Recent Advances in Production of Flame Retardant Polyamide 6 Filament Yarns

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 retardant 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

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"
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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, bioaccumulation 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., HPO₂⁻, PO⁻, PO₂⁻ and HPO−, 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
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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-((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                            | tetrathoxysilane                                                                   | [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 volatileizes 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.
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 Al(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 (BPO₄) 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 BPO₄ powder to prepare composites with 3 wt% and 10 wt% BPO₄ 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 BPO₄ slightly reduced the thermal stability of the PA6 composite fibres, which was caused by the decrease in the maximum decomposition temperatures of PA6, reducing the total heat release and increasing the amount of char residue. The latter phenomenon was more susceptible at higher BPO₄ concentrations. The incorporation of BPO₄ 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 BPO₄ 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 dialkylyphosphinate.

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
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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.

Acknowledgement
This work was supported by the Slovenian Research Agency, Slovenia (Program P2-0213, Program P2-0393 and I0-0026 Infrastructural Centre RIC UL NTF).

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