lenzing FR® |
| Modacrylic | 15–65 % vinylidene (or vinyl) chloride | Developed in the 1950s and still produced in Japan (Kanecaron) |
| Polyester | Difunctionalphosphinic acid or ester | Developed in the 1970s as Trevira CS®: the most established inherently FR polyester |
| Polypropylene | Halogen—organic synergist (ATO or tin derivatives) formulations | Recent developments of hindered amine chemistry enable single halogen-organics to be used |

The currently FR treatments and fibers come from the chemistry between 1950 and 1980. The commercial development is completely linked to changes in legislation and regulations. The evolution of these treatments and fibers has been guided by the desire to achieve better performance (fire resistance, durability) for an ever lower cost. However it is the environmental and toxicological aspects past 20 years have been responsible for banning certain products (brominated) or certain processes (release of formaldehyde or acrylamide). Thus research continues to find improvements and alternatives.

For cellulosics, the durable reactive systems with real advantages (durability even for high temperature wash cycles as in hospital) keep significant drawbacks namely on the one hand for Proban® (and derivatives) special requirement (ammonia gas cure unit) and loss in softness for the fabrics, and on the other hand for Pyrovatex® (and derivatives) losses in tensile/tear strengths and formaldehyde release during application and end-use. Despite several recent attempts [62–67], development of a reactive FR species remains a challenge where the covalent bonds with cellulose are done with easy textile processing and are resistant to hydrolysis.

Even if halogen—organic antimony III oxide still the usual formulation for back-coating, environmental concerns encourage to phosphorus-nitrogen containing species (including intumescence formulation). However, formulations with the latter need to be improved to reach in one hand the same efficiency (e.g. by obtaining FR vapor-phase activity [68]) and in other hand the same durability (reduction solubility [69]).

Several sectors including railways need more and more barrier fire resistant fabrics even when they are composed of melt fusible fibers as polyester or polypropylene. To meet this need without necessarily recourse to back-coating, attempts to develop char-promoting retardants for these fibers has been made [70–73].

Among alternatives in order to pass these different challenges, nanotechnology offers opportunities which are developed following.

## 6.4 Strategies with Nanocomposite Principle and Their Fire Properties for Textiles

Textile functionalization by material modification can be obtained following three main ways, i.e. (i) incorporation of functional additives into the polymer melt or polymer solution before spinning; (ii) chemical grafting of additives on the fiber surface with or without using linkers; and (iii) formation of a coating onto the surface of fiber or fabric. Each process has some advantages and drawbacks and the choice depends not only on the chemical nature of the substrate but also on the permanence of the treatment and the end use of the textile. Thus, spinning offers high permanence but is not practicable to natural fiber, chemical grafting requires

the presence of reactive or functional chemical groups onto the surface of the substrate; and coating, the most universal method, is independent from textile type, low amount of additives can be used and this technique allows the combination of different functionalities [74].

## 6.4.1  Spinning Processes

### 6.4.1.1  Polyolefins

As the polyamide, the polypropylene (PP) is one of the most widely used polymers in the textile field. Indeed, this polyolefin exhibits an attractive combination of low cost, low weight, easy processing, and extraordinary versatility in terms of properties (it is known for its balance of strength, modulus and chemical resistance). However, PP presents a high flammability because of its wholly aliphatic hydrocarbon structures. In the last decades, many studies were carried out to improve its flame retardancy by adding different species of nanofillers into the polymer before the spinning process.

The most frequently used nanoparticle, i.e.: layered silicates, was also investigated to enhance the flame retardancy properties of polypropylene textile articles. For example, Horrocks and co-workers evaluated by cone calorimetry the flammability of PP fabrics containing different concentrations of maleic-anhydride grafted PP and montmorillonite clay modified with dimethyl, dihydrogenated tallow quaternary ammonium Chloride (Cloisite® 20A, Southern Clay Products) [75]. Although an evident char formation in samples containing clay was seen, no clear flame retardancy properties were conferred to the PP samples. This research team continued these works by studying the impact of four different functionalized clays (tree montmorillonite clays supplied by Southern Clay Products: Cloisite® 20A, Cloisite® 30B, a montmorillonite later modified with vinyltriphenylphosphonum bromide and a bentonite clay from Elementis: Bentone 107) in the presence or absence of two types of grafted PP as well as with or without conventional phosphorous flame retardant: ammonium polyphosphate (APP, Albemarle Corporation) [76]. Due to the difficulty to obtain accurate reproducible results from thin fabrics with cone calorimeter, they performed a small scale spread test based on British Standard BS 5438. These experiments demonstrated again a change of the burning behavior in presence of clay. Whatever the clay introduced into the PP with or without compatibilizing agent, a trend of self-extinction was noticed. However, in the presence of APP, burning behavior became more erratic with no significant improvement, which reveals the absence of synergy between this fire retardant additive and clays. Apart the combination of nanofillers with conventional flame retardants, others potential synergistic associations can be imagined. Thus, based on the works of Peeterbroeck et al. [77], who showed a superior decrease of HRR for ethylene vinyl acetate containing simultaneously carbon nanotubes and clay, we studied as potential synergy the use of clay with

another carbonaceous filler, i.e.: graphite [78]. Polypropylene composites reinforced with Cloisite® 15A and/or graphite were prepared by melt blending from which multifilament yarns and knitted fabrics were produced. Despite a slight synergistic thermal effect between clay and graphite was shown from the curves of weight difference extracted from TGA experiments, no reduction in PHRR values occurred for samples containing the both fillers during mass loss calorimeter test under a heat flux of 35 kW/m$^2$.

About the use of synthetic clay i.e. polysilsesquioxanes (POSS) in PP, the latter appears not sufficient to obtain performance required in several fields of application, even if, the authors have observed some improvements in fire behavior [79]. Bourbigot et al. showed that the time to ignition of PP knitted fabric filled with FQ-POSS nanoparticles (poly(vinylsilesquioxane), Hybrid Plastics) was delayed about 50 s compared to that of virgin PP [80]. However, apart a translation of the HRR curve recorded during cone calorimeter experiment under a heat flux of 35 kW/m$^2$, no significant modification in terms of PHRR or total heat release (THR) was noticed which reveals this nanofiller act more as heat stabilizer than as flame retardant.

It is well recognized that filler geometry may play an important role on the final properties of nanocomposites fibers. Thus, in our laboratory, we were interested to fillers having fiber-like shape (carbon nanotube, sepiolite) rather than layered form such as montmorillonite, bentonite, graphite, etc. Thus, it was highlighted that the introduction of 1 wt% of multiwalled carbon nanotubes allows to increase the thermal stability and to decrease of 50 % the HRR peak of PP knitted fabrics if examined by cone calorimeter with a heat flux at 35 kW/m$^2$ [81]. However, the time to ignition decreased from 59 to 38 s for PP fabrics containing carbon nanotubes. Two reasons were proposed to explain this behavior. The first explanation was attributed to a fibrillation of the nanocomposite multifilament during the process of knitting. Indeed, the fibrils that appear at the surface of the samples can facilitate the ignition. The second one can be due to an increase in the radiation in-depth absorption coefficient induced by the addition of fillers. We again demonstrated a similar reduction of the time to ignition with polypropylene knitted fabrics filled with 0.75 wt% of modified and non-modified carbon nanotubes, without providing nevertheless a decrease of HRR [82]. In the same study, mass loss calorimeter measurements were made on PP knitted fabrics containing 0.75 wt% of functionalized sepiolite exposed to an external heat flux of 35 kW/m$^2$. Nanocomposite fabrics exhibited a decrease of about 20 % of PHRR compared with unfilled PP. Therefore, we explained this reduction by the formation of char when knitted fabrics are burnt. However, we assumed that the char was not enough to insulate the material because the THR recorded for samples with or without sepiolite was comparable.

Apart from clays such as montmorillonite, bentonite, sepiolite and carbonaceous fillers such as graphite or carbon nanotubes, other nanoparticles were introduced into PP fibers to improve their fire properties. Thus, we investigated the fire

behavior modification of PP knitted fabrics containing manganese oxides (MnO or $Mn_2O_3$) or manganese oxalate ($MnC_2O_4$) [83], while Dogan and co-workers studied by MCC the flame retardant properties of PP fibers filled with $BPO_4$ [84]. Despite the promising results achieved by these researchers for PA6 fibers containing $BPO_4$, no decrease of the PHRR or THR was seen this time for PP. The same results were obtained for PP fabrics filled with based manganese nanoparticles. In the both cases, this behavior is attributed to the absence of char formation. The aforementioned nanoparticles are not able to form a continuous shield able to protect the polymer which explains why no reduction is observed for these PP composites. The flame retardancy behavior of polypropylene/nano-$SiO_2$ composite textile filament was also investigated by Erdem et al. [85]. In this later study, the combustibility of fibers samples containing 0.3, 1 or 3 wt% of $SiO_2$ spherical nanoparticles were determined by Limit Oxygen Index (LOI) test. The authors showed that the LOI of the neat filament was about 18 % and the LOI of PP composite filaments didn't exceed 18 %, whatever the content of $SiO_2$ nanoparticles. From these experiments, it can be concluded that none of the sample reached the requirement of fire-retardant filament.

The development of fire retardant polyolefin nanocomposite fiber was undoubtedly focused on the polypropylene. However, little is known about the effects of nanoparticles on the fire properties of polyethylene fibers. Zhang et al. undertook the preparation of ultrahigh molecular weight polyethylene (UHMWPE) nanocomposite fibers by a gel-spinning process [86]. First of all, they incorporated magnesium hydroxide ($Mg(OH)_2$) nanoparticles into the polymer by dissolving UHMWPE powder in an homogeneous suspension of nanoparticle and solvent (Decalin: decahydronaphthalene, trans + cis, 98 %). Then, the polymer solutions were extruded with the help of pressurized nitrogen through an orifice of a spinneret. Finally, the filament was quenched into ice water batch to form precursor gel fiber which was subsequently hot-drawn. In order to have a better understanding of the flame retardant mechanism of $Mg(OH)_2$ nanoparticles for the UHMWPE nanocomposite fiber, the authors proposed to monitor the flaming process from thermogravimetric (TGA) and differential thermal analyses (DTA). The TGA results showed a higher thermal stability when nanoparticles are added to the polymer. Indeed, the starting decomposition temperature was increased by 30 °C and a considerable amount of residue was noticed for nanocomposite fiber. Concerning the analysis of the DTA curves the authors concluded that $Mg(OH)_2$ could act as shield to heat and oxygen because of the shift toward higher temperature of the oxidative as well as combustion exothermic peak. They referred to conventional mechanism and mode of action of metal hydroxides, i.e.: these species decompose under the form of metallic oxide at high temperature, release water and thus reduce the heat and the temperature from the material and dilute the concentration of flammable vapor and oxygen. Based on these results, they assumed that the flammability of the UHMWPE fiber can be largely reduced.

### 6.4.1.2 Polyamides

For the first time the fire behavior of a knitted structure made with nanocomposites multifilament yarn (80 monofilaments) was investigated in our laboratory [87]. To do this, multifilament yarn was produced by melt-spinning a compound of polyamide 6 (PA6) filled with an organo-modified clay (Cloisite® 30B, Southern Clay Products). The fire properties of textile fabrics having an area density of 1,020 g/$m^2$ and thickness 2.5 mm were evaluated with a cone calorimeter under a heat flux of 35 kW/$m^2$. It was first seen that the ignition of the nanocomposite material starts 50 s before the virgin material. Furthermore, although the values of total heat release (THR) was not specified, it can be estimated by comparing the non-common areas under the HRR curves recorded during the experiments that PA6 nanocomposite has more or less an equivalent THR to that of PA6. However, other promising results suggesting a modification of the burning behavior were obtained for nanocomposite fabric. Indeed, a sharply decrease of the volume of smoke production as well as the carbon monoxide or carbon dioxide generated during the combustion were measured. A decrease about 40 % of the peak of heat release rate in comparison of pure PA6 was also recorded in presence of clay. Moreover, a better char layer (more uniform and without holes) was also observed for PA6 nanocomposite fabric. This higher char formation was also achieved by McCord et al. during burn tests conducted on polyamide 6 and polyamide 12 filaments containing clay [88]. Various parameters involved in the formation of this protective char layer were also studied by Shanmuganthan et al. [89]. PA6/organoclay nanocomposite fibers were also prepared by spinning melt-pre-compounded PA6 with 8 wt% of montmorillonite modified with methyl dihydroxyethyl hydrogenated tallow ammonium. Then, single jersey fabrics were produced with a thickness less than 1 mm and different tightness factor by using drawn or undrawn multifilament yarns (26 monofilaments) and different stitch density on a circular knitting machine. Horizontal flame spread test and cone calorimeter experiments were performed to determine the impact of this nanofiller on the combustion of PA6 fabrics. The authors concluded that the inclusion of clays and fabric tightness factor play crucial roles in flame-retardancy behavior. Indeed, from the first method of characterization, they noticed that nanocomposite fabrics exhibited a decrease of dripping for those with low tightness factor and even an elimination of drops for those with high tightness factor. However, the ignition and the flame spreading are not significantly modified by the presence of clay. Various observations were made during the cone calorimeter experiments under a heat flux of 35 kW/$m^2$. First of all, a significant decrease of HRR (28 and 40 %) was noticed for samples containing montmorillonite. This trend was also more pronounced for knitting fabrics with higher tightness factor. Furthermore, due to the delay of mass loss, the authors pointed out the role of clay in the formation of a surface char able to create a mass barrier.

Apart the use of layered silicate to develop PA6 nanocomposite fibers, some works from Dogan and Bayramli were performed to introduce boron phosphate (BPO$_4$) nanoparticles into PA6 [84]. Two different contents of BPO$_4$ (3 and 10 wt%)

were mixed with the polymer in a twin screw extruder. The monofilaments obtained were then drawn with a winding unit and their mechanical, thermal and fire properties were characterized. Based on the micro combustion calorimeter results, it can be concluded that the addition of these nanoparticles changes very slightly the PHRR as well as the THR. Indeed, the reduction doesn't exceed 12 and 9 % for each parameter respectively.

Recently, there were some studies made on the production of fire retardant PA6 nanocomposite fibers by dispersing clay into appropriate solvent and by using electrospinning device. Thus, Cai et al. have produced PA6 electrospun nanofiber loaded with 4 wt% of Fe-montmorillonite which were subjected to thermogravimetric analyses (TGA) as well as carbonization experiment by using a tube-furnace in order to study the catalyzing carbonization effect of the filler on the matrix [90]. The collected results showed an increase of charring capacity in presence of clay at the end of TGA under nitrogen. This improvement of the thermal stability of PA6 fibers is assumed by Cai and co-workers to be a consequence of different mechanisms. On one hand, they reported that some transition metal as well as degradation products coming from the decomposition of alkylammonium cations in organo-modified montmorillonite following the Hofmann elimination reaction could promote an increase of molecular crosslinking. On other hand, they suggested that the clay layers play a key role in the formation of a charred ceramic surface which confines the pyrolysis products derived from polymer chain scission and lead finally to their graphitization. This presence of graphite sheets in the residue has been confirmed by X-ray diffraction, high resolution transmission electron microscopy, selected-area electron diffraction and laser raman spectroscopy. In a parallel publication, this research team has characterized respectively by TGA and Micro Combustion Calorimeter (MCC) the thermal stability and the flammability behavior of such PA6/organic-modified Fe-montmorillonite nanofiber as well as same fibers coated by silicon nanoparticles [91]. As seen for fibers filled with nanoclay, the TGA results revealed an improvement of the thermal stability of the coated nanocomposite fibers. One again, this better property was attributed by researchers to the aforementioned mechanisms (protective barriers of silicate clay layers, catalysis effect of $Fe^{3+}$, etc.). In the case of coated nanocomposite fibers, the authors also proposed an additional mechanism to explain this increased thermal stability. The improvement of charring ability was assigned to the silicon dioxide generated by hydrolysis of tetrachloride silicone resulting from the reaction between metal halide and silicon. In MCC experiments, nanocomposites fibers with 4 wt% of Fe-montmorillonite exhibited shorter time to ignition and higher initial heat release rate than unfilled fibers. This could be due to the thermal degradation of cationic surfactants of the clay. Furthermore, fibers containing montmorillonite have a reduced peak of heat release rate compared with pure or coated PA6 (~15–19 % less). The combination of clay and silicon nanoparticles reduces this value by 25 % in comparison of virgin polymer. This improved flame retardant function was attributed to the in situ generated silicon dioxide, barrier effects of silicate clay and the synergistic effects between the clay and silicon. Other synergisms between different nanoparticles or flame retardant additives were also

highlighted [92–96]. Wu showed for example that non-halogenated flame retardant additive (Exolit® OP1312, Clariant Ltd) and natural montmorillonite modified with a quaternary ammonium salt (Cloisite® 30B, Southern Clay Products) could effectively improve flame retardant properties of the material in fiber form as well as in bulk form. Thus, electrospun formulation with 2.5 wt% of montmorillonite and 10 wt% of flame retardant additive achieved a significant decrease in heat release capacity (more than 15 %) during MCC experiments. In other recent work, electrospun polyamide/boric acid nanocomposite fibers were used to confer flame-retarding property to textile material [97]. In this study, Selvakumar and co-workers showed that cotton fabrics coated with PA6 nanoweb containing different level of nanoparticles had a higher fire-spreading time and could have a 38 % increase in char formation as demonstrated by TGA.

### 6.4.1.3 Polyesters

To the best of our knowledge, the first developments of fire retardant polyester based nanocomposite fibers were published by members of our research laboratory. Thus, Solarski and co-workers introduced up to 4 wt% of Cloisite® 30B by melt blending into polylactide matrix before the spinning of these compounds to produce multifilaments yarns. After this, the yarns were used to knit textile surfaces (surface weight of 1,000 g/m$^2$ and thickness of 3 mm) which were subjected to cone calorimeter test at 35 kW/m$^2$. From these experiments, it can be concluded that this organo-modified clay modified the burning behavior of polylactid fabrics and encouraged some char formation. Indeed, an increase char yields as well as a strong decrease of the PHRR was recorded. However, although only 2 wt% of this layered silicate was enough to reduce the PHRR, it didn't prevent a reduction of the time to ignition as mentioned in previous study made on PA6 [87]. In subsequent work, by adopting the same protocol the authors evaluated another clay nanoparticle, i.e.: bentonite (Bentone 104, Elementis Specialties) [98]. An analysis of these two studies supports the same conclusions, i.e.: a reduction of time to ignition and of the PHRR. Nevertheless, it appears also the bentonite is more effective in reducing the PHRR. Indeed, the maximal values of HRR are 163 and 143 kW/m$^2$ for PLA knitted fabrics containing respectively 2 wt% of C30B and 4 wt% of bentone 104, which represents a reduction of 38 and 46 % compared to unfilled PLA fabric. Furthermore, although the THR values were not mentioned in these papers, it is obvious that the addition of C30B or bentone 104 allows a clear diminution of this parameter. Other work on the use of clay for developing effective flame retardant polyester fiber was made by Teli and Kale [99]. In this study, PET nanocomposite fibers were spun by adding master batches of linear low-density polyethylene (LLDPE) loaded with Montmorillonite (MMT) nanoclay after compatibilizing the PET and LLDPE. Given the LOI results obtained on PET/nanoclay composite made from compression molding of PET fibers, it can be suggested that the sample is flame retardant. Indeed, the LOI value increased continuously from about 20 % for neat sample

to 27 % for sample containing 2 wt% of nanoclay. LOI tests were also made after the dyeing of nancomposite fibers and a slight decrease of the different recorded values was observed and attributed to the leaching of the nanofiller present on the surface of the fiber during the finishing process.

As mentioned in different works, the research of synergy between additives seems to be an interesting way to improve the fire resistance of textiles based on polymers. Thus, recent works were done by our co-workers on fibrous materials containing a mix of phosphorous-containing additives (Exolit OP1230, Clariant) and two different POSS (OM-POSS: OctaMethyl POSS and DP-POSS: DodecaPhenyl POSS) [100]. Fire properties of knitted fabrics (area density of 1,300 g/m$^2$ and thickness 2 mm) made from multifilaments yarns produced by melt spinning various formulations of PET filled with POSS and Exolit OP1230 were characterized by UL-94. According to the results, the neat PET specimen failed due to a complete burning and the fall flaming particles whereas all knitted fabrics made with nanocomposite filaments passed successfully this fire test. Indeed, they were classified V-2, whether the sample containing 10 wt% of aluminium phosphinate or samples loaded with 9 wt% of POSS (OM-POSS or DP-POSS) and 1 wt% of phosphorous additive. The major difference of unfilled and filled sample is that the later showed a high reduction of the dripping. In order to have more details on the combustion, cone calorimeter experiments were performed on a superposition of three knitted fabrics under an external heat flux of 25 kW/m$^2$. The introduction of aluminium phosphinate leads to a relevant effect on the flame retardant properties of the PET. It is pointed out by an increase of the time to ignition from 363 to 586 s for PET and PET containing 10 wt% of Exolit OP1230. However, no significant modification of the PHRR and THR was observed when this phosphorous specie was added alone. This was totally different when 1 wt% of POSS was introduced in combination with 9 wt% of aluminium phosphinate. High decreases of PHRR and THR were recorded whatever the kind of POSS. Nevertheless, the strongest reductions in term of PHRR (49 %) and THR (38 %) were observed for OM-POSS. The authors assumed that is due to an early development of an intumescent shield. In a subsequent work, they investigated the effect of introducing another kind of phosphinate, i.e.: zinc phosphinate (Exolit OP950, Clariant) with OM-POSS [101]. Contrary to the results obtained with the aluminium phosphinate, the addition of 10 wt% of zinc phosphinate decreased significantly the PHRR (43 %) and the THR (46 %), whereas a substitution of 1 wt% of phosphinate by 1 wt% of OM-POSS didn't confer superior fire retardant properties but acted negatively on the burning behavior as indicated by a higher PHRR than fabrics containing only zinc phosphinate. Although, this study revealed that zinc-phosphinate and OM-POSS were bad candidates to create a synergy able to decrease the heat evolved during a fire, it seems that they form a good pair to decrease the toxicity and the release of fumes. Analogous studies on the combined use of metal phosphinate and clay were carried out respectively by Alongi [102] and Dogan et al. [103]. In the first publication, cone calorimeter experiments made on fabrics produced with filaments containing 0.5 wt% inorganic content revealed that the combination of zinc phosphinate and

organo-modified sepiolite is very effective in decreasing the PHRR (42 %) without affect negatively the time to ignition. Furthermore, noticeable improvement of the LOI was detected (from 22 % for neat PET to 31 % for PET filled with zinc phosphinate/sepiolite system). Based on these two characterizations, it also appears that the PET textile fabric developed with these functionalized nanoparticles and phosphinate is more interesting than the commercial fire retarded PET textile evaluated. In the later publication, Dogan and co-workers observed also during MCC test a high decrease of PHRR (62 %) in presence of zinc phosphinate (Exolit OP950, Clariant) and clay (Cloisite30B, Southern Clay Products). However, this reduction is not accompanied by a decrease of THR. Thus, the authors have drawn similar conclusions to those of previous studies which mentioned that the barrier structure created with plate-like nanoclays is able to slow down the escape of the flammable volatiles generated during combustion without allowing the creation of an "impermeable shield".

In recent works, other nanoparticles were investigated in order to improve the flame retardancy of PET. Thus, Cai et al. developed ultrafine composite fibers consisting of lauric acid (LA), PET, and silica nanoparticles via electrospinning [104]. The combustion properties of composite fibers with varied amounts of nano-$SiO_2$ were characterized by MCC. The collected results showed that the heat resistance effect and/or barrier property generated by nano-$SiO_2$ resulted in an increase of initial combustion temperature and a decrease of the heat release rate for the electrospun ultrafine composite fibers. Meanwhile, Alongi and Frache reported the compounding of PET with carbon-nanofiber [105] and expandable graphite (EG) with various montmorillonite (unmodified Cloisite® NA, Cloisite® 10A and Cloisite® 30B, Southern Clay Products) [106]. For these two studies, as the study on the synergy between zinc phosphinate and POSS nanoparticles [102], they produced filaments (173.5 dTex/f48) by melt spinning, knitted textile fabrics (152 g/m$^2$) and evaluated their combustion by cone calorimetry under a heat flux of 35 kW/m$^2$. The cone data from the fabrics showed that the time to ignition was never improved when nanoparticles were added. It can also be noticed that PHRR values were almost the same for samples containing zinc phosphinate/clay combination (PHRR = 292 ± 15 kW/m$^2$) and those filled with 0.5 wt% of carbon nanofiber (PHRR = 288 ± 31 kW/m$^2$ or 282 ± 28 kW/m$^2$ depending of the purity of nanofiber). Regarding all the results, the highest reductions of PHRR were obtained for knitted fabrics with lower content filler in clay and expandable graphite (EG), i.e.: with 0.25 wt% of unmodified cloisite (58 % reduction) or 0.25 wt% of EG (82 % reduction). In this latter study, it can also be highlighted that the synergy observed between EG and cloisite in bulk PET was not shown for PET in fibrous form.

### 6.4.1.4  Other Fibers

Among the research conducted on the development of nanocomposite fibers based on polymers other than polyolefins, polyamides and polyesters, it may

be first mentioned the work done by Horrocks et al. on polyacrylonitrile [107]. In this study, they incorporated nanoclay (various nanoparticles supplied by Southern Clay Products) either during the polymerization of the acrylic monomers or directly during a blending with a commercial polymer solution. After that, the composite polymer samples prepared from polymerization or from the commercial formulation were spun via a conventional wet-spun process. All filaments produced were collected as continuous tows and kept wet by using water before to place them in a soluble APP product (Antiblaze LR2, Rhodia Consumer Specialties). From the various experiments, the researchers showed the ability of filaments to absorb water-soluble flame retardant. Furthermore, a synergy between phyllosilicate clay and an ammonium polyphosphate was clearly demonstrated by LOI characterizations and calculation of $\Delta LOI_{nano(corr)}$, which relate only to the effect of the clay. Thus, the authors demonstrated an increase of 4.2 of this LOI value when 1 wt% of clay was added and concluded that the use of clay is an interesting way to decrease the content of flame retardant while keeping the same degree of flame retardancy. However, they noted one last challenge, which is how to avoid the removal of APP during washing.

Due to the specific properties of nanofibers and their uses in wide technical applications, some studies dedicated to the improvement of their fire properties can be found in the literature. Thus, Cai et al. investigated by MCC the effect of $FeCl_3$ on the combustion property of polyacrylonitrile nanocomposite fibers prepared by electrospinning [108]. Based on these tests, it was found that the addition of $FeCl_3$ induced the macroradicals recombination and intermolecular crosslinking via gas-phase flame retardant mechanism, and decreased distinctly the PHRR, which contributed to the improved combustion property of composite nanofibers. Other studies reported better flame retardation of nanofibers containing various layered silicate. Wang et al. showed by TGA an increase of char formation and consequently a potential flammability reduction when a montmorillonite or a synthetic, layered magnesium silicate was added to fibers of poly(MMA-co-MMA) copolymers [109] whereas Yacoob et al. demonstrated that electrospun PVA/Laponite had slower burning rate than that of pure PVA [110].

Among all previously quoted fibers, a last class of fibers can be added, i.e.: the thermostable fibers. These fibers, which can withstand high temperatures for more or less long periods without losing their mechanical properties, can be used in hi-tech sectors where improved fire properties are required. Thus, some authors have tried to extend this property by adding nanoparticles. Gladunova et al. introduced brominated and chlorinated phthalocyanine, and carbon black nano-additives at 2–5 wt% in polyoxadiazole fibers and evaluated particularly their oxygen index [111]. The authors demonstrated that the use of these additives leads to obtain filaments having oxygen index up to 34 %. As for Janowska et al., they highlighted that woven fabrics made from polyimidoamide containing 3 wt% of various montmorillonite nanoparticles can be considered as flame-retardant fibers [112, 113].

## *6.4.2  Surface Treatment and Coating*

### 6.4.2.1  Nanocoating

Nanocoating such as back coating, corresponding to the addition of a small amount of nanometers filler in a coating formulation, allows to enhance the durability of the treated fabric. Therefore, as underlined by Bourbgot et al. the inclusion of nanoclay and POSS in polyurethane coating applied to PES and cotton allows the reduction of peak heat release [114]. Wang et al. have investigates the incorporation of layer double hydroxides and nanometer titanium to polyphosphate-pentaerythritol-melamine coating, which allows to enhance the resistance of the coating [115].

Nanocoatings is also described as surface engineering processes by physical methods have attracted considerable attention, since they allow atomistic or molecular deposition films less than 100 nm of thickness from environmentally friendly technologies. Many techniques are used to accomplish the atomistic/ molecular deposition such as physical vapor deposition (PVD), chemical vapor deposition (CVD), electro platting or electroless plating, laser vaporization, plasma deposition or plasma-based CVD to realized film deposition, etc.

The sputtering technology is used to realize very thin films on the nanocomposite fibers. Cai et al. have prepared PA6 nanofibers with organic-modified Fe-montmorillonite nanocomposites and coated by silicon nanoparticles using magnetron sputter technique [91]. They found that this treatment contributes to the improved flame retardant properties.

Plasma technologies achieved in different atmospheric conditions, either low or atmospheric pressure, under various types of power, are widely used in textile either to modify the structure of the surface or to depose nanocomposites into the surface. Pappas gives a clear overview of the status of nanocoatings from atmospheric plasma [116]. The excellent adhesion of these coatings to the material substrate and the cost-effective continuous process operation are the main elements that make these coatings so interesting. Dineff et al. were the first to suggest that non-halogenated flame retardant coatings from atmospheric plasma could be the solution for the existing adhesion problems with non-halogenated flame retardant coatings [117]. Furthermore, coatings from nanoparticle adsorption after plasma pre-treatments can also be used to enhance the flame retardancy properties of PET, and cotton fabrics [118–121]. The coatings showed significant flame retardant effects and very good levels of durability of the coating [121]. The results are very promising; nevertheless the flame retardant effects achieved are still far off from the required level. Main reason is that no dedicated precursors/materials for flame retardants are available for this method yet.

### 6.4.2.2  Nanofinishing: Sol-Gel

Sol-gel technology represents a new approach to functionalize fiber for the preparation of composite materials. This process allows the creation of nanocomposite

films of functional coating on the surface of the fibers leading to new mechanical, electrical, biological and fire retardancy properties which cannot be achieved using convention finishing treatment [122, 123]. Sol-gel process is a very attractive way to gain new functionality to textile, since the small particle diameter offers the advantage to form a transparent layer, which is stable against light, heat, chemical and microbial attacks, and it improves the mechanical properties of the fabric. Furthermore, additives can be embedded in the coating and conventional process such as a pad-dry-cure method which consists of the impregnation of the textile substrate by the sol following by a drying and a curing step under appropriate conditions is used to apply the solution prepared at room temperature and normal pressure.

A sol-gel process implies the preparation of an inorganic networks through the formation of a colloidal suspension also called 'sol' by either acid or alkali catalyzed hydrolysis of silicon, metal alkoxides or organometallic compounds as precursor, and the gelation of this 'sol' to form a network. Thus, during the textiles treatment, nanoparticles condensate and aggregate on the textile surface to create a 3-D network layer and during the drying, the liquid phase containing in the cross-linked lyogel is removed to obtain a xerogel or porous layer. In the last step, the curing temperature, between 100 and 170 °C, and time, from 1 to 30 min, should be adapted with regard to the type of textile coated as well as to the applied nanosol coating to avoid any degradation [124–126].

The uses of inorganic nanosol which are inflammable are not expected to increase the flammability of the textile substrate. Therefore, for a flame retardancy application, these coatings protect the textile substrate with the creation of a physical barrier acting as an insulator, which improve the flame retardant properties and the combustion behavior of the treated surface. Thus few research groups have demonstrated that the sol-gel method improves the flame retardancy of the textile substrates in recent years [127–139]. Furthermore, the effectiveness of the thermal shielding ability is in most of case limited due to the thickness of the coating and the porosity of the xerogel which cannot act as a sufficient oxygen barrier [140]. The application of nanosol to enhance fire resistance in the textile field was only studied in the early 2000s with the use of fluorinated silane for nylon carpet, $TiCl_4$-$NH_4HF_2$ in dicarboxylic acid solution for wool [141]. It was also recognized in the literature that nanosols from $SiO_2$ have a flame retardant activity which depends on the thickness of the coating layer [129, 142]. A thinner layer is less porous than a thicker and leads to better flame retardancy properties. Tetraethyl orthosilicate (TOES) and tetramethyl orthosilicate (TMOS) have been widely used as precursors in order to enhance flame retardancy properties of viscose fibers [129], cotton-polyester blend [132] with also the aim to optimize the sol-gel process conditions. Furthermore, the sol-gel methods for textiles is not restricted in the use of silane derivative, since Alongi et al. have reported that the flame retardancy properties of cotton can be enhanced by using alumina, titania or zirconia alkoxides even if the best performances were also achieved by the silica coating on a cotton substrate [139].

Since the inorganic protective layer acts only in the condensed phase, they are suitable to interact with the release gases and smoke. Therefore, hybrid layer with active species such as phosphorus and/or nitrogen should be exploited to bring up synergistic effect [127]. Thus, a possible way to improve flame resistance is the formulation of nanosol coatings with phosphorus containing flame retardant and observed by Chapple and Ferg [143], even if this protective property decreases after rinsing due to the water leaching, and the no-covalent bonding between the phosphorous compounds and the nanosol coating. Nevertheless, the use of phosphorus hybrid as presented by Chiang et al. [144] can increase the char yield when it is introduced in epoxy. More recently, phosphorus-doped silica has been studied by Cireli et al. [128] and Brancatelli et al. [131] who added nitrogen compounds. In each case, they observed an enhancement of char-forming properties due to the synergistic effects between phosphorus and nitrogen with the silica layer. These researches were also expanded to the use of various phosphorus based compounds such as aluminium phosphinate, mixture of aluminium phosphinate, melamine polyphosphate and zinc and boron oxide, and alpha-zirconium dihydrogen phosphate. Alongi et al. have observed that the flame retardancy of cotton can be enhanced with a least 5 wt% of phosphorus compounds with respect to the sol-gel precursor [136]. They also worked for obtaining hybrid phosphorus-doped silica from diéthylphosphatoethyltriethoxysilane [137]. All these studied show that the sol-gel process is potentially interesting to enhance flame retardancy properties of cellulosic substrates and the possibility to design the coating layer in order to research synergistic effects.

### 6.4.2.3 Nanofinishing: Layer-by-Layer (LBL) Technique

Initially discovered by Iler in 1966 [145], and thereafter developed by Decher and Hong in the 90s [146], layer-by-layer technique has become a popular method to realize multifunctional coating with a thickness less than 1 μm [147]. The resulting films are used in various fields to impart oxygen barrier [148], anti-reflection [149], electrical conductivity [150], antibacterial properties [151], drug delivery [152, 153] and more recently to design flame retardant coatings [148, 154–163]. The main advantages of this technique include simplicity, universality and the control of the thickness at the nanoscale level, compared with the other traditional coating. Furthermore, it is possible to combine nanoparticles, nanosheets as well as nanowires with polymers.

Layer-by-Layer (LbL) assembly consists in the deposition of oppositely charged polyelectrolyte multilayer films onto the surface of a substrate. The self-assembly process is based on spraying or immersion (dipping method) of a charged surface in polyelectrolyte solutions followed by a rinse in water to remove surplus polymer solution adhering to the support. This technique of polymer thin film deposition allows creating uniform film with a controllable thickness. Assemblies are done through electrostatic interactions, donor/acceptor interactions, hydrogen bonding, and covalent bond. The process is mainly influenced

by the chemical nature and the chemistry of the polyelectrolyte, the molecular weight, the temperature and pH, and the ionic strength as well as the presence of the counterions. This coating method has received growing interest in the last decade and various organic of inorganic molecules can be deposited to bring new functionalities to the resulting film.

In textile application, the fabric (cotton, PET, ramie, …) was first immersed into the cationic solution for 30 s to several minutes, washed with deionized water or buffer solution, generally dried with air before being immersed into the ionic solution for 30 s to several minutes, washed with deionized water or buffer solution and dried with air to build the first bilayer architecture. The immersion period for this bilayer is optimized to promote and achieve the uniformity and stability of the coating. Thereafter the procedure was repeated until the desired number of bilayer was obtained. Finally the treated fabrics were dried under vacuum or in an oven to complete water evaporation.

According the chemical nature of the textile fabrics several strategies have been explored. Thus, to enhance flame retardancy properties of cotton fabrics, Grunlan et al. have used a branched polyethylenimine as cationic specie couples to laponite [162], sodium cloisite [161], silica nanoparticles [159] or polyhedral oligomeric silsesquioxanes [160]. Huang et al. have selected poly(acrylic acid)/montmorillonite and polyacrylamide/exfoliated grapheme oxide couples to reduce the flammability of cotton [164, 165]. Carosio et al. have investigated the PET coating from colloidal alumina/coated silica with silica [154], α-zirconium phosphate/polydia llyldimethylammonium chloride as cationic polyelectrolyte [158]. For polyester/cotton blends, Alongi et al. have realized complex architecture from ammonium polyphosphate, chitosan and silica [166]. The results of the fire tests conducted on these fabrics seems very promising since in all cases it was observed a significant improvement of their thermal stability, an increase of the time to ignition, and a decrease of the heat release rate.

### 6.4.2.4  Nanomaterials Embedded Textile

To improve the washing durability, nanomaterials can be fixed into the textile fabric. One of the methods to embed nanoparticles is to use a cross-linking agent or crosslinkable polymeric binders such as polysiloxane or carboxylic acid for carbon nanotube (MWCNT), silver particle or fumed silica. Another way is to realize the in situ synthesis of these nanoparticles such as a bottom up process. Thus, it was shown that MWCNTs improve thermal stability and provide a char barrier, these particles are incorporate into the fabrics using a process that mirrors industrial methods [167].

Nano rods can grow on any substrate by two ways. Firstly, the substrate is seeding with nano seeds and growth of nano rods by hydrothermal process. These nano seeds provide site for nucleation of nano rods [168–172]. Secondly, growth of nano rods on self-assembled monolayer (SAM) modified surface [173, 174]. Most of the time, a straightforward approach is to seed the substrate with nanoparticles

of the desired material by different techniques, such as dip coating or sol-gel coating. Once the seed layer is formed, oriented nanocrystals growth follows in a second step. In order to attach seeds on any surface, presence of polar groups on surface is very essential. Therefore different methods have been used to generate (UV treatment, sodium hydroxide). Oriented nanocrystals grow from these nucleation sites, and in subsequent reaction steps, new crystals nucleate and grow on the crystals produced in previous stages. So the initial nano rods formed at the surface can be converted into other forms (flowers) by using a secondary growth [175].

## 6.5  Conclusion

Economic, environmental, legal constraints make that research on the fire resistance of textiles is still relevant. Among the various ways of improvement, nanotechnology has been and remains a relevant possibility. This chapter presented the various nanotechnologies that have been tried to provide fire retardant properties. Nanotechnologies for textile are found either in the process of yarns or through surface treatment and coating.

Regarding the spinning, the most widely used synthetic fibers (PP, PET, PA) were studied with a wide range of nanofillers. Overall the presence of nanofillers even low rates reduces during heat/fire stress the phenomenon of melt dripping and the peak of heat release rate. However the charring effect is often insufficient with e.g. a total heat release equivalent to the untreated fiber. This feature already observed for the bulk polymers is even more pronounced for the same polymers in a fibrous state. Nanofillers were also associated with the traditional FR agents. Results are disparate where a synergistic effect has been observed only sometimes.

Except coatings containing nanofillers and plasma process (technologies already since 10 years in textile), surface treatments based on sol-gel and layer-by-layer techniques are much more recent and show the most promise for FR properties. These techniques seem to have low cost and environmental impact and to adapt to all sorts of fabrics (polymeric nature). Initial results are encouraging and demonstrate synergies with traditional FR compounds.

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