

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Flame Retardant Treatments of Nylon Textiles: A Shift towards Eco-Friendly Approaches

*Chanchal Kumar Kundu, Zhiwei Li, Lei Song and Yuan Hu*

## Abstract

Among the synthetic polymeric textiles, Nylon (Polyamide) textiles (Nylon66/ Nylon 6) are one of the most widely used materials, especially as apparel and industrial uses for their excellent properties, namely higher strength and good wear resistance. Unfortunately, due to their organic structures, they show the relative ease of burning, which poses a great risk to fire. For the flame retardant (FR) treatment of nylon textiles, several strategies have been developed throughout the years and the earlier studies show the enormous uses of petroleum-based flame retardant compounds via energy intensive application methods. However, the rapid improvement in living standards as well as the recent call for a reduction of environmental impacts during manufacturing and use have been pushed researchers to come up with environmentally benign chemistries and processes. Therefore, the challenges in search of the most sustainable, efficient and durable flame retardant treatments for nylon textiles still remain as a hot topic to be addressed. This chapter discusses the eco-friendly approaches that have been taken in escalating the fire performance of these novel nylon textiles, especially focusing on the applied compounds and the application techniques along with the durability issues of such applications.

**Keywords:** nylon textiles, flame retardancy, bio-based flame retardant, hybrid application, eco-friendliness

## 1. Introduction

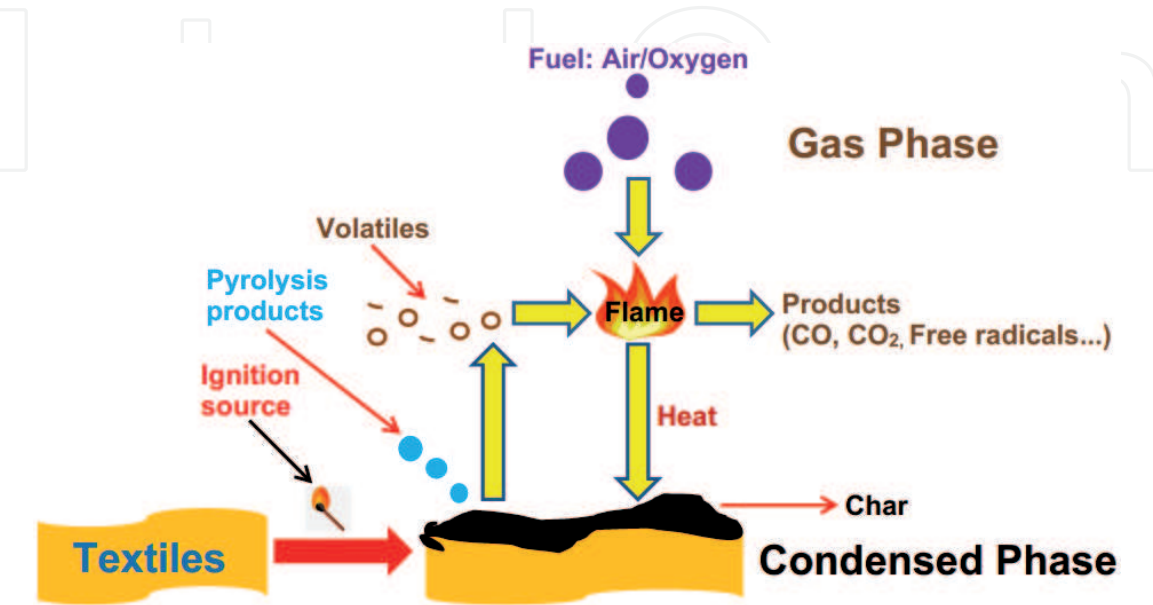
The consequences of fire related incidents leave a serious impact on human life and its property as well. Frequently, these fires are ignited from the polymeric materials, including textiles we use in our daily life as in consumer goods, home furnishings, transportation, apparel and protective clothing, etc. The world fire statistics reveal that the textiles and upholstered furniture are the first item to be ignited by small flames such as cigarettes and candles, thus producing the most common fire [1, 2]. Meanwhile, the textile materials release smoke and toxic gases while going through the combustion process, which in turn limit the evacuation in fire disasters and worsen the fire scenario [3, 4]. In addition, these fires cause huge economical losses as well as deaths of human beings [5, 6]. Thus, the researcher is making continual efforts to investigate the flammability of textiles in order to improve their fire performance. On the other hand, the growing concern over the sustainability issues infer that fire retardants should leave a low impact on health and the environment during the entire life cycle including recycling and disposal. It also demands to come up

with significant researches with a focus on alternate flame retardant chemistries and methodologies, including the use of more environmentally benign raw materials and eco-friendly approaches in the synthesis and application of new flame retardants.

Nylon is the oldest man-made fiber (MMF) among the synthetic textiles, which remains as an important fiber in the synthetic fiber community till the date. Initially Nylon, also in the name of polyamide, is developed for a limited number of end uses; however, these days, the fibers belonging to the nylon/polyamide group share a big market, from regular apparels to technical textiles. For example, carpet is a significant application for nylon and accounts for 17.5 percent of total usage globally. Other applications of nylon include airbag, heavy-duty tires, intimate apparel, military apparel, sheer hosiery and swimwear, etc. [7]. Among, different types of polyamides, polyamide 66 (Nylon 66) and polyamide 6 (Nylon 6) represents one of the most used technical fibers. Both of them possess almost similar physical properties, namely high mechanical properties (tensile strength is higher than that of wool, silk, rayon or cotton), high chemical stability, high melting point, resistance to shrinkage and abrasion [8]. However, like other common textiles these fibers are also flammable due to their organic structure; alongside they also show serious dripping. Thus, the nylon textiles cannot meet industrial and civil requirements in many cases, which ultimately limit their uses in the mentioned sectors [9–11].

2. General combustion behaviors of textiles and strategies of flame retardant mechanism

In general, combustion of a typical polymer substrate happens in contact of a fire source and in the presence of air or oxygen. Prior to the combustion process, the textile materials degrade thermally, while some of the degraded species turn into combustible volatiles and serially, in the presence of oxygen, they kindle the flame. In a logical way, while the heat generation exceeds the threshold to sustain the combustion process, the excessive heat transmitted to the textile material, usually accelerates the degradation process and form a self-sustaining combustion cycle as presented in **Figure 1** [7]. In line, we also need to study the mechanism of action of various flame retardants on textiles to evaluate a particular flame-retardant system



**Figure 1.** Combustion cycle of a typical textile material. [7], Copyright 2020. Reproduced with permission from Elsevier ltd.

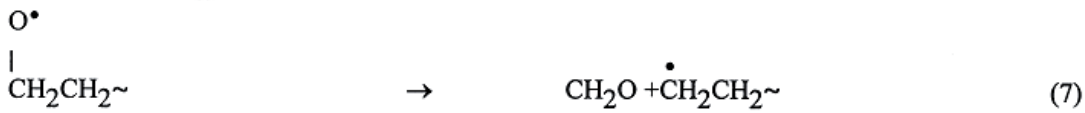
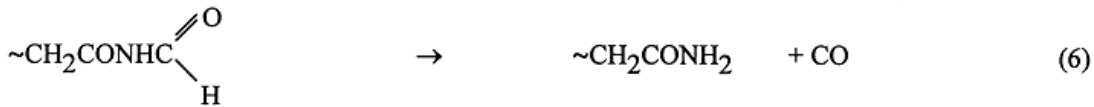
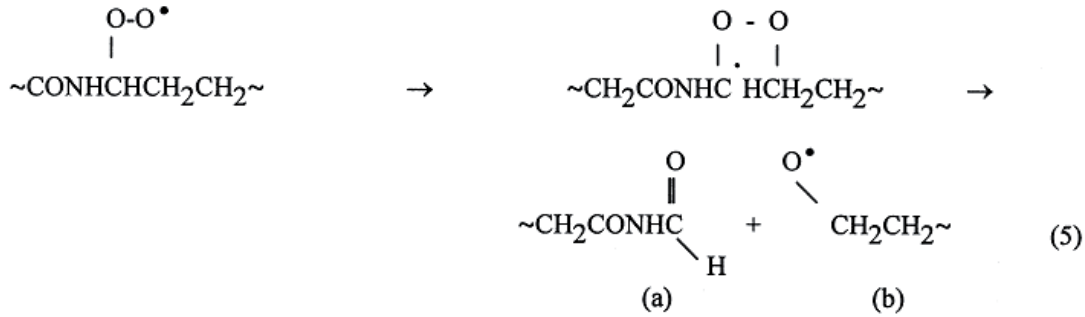
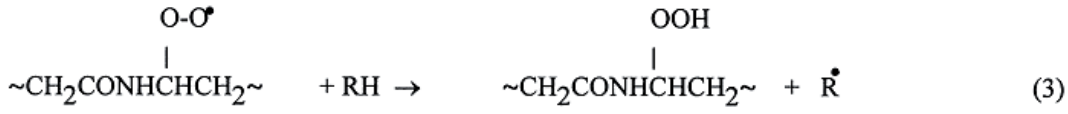
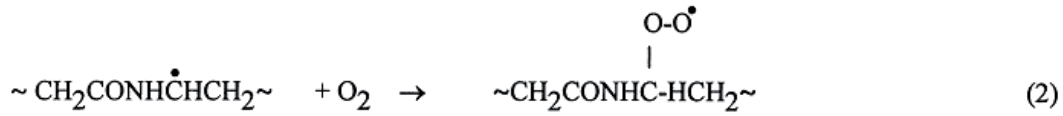
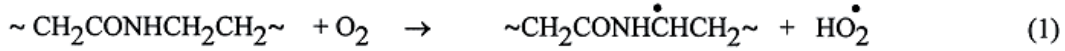
to a specific polymer. In general, the common flame retardant mechanism can be divided into two different modes of action likely (1) gas or vapor phase mechanism and (2) solid or condensed phase mechanism that break the polymer combustion cycle (see **Figure 1**). The gas phase flame retardant mechanism normally does not change the thermal decomposition of a polymeric substrate, whereas the flame-retardant compound goes for decomposition in the presence of heat and generates free radicals. These free radicals either combine with atmospheric oxygen/air through complex reactions or capture the radicals released from the polymer substrate to quench the total combustion process [12]. Meanwhile, in the condensed phase mechanism, combustion process brings structural changes in the polymer substrate via promoting polymer cross-linking to form a carbonaceous char onto the material surfaces. In line, these char residues make insulation between the polymer substrate and the flaming zone to curb the creation of new fuel and stop further burning. Another form of the condensed phase mechanism involves an additive, creating a physical barrier via releasing water during heating, which ultimately cools down the surface and slows the heat and mass transfer [13].

Briefly, a typical flame retardant (FR) compound inhibits the flammability of a polymeric/textile material in several ways mentioned as follows [14]: (i) FR compound can minimize the generation of heat to retard the combustion process, (ii) it can alter the pyrolysis pathway via lowering the generation of flammable volatiles while favoring the char formation to limit the heat and mass transfer via creating an insulation layer between the textile material and the fire source, (iii) in some extent, it can release water vapor as a byproduct to dilute the concentration of available oxygen and flammable volatiles to lower the heat flow back to the textile material, and (iv) it can release flame inhibitors in the gas phase (i.e., chlorinated, brominated and phosphorus species) to quench the intensity of combustion via capturing flammable radicals.

### 3. Combustion and thermal behaviors of nylon textiles

To come up with a suitable flame retardant approach along with an applicable flame-retarding agent for nylon textiles, it is thus needed to understand their thermal and flammability behaviors. In general, the polymeric materials release gases like CO, NO<sub>2</sub> and HCN, etc. when they are burned [15] and it is also observed that the evolution of CO differs from fiber to fiber. Meanwhile, polyamide fibers show self-extinguishing behavior due to its extensive shrinkage and dripping in combustion [16]. During burning, polyamide ignites with molten droplets and drip away from the flame; most of the heat is carried away with the droplet, making the material self-extinguishing. However, if the molten droplets burn continuously, this will encourage a greater fire hazard and pose a secondary fire risk. In inert atmosphere and at a higher temperature range (i.e., above 300°C), the main decomposition products released by polyamides are about 95% non-volatiles and the remaining volatile compounds mainly consist of CO<sub>2</sub>, CO, water, ethanol, benzene, cyclopentanone, ammonia, others aliphatic and aromatic hydrocarbons, etc. [17, 18]. However, in air atmosphere and at temperatures below 200°C, the degradation pattern of polyamide is different [17] where the volatile products to be likely water 52%, CO<sub>2</sub> 33%, CO 12%, and methanol, formaldehyde and acetaldehyde are around 1% each. Moreover, the pyrolysis process also causes de-polymerization of its structure [19]. The suggested oxidative decomposition mechanism of polyamide structure is given in **Figure 2** [20].

From **Figure 2**, it is assumed that like the oxidative degradation of hydrocarbons, the oxygen molecule initiates the chain process of oxidation of polyamides (**Eq. 1**). At first, hydrogen atom will be abstracted and subsequently, either



**Figure 2.**  
Possible oxidative decomposition mechanism for polyamides [20].

peroxide radical or a hydroperoxide will be formed (Eq. 2 and 3). Later, with the decomposition of hydroperoxide, water will be formed (Eq. 4). The formation of water can lead to the hydrolysis of the polymer and thus, on decarboxylation,  $\text{CO}_2$  will be produced. Apart from the decomposition of peroxide, the peroxide radicals may also break down in the degradation process. These radicals may also go through isomerization via making reaction with the free valence of the adjacent C-C bond. Ultimately, this kind of isomerization as well as the breakdown of peroxide radicals causes the collapse of molecular chains to form a molecule with a terminal aldehyde group (a) and a radical (b) (Eq. 5). Afterwards, these aldehyde groups go for further decomposition to the form CO (Eq. 6), while the radicals (b) cause the rupture of the C-C bond to form a secondary C-O bond and thus, in turn direct the creation of formaldehyde (Eq. 7).

#### 4. Flame retardant treatment of nylon textiles

Formerly, numerous approaches are considered to make the nylon textiles flame retardant, especially at a fiber stage. Of them, strategies like application of fire retardant additives and co-monomers during polymerization and in the spinning dope, development of inherently fire retardant fibers and fiber blending are notable [21]. However, due to the possibility of polymer degradation and leaching of flame retardant compounds at a fiber stage finishing, a kind of topical finishing or post-treatments are commonly proposed for conferring the flame retardancy of

nylon textiles in the recent time [22]. Meanwhile, the earlier applications, mostly receive the attention of halogenated species [23, 24] and petro-based flame retardant compounds containing phosphorus, nitrogen [25, 26] and sulfur elements where the uses of bio-derived flame retardants are rarely seen.

Though the nylon textiles (nylon 66/nylon 6) possess almost similar chemical, physical, thermal and fire behaviors, they belong to a different chemical structure. Thus, they have different surface functional groups and a varied level of crystallinity, which ultimately affects the processing of these textiles during finishing. As we know that nylon 66 is made from two monomers namely, hexamethylenediamine and adipic acid; each containing 6 carbon atoms and carries amino and carboxylic acid as functional groups. While, nylon 6 is synthesized from a single monomer namely caprolactam (also called  $\epsilon$ -caprolactam) having 6 carbons via ring-opening polymerization and only carries amino functional groups.

In the following section, the very common flame retardant finishes applied to nylon 66/nylon 6 textiles both at the fiber and fabric stage are discussed.

#### **4.1 Flame retardant (FR) treatment of nylon 66 (polyamide 66) textiles**

##### *4.1.1 FR treatment at fiber stage*

The fiber stage flame retardant finishing of Nylon 66 textiles is usually done using polymerization, electrospinning, mixing or blending techniques. In some applications, halogen free flame retardant compounds, namely a mixture; comprising of phosphorus and boron esters via ionic introduction [27] and melamine cyanurate (MCA) via in situ polymerization [28] are considered. While, a kind of condensation polymerization using nylon salt and 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-based flame retardant working in gas phase is also exploited [29] to prepare the flame retardant nylon 66 fibers. Recently, a hybridized flame retardant compound [30], namely a kind of encapsulated nanoscale graphene with red phosphorus is used to prepare core-shell structured polyamide 66 nanofiber via a coaxial electrospinning method. However, till the date, the application of fully green compounds as a flame retardant is still absent in preparing the flame retardant nylon 66 fibers. The main results of these applications are presented in **Table 1**.

##### *4.1.2 FR treatment at fabric stage*

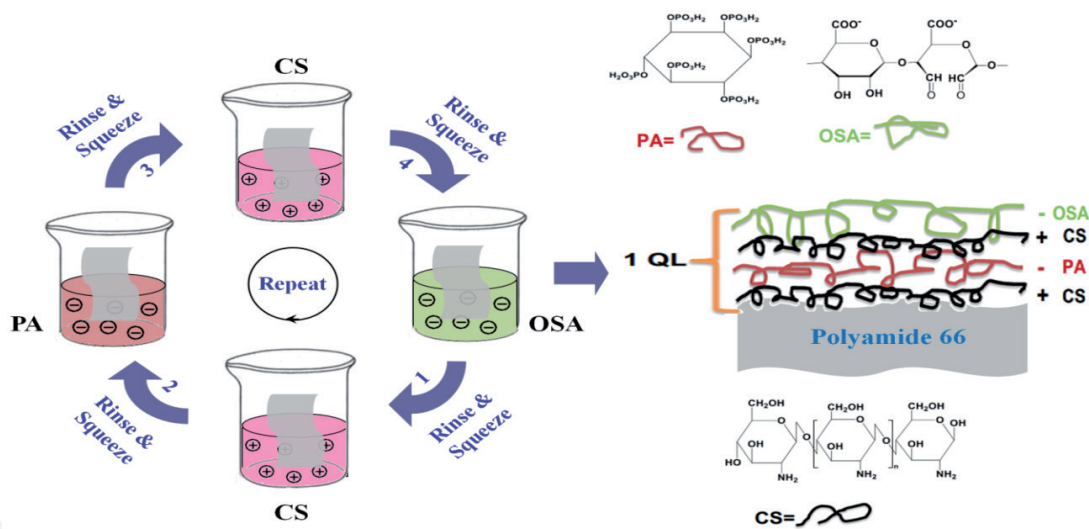
The flame retardant treatment of nylon 66 textiles at the fabric stage is usually done in the form of surface coatings via numerous techniques, namely pad-dry-cure, UV grafting, plasma deposition, layer-by-layer assembly and sol-gel process [31–34]. In earlier applications, petro-based compounds are widely used, however, with the growing concern of adverse impacts posed by petro-based flame retardants, researchers are paying attention on the green flame retardants and in some extent, semi-green application approaches are also seen in the recent time.

###### *4.1.2.1 Application of fully bio-based flame-retardants*

The flame retardant treatment of nylon textiles using fully bio-based compounds are yet to be in extensive uses as a very few work focuses on it. For example, Kundu et al. [35] consider all green compounds, namely bio-derived chitosan (CS), phytic acid (PA) and oxidized sodium alginate (OSA) for the first time ever to improve the flame retardancy of nylon 66 textiles. These coatings with a 10 to 15 quadra-layer (QL; deposition of consecutive four layers constructs a single quadra-layer) (see **Figure 3**) depositions stop the melt dripping of fabric materials.

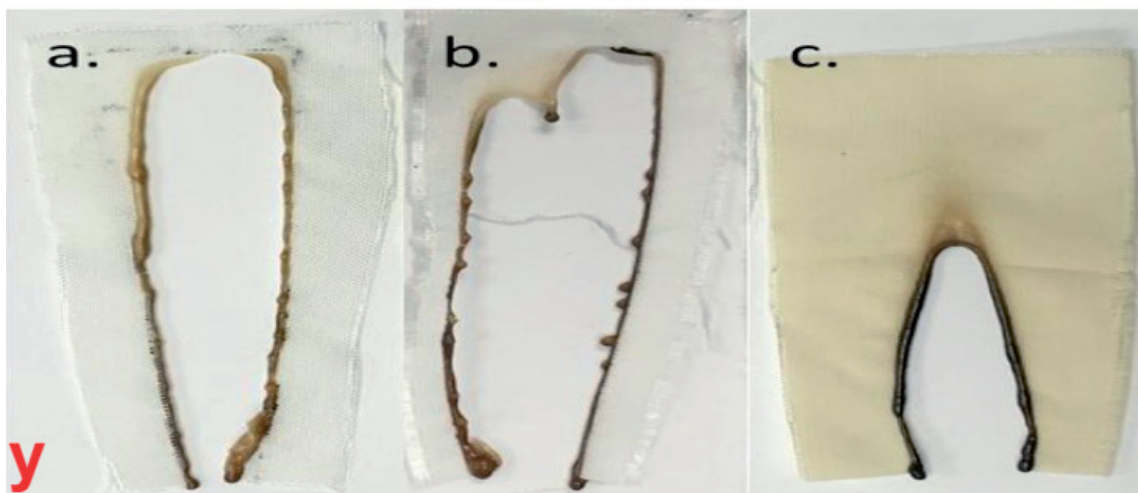
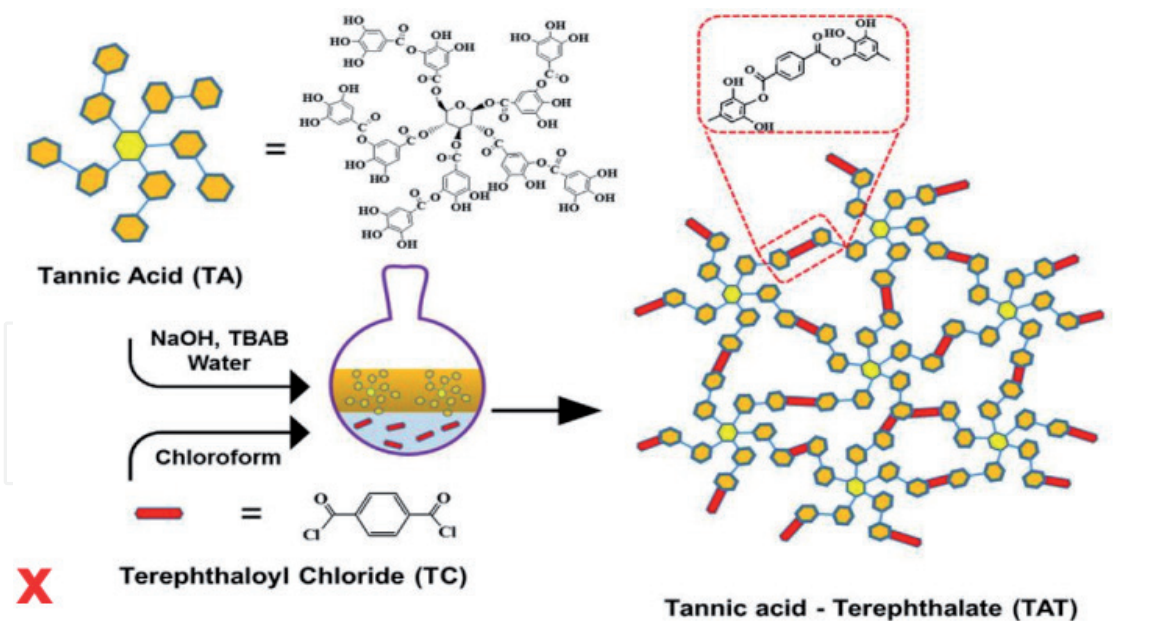
Substrate	FR compounds	Application technique	Main results	Eco-friendliness
Nylon 66 fiber [27]	Phosphorus and boron esters	Open air grafting (cold)/ultraviolet irradiation grafting (hot) and hot vacuum oven grafting	Improved charring by about 25.67%	No
Nylon 66 fiber [28]	Melamine cyanurate (MCA)	In-situ polymerization	LOI upto 31.5% and UL94 V-0 rating in VBT	No
Nylon 66 fiber [29]	DOPO-based flame retardant	Condensation polymerization	LOI upto 32.9% and UL94 V-0 rating in VBT	No
Nylon 66 fiber [30]	Graphene and red-Phosphorus	Encapsulation	THR and pHRR reduction by about 50.5 and 26.9% respectively	No

**Table 1.**  
Collected results of flame retardant treatment for nylon 66 fiber.



**Figure 3.**  
Schematic representation of Quadra-layer (QL) deposition.

Here, the use of these green polyelectrolytes plays a multiple role as an acid source, a carbon source and a foaming agent and thus, their interactions facilitate the intumescent process in a condensed phase mechanism to control the flame spread process. More importantly, it is found that the use of OSA improves the durability of this multilayered nanocoating via offering covalent interactions. This is the first attempt to use fully renewable and environmentally friendly intumescent LbL coating in improving the flame retardant properties of a thermoplastic textile like nylon 66. In addition, this is also a very first attempt to improve the durability of LbL assembled coatings for nylon textiles against home laundering as the coatings developed via non-covalent forces (i.e., ionic interaction) show poor wash durability. In line, another environmentally friendly and fully bio-based synthesized compound, namely tannic acid-terephthalate (TAT) (see **Figure 4x**) obtained from tannic acid, is applied onto the nylon 66 fabric surfaces via pad-dry-cure process [36]. This kind of green coating surely imparts excellent flame retardancy to the textile substrate in terms of obtaining self-extinguishing behavior and reduced char length in the



**Figure 4.** Proposed reaction scheme of tannic acid and terephthaloyl chloride (top-x) and vertical flame test samples after burning, a. neat nylon 66 fabric, b. TA-coated nylon 66 fabric (after washing), c. TAT-coated nylon 66 fabric (after washing) (bottom-y) [36], copyright 2018. Reproduced with permission from Elsevier ltd.

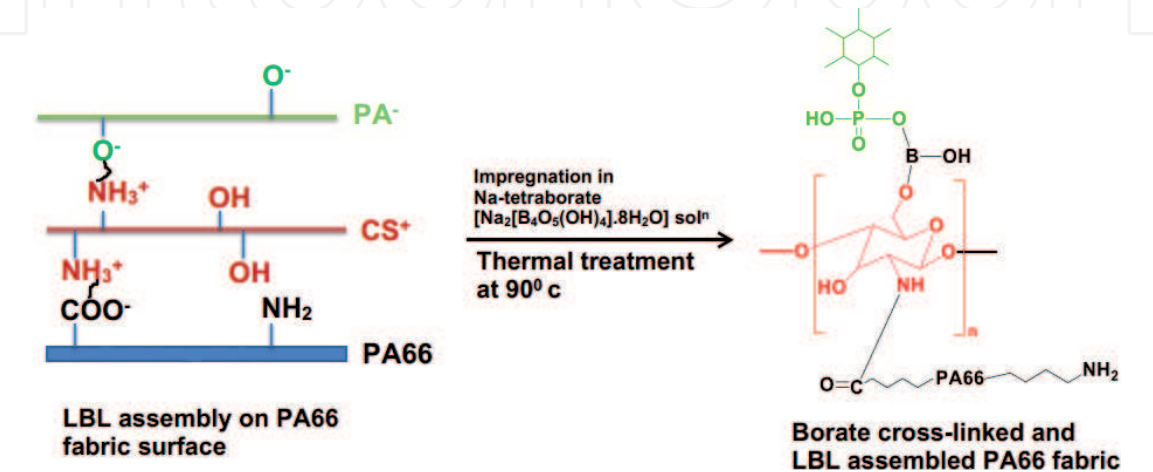
vertical flame test (see **Figure 4y**). Here, the cross-linked phenol species belonging to TAT structure helps to build up charring in the solid phase and exhibits a positive impact in enhancing flame retardancy of nylon substrate. Just a very thin layer of such coating (i.e., only add-on of 6 wt.%) helps to obtain self-extinguishing behavior and brings a considerable decrease (i.e., 20–25%) in heat release rate. The main results of these applications are summarized in **Table 2**.

#### 4.1.2.2 Application of hybrid flame-retardants

To address the environmental issues, researchers equally put focus on the numerous hybrid application techniques, namely they consider the combined use of both the bio-derived and petro-based compounds, even in some applications, they opt to blend the mineral with the bio/petro-based compounds in a semi eco-friendly application. For example, Kundu et al. [37] combine an inorganic boron compound like sodium tetraborate with the bio-derived compounds like chitosan (CS) and phytic acid (PA) to simultaneously improve the flame retardant properties of PA66 textiles and to stabilize the ionically assembled coatings (see **Figure 5**). Here, the modification of nylon 66 textile with chitosan, phytic

Substrate	FR compounds	Application technique	Main results	Eco-friendliness
Nylon 66 fabric [35]	Chitosan, phytic acid and oxidized sodium alginate	LbL assembly	A maximum of 24% reduction in pHRR	Full
Nylon 66 fabric [36]	Tannic acid terephthalate (TAT)	Pad-dry-cure	Improved charring and self-extinguishing behavior	Full

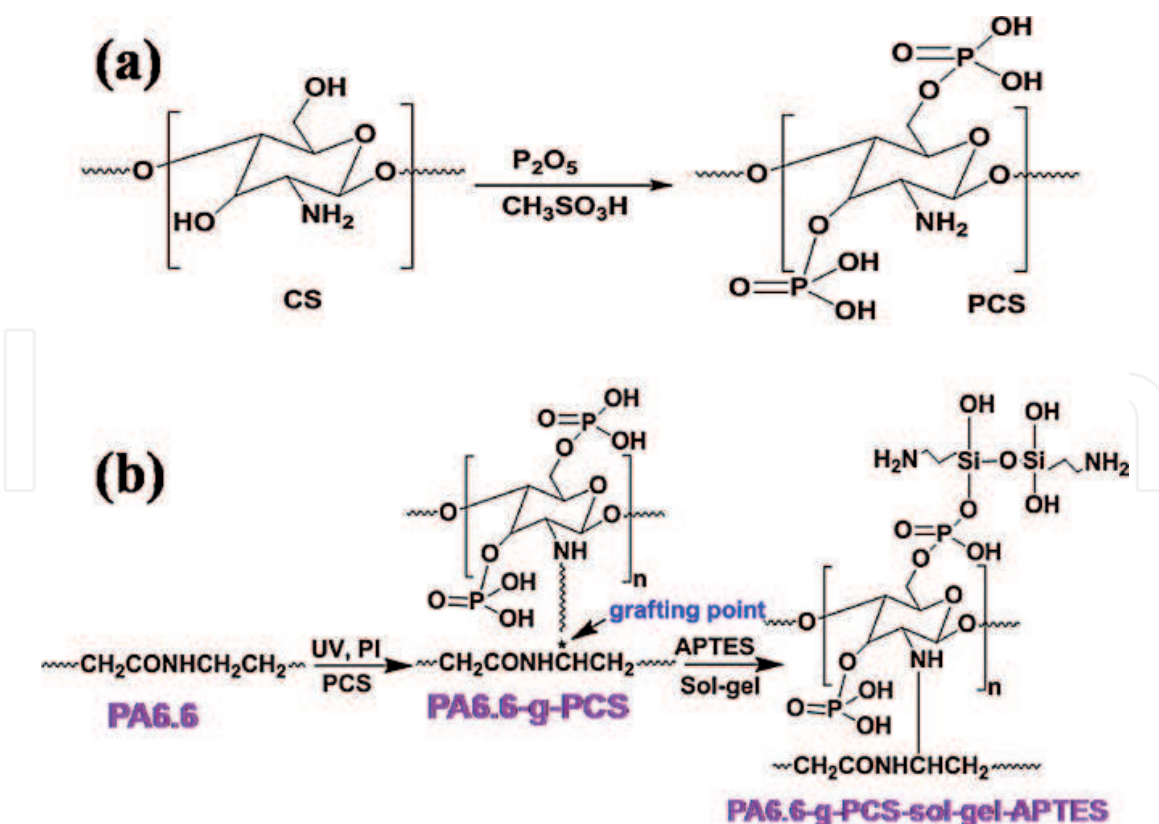
**Table 2.**  
Collected results of flame retardant treatment for nylon 66 fabric.



**Figure 5.**  
Schematic illustration for the interactions among chitosan, phytic acid, borate compound and PA66 fabric during the LbL deposition and after the thermal treatment [37], copyright 2018. Reproduced with permission from Elsevier B.V.

acid and borate compounds boosts up the charring of the same while providing enhanced stability of char residues. In addition, the borate induced cross-linking offers added stability of as-prepared coating in detergent solution.

Presently, this hybrid methodology has been expanded further in several works where Kundu et al. [38] come up with the hybridization of some alkoxy silane based compounds, namely (3-Aminopropyl) triethoxysilane (APTES) and boron doped APTES sol solutions with some bio-originated compounds like chitosan and phytic acid in the hybrid application (i.e., LbL deposition/sol-gel process). Here, the simultaneously APTES and B-d-APTES sols treated and LbL deposited fabrics stop the melt-dripping in the vertical burning test. Meanwhile, the boron doped APTES sol treated fabrics reveal improved charring and thermal stability in TG analysis. It is speculated that the phytic acid, being a phosphorus compound, catalyzes the charring while the silicon and boron compounds endow with excellent shielding to these char residues. Thus, an added level of char yield% is experienced and finally, this thermally stable char residues impart enhanced flame retardancy to the nylon textile. In addition, this kind of hybrid application, namely LbL assembly (i.e., 5 bi-layers deposition) and simultaneous sol-gel treatment offers durability to the applied finish against home laundering. In another application, Kundu et al. [39] introduce a hybrid methodology via using a chitosan derivative, namely phosphorylated chitosan (PCS) along with an alkoxy-silane like (3-aminopropyl) triethoxysilane (APTES). Here, the PCS is grafted onto the surface of nylon 66 fabrics via UV-induced grafting polymerization and subsequently, these grafted fabrics are further modified by APTES through sol-gel process in order to form a cross-linked coating (see **Figure 6**). The obtained results indicate that the simultaneous PCS



**Figure 6.**  
 Synthetic route of PCS (a) and schematic illustration of UV grafting and sol-gel treatment of PA66 fabrics (b) [39], copyright 2017. Reproduced with permission from Elsevier Ltd.

grafting and sol-gel treatment stop the melt dripping and improve other flame retardant parameters. The prominent flame retardant properties for the simultaneous PCS and APTES treated PA66 fabrics are due to the joint effect of thermal shielding exerted by the silica and char-forming effect derived from PCS.

Hybridization in the deposition method, namely synchronization of layer by layer (LBL) assembly with the pad-dry-cure technique is seen in preparing a flame retardant hybrid coating for nylon 66 fabric [40]. Here, some bio-derived compounds like chitosan and phytic acid are combined with melamine and graphene oxide (GO). This hybrid application significantly improves the flame retardancy with a considerable improvement in thermal stability and char yield%. Furthermore, the application of a nanocomposite layer prepared from chitosan/graphene oxide on top of the LbL assembled film offers covalent cross-linking to the underneath ionic-assembled coating, which impart considerable durability to the applied finishing to retain flame retardant performance even after 10 laundering cycles. In line, graphene oxide (GO) is functionalized with some plant derived biomolecules namely, lignin (L) and phytic acid (PA) (see **Figure 7**) and used accordingly in modifying the fire performance of nylon 66 fabrics in a one pot deposition [41]. Here, in some formulations, chitosan as a naturally derived charring agent is also considered to enhance the charrability of such finishing further. The as prepared thin film (i.e., add on is less than 10%) barely alters the physical properties (i.e., color, handle and tensile strength, etc.) of treated fabrics. Meanwhile, this kind of application offers better thermal stability and improved fire performance alongside the wash durability of applied finishes. Here, the inclusion of citric acid as a cross-linking agent extends some cross-linking interaction among the applied compounds to retain the flame retardancy even after 5 washing cycles.

Another bio-derived compound, namely soybean protein isolation (SPI) is used with thiourea via a simple pad-dry process to impart flame retardant properties to

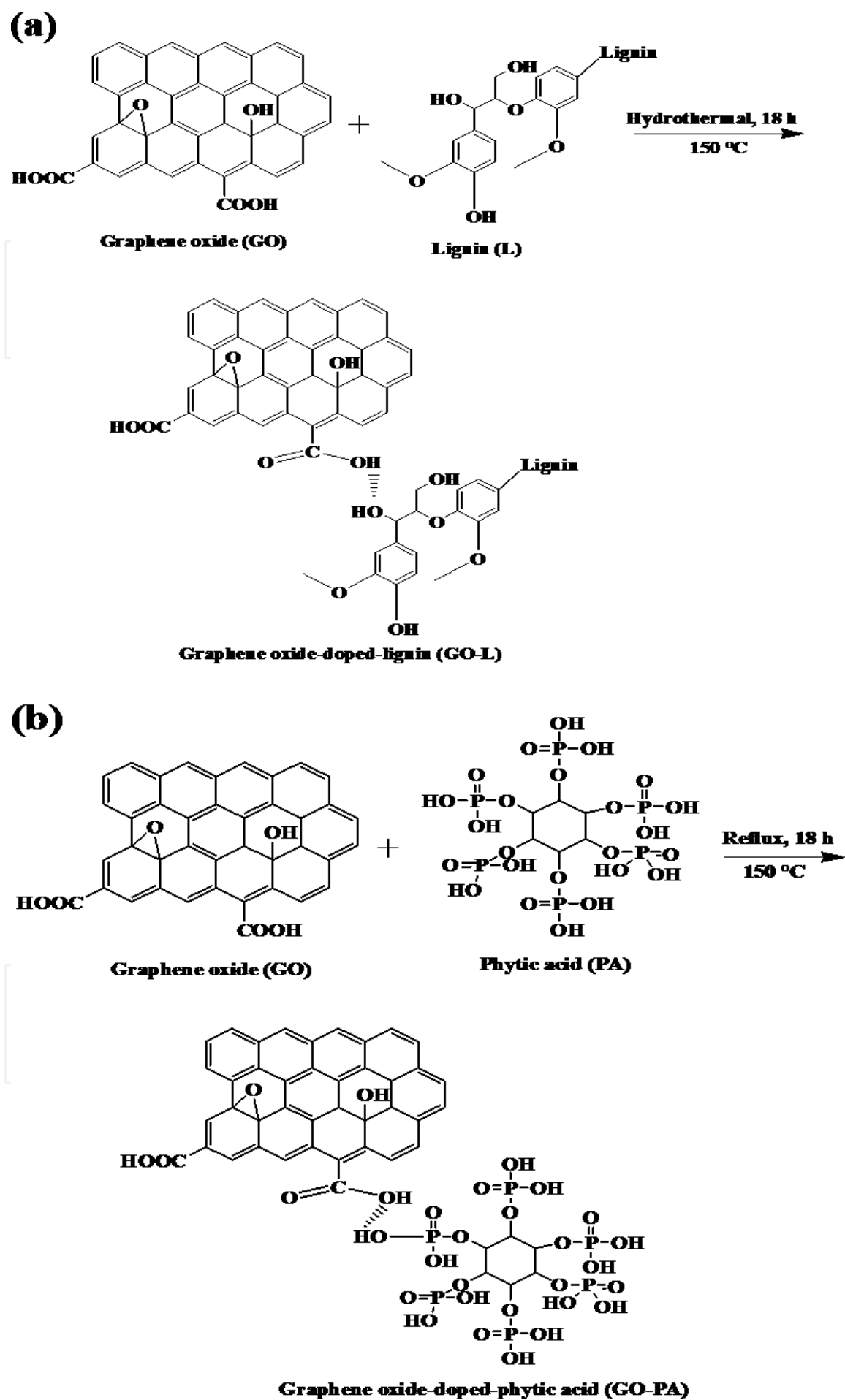
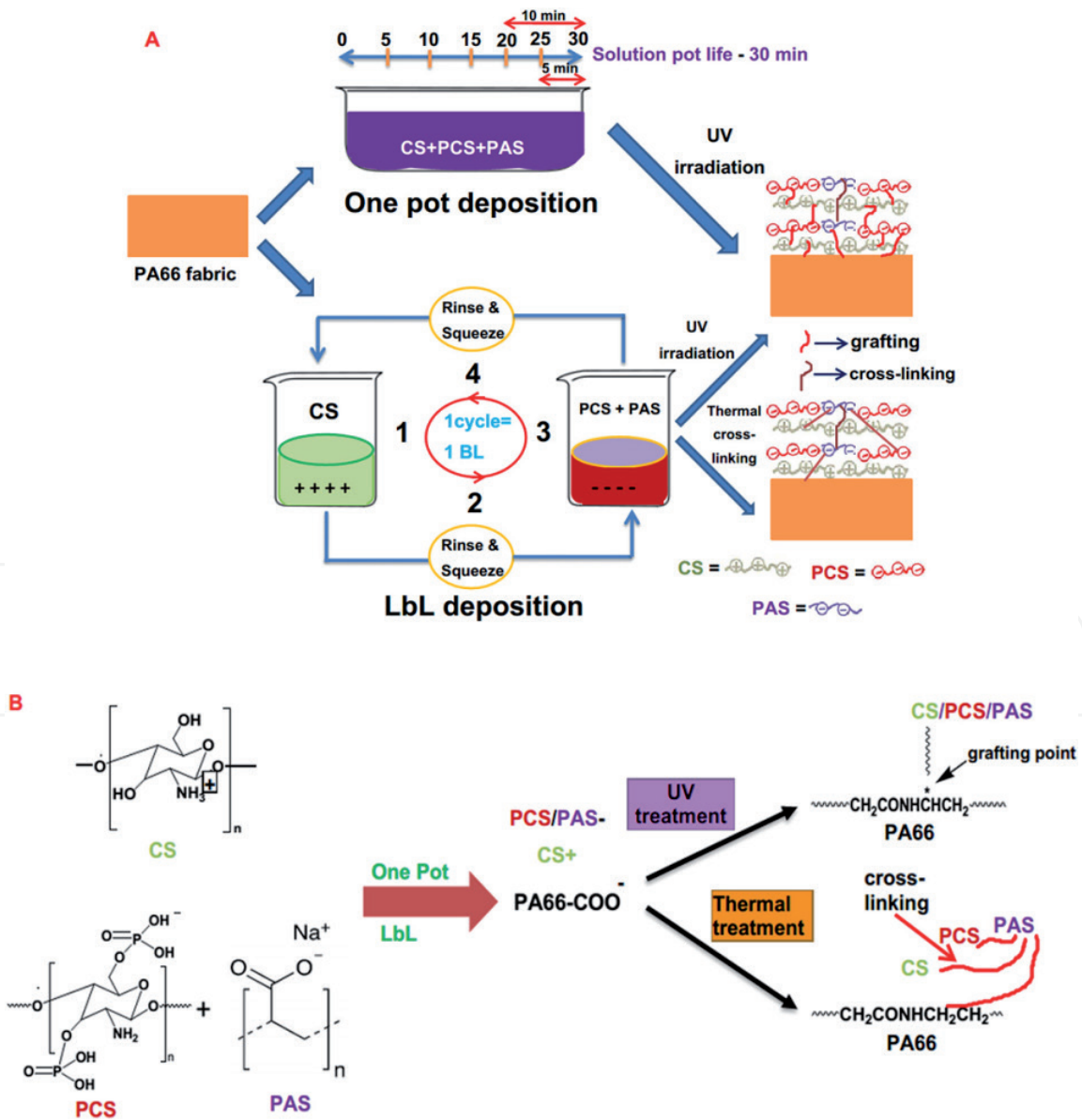


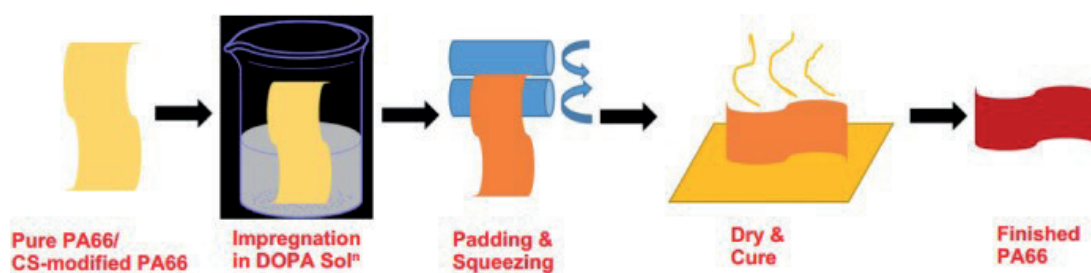
Figure 7.  
 Synthesis route of graphene oxide-doped-lignin (GO-L) (a) and graphene oxide-doped-phytic acid (GO-PA) (b) [41], copyright 2020. Reproduced with permission from Elsevier B.V.

nylon 66 fabrics [42]. This kind of hybridization in the applied compounds comes up with reduced burning length and no dripping for the modified textiles. Here, it is speculated that these hybrid compounds may release non-combustible gases like  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in the gas phase and produce compact char residues in the solid phase during burning. In line, these noncombustible gases dilute the fuel/oxygen concentration and the obtained char layers provide insulation between the fire zone and textile substrate to prevent the transfer of heat and oxygen. Therefore, it is perceived that the N, P, S and metal elements in SPI play a vital role in modifying the fire behaviors of polymeric substrates and offer better flame retardancy in a sustainable manner.

In some application, pure chitosan (CS) along with its phosphorus-derivative, namely phosphorylated chitosan (PCS) are used to construct a flame retardant coating for nylon 66 textiles while poly-acrylate sodium (PAS) is accompanied with them as a cross-linking agent [43]. The coating is prepared both in LbL assembly and one pot deposition method to make a comparison between the application method (see **Figure 8**). Here, the LbL assembled coatings possess superior homogeneity in the coating structure over the one pot deposited one. Meanwhile, the LbL assembled coatings with a higher add on% offer an improved LOI value and also bring a considerable



**Figure 8.**  
Schematic representation of the 'one-pot', and LbL deposition of PA 66 fabrics (A) and the mechanism of reactions (B) [43], copyright 2019. Reproduced with permission from Elsevier B.V.



**Figure 9.**

*Schematic representation of DOPA application [44], copyright 2020. Reproduced with permission from Elsevier Ltd.*

reduction in pHRR for the nylon substrate. In addition, the PAS cross-linking via thermal treatment stabilizes the deposited coatings to a certain extent; as the fabrics prepared in this process retain the UL-94-V1 rating after the 5 times washing in laundering. It is also found that the LbL assembly imparts better flame retardancy than the one-pot deposition technique as a higher weight gain% in LbL deposition offer this superior flame retardant properties irrespective of deposition techniques.

In another application [44], a petro-based P-compound, namely DOPA, a DOPO derivative, is combined with the bio-based chitosan (CS) in a semi bio-based flame retardant application via a simple pad-dry-cure method as shown in **Figure 9**. Here, the nylon 66 modified with chitosan and 10 wt. % of DOPA reveals an excellent flame retardancy in terms of significant reduction in pHRR compared to the nylon 66 modified only with DOPA. It is speculated that the P and N elements available from DOPA and chitosan respectively appear to be involved synergistically to offer enhanced flame retardancy. In line, the co-presence of DOPA and CS ensures a synergistic gas phase and solid phase activity where DOPA exhibits a quenching effect in the gas phase and chitosan takes part in the charring process in the condensed phase.

Even in some applications, several novel nanoparticles (NPs) namely,  $\text{TiO}_2$  and  $\text{SiO}_2$  are blended with naturally derived phytic acid (PA) and chitosan (CS) via a pad-dry-cure technique [45]. The blended formulation of PA- $\text{TiO}_2$  enhances the limiting oxygen index (LOI) and increases char yield% of treated textiles. Conversely, the introduction of chitosan (CS) into the PA- $\text{TiO}_2/\text{SiO}_2$  formulations brings a significant reduction in the peak heat release rate (pHRR). In addition, the formulations containing nanoparticles ( $\text{TiO}_2/\text{SiO}_2$ ) along with phytic acid boost up the tensile strength of treated textiles. Here, it is realized that the hybrid complexes of nanoparticles and bio-based compounds can be considered as a big alternative of the traditional halogen and phosphorus containing synthetic compounds. The main results of these applications are presented in **Table 3**.

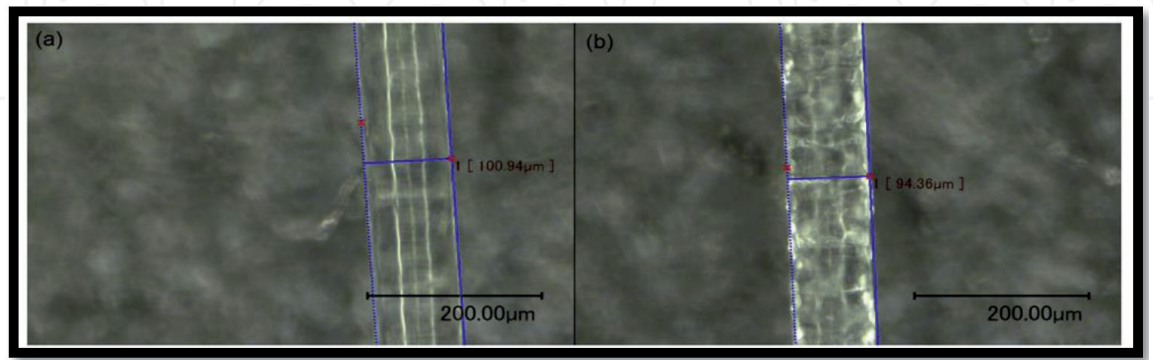
## 4.2 Flame retardant (FR) treatment of nylon 6 (polyamide 6) textiles

### 4.2.1 FR treatment at fiber stage

At the fiber stage finishing, a higher loading of a typical flame retardant is usually considered in imparting a satisfactory level of flame retardancy, which ultimately affects the mechanical properties of treated fibers and causes the spinning process difficult. For example, Coquelle et al. [46] use ammonium sulfamate (AS) as an additive flame retardant for nylon 6. Here, a loading of 5 wt.% AS in PA6 matrix leaves no significant changes since the pure PA6 and modified PA6 fiber come up with an almost similar fiber diameter (see **Figure 10**). An investigation based on the loading % of AS on the physical properties of modified nylon 6 fibers show that the fibers modified with less than 7 wt. % of AS are quite spinnable without alteration of the mechanical properties. In contrast, a higher loading (i.e., 10 wt. %) makes the material brittle and

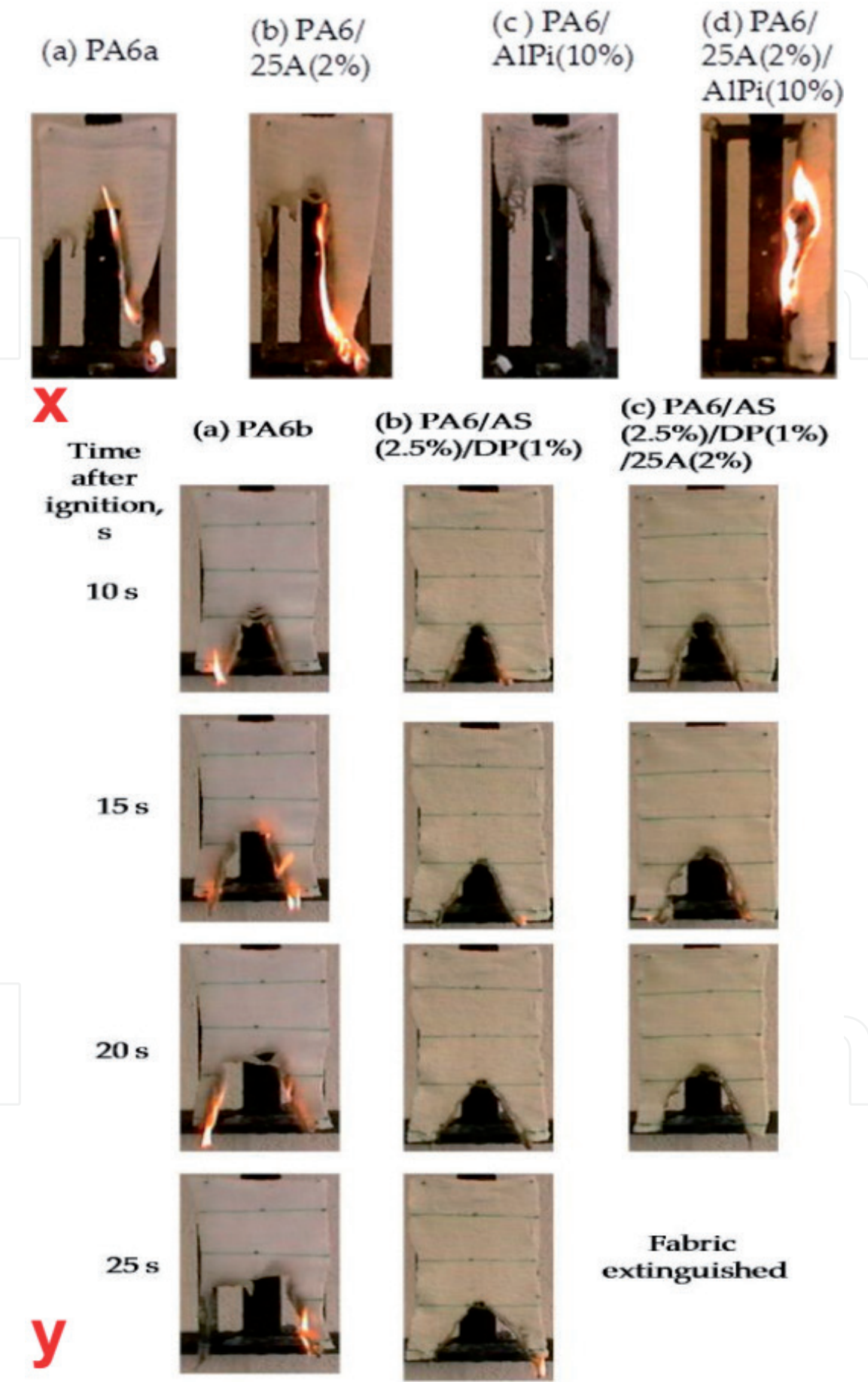
Substrate	FR compounds	Application technique	Main results	Eco-friendliness
Nylon 66 fabric [37]	Chitosan, phytic acid and Na-metaborate	LbL assembly/dipping	LOI up to 21.5%, reduction by 31% in pHRR	Partial
Nylon 66 fabric [38]	Chitosan, phytic acid, APTES and B-d-APTES	LbL assembly/sol-gel process	LOI up to 20.6%, 30% reduction in pHRR	Partial
Nylon 66 fabric [39]	P-chitosan (PCS) and APTES	UV-grafting/sol-gel process	LOI up to 24.3%, reduction by 30% in pHRR	Partial
Nylon 66 fabric [40]	Chitosan, phytic acid, melamine, urea and GO	Pad-dry-cure	LOI up to 25%, pHRR reduction by about 56%	Partial
Nylon 66 fabric [41]	Lignin, phytic acid, chitosan and GO	One pot deposition	LOI up to 27%, reduction in pHRR by 25%	Partial
Nylon 66 fabric [42]	Soybean protein isolation (SPI) and thiourea	Pad-dry-cure	LOI up to 25.5%, no dripping	Partial
Nylon 66 fabric [43]	Chitosan, P-chitosan and PAS	One pot deposition/LBL assembly	LOI up to 23%, 25% reduction in pHRR	Partial
Nylon 66 fabric [44]	DOPA and chitosan	UV grafting/ pad-dry-cure	LOI up to 24.5%, reduction in pHRR by 40%	Partial
Nylon 66 fabric [45]	Phytic acid, chitosan, TiO <sub>2</sub> and SiO <sub>2</sub>	Pad-dry-cure	LOI up to 24.5%, reduction in pHRR by 25%	Partial

**Table 3.**  
Collected results of flame retardant treatment for nylon 66 fabric.



**Figure 10.**  
Optical microscope photographs of PA6 (a) and PA6/AS 5% (b) fibers [46], copyright 2014. Reproduced with permission from Elsevier ltd.

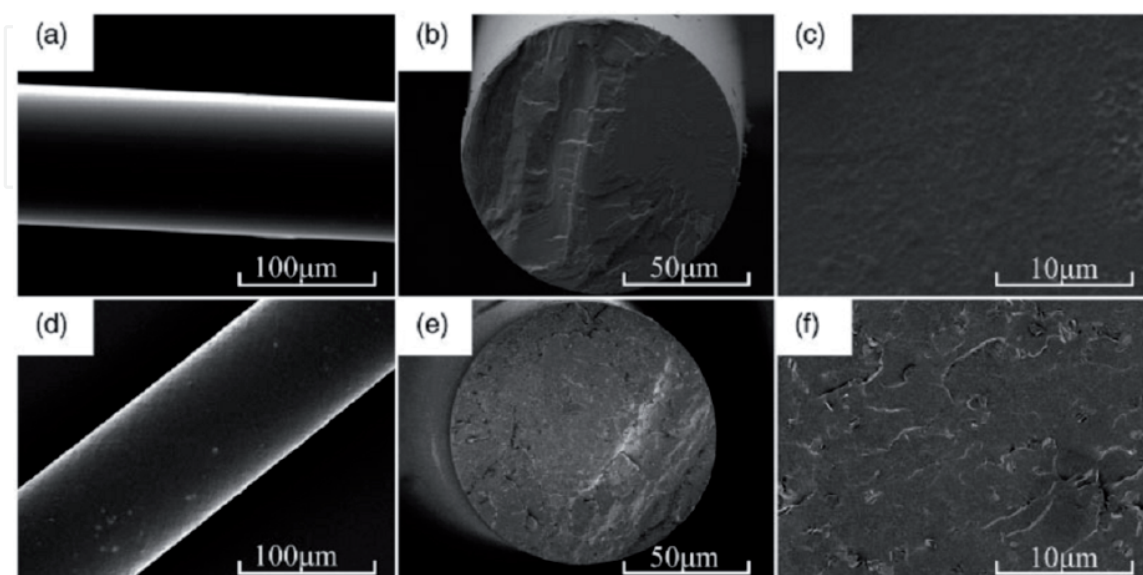
thus, it is impossible to spin it into fibers. This phenomenon exhibits the expected negative impact of higher loading % on the physical properties of synthetic fibers and thus, it is not beneficial to add the flame retardant compounds in the bulk state via additive mixing to impart flame retardant finishing at the fiber stage.



**Figure 11.** Selected images of burning PA6 fabrics comprising ALPi and/or Cloisite 25a 40 s after extinction of igniting flame (top-x) and burning and extinguishing behavior of ignited PA6/DP/AS/clay-based fabric samples: 10, 15, 20 and 25 s after extinction of the igniting flame (bottom-y) [47], copyright 2016. Reproduced with permission from [www.mdpi.com/journal/polymers](http://www.mdpi.com/journal/polymers).

So, a low loading of additive compounds is preferable (i.e., less than or equal 10 wt. %) to retain spinability of fibers to make the fabric from them and thus, a kind of trade-off between the loading of FR compounds and mechanical properties of fibers should be maintained in the fire retardant finishing of nylon 6 fibers. This low loading approach has been materialized in some application [47] where two different formulations are considered working in the different flame retardant mechanism (i.e., gas/solid). For example, aluminum diethyl phosphinate (AlPi) working primarily in the gas phase is mixed up with some clay additives like nanoclay, organically modified montmorillonite clay and Cloisite 25A active in the condensed phase. While, in another formulation, ammonium sulphamate (AS)/dipentaerythritol (DP) at 2.5/1 wt. % supposed to be active in the condensed phase, are blended with the same clay-based additives as mentioned earlier. Here, the different formulations come up with different level of flame retardancy as the AlPi-based formulation is incapable to impart self-extinguishability, though the clay-based additives can minimize the burning rate and modify the melt dripping phenomenon. In contrast, the AS/DP-based formulation at a loading of 5.5 wt. % or less offers better flame retardancy and in addition, the clay additives helps to rectify the dripping phenomenon remarkably. From the images of burning fabrics, it is observed that the PA6/AS/DP/clay-containing fabrics (see **Figure 11y**) show definite self-extinguishing characteristics unlike the PA6/AlPi/clay-containing fabric substrates (see **Figure 11x**) and thus, the PA6/AS/DP/clay formulation exhibits potential to be considered in the commercial scale.

Another clay based (i.e., MMT) additive approach is considered [48] to prepare the flame retardant nylon 6 nanocomposite nanofibers. Here, the MMT platelets as a nano-filler is blended with Exolit OP1312; a phosphorus-based non-halogenated additive via electrospinning. In this application, a higher loading of filler material (i.e., nanoclay particles) also affects the electrospinnability of this nanocomposite like other ordinary additive compounds. In another application [49], flame retardant PA6 fiber is developed using a composite formulation, namely via incorporation of melamine cyanurate (MCA) in nylon 6 matrix through in-situ polymerization process. Here, the MCA disperses into the nylon 6 matrix in a homogeneous manner without agglomeration as seen in the SEM images (see **Figure 12**) and thus, the interfacial interaction with the matrix is amplified in many folds. The as prepared composite fiber with a

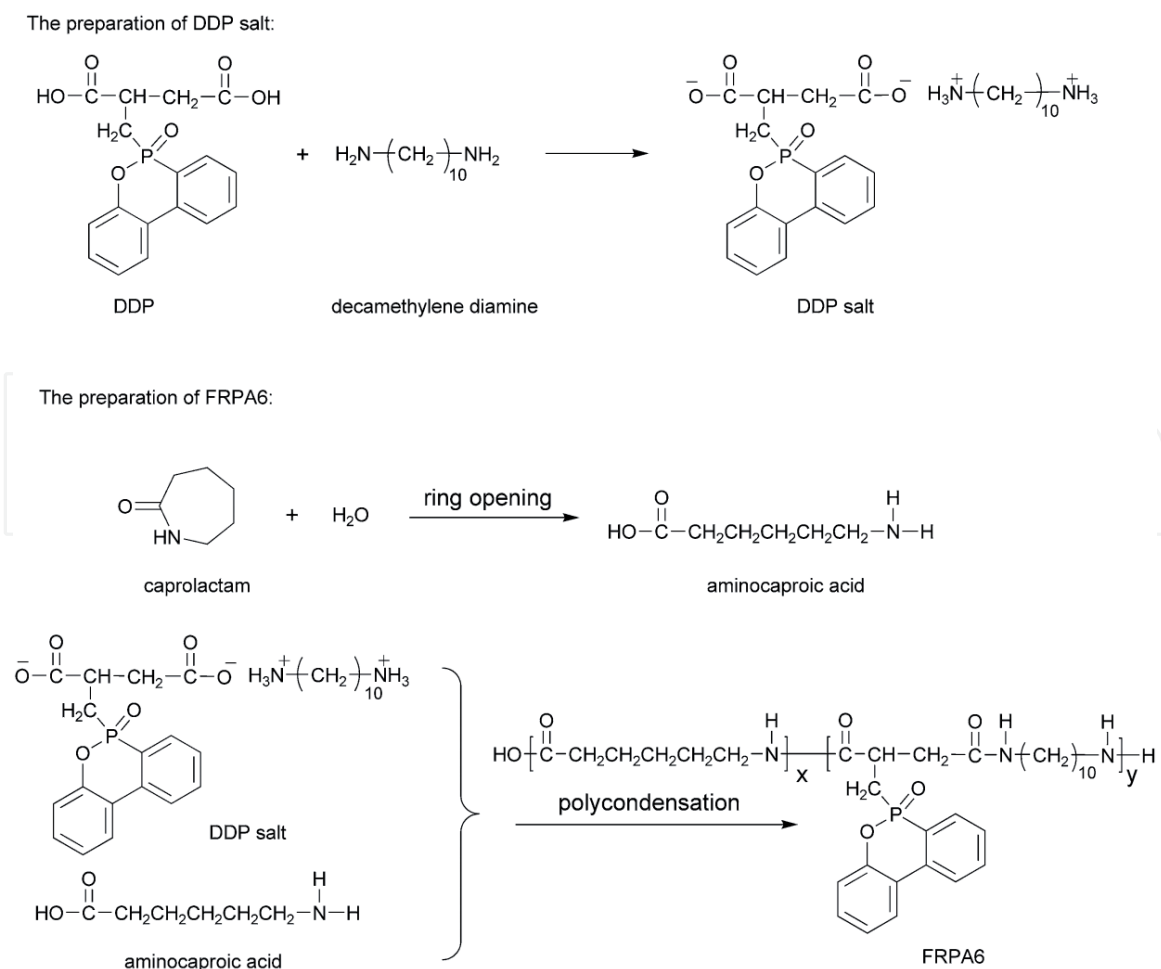


**Figure 12.**  
 The scanning electron micrographs of the surface and cross-section of polyamide 6 (PA6) fiber (a), (b), (c) and melamine cyanurate (MCA)/PA-6-8 fiber (d), (e), (f) [49], copyright 2016. Reproduced with permission from [sagepub.co.uk/journalsPermissions.nav](http://sagepub.co.uk/journalsPermissions.nav).

loading of only 8 wt. % of MCA shows satisfactory flame retardancy. Even, this lower loading % deteriorates the physical properties of the composite fiber as the tenacity at break decreases from 4.85 to 3.11 cN.dtex<sup>-1</sup>, but still meet the requirements of fabric preparation. Moreover, this in-situ polymerization approach opens the way for the preparation of flame retardant nylon 6 fibers with good spinnability.

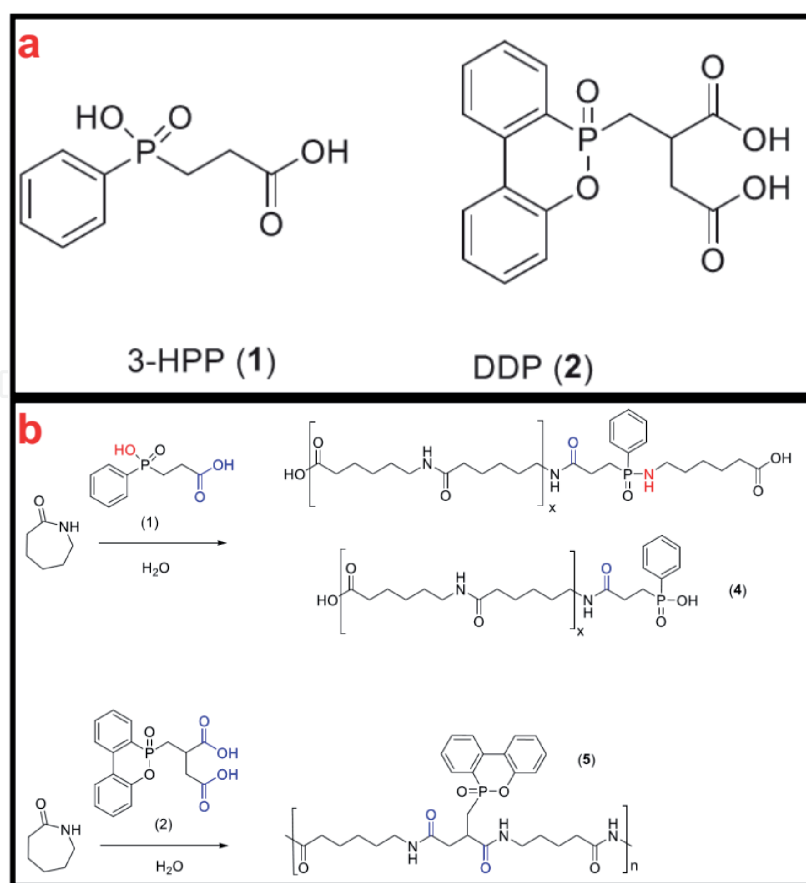
Apart from these, a phosphorus-based DOPO derivative, namely 9, 10-dihydro-10- [2, 3 di (hydroxycarbonyl) propyl]-10-phosphaphenanthrene-10-oxide (DDP), active in the gas phase, goes through the polycondensation reaction with caprolactam (see **Figure 13**) to develop intrinsically flame retardant nylon 6 fibers [50]. The melt-spun fiber prepared with a loading of 5 wt. % DDP attains a V-0 rating and also obtains a significant increase in LOI value. In addition, this kind of modification does not alter much the spinnability of such fibers in fabric preparation. Here, DDP acts both in the solid and gas phase via escalating charring and producing noncombustible gases respectively to impart fire retardant properties to the modified nylon 6 fibers.

The application of petro-based phosphorus compounds are further extended to develop flame-retarded nylon 6 fibers [51]. Here, at the first stage, co-condensation of ε-caprolactam is carried out via melt-polymerization process and later, a low loading of phosphorus-based FR co-monomer is introduced into the polymer chain with an aim to keep the tensile properties less hampered. Two different phosphorus compounds, namely 3 hydroxyphenylphosphinylpropanoic acid (3-HPP, 1) and 9,10-dihydro-10- [2,3 di(hydroxycarbonylpropyl) -10-phosphaphenanthrene-10-oxide (DDP, 2) are considered (see **Figure 14a**) and finally, they are integrated into the nylon 6 backbones (see **Figure 14b**). Such treatment eases the processing of flame



**Figure 13.**

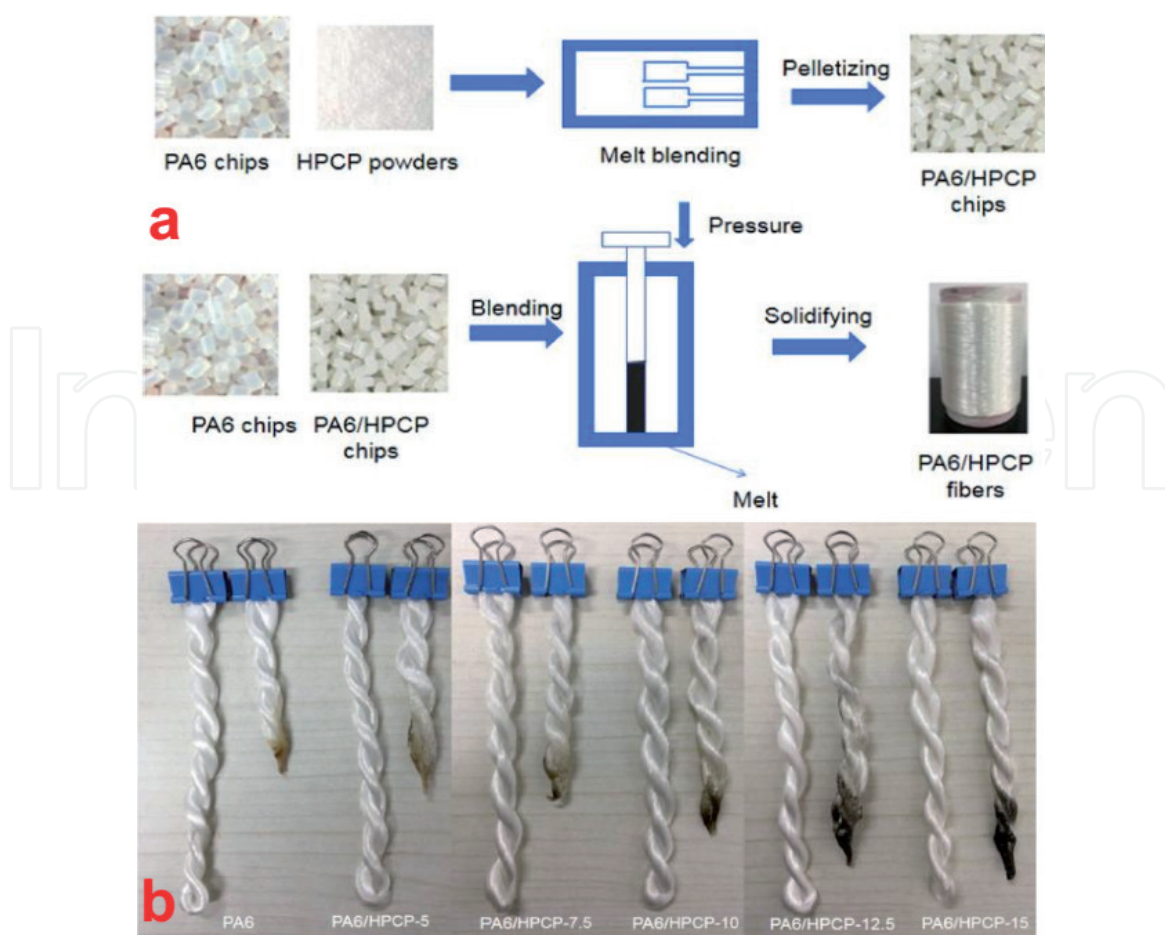
Preparation process of FR-PA6 [50], copyright 2018. Reproduced with permission from the Royal Society of Chemistry.



**Figure 14.** Chemical formulae of 1 and 2 (top-a) and installation options of the flame retardants into the nylon 6 backbone (bottom-b) [51], copyright 2019. Reproduced with permission from Wiley periodicals, Inc.

retardant nylon 6, especially at the fiber stage. In addition, this kind of facile application rarely alters the tensile properties of nylon substrate, which usually happens in the bulk state application of flame retardant compounds. In line, hexaphenoxycyclo-triphosphazene (HPCP) [52], a petro-based phosphorus compound, is considered to modify the flame-retardant properties of nylon 6 fibers (see **Figure 15a**). Here, the nylon 6 chips are blended with the flame retardant compound (HPCP) and fibers are prepared via melt spinning process. It is found that a loading up to 15 wt. % of HPCP does not deteriorate the spinnability of the modified fibers while a slight reduction of tensile properties is observed. Meanwhile, such modification imparts added flame retardancy to the nylon 6 fibers, especially in terms of increased LOI value and improved charring. In addition, the burning behavior is modified as the damaged length and burning time become shortened while dripping rate is minimized and no smoldering effect is observed (see **Figure 15b**). Here, HPCP primarily acts in the condensed phase via producing aromatic char residues along with the release of noncombustible gases like CO, CO<sub>2</sub> and NH<sub>3</sub> in the gas phase.

Apart from the previous techniques, a newly adopted technique, namely electron beam irradiation [53] is also considered in several applications to develop flame retarded nylon 6 fibers. Using this irradiation, some sort of cross-linking is induced to the polymer structure to alter the physical-chemical and thermal behaviors of the same. In some occasion, this irradiation-based cross-linking is carried out in presence of triallylcyanurate (TAC) to avail added benefits. As this kind of cross-linking usually improves the anti-dripping properties of nylon fibers while enhancing the physical properties like breaking strength and elongation at break, especially at a lower dosing. In line, such irradiation is also carried out in the presence of  $\gamma$ -rays along with some sensitizers like trimethallylisocyanurate (TMAIC)



**Figure 15.** The preparation process of PA6/HPCP fibers (top-a) and photos of the representative PA6 and PA6/HPCP fiber samples before and after the vertical oriented burning test (bottom-b) [52], copyright 2019. Reproduced with permission from Wiley periodicals, Inc.

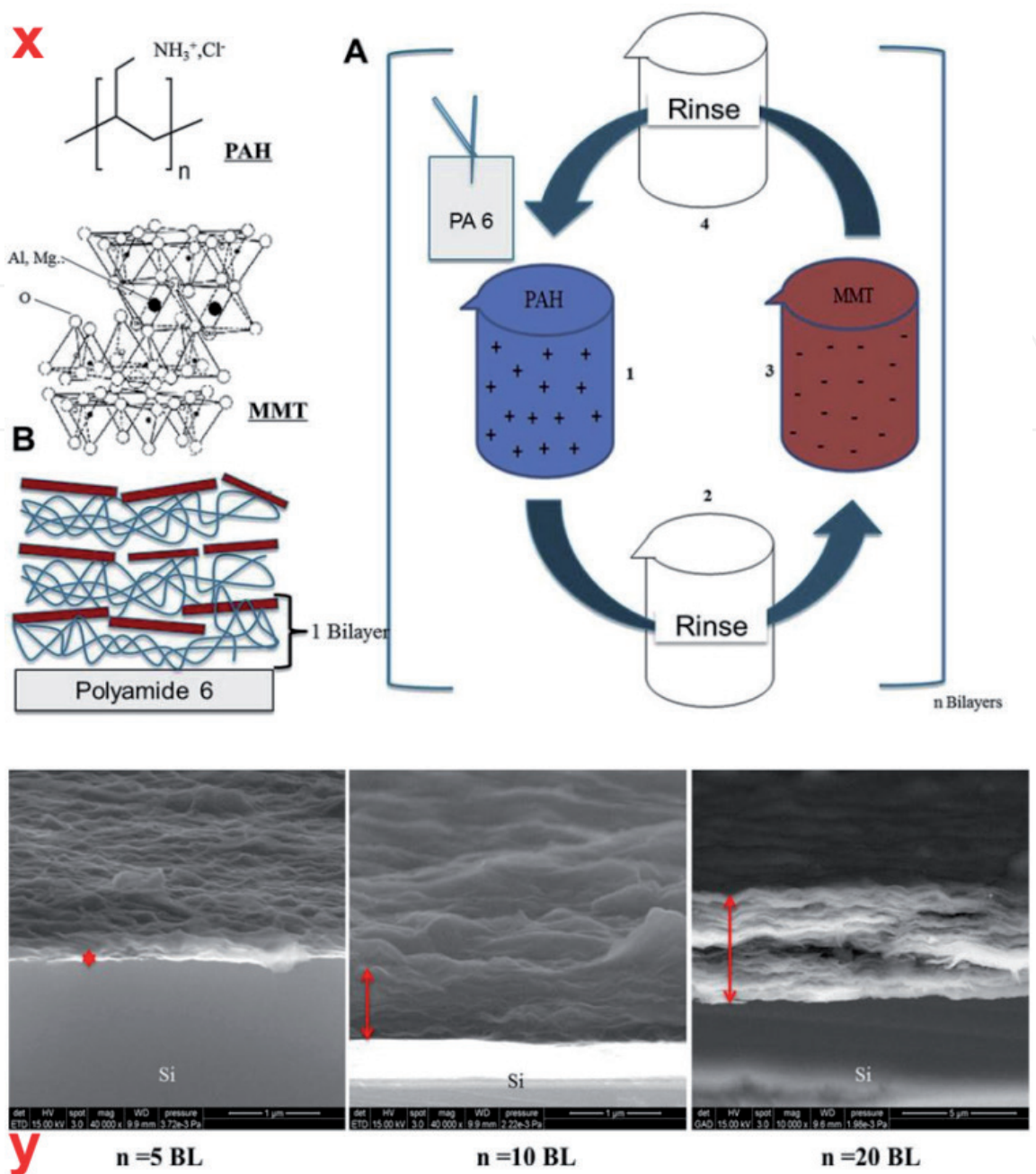
and trimethylolpropanetrimethylacrylate (TMPTMA) [54]. In order to overcome the low yield % in cross-linking reaction under the low radiation technique, different types of sensitizers are associated to overcome this shortcoming [55]. Meanwhile, this sensitizer assisted cross-linking alters the nylon 6 fiber structure into a three-dimensional network, which imparts improved anti-dripping properties to the modified fibers. The major results of the above section are summarized in **Table 4**.

#### 4.2.2 FR treatment at fabric stage

A very few attempts have been adopted so far to modify the flame retardant behaviors of nylon 6 textiles at fabric stage. Apaydin et al. [56] first take the initiative to come up with surface finishing of nylon 6 fabrics and introduce layer by layer (LbL) technique in preparing a flame retardant coating using two different types of polyelectrolytes (see **Figure 16x**). One is petro-based organic compound, namely polyallylamine (PAH) (polycation) and the other is an inorganic mineral compound like montmorillonite (MMT) (polyanion). The prepared coatings come up with a homogeneous distribution of coating ingredients with some roughness while in 20 bilayers deposited fabric sample, the MMT platelets lay in a parallel alignment (see **Figure 16y**). And this parallel distribution of MMT platelets ultimately imparts better mechanical and barrier properties to the coating structure. Meanwhile, the as prepared coatings, especially with 10 and 20 bilayers deposition offer enhanced thermal stability of the fabric substrate with a significant reduction in pHRR.

Substrate	FR compounds	Application technique	Main results	Eco-friendliness
Nylon 6 fiber [46]	Ammonium sulfamate (AS)	Additive mixing	30% reduction in pHRR	No
Nylon 6 fiber [47]	Cloisite 25A, aluminum diethyl phosphinate (ALPi), ammonium sulphamate/dipentaerythritol	Additive mixing	Low burning rate and the lowest level of melt-dripping.	No
Nylon 6 fiber [48]	MMT and Exolit OP1312	Additive mixing	Suppress peak heat release rate and improve charring	Partial
Nylon 6 fiber [49]	$\epsilon$ -caprolactam, adipic acid-melamine salt and cyanuric acid-hexane diamine salt	In-situ polymerization	Effectively suppress the propagation of flame	No
Nylon 6 fiber [50]	Caprolactam and DDP	Melt-polymerization	LOI value up to 33.7%, V-0 rating	No
Nylon 6 fiber [51]	$\epsilon$ -caprolactam, 3-HPP and DDP	Melt-polymerization	LOI up to 35%, good thermal properties	No
Nylon 6 fiber [52]	PA6/hexaphenoxycyclotriphosphazene (HPCP)	Blending technique	LOI up to 28.6%, no smoldering in the vertical burning.	No
Nylon 6 fiber [53]	Triallylcyanurate (TAC)	Electron beam irradiation	Nonvolatile residue increases	No
Nylon 6 fiber [54]	Trimethallylisocyanurate (TMAIC) and trimethylolpropane trimethylacrylate (TMPTMA)	$\gamma$ -irradiation	Improved anti-dripping performance	No

**Table 4.**  
*Collected results of flame retardant treatment for nylon 6 fiber.*



**Figure 16.** x) Schematic representation of layer-by-layer deposition. We repeated the steps 1–4 until the desired number of bilayers and y) a cross-sectional assemblies (top-x) and SEM cross-section of 5, 10 and 20 BL coated samples (bottom-y) [56], copyright 2012. Reproduced with permission from Elsevier Ltd.

Apart from the LbL assembly, a sol-gel technique using DOPO-VTS and TEOS is also adopted in developing flame retardant finishes onto the nylon 6 fabric surfaces [57]. The co-application of silicon compounds with a DOPO derivative ensures added charring while providing thermal stability to these residues, which acts positively to stop the melt-dripping of nylon fabrics.

Moreover, flame-retarded nylon 6 textiles with a knitted structure is developed using a different technique [58]. Here, a blending technique is adopted to mix three different components, namely nylon 6 multifilament, commercially available nylon 6 polymer chips and synthesized flame-retarded nylon 66. Initially, the flame-retarded nylon 66 is developed through the co-condensation reaction of hexamethylenediammoniumadipate (AH-salt) with the salts of hexamethylene diamine and two different organophosphorus compounds

Substrate	FR compounds	Application technique	Main results	Eco-friendliness
Nylon 6 fabric [56]	Polyallylamine and MMT	LbL assembly	62% reduction in pHRR for 20 BL deposition	Partial
Nylon 6 fabric [57]	DOPO-VTS and TEOS	Pad-dry-cure	Impart non-dripping behavior, decrease the THR value and increase the char yield%	No
Nylon 6 fabric [58]	FR-PA66 + PA6	Blending technique	LOI up to 38%, V-0 rating in horizontal burning test	No

**Table 5.**  
*Collected results of flame retardant treatment for nylon 6 fabric.*

like 3 hydroxyphenylphosphinylpropanoic acid (3-HPP) and 9,10-dihydro-10-[2,3-di(hydroxycarbonylpropyl)-10-phosphaphenanthrene-10-oxide (DDP). Here, the mixing of flame retardant compounds with varied polyamides ensures better miscibility and compatibility of the composites, which help the modified nylon 6 fiber to retain its physical properties as well as overcoming the post-synthesis shortcomings related to bleeding and higher loading of flame retardant compounds. Finally, the prepared fabric with a knitted structure using these flame-retarded nylon 6 fibers come up with a very high LOI value (i.e., 36–38) and reveals improvements in other parameters. The key results of this section are presented in **Table 5**.

5. Conclusions

The flame retardant treatment of nylon textiles is getting constant development with time and becoming more sustainable in terms of uses of bio-derived flame retardant compounds and the green application processes. However, in the earlier applications, the use of petro-based flame retardant compounds has been more prominent. Additionally, it is seen that the fiber stage finishing has been more preferable over the topical finishing in the previous applications. Nonetheless, this fiber stage finishing still exists at a limited scale while some sort of modification is initiated in the current applications to convert this process more eco-friendly. However, due to the limitation of fiber stage finishing method related to the poor mechanical or physical properties in the modified fibers, the topical finishing has become very popular in today’s applications. Meanwhile, the green practices in topical/surface finishing, especially in terms of flame retardant compounds and application methods are increasing day by day. These bio-derived compounds show efficacy in improving some crucial flame retardant parameters, namely reducing pHRR and enhancing the char yield % as their polyalcoholic aromatic structure favors the condensed phase mechanism. However, they are yet to show the potency in improving LOI values and thermal stability. Even in some extent, coatings developed from bio-derived polyelectrolytes via ionic interaction suffer from poor wash durability, which need to be optimized further. In line, some sort of hybridization, both in application methods (i.e., sol–gel/layer-by-layer assembly, etc.) and in flame retardant compounds (i.e., organic/inorganic/nanocompounds) have been enormously used in these days. In a typical application, flame retardant compounds belonging to organic species produce charring while the inorganic species offer shielding effect to these char residues to safeguard the underneath textiles from further burning. Such kind of hybridization has been found beneficial in improving

the charring ability of nylon textiles as the nylon polymers show poor charring due to their typical aliphatic structures. Though some recent works have already shown promise in imparting flame retardant properties to the nylon textiles considering the environmental impacts and durability issues of such finishing methods, still there are challenges to imply them commercially.

### **Author details**

Chanchal Kumar Kundu<sup>1,2</sup>, Zhiwei Li<sup>1\*</sup>, Lei Song<sup>2</sup> and Yuan Hu<sup>2</sup>

1 National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng, P.R. China

2 State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, P.R. China

\*Address all correspondence to: zhiweili@henu.edu.cn

### **IntechOpen**

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

## References

- [1] N.N. Brushlinsky, S.V. Sokolov, P. Wagner, J.R. Hall, in: World Fire Statistics. Report No. 10. Centre of Fire Statistics, International Association of Fire and Rescue Service, 2006. [www.ctif.org](http://www.ctif.org).
- [2] M. Kobes, K. Groenewegen, in: Consumer Fire: European Statistics and Potential Fire Safety Measures, Austrian Federal Ministry Labor, Social Affairs and Consumer Protection, 2009.
- [3] H. Frantzich, in: A Model for Performance-Based Design of Escape routes, Technical Report, Department of Fire Safety Engineering, Lund Institute of Technology, Lund University, 1994.
- [4] R.G. Gann, Estimating Data for Incapacitation of People by Fire Smoke, *Fire Technology* 40 (2004) 201-207.
- [5] J.H. Cho, V. Vasagar, K. Shanmuganathan, A.R. Jones, S. Nazarenko, C.J. Ellison, Bioinspired Catecholic Flame Retardant Nanocoating for Flexible Polyurethane Foams, *Chem. Mater.* 27 (2015) 6784-6790.
- [6] G. Laufer, C. Kirkland, A.B. Morgan, J.C. Grunlan, Exceptionally Flame Retardant Sulfur-Based Multilayer Nanocoating for Polyurethane Prepared from Aqueous Polyelectrolyte Solutions, *ACS Macro Lett.* 2 (2013) 361-365.
- [7] C.K. Kundu, Z. Li, L. song, Y. Hu, An overview of fire retardant treatments for synthetic textiles: From traditional approaches to recent applications, *Eur. Polym. J* 137 (2020) 109911.
- [8] A. Dahiya, M. G. Kamath, R. Hegde, MSE 554, University of Tennessee, Nonwovens science and technology II (2004).
- [9] A. R. Horrocks, B. K. Kandola, P. Davies, S. Zhang, S. Padbury, Developments in flame retardant textiles—a review, *Polymer Degradation and Stability*, 88 (2005) 3-12.
- [10] L. Li, G. Chen, W. Liu, J. Li, S. Zhang, The anti-dripping intumescent flame retardant finishing for nylon-6, 6 fabric, *Polymer Degradation and Stability*, 94 (2009) 996-1000.
- [11] E.D. Weil, S. Levchik, Current practice and recent commercial developments in flame retardancy of polyamides, *Journal of fire sciences*, 22 (2004) 251-264.
- [12] J. Green, Brominated phosphate ester flame retardants for engineering plastics, in *Fire Retardant Engineering Polymers and Alloys, Products and Applications—Compounding—Testing and Evaluation*, papers presented at La Mansion del Rio, San Antonio, Texas, March 12-15 (1989) 69-100.
- [13] G.L. Nelson, Fire and polymers—an overview, in *Fire and Polymers II* (G. L. Nelson, Ed.), ACS Symposium Series 599, American Chemical Society, Washington, DC (1995) 1-28.
- [14] A. Dasari, Z.Z. Yu, G.P. Cai, Y.W. Mai, Recent developments in the fire retardancy of polymeric materials, *Prog. Polym. Sci.* 38 (2013) 1357-1387.
- [15] G.L. Nelson, Fire toxicity, in *Fire and Polymers II* (G. L. Nelson, Ed.), ACS Symposium Series 599, American Chemical Society, Washington, DC (1995) 291-292.
- [16] D.W. Van Krevelen, Flame resistance of chemical fibers, *Journal of Applied Polymer Science*, 31 (1977) 269-292.
- [17] M.S. Subbulakshmi, N. Kasturiya H. P. Bajaj, A. K. Agarwal, Production of flame-retardant nylon 6 and 6.6, *Journal of Macromolecular Science*, 40 (2000) 85-104.

- [18] Interscience (Ed.), Man Made Textile Encyclopedia, J. J. Press, New York (1959) 143-144.
- [19] W.H. Sharkey, W. E. Mochel, Mechanism of the Photooxidation of Amides, Journal of the American Chemical Society, 81 (1959) 3000-3005.
- [20] Y. Shinohara, D. Ballantine, Free radicals in irradiated nylon, The Journal of Chemical Physics, 36 (1962) 3042-3049.
- [21] B.K. Kandola, Flame Retardancy Design for Textile. In Fire Retardancy of Polymeric Materials, 2 ed.; Wilkie, C. A.; Morgan, A. B., Eds. CRC Press Taylor and Francis Group: Boca Raton (2010) 725-762.
- [22] J. Alongi, F. Carosio, P. Kiekens, Recent advances in the design of water based-flame retardant coatings for polyester and polyester-cotton blends, Polymers, 8 (2016) 357.
- [23] E.D. Weil, S. Levchik, Current practice and recent commercial developments in flame retardancy of polyamides, J. Fire Sci. 22 (2004) 251-264.
- [24] S.V. Levchik, E.D. Weil, Combustion and fire retardancy of aliphatic nylons, Polym. Int. 49 (2000) 1033-1073.
- [25] S.V. Levchik, E.D. Weil, A review of recent progress in phosphorus-based flame retardants, J. Fire Sci. 24 (2006) 345-364.
- [26] S.V. Levchik, A.I. Balabanovich, G.F. Levchik, L. Costa, Effect of melamine and its salts on combustion and thermal decomposition of polyamide 6, Fire Mater. 21 (1997) 75-83.
- [27] F. Mohaddes, L. Wang, R.A. Shanks, S.M. Fergusson, Elevation of charring level of polyamide-6,6 films via ionic introduction of phosphoric acid and boric acid esters, Green Chem. Lett. Rev. 7 (2014) 184-190.
- [28] Y. Li, K. Liu, R. Xiao, Preparation and characterization of flame-retarded polyamide 66 with melamine cyanurate by in situ polymerization, Macromol. Res. 25 (2017) 779-785.
- [29] Y.Y. Li, K. Liu, R. Xiao, Preparation and characterizations of flame retardant polyamide 66 fiber, 2017 Global Conference on Polymer and Composite Materials (PCM 2017) IOP Publishing IOP Conf. Series: Materials Science and Engineering 213, 2017.
- [30] L. Xiao, L. Xu, Y. Yang, S. Zhang, Y. Huang, C.W. Bielawski, J. Geng, Core-Shell Structured Polyamide 66 Nanofibers with Enhanced Flame Retardancy, ACS Omega 2 (2017) 2665-2671.
- [31] J. Alongi, F. Carosio, G. Malucelli, Current emerging techniques to impart flame retardancy to fabrics: an overview, Polymer Degradation and Stability, 106 (2014) 138-149.
- [32] S.Y. Liang, N. M. Neisius, S. Gaan, Recent developments in flame retardant polymeric coatings, Progress in Organic Coatings, 76 (2013) 1642-1665.
- [33] B. Mahltig, H. Haufe, H. Böttcher, Functionalisation of textiles by inorganic sol-gel coatings, Journal of Materials Chemistry, 15 (2005) 4385-4398.
- [34] C.K. Kundu, B. Yu, C. S. R. Gangireddy, X. Mu, B. Wang, X. Wang, L. song, Y. Hu, UV Grafting of a DOPO-Based Phosphoramidate Monomer onto Polyamide 66 Fabrics for Flame Retardant Treatment, Industrial & Engineering Chemistry Research, 56 (2017) 1376-1384.
- [35] C.K. Kundu, W. Wang, S. Zhou, X. Wang, H. Sheng, Y. Pan, L. song, Y. Hu, A green approach to constructing

multilayered nanocoating for flame retardant treatment of polyamide 66 fabric from chitosan and sodium alginate, *Carbohydr. Polym.* 166 (2017) 131-138.

[36] Z. Xia, W. Kiratitanavit, P. Facendola, S. Thota, S. Yu, J. Kumar, R. Mosurkal, R. Nagarajan, Fire resistant polyphenols based on chemical modification of bio-derived tannic acid, *Polym. Degrad. Stab.* 153 (2018) 227-243.

[37] C.K. Kundu, X. Wang, L. song, Y. Hu, Borate cross-linked layer by layer assembly of green polyelectrolytes on polyamide 66 fabrics for flame-retardant treatment, *Prog. Org. Coat.* 121 (2018) 173-181.

[38] C.K. Kundu, X. Wang, L. Liu, L. song, Y. Hu, Few layer deposition and sol-gel finishing of organic-inorganic compounds for improved flame retardant and hydrophilic properties of polyamide 66 textiles: A hybrid approach, *Prog. Org. Coat.* 129 (2019) 318-326.

[39] C.K. Kundu, X. Wang, Y. Hou, Y. Hu, Construction of flame retardant coating on polyamide 6.6 via UV grafting of phosphorylated chitosan and sol-gel process of organo-silane, *Carbohydr. Polym.* 181 (2018) 833-840.

[40] M.Z. Rahman, C.K. Kundu, H. Nabipoura, X. Wang, L. song, Y. Hu, Hybrid coatings for durable flame retardant and hydrophilic treatment of Polyamide 6.6 fabrics, *Prog. Org. Coat.* 144 (2020) 105640.

[41] C.K. Kundu, Z. Li, X. Li, Z. Zhang, Y. Hu, Graphene oxide functionalized biomolecules for improved flame retardancy of Polyamide 66 fabrics with intact physical properties, *Int. J. Biol. Macromol.* 156 (2020) 362-371.

[42] D. Meng, J. Guo, A. Wang, X. Gu, Z. Wang, S. Jiang, S. Zhang, The fire

performance of polyamide66 fabric coated with soybean protein isolation, *Prog. Org. Coat.* 148 (2020) 105835.

[43] C.K. Kundu, X. Wang, L. song, Y. Hu, Chitosan-based flame retardant coatings for polyamide 66 textiles: One pot deposition versus layer-by-layer assembly, *Int. J. Biol. Macromol.* 143 (2020) 1-10.

[44] C.K. Kundu, X. Wang, M.Z. Rahman, L. song, Y. Hu, Application of Chitosan and DOPO derivatives in fire protection of polyamide 66 textiles: Towards a combined gas phase and condensed phase activity, *Polym. Degrad. Stab.* 176 (2020) 109158.

[45] C.K. Kundu, L. song, Y. Hu, Nanoparticles based coatings for multifunctional Polyamide 66 textiles with improved flame retardancy and hydrophilicity, *J. Taiwan Inst. Chem. Eng.* 112 (2020) 15-19.

[46] M. Coquelle, S. Duquesne, M. Casetta, J. Sun, S. Zhang, S. Bourbigot, Investigation of the decomposition pathway of polyamide 6/ammonium sulfamate fibers, *Polym. Degrad. Stab.* 106 (2014) 150-157.

[47] R. Horrocks, A. Sitpalan, C. Zhou, B.K. Kandola, Flame Retardant Polyamide Fibres: The Challenge of Minimising Flame Retardant Additive Contents with Added Nanoclays, *Polymers* 8 (2016) 288.

[48] H. Wu, M. Krifa, J.H. Koo, Flame retardant polyamide 6/nanoclay/intumescent nanocomposite fibers through electrospinning, *Text. Res. J.* 84 (2014) 1106-1118.

[49] Y. Li, Y. Lin, K. Sha, R. Xiao, Preparation and characterizations of flame retardant melamine cyanurate/polyamide 6 composite fibers via in situ polymerization, *Text. Res. J.* 87 (2017) 561-569.

- [50] K. Liu, Y. Li, L. Tao, R. Xiao, Preparation and characterization of polyamide 6 fibre based on a phosphorus-containing flame retardant, *RSC Adv.* 8 (2018) 9261-9271.
- [51] E. Giebel, T. Schneck, J. Unold, M.R. Buchmeiser, Syntheses of intrinsically flame-retardant polyamide 6 fibers and fabrics, *J. Appl. Polym. Sci.* 136 (2019) 47829.
- [52] Y. Di, X. Wu, Z. Zhao, W. Wang, Experimental investigation of mechanical, thermal, and flame-retardant property of polyamide 6/ phenoxyphosphazene fibers, *J. Appl. Polym. Sci.* 137 (2019) 48458.
- [53] S. Zhu, M. Shi, M. Zhu, Effects of Electron-Beam Irradiation Crosslinking on PA6 Fibers, *Fiber Polym.* 14 (2013) 525-529.
- [54] S. Zhu, M. Shi, M. Zhu, Thermal and anti-dripping properties of g-irradiated PA6 fiber with the presence of sensitizers, *Mater. Lett.* 99 (2013) 28-30.
- [55] N.K. Pramanik, R.S. Haldar, Y.K. Bhardwaj, Radiation processing of Nylon 6 by e-beam for improved properties and performance, *Radiat. Phys. Chem.* 78 (2009) 199-205.
- [56] K. Apaydin, A. Laachachi, V. Ball, M. Jimenez, S. Bourbigot, V. Toniazzi, D. Ruch, Polyallylamine-montmorillonite as super flame retardant coating assemblies by layer-by-layer deposition on polyamide, *Polym. Degrad. Stab.* 98 (2013) 627-634.
- [57] A. Sehi, B. Tomsic, I. Jerman, J. Vasiljevic, J. Medved, B. Simoncic, Synergistic inhibitory action of P- and Si-containing precursors in sol-gel coatings on the thermal degradation of polyamide 6, *Polym. Degrad. Stab.* 128 (2016) 242-252.
- [58] G. Mourgas, E. Giebel, V. Bauch, T. Schneck, J. Unold, M.R. Buchmeiser, Synthesis of intrinsically flame-retardant copolyamides and their employment in PA6-fibers, *Polym. Adv. Technol.* (2019) 1-11.