Jelena Vasiljević[1], Marija Čolović[2], Ivan Jerman[2], Barbara Simončič[1]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva 12, 1000 Ljubljana, Slovenia
[2]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Recent Advances in Production of Flame Retardant Polyamide 6 Filament Yarns
Najsodobnejše raziskave na področju proizvodnje ognjevarnih poliamidnih 6 filamentnih prej

Abstract

Polyamide 6 is one of the key engineering polymers with excellent mechanical properties and resistance which enable its global production and wide use in the industrial and domestic plastic manufacturing. Polyamide 6 also represents an important raw material for the production of technical filament yarns. However, an important drawback associated with the flammability of PA6 fibres has not been resolved yet. This paper reviews the most common halogen-free flame retardant additives for polyamide 6, their mode of action as well as different strategies for the incorporation of flame retardant additives in the production process of flame ratardant polyamide 6 fibres. The most recent research and patents on this topic are critically discussed.
Keywords: textile, bulk polymers, flame retardancy, flame retardant additives, production strategies

Izvleček

Poliamid 6 je eden ključnih inženirskih polimerov z odličnimi mehanskimi lastnostmi in visoko odpornostjo, ki omogoča njegovo široko uporabo pri proizvodnji industrijskih in gospodinjskih plastičnih mas. Poliamid 6 predstavlja tudi pomembno surovino za proizvodnjo filamentnih prej za tehnične namene. Vendar pa pomembna pomanjkljivost, povezana z vnetljivostjo poliamidnih 6 vlaken, še ni bila odpravljena. Članek vključuje pregled najpogosteje uporabljenih ne-halogenih ognjevarnih aditivov za poliamid 6, njihovega načina delovanja in različnih pristopov za vgradnjo ognjevarnih aditivov v proizvodnem procesu ognjevarnih vlaken iz poliamida 6. Predstavljena je kritična razprava o najsodobnejših raziskavah in patentih na področju.
Ključne besede: tekstilije, plastične mase, ognjevarnost, ognjevarna sredstva, proizvodne strategije

1 Introduction

Polyamide 6 (PA6) is one of the key engineering polymers with excellent mechanical properties and resistance which enable its global production and wide use in the industrial and domestic plastic manufacturing. Excellent processing properties, low moulding shrinkage and simple and low cost processing on one hand as well as its toughness, high tensile strength, abrasion and creep resistance on the other hand enabled PA6 to become one of the most important raw materials in the production of textile fibres for technical applications, such as technical clothing, carpets and carpet paddings, fabrics for furniture upholstery, transport seats, floor coverings and air bags [1]. Whereas PA6 plastics represent the largest segment of the global polyamide market, the PA6 textile fibre application segment is the fastest growing [2]. Furthermore, PA6 has an exceptional feature, i.e., its chemical recyclability back to monomer ε-caprolactam, which classifies PA6 as a "sustainable polymer"

and, consequently, dramatically enhances its reusability and added value [3].

Despite the widespread use of PA6 in various economic areas, a problem associated with the flammability of PA6 fibres has not been solved yet. Specifically, a very hazardous drawback of PA6 is its inherent flammability, which can lead to rapid burning with an intensive flammable melt-dripping and a release of toxic smoke, which may present a great risk and danger for lives and material goods. Despite the rather successful production of flame retardant (FR) PA6 moulding plastic materials, the development of FR PA6 textile fibres remains a challenging scientific problem, and commercially available FR PA6 textile fibres still do not exist [4].

Much effort has been put into the production of FR PA6 fibres during the last decades [4–8]. For effective FR action, it is crucial that the FR additive matches the processing and pyrolysis specifics of PA6. Accordingly, the FR additive needs to be thermally stable and non-volatile at the processing temperatures of PA6 composites and filaments. The thermal stability and mode of action of the FR additive must match those of PA6 during pyrolysis, during which the mostly volatile cyclic monomer ε-caprolactam, alkyl cyanides and ammonia are produced, leaving no charred residue in the condensed phase [9]. According to the literature, FR loadings higher than 15 wt% are required to achieve an effective FR action in the PA6 bulk polymers [4], but these high loadings are unacceptable for the textile fibres because of their impaired spinnability and tensile properties. These represent the most important limitations in the production of FR PA6 fibres in comparison with PA6 bulk polymers. Furthermore, compared to bulk plastic, the lightweight PA6 textile fibres and fabrics have an open structure with a much higher surface, which intensifies the burning rate.

2 Structures of FR additives and their mode of action

Although halogenated FR additives are very effective and have been some of the most important FR additives for PA6 over the decades, they have been prohibited as substances of Very High Concern (REACH SVCH), and due to their persistence, bio-accumulation and high toxicity (PBT), there is a gap in the market for FR additives. The most intensively investigated halogen-free FR additives for PA6 include phosphorus (P)- and nitrogen (N)-based FRs, inorganic hydroxides and different nanoparticles [4–8, 10–12]. The most common FRs for PA6 are summarised in Table 1, and some of them are presented in Figure 1.

FR mechanisms and modes of action depend on the chemical structures of the FR additives as well as the structure and thermal decomposition pathway of the polymers. Accordingly, FR additives act chemically and/or physically in the gas phase and/or in the condensed phase (Figure 2) [4–8, 10–12]. It is known that the same FR additive can provide different flame retardancy for different polymers. In general, P-based FR additives are active in both the condensed phase and the gas phase depending on the oxidation state of the P atom [67]. According to the condensed-phase mode of action, phosphorous compounds, i.e., phosphates and phosphonates, promote char formation by influencing the decomposition pathway of the polymers. If this reaction is accompanied by the release of water, the combustive vapours are also diluted. According to the gas-phase mechanism, phosphorous compounds, i.e., phosphinates and phosphine oxides, decompose to radical scavengers, which terminate the oxidative radical chain reactions in the combustion cycle. In the case of PA6, the gas phase contributes more to flame retardancy than char formation because the polymer chain scission, which occurs during thermal decomposition, leads to the generation of ε-caprolactam and other volatiles from the shorter chain fragments, and very little char residue is formed. Therefore, char-promoting phosphorous FRs alone are not enough to be effective in PA6. In contrast, the gas phase active P-based FR additives are of great importance for the protection of PA6. Specifically, phosphorous radicals in the flame, i.e., $HPO_2\cdot$, $PO\cdot$, $PO_2\cdot$ and $HPO\cdot$, can scavenge H· and OH· radicals that propagate fuel combustion. This leads to a reduction in concentrations of H· and OH· radicals and the quenching of the flame.

Among N-based FR additives, MeCy has special importance since it is considered as one of the most effective FR additives for aliphatic polyamides [68]. MeCy exhibits a strong condensed-phase mode of action; however, it is also active in the gaseous phase [18]. At higher temperatures, MeCy undergoes

Table 1: The most common halogen-free FR additives for PA6

FR-active chemical element or group	Chemical structure	Reference
Phosphorous	6-((6-oxidodibenzo[c,e][1,2]-oxaphosphinine-6-yl) methoxy)dibenzo[c,e][1,2]-oxaphosphinine-6-oxide) (Di-DOPO-MeO)	[13]
Nitrogen	ammonium sulfamate (AS)	[14–17]
	melamine cyanurate (MeCy)	[18–27]
Phosphorous, nitrogen	ammonium polyphosphate (APP)	[28]
	melamine polyphosphate (MPP)	[29–32]
	6-(2-(4,6-diamino-1,3,5-triazin-2-yl)ethyl)dibenzo[c,e][1,2]oxaphosphinine-6-oxide (DTE-DOPO)	[33]
	6, 60-(ethane-1,2-diylbis(azanediyl))bis(dibenzo[c,e][1,2]-oxaphosphinine-6-oxide) (Di-DOPO-EDA)	[13]
	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-based diepoxide (DEP)	[34, 35]
	cyclotriphosphazene	[36–38]
Phosphorous, aluminium	aluminium dialkylphosphinate (AlPi)	[16, 28–31, 33, [38–46]
	aluminium hypophosphite	[41, 42, 47]
Phosphorous, boron	boron phosphate	[44, 48, 49]
Phosphorous, silicon	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-functionalised triethoxysilane (SiDOPO)	[50, 51]
	diethylphosphatoethyltriethoxysilane (SiP)	52
Boron	zinc borate	44, 53
Group II or III hydroxides	alumina monohydrate, AlO(OH)	[4, 54, 55]
	magnesium hydroxide, $Mg(OH)_2$	[55, 56]
Silicon	tetraethoxysilane	[52]
Aluminium, silicon	pristine clays (bentonite, kaolinite, zeolite), pristine nanoclays (halloysite nanotubes)	[14, 27, 57–60]
	organically modified nanoclays (montmorillonite (MMT))	[30, 31,61,62]
Carbon	carbon nanotubes (CNTs)	[63–66]

endothermic decomposition to melamine and cyanuric acid. Melamine partially sublimes at approximately 350 °C, which is accompanied by a significant absorption of energy. In the condensed phase, melamine undergoes endothermic self-condensation with the release of ammonia, which volatilises and dilutes the fuel gases that support combustion. MeCy also decreases the thermal stability of PA6 and catalyses the chain scission of PA6 macromolecules to oligomeric segments, which are less flammable than caprolactam. The chain scission also decreases the melt viscosity and accelerates melt flow and dripping. Because the melt drips remove heat from the polymer matrix, the phenomenon of flame self-extinguishment occurs. MeCy also promotes the formation of a cross-linked structure in the self-condensation reaction with the generated oligomers. This promotes the formation of a closed char layer.
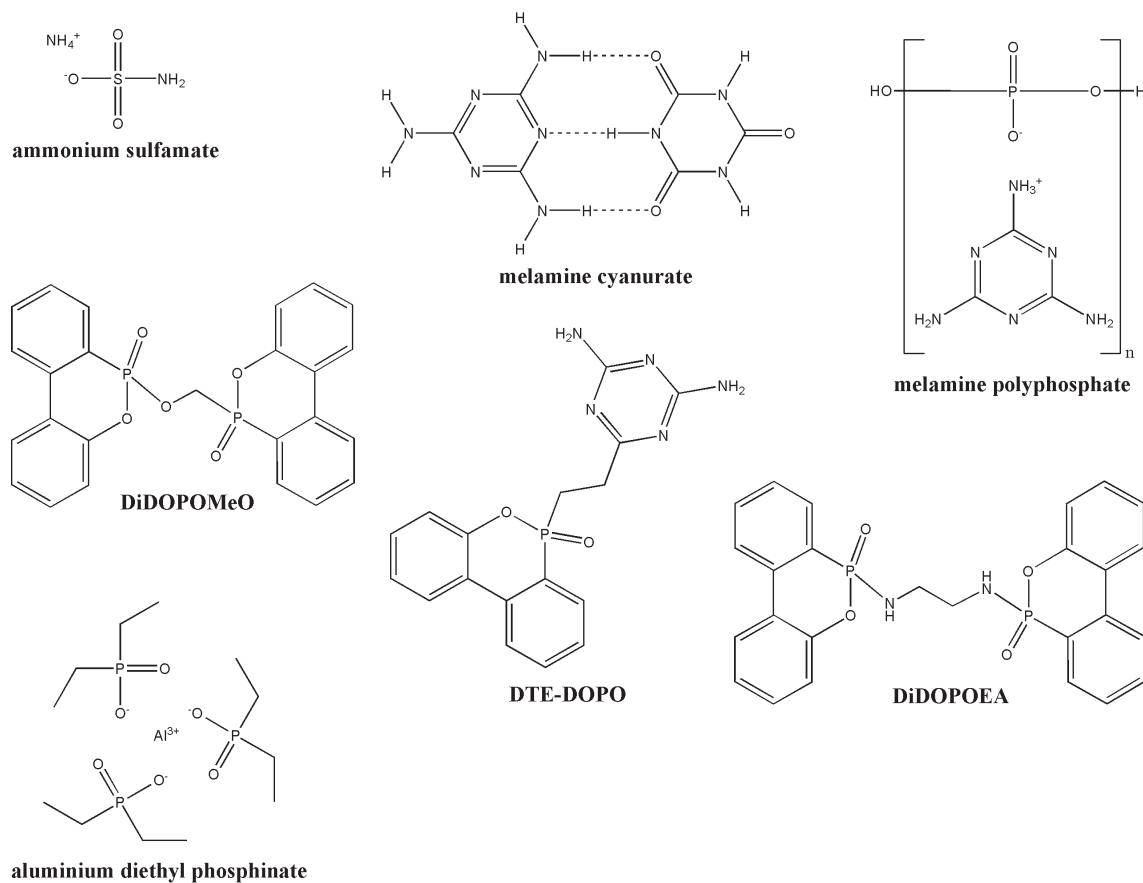
Figure 1: Chemical structures of some representative FR additives for PA6
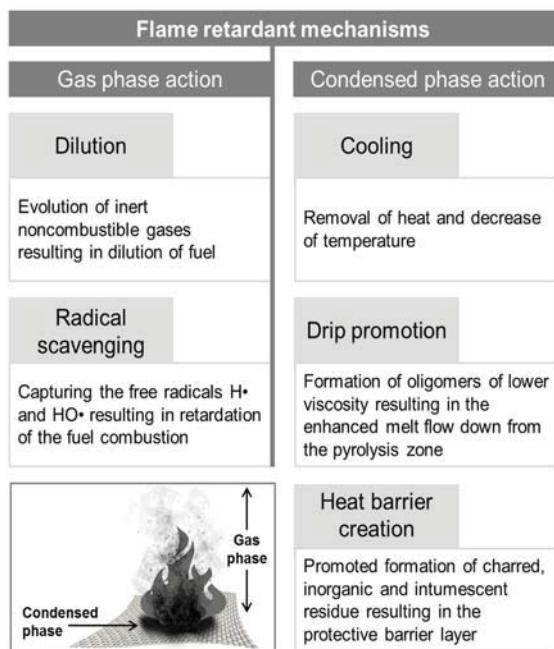
Figure 2: Flame retardant mechanisms of FR additives

MPP, as a representative of the P/N-based FR additives, was developed as a char former in the intumescent FR action. The latter is characterised by swelling and expanding at temperatures higher than critical temperature, leading to the formation of a foamed cellular charred layer [4, 9, 69]. In the intumescent FR formulations, MPP acts as an acid source because the release of phosphoric acid promotes the creation of a carbonaceous shield on the polymer surface, which acts as a heat-barrier and physically prevents contact between the polymer and the flame and hinders the flow of oxygen and heat to the polymer surface. As an acid source, ammonium phosphate, ammonium polyphosphate or AS can also be used [8]. For effective intumescent FR action, the acid source-containing FR additives are usually combined with the carbon source-containing additives, for instance, pentaerythritol, as well as a blowing agent, mostly melamine or guanidine, which releases non-combustible gases.

The FR action of inorganic hydroxides, such as AlO(OH) and Mg(OH)$_2$, involves heat sink and heat-barrier effects [8, 54, 56]. At temperatures between 340–350 °C and above 300–320 °C, boehmite and magnesium hydroxide, respectively, undergo endothermic decomposition (absorbing heat) in which free water is produced. This results in the cooling of the polymer and the diluting of the combustive gas mixture by the release of the vapours. The water release could also enhance the decomposition of PA6. In addition, a mineral layer formed on the polymer surface acts as a barrier that prevents contact between the heat and the polymer.

Silica as well as different clays exhibit the heat-barrier FR effect. They contribute to the formation of a reinforced insulating charred layer, which acts as a heat and gas barrier and protects the polymer against thermal oxidation and mass loss during combustion [30, 61, 70]. The presence of the protective layer increases the thermal stability of PA6 and significantly reduces the heat release rate during combustion relative to pristine PA6, suggesting improved fire behaviour. Additionally, smoke obscuration is significantly lowered in the presence of clays. Well-dispersed particles of clay can act as nucleating sites for bubble formation in the residue during the decomposition process, leading to an expanded carbonized material composed of a large bubble covering the residue. The gases trapped under the bubble insulate the surface of the polymer [30].

The FR mechanism of CNTs differs from that of clays [63]. It is assumed that CNTs act as inert fillers that do not significantly influence the thermal decomposition behaviour of PA6. The presence of CNTs in the PA6 composite increases the time to ignition and decreases the heat release rate but does not significantly lower the total heat release in comparison to pristine PA6. The reason for the increase in the time to ignition is attributed to the improved thermal conductivity or the increased melt viscosity of the composite. A decreased heat release rate caused by the CNTs in the composite would indicate a reduction in flammability. However, on the contrary, during ignition, the CNTs form a thermally stable interconnected network structure, which fixes the molten material in the pyrolysis zone and prevents melt-dripping. This results in the increase in the composite burning intensity. Since CNTs subsequently decompose in the thermo-oxidative reaction, no charred residue is created during the thermal decomposition of the PA6 composite.

3 Strategies for the production of FR PA6 fibres

The most common strategy for the production of FR PA6 fibres includes the use of the melt-compounded PA6/FR composites in the melt-spinning process [71]. However, there are several drawbacks in the fibre production process when using the "melt-compounding approach" related to the agglomeration of FR additives in the PA6 matrix [26, 32]. Specifically, the high melt reactivity of PA6 and its poor compatibility with FRs due to the strong intermolecular hydrogen bonds between the polymer chains cause the agglomeration of FR additive species. This results in the non-uniformly dispersed and low-dispersed micro-sized FR additive particles in the PA6 matrix. The flame-retardant action of the FR molecules entrapped in the micro-sized agglomerates is inhibited because of the inability of the entrapped FR molecules to actively participate in the flame retarding action. The flame retarding action occurs at the nanoscopic level. In the case of the micro-sized aggregates, only the outermost molecules can efficiently participate in the flame retarding action. Thus, in the case of the aggregated FRs, increased weight percent loading of the FR additive is unavoidable for efficient flame retardancy. Furthermore, the micro-sized FR agglomerates impair the spinnability of the PA6 composite filaments since they cause clogging of the filters and spinnerets at higher FR additive loadings. The agglomerates also significantly impair the physical and mechanical properties of the fibres. Consequently, the loading of FR additives that are acceptable for the continuous melt-spinning process provides only a poor FR effect. To solve these problems, three main approaches in the production process of FR PA6 fibres have been introduced: (i) preparation of the melt-compounded PA6/FR composites with the incorporation of FR nanoparticles as well as FR mixtures with a synergistic action, (ii) *in situ* polymerisation of ε-caprolactam in the presence of the FR additives, and (iii) synthesis of PA6 copolymers with the incorporation of reactive FR co-monomers.

3.1 Melt-compounded PA6/FR composites with the incorporation of nanoparticles and synergistic FR mixtures

The incorporation of nanoclays into the PA6 composite fibres was first reported by Bourbigot et al. [61], who prepared a PA6 nanocomposite with 5 wt%

Cloisite 30B (Southern Clay Products Inc., USA), which is organically modified montmorillonite. The composite masterbatch was used in a melt-spinning process for the production of multifilament yarn, which was afterwards knitted into knit fabric. Flame retardancy was evaluated in terms of cone calorimetric analysis. The results show that the presence of nanoclay reduced the heat release rate by 40% and significantly lowered smoke obscuration in comparison with the pristine PA6 fabric. However, the flame spread test was not carried out.

Onder et al. [62] also used two types of nanoclays, i.e., a commercially available organically modified montmorillonite, SA682640 (Sigma-Aldrich, UK), and a self-produced organoclay, and melt spun PA6 nanocomposite monofilaments comprising varying amounts of the organoclay ranging between 0.5 and 5 wt%. The results of the thermogravimetric (TG) analysis reveal that the presence of both nanoclays considerably improves the thermal stability of the nanocomposite structures, which is caused by the shift of their mass loss to higher temperatures by 25 to 33 °C. In addition to improved thermal properties, the mechanical properties of the PA6 composite yarns met the requirements of many textile applications.

Dogan and Bayramli [49] investigated the influence of boron phosphate (BPO_4) particles of spherical shapes with diameters of approximately 200 nm on the thermal and mechanical properties of the PA6 fibres. They mixed the PA6 pellets with the BPO_4 powder to prepare composites with 3 wt% and 10 wt% BPO_4 from which monofilament fibres were melt spun. The flame retardancy of the fibres was investigated by TG analysis and micro-combustion calorimetry. The results show that the presence of BPO_4 slightly reduced the thermal stability of the PA6 composite fibres, which was caused by the decrease in the maximum decomposition temperature of PA6, reducing the total heat release and increasing the amount of char residue. The latter phenomenon was more susceptible at higher BPO_4 concentrations. The incorporation of BPO_4 deteriorated the mechanical properties of the PA6 composite fibres, resulting in a decrease in the Young's modulus, stress at break and elongation of break. The deterioration of the mechanical properties increased with the increase in BPO_4 concentration.

Coquelle et al. [15] prepared PA6 composite monofilament fibres with the addition of 3 wt%, 5 wt%, 7 wt% and 10 wt% of AS (Sigma-Aldrich, Germany) as the FR additive. The results of the TG and a pyrolysis combustion flow calorimetric analyses show that 7 wt% AS reduced the peak of heat release rate by 30 % due to the combined gas and condense phases action of AS. However, fibres containing 7 wt% of AS were spinnable but were very brittle, therefore lower AS loadings were recommended for the production of PA6/AS fibres for the textile applications.

Sun et al. [32] studied the influence of MPP in the form of the commercial product, Melapur 200 (BASF, Germany), and halloysite nanotubes (Sigma-Aldrich, Germany) on the flammability and thermal stability of PA6 composites as well as the spinnability of PA6 composite fibres. To assure good spinnability, the total amount of FR additives was fixed at 12 wt% with different ratios of both MMP and halloysite nanotubes. The flame-retardant properties of the PA6 composites, but not of the composite fibres, were characterised by the limiting oxygen index (LOI) test, UL 94 vertical burning test and cone calorimetry. The results show that the presence of all the FR additive mixtures increased the LOI values of the composites but did not significantly improved the UL 94 test ratings, which remained at the V2 level. The increase in the wt% ratio of halloysite nanotubes in the FR mixture delayed the time to ignition, decreased the heat release rate and increased the char residue. These results confirm the existence of FR synergism between MPP and halloysite nanotubes in PA6.

Horrocks et al. [16] produced PA6/FR composite multifilament yarns by using 2 wt% organically modified montmorillonite nanoclay (NC), Cloisite 25A (Southern Clay Products Inc., USA), together with two types of FR formulations: the vapour phase active micro-sized particles of AlPi, Exolit OP935 (Clariant, Switzerland), at 10 wt%; and the condensed-phase intumescent active mixture of AS (Sigma-Aldrich, UK) and dipentaerythritol (DP) (Fisher Scientific, UK) at 2.5 wt% and 1 wt%, respectively. All the yarns had acceptable tensile properties and were knitted into knit fabrics. This paper is the first to report the burning and extinguishing behaviour of the knit fabrics using the vertical flame spread test. Since not all fabrics burned the entire length, the respective burn lengths, the time to burn that length (or extinguishment time), the rate of flame spread and the average number of molten drops were recorded for each fabric. The results

showed that the presence of NC with AlPi in the PA6 composite fabric sample impaired the flame retardant activity of AlPi, which resulted in increases in the total burning time and the burn length compared to fabric samples with only AlPi. The PA6/AlPi/NC fabric sample did not show any tendency to self-extinguish. In contrast, the presence of NC with the AS/DP mixture in the PA6 composite fabric further decreased the self-extinction time from 31 s to approximately 23 s and the burn length compared to that of the AS/DP mixture, which confirmed the compatibility of the FR additives. However, the authors addressed the water solubility of ammonium sulphamate as a possible limitation regarding the wash durability of these fibres.

Šehić et al. [27] investigated the influence of two FR mixtures consisting of MeCy, Mastertek (Campine, Belgium) and AlPi, Exolit OP931 (Clariant, Switzerland), MeCy and sodium aluminosilicate (SASi), and Zeolite ZP–4A TSR (Silkem, Slovenia) at different weight ratios on the flammability, thermal behaviour and mechanical properties of PA6 composite yarns produced by melt-spinning. The results of the UL-94 vertical burning test indicate that, within the V2 rating, the incorporation of the MeCy+SASi mixture significantly decreased the after-flame time of the PA6/FR yarns relative to pristine PA6, indicating an improvement of the flame retardant properties. The MeCy+SASi mixture also enhanced the thermo-oxidative stability of the PA6/FR yarns compared to when MeCy was the only component, suggesting that the additive has a slightly synergistic effect with the 8 wt% MeCy and 2 wt% SASi mixture. In contrast, the performance of the MeCy+AlPi mixture was antagonistic, irrespective to their concentrations. The tensile properties of the studied PA6/FR composite filament yarns were not significantly deteriorated, and these yarns could be appropriate for knitting into the knit fabrics. There results confirmed the Horrocks's observations that silica-based FR additives improved the FR action of condensed-phase active FR additives but not the gas-phase active aluminium dialkylphosphinate.

3.2 In situ polymerization of ε-caprolactam in the presence of FR additives

There is little research that reports on the in situ polymerisation of ε-caprolactam in the presence of FR additives [20, 21, 23, 24, 26, 72, 73]. However,

the in situ polymerisation of ε-caprolactam in the presence of additives is advantageous over the melt-compounding method as it enables the production of PA6 nanocomposites with nanodispersed additives [33–38]. According to our knowledge, Alfonso et al. [74] were the first to report results regarding the in situ polymerisation of ε-caprolactam in the presence of FR additives. They found that, contrary to MeCy and APP, which strongly inhibit polymerisation, red P and magnesium oxide do not have an adverse effect on kinetics or thermodynamics and enhance fire performance by the thorough distribution of the additives. According to the preparation method introduced by Wu et al. [21], Li et al. [26] synthesised melamine/adipic acid salt and cyanuric acid/hexane diamine salt and used them in the in situ polymerisation of ε-caprolactam. The obtained results for the bulk nanocomposite confirmed the formation of uniformly dispersed MeCy nanoparticles in the PA6 matrix [21]. This nanocomposite showed superior flame retardancy and significantly less deterioration of the mechanical properties compared to the composite prepared by the common melt-compounding of PA6 with commercial MeCy. The PA6/MeCy composites were pelleted and melt spun into the FR composite filament yarns [26]. Unfortunately, the flame retardant performance of the knitted fabrics was discussed only qualitatively.

3.3 Synthesis of PA6 copolymers with the incorporation of FR reactive comonomers

In recent years, a new approach for the preparation of FR PA6 fibres has been developed based on the introduction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide DOPO-based reactive co-monomers during the melt polycondensation of ε-caprolactam [75, 76]. This approach was inspired by the synthesis procedure of a DOPO-containing co-polyester [77–79], which was commercialised as the DOPO-based FR reactive additive, Ukanol ES, and a co-polyester, Ukanol ES-CoPET (Schill+Seilacher GmbH, Germany). Accordingly, DOPO was first reacted with itaconic acid to prepare a phosphorus-containing diacid, 9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]- 10-phosphaphenanthrene-10-oxide (DDP) (Figure 3). In the second step, DDP was reacted with a diamine to form a salt containing an amidogen and a carboxyl group at each end. The salt was then mixed
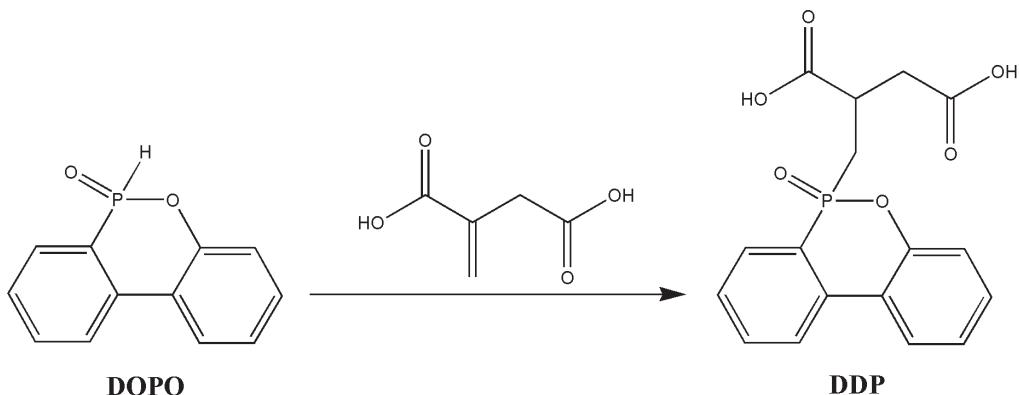
Figure 3: Preparation of DDP
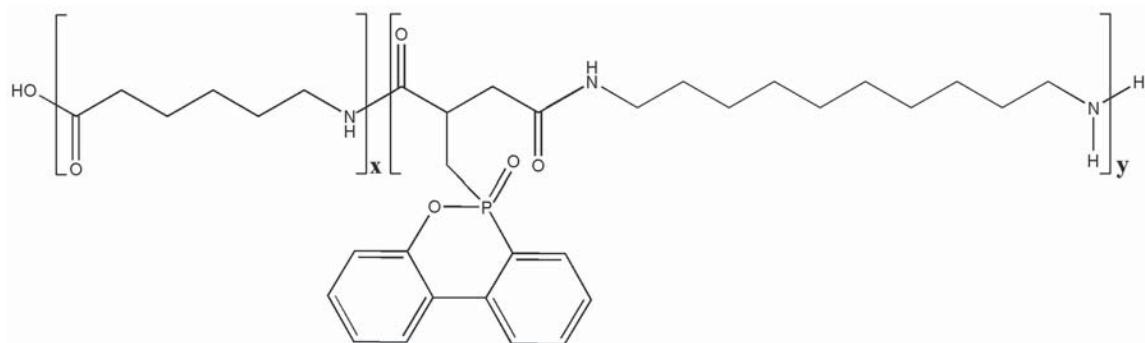
Figure 4: Chemical structure of PA6/DDP copolymer

with ε-caprolactam, and the polymerisation process was carried out under the appropriate conditions. The synthesised FR PA6 includes polyamide chain segments and DOPO-based FR chain segments of different weight ratios (Figure 4).

According to this procedure, Liu et al. [76] prepared the PA6/DDP composites containing 2 wt% to 5 wt% DDP, and their thermal stability and flame retardancy were determined by thermogravimetry, the UL 94 test and cone calorimetry. To study the mechanical properties as well as flame retardancy using the vertical burning test, filament fibres and knit fabric samples were prepared. The results show that the introduction of DDP decreased the initial temperature of the composite decomposition and simultaneously increased its thermal oxidative stability. The presence of 5 wt% DDP decreased the total heat release during combustion and significantly increased the LOI value in comparison with pristine PA6. The results of the vertical burning test show that the after-flame time of the knit fabric samples decreased when the concentration of DDP increased and that 5 wt% DDP

was enough to preserve the self-extinguishment of the melt drops and reach the LOI value of 28.4 for the fabric. The incorporation of DDP decreased the tenacity at break of the fibres, but it still met the requirements of textiles.

4 Conclusion

Since halogenated FR additives have been prohibited due to health and environmental concerns, phosphorus (P) and nitrogen (N) based FRs, inorganic hydroxides as well as nanoparticles have been established for PA6. Among them, AlPi, MeCy, AS and DOPO derivatives alone or in combination with nanoclays have been mainly used. FR additives were incorporated into the polymer matrix by mixing FR additives with PA6 pellets in the process of the preparation of melt-compounded PA6/FR composites prior to the melt-spinning of PA6 composite fibres or by introducing FR additives during the polymerisation of ε-caprolactam. Whereas the *in situ* polymerisation was characterised for the MeCy incorporation, the

reactive DOPO derivatives were included as comonomers in the synthesis of PA6 copolymers. The latter approach is the most promising and will therefore provide important research challenges in the future. It represents a powerful tool for highlighting the flame retardant mechanisms of the nanodispersed FRs in the PA6 matrix and how these mechanisms function in the open high surface structure textile materials. This knowledge will provide the missing blocks to the current state of the art. Development of the flame retardant PA6 nanocomposite also provides very important solution for the lowering FR additive loadings in the bulk polymers, which will increase their sustainability.

References

1. RICHARDS, A.F. Nylon fibres. In *Synthetic fibres: nylon, polyester, acrylic, polyolefin*. Edited by J. E. McIntyre. Cambridge : Woodhead Publishing, 2005, pp. 20–94.

2. Market research report: Polyamide market by application (engineering plastics, fiber), type (PA 6, PA 66, bio-based & specialty polyamides), and region (Asia-Pacific, North America, Europe, Middle East & Africa, South America) - Global forecast to 2021 [online] [accessed 19. 06. 2018]. Available on World Wide Web: <https://www.giiresearch.com/report/mama270202-polyamide-market-by-type-polyamide-6-polyamide-6-6.html>.

3. Circular economy: Implementation of the circular economy action plan [online] [accessed 19. 06. 2018]. Available on World Wide Web: <http://ec.europa.eu/environment/circular-economy/index_en.htm>.

4. WEIL, E. D., LEVCHIK S. V. *Flame retardants for plastics and textiles: Practical applications* (Second edition), Munich : Hanser, 2016.

5. LEVCHIK, S. V., LEVCHIK, G. F., BALABANOVICH, A. I., CAMINO, G., COSTA, L. Mechanistic study of combustion performance and thermal decomposition behaviour of nylon 6 with added halogen-free fire retardants. *Polymer Degradation and Stability*, 1996, **54**(2–3), 217–222, doi: 10.1016/S0141-3910(96)00046-8.

6. HORROCKS, A. R., KANDOLA, B. K., DAVIES, P. J., ZHANG, S., PADBURY, S. A. Developments in flame retardant textiles – a review. *Polymer Degradation and Stability*, 2005, **88**(1), 3–12, doi: 10.1016/j.polymdegradstab.2003.10.024.

7. HORROCKS, A. R. Technical fibres for heat and flame protection. In *Handbook of technical textiles: Technical textile applications.* Edited by A. R. Horrocks, S. C. Anand, Cambridge : Woodhead Publishing, 2016.

8. *Update on flame retardant textiles: State of the art, environmental issues and innovative solutions.* Edited by Alongi, J., Horrocks, A. R., Carosio, F., Malucelli, G. Shawbury : Smithers Rapra Technology, 2013.

9. LEVCHIK, S. V., WEIL, E. D., LEWIN, M. Thermal decomposition of aliphatic nylons. *Polymer International*, 1999, **48**, 532–557; doi: 10.1002/(SICI)1097-0126(199907)48:7<532::AID-PI214>3.0.CO;2-R.

10. *Fire retardant materials.* Edited by A. R. Horrocks, D. Price. Cambridge : Woodhead Publishing, 2001.

11. LEVCHIK, Sergei V., WEIL, Edward D. A review of recent progress in phosphorus-based flame retardants. *Journal of Fire Sciences*, 2006, **24**, 345–364, doi: 10.1177/0734904106068426.

12. van der VEEN, Ike, de BOER, Jacob. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*, 2012, **88**(10), 1119–1153, doi: 10.1016/j.chemosphere.2012.03.067.

13. BUCZKO, A., STELZIG, T., BOMMER, L., RENTSCH, D., HENECZKOWSKI, M., GAAN, S. Bridged DOPO derivatives as flame retardants for PA6. *Polymer Degradation and Stability*, 2014, **107**, 158–165, doi: 10.1016/j.polymdegradstab.2014.05.017.

14. DAHIYA, J. B., KANDOLA, B. K., SITPALAN, A., HORROCKS, A. R. Effects of nanoparticles on the flame retardancy of the ammonium sulphamate-dipentaerythritol flame-retardant system in polyamide 6. *Polymers for Advanced Technologies*, 2013, **24**(4), 398–406, doi: 10.1002/pat.3095.

15. COQUELLE, M., DUQUESNE, S., CASETTA, M., SUN, J., ZHANG, S., BOURBIGOT, S. Investigation of decomposition pathway of polyamide

6/ammonium sulfamate fibers. *Polymer Degradation and Stability*, 2014, **106**, 150–157, doi: 10.1016/j.polymdegradstab.2014.02.007.

16. HORROCKS, R., SITPALAN, A., ZHOU, C., KANDOLA, B. K. Flame retardant polyamide fibres: The challenge of minimising flame retardant additive content with added nanoclays. *Polymers*, 2016, **8**(8), 288, doi: 10.3390/polym8080288.

17. XIANG, Hengxue, LI, Lili, CHEN, Wei, YU, Senlong, SUN, Bin, ZHU, Meifang. Flame retardancy of polyamide 6 hybrid fibers: Combined effects of α-zirconium phosphate and ammonium sulfamate. *Progress in Natural Science: Materials International*, 2017, **27**(3), 369–373, doi: 10.1016/j.pnsc.2017.04.013.

18. GIJSMAN, P., STEENBAKKERS, R., FURST, C., KERSJES, J. Differences in the flame retardant mechanism of melamine cyanurate in polyamide 6 and polyamide 66. *Polymer Degradation and Stability*, 2002, **78**(2), 219–224, doi: 10.1016/S0141-3910(02)00136-2.

19. CHEN, Y., WANG, Q., YAN, W., TANG, H. Preparation of flame retardant polyamide 6 composite with melamine cyanurate nanoparticles in situ formed in extrusion process. *Polymer Degradation and Stability*, 2006, **91**(11), 2632–2643, doi: 10.1016/j.polymdegradstab.2006.05.002.

20. WU, Z.-Y., XU, W., XIA, J. K., LIU, Y.-C., WU, Q.-X., XU, W.-J. Flame retardant polyamide 6 by in situ polymerisation of ε-caprolactam in the presence of melamine derivatives. *Chinese Chemical Letters*, 2008, **19**(2), 241–244, doi: 10.1016/j.cclet.2007.12.012.

21. WU, Z. Y., XU, W., LIU, Y. C., XIA, J. K., WU, Q. X., XU, W. J. Preparation and characterisation of flame-retardant melamine cyanurate/polyamide 6 nanocomposites by *in situ* polymerisation. *Journal of Applied Polymer Science*, 2009, **113**(4), 2109–2116, doi: 10.1002/app.30022.

22. ISBASAR, C., HACALOGLU, J. Investigation of thermal degradation characteristics of polyamide-6 containing melamine or melamine cyanurate via direct pyrolysis mass spectrometry. *Journal of Analytical and Applied Pyrolysis*, 2012, **98**, 221–230, doi: 10.1016/j.jaap.2012.09.002.

23. MU, Jun Qian, YANG, Yi, PENG, Zhi Han. Preparation and characterization of a novel flame retarded mca-pa6 resin by *in situ* polymerization. *Advanced Materials Research*, 2012, **399-401**, 444-448, doi: 10.4028/www.scientific.net/AMR.399-401.444.

24. SHA, K., HU, Y. L., WANG, Y. H., XIAO, R. Preparation and flame retardant polyamide 6/melamine cyanurate via *in situ* polymerisation and its characterisation. *Materials Research Innovations*, 2014, **18**, S4-843–S4-847, doi: 10.1179/1432891714Z.000000000804.

25. TANG, S., QIAN, L., QIU, Y., SUN, N. The effect of morphology on the flame-retardant behaviors of melamine cyanurate in PA6 composites. *Journal of Applied Polymer Science*, 2014, **131**(15), 40558, doi: 10.1002/app.40558.

26. LI, Y., LIN, Y., SHA, K., XIAO, R. Preparation and characterisation of flame retardant melamine cyanurate/polyamide 6 composite fibres via *in situ* polymerisation. *Textile Research Journal*, 2017, **87**(5), 561–569, doi: 10.1177/0040517516632478.

27. ŠEHIĆ, Alisa, VASILJEVIĆ, Jelena, JORDANOV, Igor, DEMŠAR, Andrej, MEDVED, Jožef, JERMAN, Ivan, ČOLOVIĆ, Marija, HEWITT, Fiona, HULL, T. Richard, SIMONČIČ, Barbara. Influence of N-, P- and Si-based flame retardant mixtures on flammability, thermal behavior and mechanical properties of PA6 composite fibers. *Fibres and Polymers*, 2018, Accepted Article doi: 10.1007/s12221-000-0000-0.

28. HORROCKS, A. R., KANDOLA, B., MILNES, G. J., SITPALAN, A., HADIMANI, R. L. The potential for ultrasound to improve nanoparticle dispersion and increase flame resistance in fibre-forming polymers. *Polymer Degradation and Stability*, 2012, **97**(12), 2511–2523, doi: 10.1016/j.polymdegradstab.2012.07.003.

29. BRAUN, U., BAHR, H., SCHARTEL, B. Fire retardancy effect of aluminium phosphinate and melamine polyphosphate in glass fibre reinforced polyamide 6. *e-Polymers*, 2010, **10**(1), 443–456, doi: 10.1515/epoly.2010.10.1.443.

30. SAMYN, F., BOURBIGOT, S. Protection mechanism of a flame retarded PA6 nanocomposite, *Journal of Fire Sciences*, 2013, **32**(3), 241–256, doi: 10.1177/0734904113510685.

31. SAMYN, F., BOURBIGOT, S. Thermal decomposition of flame retarded formulations PA6/aluminium phosphinate/melamine polyphosphate/organomodified clay: Interactions between the constituents? *Polymer Degradation and Stability*, 2012, **97**(11), 2217–2230, doi: 10.1016/j.polymdegradstab.2012.08.004.

32. SUN, J., GU, X., ZHANG, S., COQUELLE, M., BOURBIGOT, S., DUQUESNE, S., CASETTA, M. Effects of melamine polyphosphate and halloysite nanotubes on the flammability and thermal behaviour of polyamide 6. *Polymers for Advanced Technologies*, 2014, **25**(12), 1552–1559, doi: 10.1002/pat.3400.

33. BUTNARU, Irina, FERNÁNDEZ-RONCO, María P., CZECH-POLAK, Justyna, HENECZ-KOWSKI, Maciej, BRUMA, Maria, GAAN, Sabyasachi. Effect of meltable triazine-dopo additive on rheological, mechanical, and flammability properties of PA6. *Polymers*, 2015, **7**(8), 1541–1563, doi: 10.3390/polym7081469.

34. WIRASAPUTRA, Alvianto, ZHENG, Lijun, LIU, Shumei, YUAN, Yanchao, ZHAO, Jianqing. High-performance flame-retarded polyamide-6 composite fabricated by chain extension. *Macromolecular materials and Engineering*, 2016, **301**(5), 614–624, doi: 10.1002/mame.201500357.

35. CAI, Jianan, WIRASAPUTRA, Alvianto, ZHU, Yaming, LIU, Shumei, ZHOU, Yubin, ZHANG, Chunhua, ZHAO, Jianqing. The flame retardancy and rheological properties of PA6/MCA modified by DOPO-based chain extender. *RSC Advances*, 2017, **7**, 19593–19603, doi: 10.1039/C6RA28293H.

36. SUN, J., GU, X., ZHANG, S., COQUELLE, M., BOURBIGOT, S., DUQUESNE, S., CASETTA, M. Improving the flame retardancy of polyamide 6 by incorporating hexachlorocyclotriphosphazene modified MWNT. *Polymers for Advanced Technologies*, 2014, **25**(10), 1099–1107, doi: 10.1002/pat.3358.

37. HÖHNE, Carl-Christoph, WENDEL, Rainer, KÄBISCH, Bert, ANDERS, Thorsten, HENNING, Frank, KROKE, Edwin. Hexaphenoxy-cyclotriphosphazene as FR for CFR anionic PA6 via T-RTM: a study of mechanical and thermal properties. *Fire and Materials*, 2017, **41**(4), 291–306, doi: 10.1002/fam.2375.

38. XU, Miao-Jun, LIU, Chuan, MA, Kun, LENG, Yang, LI, Bin. Effect of surface chemical modification for aluminum hypophosphite with hexa-(4-aldehyde-phenoxy)-cyclotriphosphazene onthe fire retardancy, water resistance, andthermal properties for polyamide 6. *Polymers Advanced Technologies*, 2017, **28**(11), 1382–1395, doi: 10.1002/pat.4015.

39. LIN, G. P., CHEN, L. I., WANG, X. L., JIAN, R. K., ZHAO, B., WANG, Y. Z. Aluminum hydroxymethylphosphinate and melamine pyrophosphate: synergistic flame retardance and smoke suppression for glass fiber reinforced polyamide 6. *Industrial & Engineering Chemistry Research*, 2013, **52**(44), 15613–15620, doi: 10.1021/ie402396x.

40. SEEFELDT, H., DUEMICHENB, E., BRAUN, U. Flame retardancy of glass fiber reinforced high temperature polyamide by use of aluminium diethylphosphinate: thermal and thermo-oxidative effects. *Polymer International*, 2013, **62**(11), 1608–1616, doi: 10.1002/pi.4497.

41. ZHAO, B., CHEN, L., LONG, J. W., CHEN, H. B., WANG, Y. Z. Alumunium hypophosphite versus alkyl-substituted phosphinate in polyamide 6: flame retardance, thermal degradation and pyrolysis behaviour. *Industrial & Engineering Chemistry Research*, 2013, **52**(8), 2875–2886, doi: 10.1021/ie303446s.

42. ZHAO, B., CHEN, L., LONG, J. W., JIAN, R. K., WANG, Y. Z. Synergistic effect between aluminum hypophosphite and alkyl-substituted phosphinate in flame-retarded polyamide 6. *Industrial & Engineering Chemistry Research*, 2013, **52**(48), 17162–17170, doi: 10.1021/ie4009056.

43. HORROCKS, A. R., SMART, G., KANDOLA, B., PRICE, D. Zinc stannate interactions with flame retardants in polyamides; Part 2: Potential synergies with non-halogen-containing flame retardants in polyamide 6 (PA6). *Polymer Degradation and Stability*, 2012, **97**(4), 645–652, doi: 10.1016/j.polymdegradstab.2012.01.004.

44. DOGAN, E. Bayramli. The flame retardant effect of aluminum phosphinate in combination with zinc borate, borophosphate, and nanoclay in polyamide-6. *Fire and Materials*, 2014, 38(1), 92–99, doi: 10.1002/fam.2165.

45. KAYNAK, Cevdet, POLAT, Osman. Influences of nanoclays on the flame retardancy of fiber-filled and unfilled polyamide-6 with and without aluminium diethylphosphinate. *Journal of Fire Sciences*, 2015, 33(2), 87–112, doi: 10.1177/0734904114555961.

46. MA, Kun, LI, Bin, XU, Miaojun. Simultaneously improving the flame retardancy and mechanical properties for polyamide 6/aluminum diethylphosphinate composites by incorporating of 1,3,5-triglycidyl isocyanurate. *Polymers*

Advanced Technologies, 2018, **29**(3), 1068–1077, doi: 10.1002/pat.4218.

47. GE, H., TANG, G., HU, W.Z., WANG, B. B., PAN, Y., SONG, L., HU, Y. Aluminum hypophosphite microencapsulated to improve its safety and application to flame retardant polyamide 6. *Journal of Hazardous Materials*, 2015, **294**, 186–194, doi: 10.1016/j.jhazmat.2015.04.002.

48. DOGAN, M., BAYRAMLI, E. Effect of boron-containing materials on the flammability and thermal degradation of polyamide 6 composites containing melamine. *Journal of Applied Polymer Science*, 2010, **118**(5), 2722–2727, doi: 10.1002/app.32637.

49. DOGAN, M., BAYRAMLI, E. Effect of boron phosphate on the mechanical, thermal and fire retardant properties of polypropylene and polyamide-6 fibers. *Fibers and Polymers*, 2013, **14**(10), 1595–1601, doi: 10.1007/s12221-013-1595-0.

50. SAHYOUN, J., BOUNOR-LEGARÉ, V., FERRY, L., SONNIER, R., Da CRUZ-BOISSON, F., MELIS, F., BONHOMMÉ, A., CASSAGNAU, P. Synthesis of a new organophosphorous alkoxysilane precursor and its effect on the thermal and fire behavior of a PA66/PA6 copolymer. *European Polymer Journal*, 2015, **66**, 352–366, doi: 10.1016/j.eurpolymj.2015.02.036.

51. LI, Maolin, ZHONG, Yuhua, WANG, Zheng, FISCHER, Andreas, RANFT, Florian, DRUMMER, Dietmar, WU, Wei. Flame retarding mechanism of Polyamide 6 with phosphorus-nitrogen flame retardant and DOPO derivatives. *Journal of Applied Polymer Science*, 2016, **133**(6), 42932 DOI: 10.1002/APP.42932.

52. NIEUWENHUYSE, P., BOUNOR-LEGARÉ, V., BARDOLLET, P. Phosphorylated silica/polyamide 6 nanocomposites synthesis by in situ sol-gel method in molten conditions: Impact on the fire-retardancy. *Polymer Degradation and Stability*, 2013, **98**(12), 2635–2644, doi: 10.1016/j.polymdegradstab.2013.09.027.

53. SI, Gaojie, LI, Duxin, YOU, Yilan, HU, Xi. Investigation of the influence of red phosphorus, expansible graphite and zinc borate on flame retardancy and wear performance of glass fiber reinforced PA6 composites. *Polymer Composites*, 2017, **38**(10), 2090–2097, doi: 10.1002/pc.23781.

54. HULL, T. R., WITKOWSKI, A., HOLLINGBERY, L. Fire retardant action of mineral fillers. *Polymer Degradation and Stability*, 2011, **96**(8), 1462–1469, doi: 10.1016/j.polymdegradstab.2011.05.006.

55. LI, Minghui, CUI, Huijuan, LI, Qunying, ZHANG, Qian. Thermally conductive and flame retardant polyamide 6 composites. *Journal of Reinforced Plastics and Composites*, 2016, **35**(5), 435–444, doi: 10.1177/0731684415618538.

56. CASETTA, M., MICHAUX, G., OHL, B., DUQUESNE, S., BOURBIGOT, S. Key role of magnesium hydroxide surface treatment in the flame retardancy of glass fiber reinforced polyamide 6. *Polymer Degradation and Stability*, 2018, **148**, 95–103, doi: 10.1016/j.polymdegradstab.2018.01.007.

57. BATISTELLA, M. A, SONNIER, R., OTAZA-GHINE, B., PETTER, C. O., LOPEZ-CUESTA J.-M. Interactions between kaolinite and phosphinate-based flame retardant in Polyamide 6. *Applied Clay Science*, 2018, **157**, 248–256, doi: 10.1016/j.clay.2018.02.021.

58. DEMIR, H., ARKIS, E., BALKOSE, D., ULKU, S. Synergistic effect of natural zeolites on flame retardant additives. *Polymer Degradation and Stability*, 2005, **89**(3), 478–483, doi: 10.1016/j.polymdegradstab.2005.01.028.

59. MARNEY, D. C. O., RUSSELL, L. J., WU, D. Y., NGUYEN, T., CRAMM, D., RIGOPOULOS, N., WRIGHT, N., GREAVES, M. The suitability of halloysite nanotubes as a fire retardant for nylon 6. *Polymer Degradation and Stability*, 2008, **93**(1), 1971–1978, doi: 10.1016/j.polymdegradstab.2008.06.018.

60. LI, L., WU, Z., JIANG, S., ZHANG, S., LU, S., CHEN, W., SUN, B., ZHU, M. Effect of halloysite nanotubes on thermal and flame properties of polyamide 6/melamine cyanurate composites. *Polymer Composites*, 2015, **36**(5), 892–896, doi: 10.1002/pc.23008.

61. BOURBIGOT, S., DEVAUX, E., FLAMBARD, X., FLAMBARD, X. Flammability of polyamide-6 /clay hybrid nanocomposite textiles. *Polymer Degradation and Stability*, 2002, **75**(2), 397–402, doi: 10.1016/S0141-3910(01)00245-2.

62. ONDER, E., SARIER, N., ERSOY, M. S. The manufacturing of polyamide– and polypropylene–organoclay nanocomposite filaments and their suitability for textile applications. *Thermochimica Acta*, 2012, **543**, 37–58, doi: 10.1016/j.tca.2012.05.002.

63. SCHARTEL, B., PÖTSCHKE, P, KNOLL, U., ABDEL-GOAD, M. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites.

European Polymer Journal, 2005, **41**(5) 1061–1070, doi: 10.1016/j.eurpolymj.2004.11.023.

64. LI, Juan, TONG, Lifang, FANG, Zhengping, GU, Aijuan, XU, Zhongbin. Thermal degradation behavior of multi-walled carbon nanotubes/polyamide 6 composites. *Polymer Degradation and Stability*, 2006, **91**(9), 2046–2052 doi: 10.1016/j.polymdegradstab.2006.02.001.

65. SCAFFARO, R., MAIO, A., TITO, A. C. High performance PA6/CNTs nanohybrid fibers prepared in the melt. *Composites Science and Technology*, 2012, **72**(15), 1918–1923, doi: 10.1016/j.compscitech.2012.08.010.

66. KHUN, Nay Win, CHENG, Henry Kuo Feng, LI, Lin, LIU, Erjia. Thermal, mechanical and tribological properties of polyamide 6 matrix composites containing different carbon nanofillers. *Journal of Polymer Engineering*, 2015, **35**(4), 367–376, doi: 10.1515/polyeng-2013-0241.

67. VELENCOSO, Maria M., BATTIG, Alexander, MARKWART, Jens C., SCHARTEL, Bernhard, WURM, Frederik R. Molecular firefighting – how modern phosphorus chemistry can help solve the flame retardancy task. *Angewandte Chemie*, 2018, Accepted Article, doi: 10.1002/anie.201711735.

68. WEIL, E. D., LEVCHIK, S. V. Flame retardants in commercial use or development for textiles. *Journal of Fire sciences*, 2008, **26**, 243–281, doi: 10.1177/0734904108089485.

69. BOURBIGOT, Serge, DUKUESNE, Sophie. Intumescence and nanocomposites: a novel route for flame-retarding polymeric materials. In *Flame retardant polymer nanocomposites*. Edited by Alexander B. Morgan, Charles A. Wilkie. New Jersy : John Wiley & Sons, 2007, pp. 131–162.

70. GILMAN, Jefrey W. Flame retardant mechanism of polymer-clay nanocomposites. In *Flame retardant polymer nanocomposites*. Edited by Alexander B. Morgan, Charles A. Wilkie. New Jersy : John Wiley & Sons, 2007, pp. 67–87.

71. *Manufactured fibre technology*. Edited by V. B. Gupta, V. K. Kothari. Dordrecht : Springer Science & Business Media, 2012.

72. XIAO, Ru; SHA, Kai; CHEN, Xin; CHEN, Jizong, GU, Liqin, WANG, Huaping, LI, Xilin, ZHENG, Xiaoting, HUANG, Jianhua, CAO, Xiaoyu, QIAO, Jiaxin, LI, Yue, TANG, Youhao, LIN, *Huagang. MCA flame-resistant polyamide 6 fibers and preparation method thereof. CN patent, no. CN104294392 (A). 2015-01-21.*

73. LIANG, Weidong, XIAO, Ru, QIAO, Jiaxin, CHEN, Xin, CHEN, Jizong, LI, Xilin, SHA, Kai, HU, Yulong, LIU, Peng, LIU, Ke, TANG, Youhao, TAO, Lei. *Preparation method of flame-retarded polyamide 6 fiber. CN patent, no. CN104499076 (A). 2015-04-08.*

74. ALFONSO, Giovanni Carlo, COSTA, Giovanna, PASOLINI, Massimo, RUSSO, Saverio, BALLISTRERI, Alberto, MONTAUDO, Giorgio, PUGLISI, Concetto. Flame-resistant polycaproamide by anionic polymerization of ε-caprolactam in the presence of suitable flame-retardant agents. *Journal of Applied Polymer Science*, 1986, **31**(5), 1373–1382, doi: 10.1002/app.1986.070310521.

75. XIAO, Ru, LIU, Ke, LI, Yuanyuan, LI, Taotao, WANG, Huaping. *Flame-retarded polyamide 6 and preparation method thereof. CN patent, no. CN106675007 (A). 2017-05-17.*

76. LIU, Ke, LI, Yuanyuan, TAO, Lei, XIAO, Ru. Preparation and characterization of polyamide 6 fibre based on a phosphorus-containing flame retardant. *RSC Advances*, 2018, **8**, 9261–9271, doi: 10.1039/C7RA13228J.

77. SEIJI, Endo, TAKAO, Kashihara, AKITADA, Osako, TATSUHIKO, Shizuki, TADASHI, Ikegami. *Neue phosphor-enthaltende verbindungen. DE patent, no. DE2646218 (A1). 1977-04-28.*

78. CHANG, Shinn-Jen, CHANG, Feng-Chih. Characterizations for blends of phosphorus-containing copolyester with poly(ethylene terephthalate). *Polymer Engineering and Science*, 1998, **38**(9), 1471–1481, doi: 10.1002/pen.10318.

79. CHEN, Hong-Bing, ZHANG, Yi, CHEN, Li, SHAO, Zhu-Bao, LIU, Ya, WANG, Yu-Zhong. novel inherently flame-retardant poly(trimethylene terephthalate) copolyester with the phosphorus-containing linking pendent group. *Industrial & Engineering Chemistry Research*, 2010, **49**(15), 7052–7059, doi: 10.1021/ie1006917.