

The flame retardancy of polyamide 6—prepared by in situ polymerisation of ϵ -caprolactam—For T-RTM applications

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ABSTRACT

The complexity of recycling crosslinked polymer composites has promoted the use of thermoplastic in situ polymerisable matrices, including ϵ -caprolactam-based polyamide 6 (PA6) in long-fibre reinforced composites. Their uptake by the automotive industry has created a need for adequate flame retardancy, which poses several challenges: flame retardants may hinder the in situ polymerisation reaction; moreover, the fibre reinforcement can filter out the additives not soluble in ϵ -caprolactam during liquid moulding composite processing, such as thermoplastic resin transfer moulding (T-RTM). We discussed the feasibility of the flame retardancy of ϵ -caprolactam-based PA6 and its composites, including the solubility of the additives in ϵ -caprolactam and their effect on the polymerisation reaction and fire performance. We evaluated the correlations between the flame retardant structure and the inhibition of polymerisation. Finally, we briefly summarised the composite processing and coating technologies suitable for preparing flame retarded ϵ -caprolactam-based PA6 matrix and composite systems, as well as the most often used tests for their characterisation.

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1. Introduction

With more and more considerable and easier recycling and more efficient production due to shorter cycle times, long fibre reinforced thermoplastic polymer composites are becoming more and more widespread [1]. They are produced by in situ polymerisation, where a low viscosity monomer is impregnated into the reinforcing fabrics, and polymerisation occurs in the mould. A typical low-viscosity monomer applied is ϵ -caprolactam, which can be used to produce PA6 by ring-opening polymerisation in the presence of an initiator and an activator [2]. The emerging use of ϵ -caprolactam-based PA6 matrix material for long-fibre reinforced automotive composites requires an effective reduction of flammability [3]. Stringent safety regulations require flame retardants to prevent the spread of flames, heat release, the formation of toxic fumes and at the same time maintain the load-bearing capacity of the composite. Flame retardants are typically added to the polymer matrix, thus they can affect the viscosity of the matrix, and consequently, the available processing techniques [4]. In the case

of reactive polymer processing, such as the in situ polymerisation of ϵ -caprolactam, they may even interfere with the polymerisation mechanism. In addition, in the case of composites prepared by liquid moulding techniques, the filtration and inhomogeneous distribution of solid flame retardants can be an issue, and fibre reinforcement can prevent the formation of a continuous protective layer as well [5,6]. These problems can be avoided by using liquid flame retardants and/or flame-retardant coatings [7,8].

Being a relatively novel area, literature resources on the flame retardancy of ϵ -caprolactam-based PA6 are rather scarce. In this review article, after a short description of the synthesis of ϵ -caprolactam and the polymerisation reactions, we focused on the flame retardants tested in ϵ -caprolactam systems up to now, their solubility, their effect on the polymerisation reaction and on the flammability of the resulting PA6 and its composites. We also summarised the main composite processing technologies, which can be used for the reactive processing of ϵ -caprolactam-based flame retarded PA6 systems, and the coating technologies for flame retardant coatings on the composites. After that, we reviewed the most important characterisation methods of ϵ -caprolactam-based PA6 matrix and composite systems, including the flame retardancy tests.

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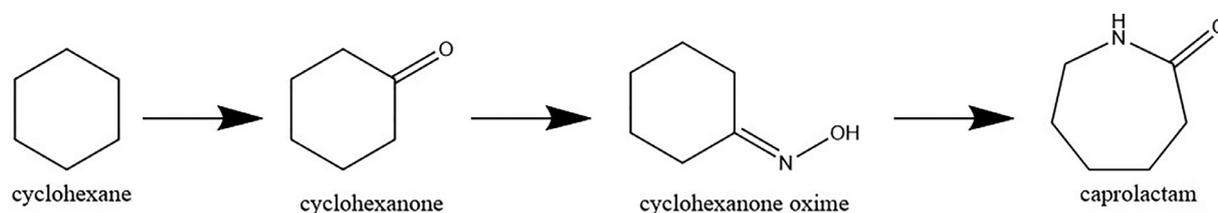


Fig. 1. Production of caprolactam.

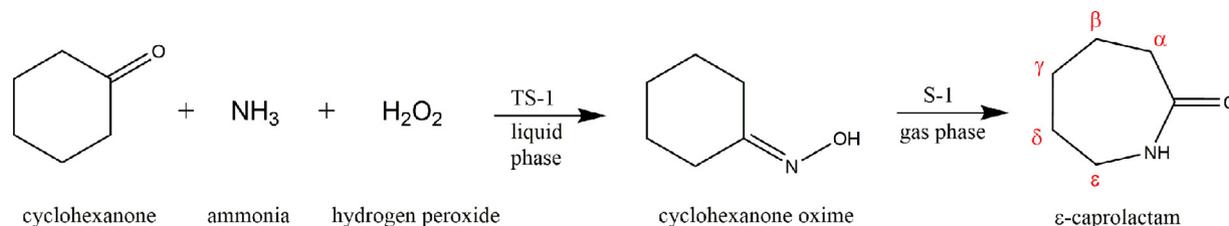


Fig. 2. Green production of caprolactam based on [13].

2. Synthesis and flame retardancy of ϵ -caprolactam-based polyamide 6

The use of ϵ -caprolactam-based PA6 in the production of advanced recyclable composites is an emerging technology. Additives such as flame retardants are often needed to achieve the properties required by industry standards. However, the effect of additives on in situ polymerisation is not yet sufficiently understood. Understanding the whole process is worth going back to basics, which includes the synthesis and polymerisation of ϵ -caprolactam.

Therefore, before discussing the flame retardancy solutions for ϵ -caprolactam, we will briefly summarise the synthesis of ϵ -caprolactam and the polymerisation in ϵ -caprolactam reactions.

2.1. Synthesis of ϵ -caprolactam

ϵ -caprolactam ($C_6H_{11}ON$) has been known since the 19th century. However, commercial interest in it did not grow until 1938 when German chemist Paul Schlack (IG Farbenindustrie) first produced PA6 by polycondensation of caprolactam. ϵ -caprolactam is one of the most important lactams from an industrial point of view. It is a cyclic amide of aminocaproic acid [9]. ϵ -caprolactam is a white, hygroscopic, crystalline compound with a characteristic odour. Acute exposure to ϵ -caprolactam may lead to the irritation of the eyes, nose, throat, and skin in humans. It has a melting point of 69°C, a boiling point of 268°C, and a density of 1.014 g/cm³ [10,11].

Several methods have been developed to produce ϵ -caprolactam. These are mainly multistep processes in which ammonium sulphate is formed as a by-product. The first step in the process is the production of cyclohexanone. Cyclohexanone can be obtained either by the catalytic oxidation of cyclohexane with air or by hydrogenating phenol, followed by the dehydrogenation of the cyclohexanol obtained. The next step is the production of cyclohexanone oxime. In this process, cyclohexanone reacts with a hydroxylamine salt (usually a sulphate). Finally, the Beckmann rearrangement produces the ϵ -caprolactam. The compounds formed in each step are shown in Fig. 1 [9,12].

The disadvantage of this process is that the production of 1 kg of caprolactam leads to the formation of 5 kg of ammonium sulphate as a by-product that can be primarily used as a low-value fertiliser. Its decomposition produces sulphuric acid (H_2SO_4), which can cause soil acidification [12]. The environmentally friendly Sumitomo process has been developed to overcome these environmental and economic problems (Fig. 2). This process

combines the method developed by EniChem and the Beckmann rearrangement [13].

In the first step (EniChem method), cyclohexanone oxime is synthesised from cyclohexanone in the presence of ammonia (NH_3) and hydrogen peroxide (H_2O_2). A microporous titanium silicalite (TS-1) catalyst is used. The next step is the Beckmann rearrangement using a silicalite (S-1) catalyst [13]. According to Zong et al. [14], using this procedure, the conversion of cyclohexanone is no less than 99.9%, the selectivity of cyclohexanone oxime is no less than 99.3%, while the H_2O_2 consumption is about 90%. The advantages of the reaction include simplifying the procedure, the high atomic efficiency (ratio of molecular mass of the final product to the starting materials), and the fact that the only by-product of the reaction is water. While the atomic efficiency of conventional methods is in the range of 25–40%, this friendly green process has an atomic efficiency of 75% [15].

2.2. In situ polymerisation mechanisms and the components of ϵ -caprolactam systems

The short polymerisation time of ϵ -caprolactam enables the production of thermoplastic fibre reinforced composite via T-RTM method which involves the polycondensation reaction of the low-viscosity monomer in the mould between the reinforcing layers [16]. The polymerisation time of these ϵ -caprolactam-based matrices is generally shorter than the formation of crosslinks in thermosetting polymers, resulting in faster cycle times and more efficient production.

The polymerisation of lactams can be an anionic process (initiated by a base) and a cationic process (initiated by acids). However, the cationic mechanism of lactam polymerisation is limited by the low conversion, low molar masses, and side reactions. For this reason, PA6 is mainly prepared by the anionic ring-opening polymerisation (AROP) of ϵ -caprolactam. AROP is the fastest process for the production of polyamide, as its activation energy is relatively low. In addition to the monomer, an activator and initiator are needed to initiate and maintain the reaction. The initiator is usually the sodium or magnesium salt of caprolactam, and it starts the polymerisation chain reaction. Such commercially available initiators are Bruggolen® C10 (C10) (containing sodium) and caprolactam magnesium bromide, under the trade name Nyrin® C1 (C1). Another initiator that can be used is Dilactamate® (DL), which is less sensitive to moisture and allows a high degree of polymerisation without a nitrogen atmosphere. The use of DL initiator may be particularly favourable when using hygroscopic flame

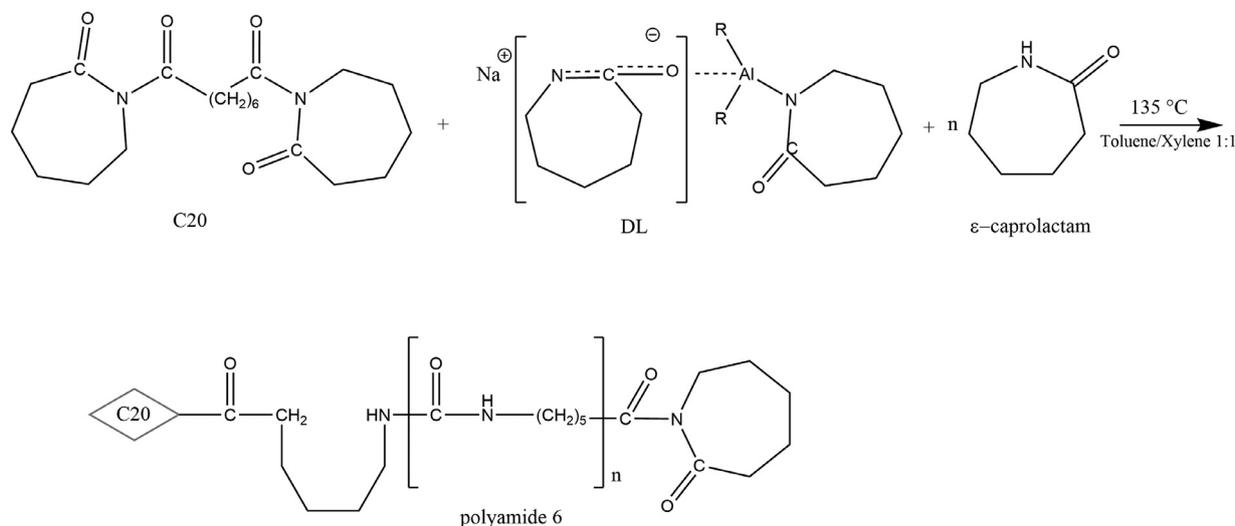


Fig. 3. Preparation of polyamide 6 (PA6) from ϵ -caprolactam (CL) with dilactamate (DL, dicaprolactamate bis(2-methoxyethoxy)aluminum, R=OCH₂CH₂OCH₃) initiator and Bruggolen C20 activator based on [18].

retardants. The function of the activator is to increase the polymerisation rate. The effects induced by the activator are complex; it forms a bond with the growing polymer chain and can affect the reaction medium, altering its alkalinity during polymerisation, promoting or limiting side reactions. The characteristics of the polyamide depend mainly on the nature and concentration of the activator, which significantly influences the molecular mass distribution, the presence of structural irregularities, crosslinking, and the degree of crystallinity. The activator can be direct or indirect. Direct activators have an N-acyl lactam structure, while indirect activators are compounds that are converted to such a structure by in situ reactions and continue to function as growth centres. One of the most widely used activators is Bruggolen® C20 (C20) [17–19]. Fig. 3 illustrates the preparation of PA6 from ϵ -caprolactam with DL initiator and C20 activator.

Höhne [20] et al. investigated flame retarded carbon fibre reinforced PA6 composites. In the production using T-RTM, ϵ -caprolactam with 4% Bruggolen C20P activator, and ϵ -caprolactam with 2% Bruggolen C10 initiator and the flame retardant were added to the dosing unit. Alonso et al. [21] used Na and Li caprolactamate initiator and N-acetylcaprolactam in the presence of flame retardant to produce PA6.

2.3. Parameters influencing the in situ polymerisation of ϵ -caprolactam

According to Barhomi et al. [22], these three main parameters control the anionic polymerisation of caprolactam:

- initiator (type and concentration)
- activator (type and concentration)
- initial polymerisation temperature.

In their study, Rijswijk et al. [23] investigated the choice of initiator, activator and polymerisation temperature in the preparation of PA6. The authors described that the polymerisation reaction consists of three steps:

- dissociation of the initiator to form the anion necessary to initiate polymerisation,
- complex formation between the activator and the initiator,
- polymerisation by anions, during which an anion is regenerated on the addition of each monomer.

By examining different activator-initiator pairings, they concluded that the reaction mechanism is more or less determined

by the combination of activator and initiator, not by the complex formed in all pairings. However, the reaction rate and the physical properties of the polymer are influenced by the polymerisation temperature, the concentration of the activator and the initiator. The polymerisation temperature affects the reaction in two ways: High temperatures increase the degree of polymerisation and decrease the rate of crystallisation. Below 130 °C, the crystallisation rate is high so that reactive groups can be "trapped" inside the growing crystals, resulting in a polymer with inferior mechanical properties. Above 180 °C, the initial temperature of the reaction mixture exceeds the melting temperature of PA6 (220 °C), which results in different properties and morphology of the polymer after cooling. Thus, the optimum polymerisation temperature is between 140 and 150 °C [23]. This optimal temperature region also affects the choice of flame retardants, namely, in the case of solid flame retardants it is advantageous if the flame retardant has a melting point below 130 °C, as this allows proper dispersion and prevents the filtering of the additive.

The choice of the initial polymerisation temperature is crucial during in situ polymerisation. Therefore, many studies have been devoted to the determination of the appropriate mould temperature. Gong and Yang [24] prepared all-polyamide composites and found that the higher the mould temperature, the lower the conversion of the monomer is. Furthermore, they concluded that the faster the monomer conversion occurred, the more air bubbles remained in the product. The consequent high void fraction negatively affected the mechanical properties, as well as surface quality.

Osváth et al. [25] studied the effect of post-polymerisation heat on the conversion and molecular mass distribution of PA6 prepared by solventless anionic ring-opening polymerisation of ϵ -caprolactam. They obtained higher monomer conversions and molecular masses for PA6 produced without quenching than for the quenched PA6 at the same reaction times.

In his thesis, Khodabakhshi [26] carried out extensive research on the factors influencing the polymerisation process, investigating the degree of polymerisation between 110 and 150 °C. He determined monomer conversion by differential scanning calorimetry (DSC) (Table 1) using the following Eq. (1):

$$\text{Monomer conversion} = \frac{\text{sample mass after DSC}}{\text{sample mass before DSC}} \quad (1)$$

Table 1
Monomer conversion of samples polymerised at temperatures between 110 and 150 °C [26].

Polymerisation temperature [°C]	Monomer conversion from DSC ¹	Monomer conversion from extraction ²
110	83	85
115	91	89
120	93	92
125	98	97
130	87	97
135	90	89
140	92	93
145	93	92
150	96	95

¹ determined from eq. (1).

² data from literature [27].

He compared these results to the monomer conversions determined by extraction, available in the literature [27]. High monomer conversion can be achieved at a polymerisation temperature of 125 °C, but the mechanical properties (flexural strength, tensile strength) of the specimens are inferior. Thus, he considered 150 °C the best polymerisation temperature [26].

Anionic ring-opening polymerisation is also affected by moisture content. As oxygen in water and air inhibits the reaction, dry and oxygen-free manufacturing conditions are recommended. The raw materials and additives, including flame retardants, should be dried to achieve a water content at least below 200 ppm. Wendel et al. [28] investigated polyamide produced by active ring-opening polymerisation using T-RTM technology. They observed the effect of water at different activator and catalyst concentrations. They concluded that the residual monomer content increased in all cases in the presence of water and the polymerisation process was much slower as moisture content increased. The most significant changes were observed with 1% C20 and 2% C10, where the residual monomer content increased to 12% at 0.02% water content compared to the initial 0.6%. Results obtained at 0% moisture content show significant differences in viscosity in the presence of different concentrations of activator and catalyst. For all concentrations tested, viscosity decreased in the presence of water. Above a certain moisture content, strength also decreased.

Besides the main parameters, as the type and concentration of initiator and activator, initial polymerisation temperature and moisture content, the applied additives may also influence the reaction. The in situ polymerisation of ϵ -caprolactam in the presence of various additives is intensively studied nowadays to achieve short reaction times appropriate for advanced composite manufacturing via T-RTM method [2]. Some additives, including some flame retardants, inhibit the in situ polymerisation reaction, but, up to now, only a few studies have addressed the causes of this inhibition. We will discuss these issues along with the structure and fire performance of flame retardants in the next chapter.

2.4. Flame retardancy of ϵ -caprolactam-based polyamide 6

Although the high nitrogen content of polyamides may imply some inherent flame retardancy, as thermoplastic materials, they melt easily in flames, causing dripping and rapid fire spread. Therefore, flame retardancy is a crucial requirement for polyamides. Accordingly, this chapter intends to summarise the structure and properties of the flame retardants used for this purpose, including their solubility in molten ϵ -caprolactam, their effect on the polymerisation reaction in relation to their structure, and last but not least, their fire performance.

Alfonso et al. [21] searched for commercially available flame retardants that do not inhibit the polymerisation reaction of ϵ -caprolactam. Of the many flame retardants tested (Table 7), including ammonium polyphosphate and melamine derivatives com-

monly used for the flame retardancy of PA6, only red phosphorus (P), magnesium oxide (MgO), and a polyhalogenated cyclopentadiene derivative, Dechlorane plus (DP), did not inhibit the polymerisation process. The low moisture content (preferably below 50 ppm), and consequently the dryability of the additives is of utmost importance for the feasibility of polymerisation. Furthermore, they highlighted the importance of microencapsulating red phosphorus powder (having sizes below 40 μ m) with a melamine resin obtained from melamine, formaldehyde, triethanolamine and methanol [29,30], which minimises the phosphine formation, which affects the anionic polymerisation reactions negatively. This patented coating also allowed to keep the moisture content of red phosphorus at an extremely low level. As for the effect on the polymerisation itself, they observed that up to 10% P content, high monomer conversion could be achieved in a short time, but at higher percentages, conversion decreases, and the polymerisation time increases. Better results were obtained when red phosphorus was combined with MgO. They also investigated the effects of flame retardants on thermal and mechanical properties (Table 2). Irrespective of concentration, none of the flame retardants significantly affected the melting, glass transition, and crystallisation temperatures. No significant differences were observed in tensile strength and elastic modulus. The minor differences can be attributed to errors due to the absorption of moisture by the polyamides [21].

For flame retardancy testing, UL-94 and LOI tests were performed (Table 3). For LOI, the highest value was obtained at 5% P+5% MgO (28.5). For UL-94, three combinations were rated V-0: 1% P+5% DP, 8–15% P, 5% P+5% MgO. Based on these results they concluded that the combination of P with MgO or DP has a synergistic effect on the fire performance. They explained this effect in the case of MgO by the ability of MgO to increase the rate of phosphoric acid formation which led to a higher charring rate on the surface of the burning polymer. While in the case of DP, in the presence of O₂ and HCl, the phosphorus-containing species from the thermal decomposition of hydrochlorinated hydrocarbon can form PCl₃, a well-known flame poison [21].

Höhne et al. [20] investigated the flame retardancy of PA6 composite produced by in situ anionic polymerisation of ϵ -caprolactam with T-RTM technology. Several flame retardants were investigated including amongst others red phosphorus, ammonium polyphosphate, phosphinates, melamine, aluminium and magnesium hydroxide, expandable graphite (Table 6), but only hexaphenoxycyclotriphosphazene, brand name Rabitle FP110, was compatible with T-RTM. Of the 12 flame retardants tested, 9 were not soluble in caprolactam and were therefore filtered by the carbon fibre reinforcement. Of the remaining three flame retardants, including methyl DOPO and a diphospha-spirocompound, hexaphenoxycyclotriphosphazene was the only one that did not inhibit polymerisation when used in higher amounts (up to 25 mass%). This was explained by the difficulty the reactive anionic polymer chain had

Table 2

The glass transition (T_g), crystallisation (T_c) and melting (T_m) temperatures, initial modulus (E) and tensile strength (σ) of polycaprolactam in the presence of different flame retardants [21].

Flame retardant	mass% ^a	T_g [°C]	T_c [°C]	T_m [°C]	E [GPa]	σ [MPa]
Reference	0	49	187	217	1.9	67
P	1	47	186	219	1.7	60
P	5	48	186	219	1.7	58
P	10	47	187	220	2.1	56
P+MgO	1+1	48	186	217	1.8	67
P+MgO	3+3	47	186	217	1.9	66
P+MgO	5+5	48	186	217	2.1	65
DP	1	50	186	219	1.8	60
DP	5	48	186	217	2.1	60
DP	10	51	186	220	2.1	60
P+DP	4 ^b	51	186	220	2.0	67
P+DP	6 ^b	49	186	217	1.9	60
P+DP	4 ^c	- ^d	- ^d	- ^d	1.9	65
P+DP	6 ^c	- ^d	- ^d	- ^d	1.9	63

^a relative to initial monomer concentration.

^b Cl/P atomic ratio 3:1.

^c Cl/P atomic ratio 2:1.

^d no data.

Table 3

LOI and UL-94 test results in the presence of different flame retardants [21].

P [mass%]	DP [mass%]	MgO [mass%]	LOI	UL-94 ^a
-	-	-	21	FB
-	1	-	21	FB
-	5-15	-	22-23	FB
1	-	-	23	FB
1 ^b	5 ^b	-	24	V-0
5	-	-	23	V-1
8-15	-	-	25-27	V-0
-	-	5	22	FB
5	-	5	28.5	V-0

^a Free burning.

^b Cl/P ratio 3:1.

accessing the nucleophilic P atom due to the spatial inhibition of the six phenoxy groups in hexaphenoxycyclotriphosphazene. Both in the case of methyl DOPO and the diphospha-spirocompound the P atom was easily accessible, therefore the polymerisation reaction was feasible only up to 5 and 1 mass% additive content, respectively.

Five different hexaphenoxycyclotriphosphazene (FP110) contents were tested with the use of a cone calorimeter, the results of which are shown in Fig. 4. For each sample, ignition takes about 50 s, and higher flame retardant contents reduce the total burn time and the peak heat release rate. Total heat release decreases as the amount of flame retardant increases [20].

FP110 reduced the heat release after ignition, as the addition of the flame retardant reduced the proportion of combustible polymer in the sample. The formation of a protective char layer on the surface of the sample due to the solid phase effect of the flame retardant is initiated at the same time as ignition. Although this char layer is not sufficient to extinguish the flame, as measured by mass loss, it prevents the reignition of the sample. The gas phase mechanism of combustion inhibition produces P-O and N-O radicals. The resulting reduction in oxygen makes combustion incomplete, resulting in higher smoke emissions and CO ratios. In LOI testing, the highest value (38.4) was achieved at 15% flame retardant content, while in UL-94 testing, self-extinguishing, V-0 ratings were achieved at 15% and 25% flame retardant content. The authors also found that FP110 behaves as a passive filler in the polymer matrix, so it has no reinforcing interaction with the polymer. It is assumed that it disrupts the polymer chain interactions (e.g.

hydrogen bonds), and therefore the defects generated by FP110 reduce the resistance of the matrix to mechanical stress [20].

These discussed flame retarded of ϵ -caprolactam-based PA6 systems are characterised by short polymerisation times, which enable the production of fibre reinforced composites via T-RTM with short cycle times. Nevertheless, it has to be mentioned that flame retardancy solutions have been elaborated for PA6 prepared by in situ water catalysed anionic ring-opening polymerisation systems as well [31-34]. These reactions require long reaction times at elevated temperatures, and the flame retarded systems produced this way are typically used for melt-spinning applications. Although these systems are not suitable for composite production via T-RTM due to long polymerisation times, their presentation may inspire the development of further flame retardancy solutions.

Vasiljević et al. [31] investigated PA6/bridged 9,10-dihydro-9-oxa-10-phosphanthrene-10-oxide (DOPO)-derivate (PHED) nanocomposites. They proposed a one-step production method for PA6 with a well-dispersed physically incorporated additive, which provided effective flame retardancy at low concentrations. The in situ ring-opening polymerisation process was carried out in a hydrothermal autoclave reactor at 250 °C for 10 h in the presence of PHED. This DOPO derivative does not have any chemical groups which could interact during the polymerisation reaction, melts at a lower temperature (187 °C) than the temperature of polymerisation and consequent melt-spinning; furthermore, during its pyrolysis, radical scavengers are formed at temperatures that match the decomposition temperature of PA6, which is a key factor in providing appropriate gas phase flame retardant effect. After the polymerisation, the product was ground, nanocomposite filaments containing 10% and 15% PHED additives were prepared by melt-spinning and flame retarded PA6 fabric was obtained by knitting (Fig. 5).

It was found that PHED only slightly reduced the crystallisation and melting temperatures and did not significantly affect the crystallisation of the polymer. Based on thermogravimetric studies, it was found that both the initial and the maximum decomposition temperature were slightly reduced compared to the reference PA6. A UL-94 test was also carried out in a vertical arrangement, as shown in Table 4. It was observed that the samples achieved a V-0 classification in the presence of PHED [31].

In their further study, Vasiljević et al. [32] investigated the effect of three different flame retardant bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives (Table 6) on PA6 systems produced by the in situ water-catalysed

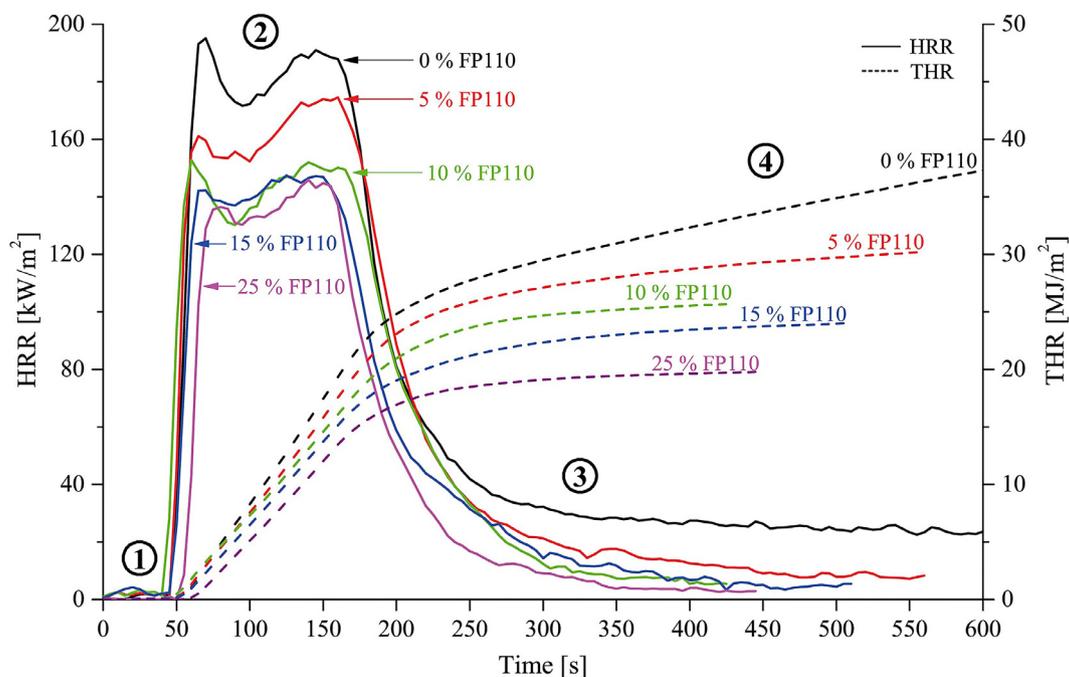


Fig. 4. Heat release rate (HRR, continuous) and total heat release rate (THR, dashed) of carbon fibre reinforced PA6 composites [20].



Fig. 5. Production of FR PA6 nanocomposite from ϵ -caprolactam and PHED additive [31].

Table 4
UL-94 test results of PA6, PA6/10PHED and PA6/16PHED [31].

Sample	t_1 [s]	t_2 [s]	Weight loss [%]	CI ignition	Classification
PA6	1.1 ± 0.4	0.5 ± 0.2	55 ± 5.9	Yes	V-2
PA6/10PHED	0	0	53 ± 11.1	No	V-0
PA6/16PHED	0	0	52 ± 5.2	No	V-0

t_1 : combustion time after ignition, t_2 : combustion time after the second ignition, CI: cotton indicator.

polymerisation of ϵ -caprolactam. Of the DOPO derivatives studied, one was a P-N bonded phosphonamidate derivative (6,6'-(Ethane-1,2-diybis(azanediyl))bis(dibenzo[c,e][1,2]oxaphosphinine-6-oxide) - ED), and the other two were P-C bonded phosphinate derivatives (6,6'-(1-(2-Naphthyl)ethane-1,2-diybis(dibenzo[c,e][1,2]oxaphosphinine-6-oxide) - NED and 6,6'-(1-Phenylethane-1,2-diybis(dibenzo[c,e][1,2]oxaphosphinine-6-oxide) - PHED). The polymerisation was strongly inhibited in the presence of ED, as the hydrogen bonding between the carbonyl group in caprolactam and the NH from the phosphonamidate groups hindered the chain propagation reaction. In NED and PHED no reactive chemical groups are present, and the access to P atoms is sterically hindered, so the polymerisation was only slightly influenced.

However, it was noted that the average molecular mass of PA6 decreased as the size of the additive molecules increased (in PHED benzyl groups are attached to the ethylene bridge connecting two DOPO groups, while in NED naphthyl groups), because the increasing steric effects hindered the condensation between polyamide chains. DSC studies confirmed that PHED and NED did not markedly influence the temperature and degree of crystallisation, melting and glass transition temperature as these additives minimally influence the hydrogen bonding between the PA6 chains. Contrary to PHED and NED, ED decreased the temperature of crystallisation by 12 °C, decreased the degree of crystallisation by 35% and increased the glass transition temperature by 7 °C compared to the reference PA6. In accordance with the dominant

Table 5
Cone calorimetry results of the reference and flame retardant samples [33].

Sample	PHRR [kW/m ²]	MHRR [kW/m ²]	THR [MJ/m ²]	PMLR [g/s]	MMLR [g/s]	TPHRR [s]	SEA [m ² /kg]
PA6	745.10	263.22	89.24	0.35	0.15	145	80.25
PA6/PTCDA (1%)	650.16	243.27	82.17	0.27	0.098	173	82.09
PA6/PTCDA (1.5%)	530.38	213.05	74.01	0.19	0.062	190	82.19
PA6/PTCDA (2%)	503.45	207.73	70.23	0.15	0.054	199	84.53

PHRR: peak heat release rate, MHRR: mean heat release rate, THR: total heat release rate, PMLR: peak mass loss rate, MMLR: mean mass loss rate, TPHRR: time of peak heat release rate, SEA: specific extinction area.

gas phase activity of these flame retardants, the decomposition of PA6 was shifted to lower temperatures, but the residual mass at 500 °C increased by approximately 50% [31]. 15% PHED-containing PA6 samples reached V-0 UL-94 rate, ED and NED decreased the complex viscosity of PA6 melt to the extent that melt-spinning was not feasible, therefore the fire performance was not tested.

Zhang et al. [33] investigated the in situ polymerisation of ϵ -caprolactam in the presence of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). Contrary to the procedures discussed previously, this approach provides a reactive flame retardancy solution as the amino functional group of PA6 and the anhydride functional group in PTCDA react with each other. First, ϵ -caprolactam was hydrolysed to amino acids at 180 °C for 1 hour, then polycondensation and grafting of PTCDA was carried out at 200 °C for 2 h and at 260 °C for 4 h. The addition of PTCDA destroyed the regularity of PA6 chains and decreased the degree of crystallinity. As PTCDA acted as an end-capping agent for PA6, it shortened the molecular chains, resulting in a decrease in the thermal stability of PA6/PTCDA composites. Due to the char forming ability, the residual mass increased, and the thermal degradation was slowed down at higher temperatures. The LOI value increased from 22 to 29.5 due to the addition of 2.5% PTCDA. In the vertical burning test, the reference and the 1% PTCDA containing sample achieved V-2 UL-94 classification, while 1.5% and 2% PTCDA content resulted in V-1 rate [32]. The results of the cone calorimetry tests are shown in Table 5.

PTCDA decreased the peak and total heat release rate. The mass loss rate and specific extinction area results confirmed the dominant condensed-phase activity of PTCDA [33].

Liu et al. [34] introduced a reactive flame retardant, 2,3-dicarboxy propyl diphenyl phosphine oxide (DPDPO) into the chain of PA6. First, they reacted DPDPO with decamethylene diamine to form a salt that reacted with aminocaproic acid (obtained from the hydrolysis of ϵ -caprolactam) at 250 °C for 3 h and at 240 °C for 5 h. The steric hindrance of the adjacent benzene rings reduced the reactivity of the functional groups of DPDPO salt and resulted in lower molecular mass and viscosity. The degree of crystallization remained similar, but the glass transition temperature and thermal stability decreased due to the introduction of DPDPO. 5 mass% of DPDPO resulted in V-0 UL-94 rating and an LOI of 31.7%, but the peak and total heat release rate was not reduced significantly as amount of char was not sufficient to form an effective barrier layer, namely, DPDPO acts mainly in the gas phase.

The properties and the structure of the flame retardants used in the reviewed literature [20,21,29–34] are listed in Table 6.

Based on the reviewed literature review among the phosphorus-containing flame retardants, the bulkier heterocyclic structures where the access to P atom is sterically hindered do not significantly interfere with the polymerisation reaction of ϵ -caprolactam. It should be noted that even if stoichiometric hindrance is beneficial when it restricts access to P atoms, after a certain size, bulky molecules can hinder the polycondensation reaction of polyamide chains. Furthermore, the possible formation of secondary bonds, e.g. hydrogen bonds between the carbonyl group of caprolactam and -NH group of the flame retardant may

also hinder the chain propagation. If these P-containing flame retardants are soluble in molten ϵ -caprolactam or their appropriate dispersion is possible, polymerisation and composite production via injection techniques is feasible. Metal oxides, in general, do not hinder the polymerisation itself, but they are not soluble molten ϵ -caprolactam and tend to sediment and filter out during composite production, therefore they are not appropriate for composite production.

3. Processing technologies of ϵ -caprolactam-based flame retarded polyamide 6 systems

The use of fibre reinforced (especially carbon fibre reinforced) PA6 composites as structural materials is growing, but the flammability of the matrix requires flame retardancy. Flame retardants can be added to the matrix, which can be problematic as solid flame retardants can be filtered out during production. In addition, in the case of solid-phase flame retardants, the reinforcement can prevent the formation of a char layer, and even this limited charring can lead to the delamination of the reinforcement layers. In the case of carbon fibre reinforcement, the high thermal conductivity can also be a problem, as it can promote matrix ignition. Furthermore, both liquid and solid additives affect the viscosity of the matrix, which thus can fall outside the range of processability. The use of flame retardant coatings may be a solution to these issues [5]. The problems listed above should be taken into account in the processing technologies of PA6 systems. The selection of additives (e.g. flame retardants) used during processing and producing a good quality product requires knowledge of the advantages, limitations and operation of the production technologies. This chapter briefly summarises the most important composite processing technologies, which can be used for the reactive processing of ϵ -caprolactam-based flame retarded PA6 systems, and the coating technologies suitable for depositing flame retardant coatings on the surface of the composite.

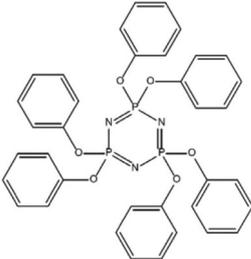
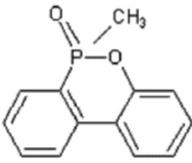
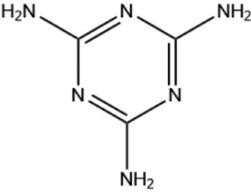
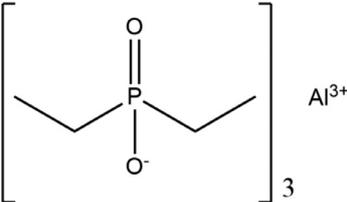
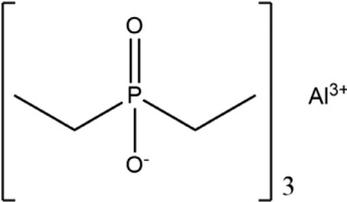
3.1. Composite processing technologies

Amongst composite processing technologies, vacuum injection and thermoplastic resin transfer moulding (T-RTM) are the main methods found in the literature for reactive processing of ϵ -caprolactam.

3.1.1. Vacuum injection technologies

Vacuum injection is a commonly used manufacturing technique for crosslinked composites, where the pressure gradient is created by the vacuum. The process involves first placing the dry, cut-to-size reinforcing material into the mould. A single-sided mould can be used to reduce costs; the other side of it is covered with vacuum foil using sealing tape. Once the mould is hermetically sealed, the vacuum causes the resin to flow from the inlet to the outlet. Thanks to the closed system, no volatile organic compound (VOC) emissions are produced during vacuum injection. A significant drawback of the technology is its susceptibility to leakage. Leakage causes air to flow into the mould, resulting in hollow air bubble areas [52,53].

Table 6
Used flame retardants [20,21,29-34].

Flame retardant	Manufacturer	Country	P content	Main component	Main component formula	Soluble in molten ϵ -caprolactam	Polymerisable	Ref.
Rabitle FP 110	Fushimi Pharmaceutical Co., Ltd	Japan	13,4	80% hexaphenoxycyclotriphosphazene and 20% phenoxycyclotetra to phenoxycyclooctaphosphazene		Yes (tested: up to 50 mass%)	Yes	[35]
Aflammit PCO 960	Thor GmbH	Germany	24	2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane,3,9-dimethyl-,3,9-dioxide		Yes (tested: up to 10 mass%)	Yes (up to 1 mass%)	[36,37]
Methyl-DOPO	commercially n.a.	-	13,5	Methyl-DOPO		Yes (tested: up to 10 mass%)	Yes (up to 5 mass%)	[38]
Melamine Expandable graphite	Sigma-Aldrich NGS Naturgraphit GmbH (it was renamed NGS Trading & Consulting GmbH)	USA Germany	- -	Melamine Expandable graphite		No No	No No	[39] [40]
Exolit OP 935	Clariant	Switzerland	23,3-24	Aluminium diethylphosphinate		No	No	[41]
Exolit OP 1312	Clariant	Switzerland	18,7-19,7	Aluminium diethylphosphinate		No	No	[42]

(continued on next page)

Table 6 (continued)

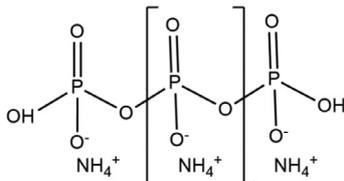
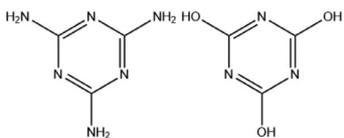
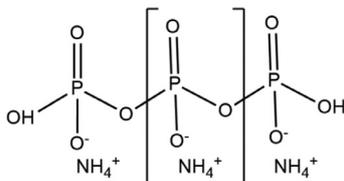
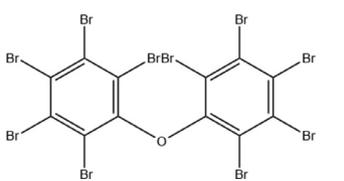
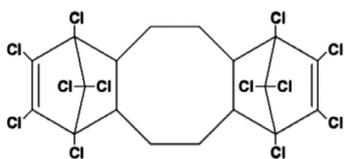
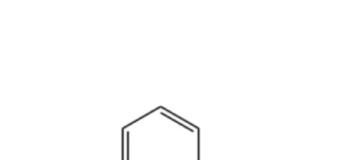
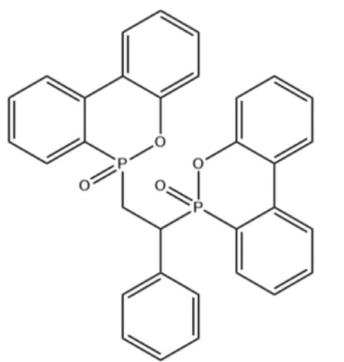
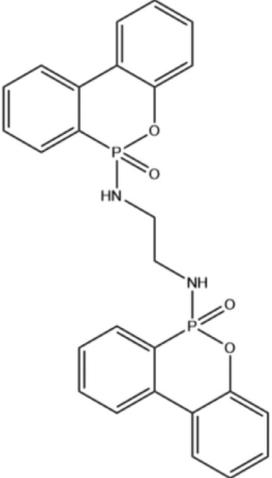
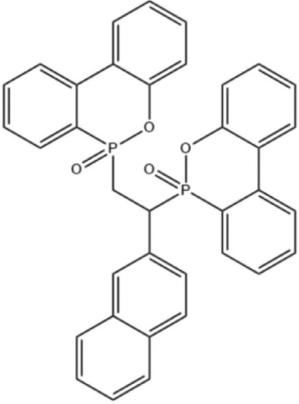
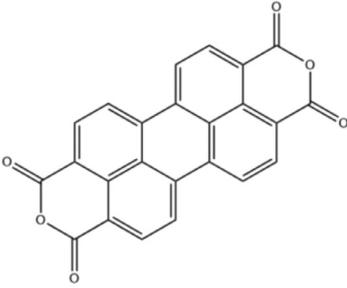
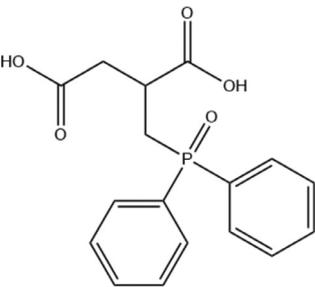
Flame retardant	Manufacturer	Country	P content	Main component	Main component formula	Soluble in molten ϵ -caprolactam	Polymerisable	Ref.
Exolit AP 462	Clariant	Switzerland	29–31	Ammonium polyphosphate		No	Yes	[43]
Apyral 40 CD	NabalTec	Germany	–	Aluminium hydroxide		No	Yes	[44]
Apyral 40 VS1	NabalTec	Germany	–	Aluminium hydroxide		No	Yes	[45]
Magnifin H5 IV	Albemarle	USA	–	Magnesium hydroxide		No	Yes	[46]
Red phosphorus	ItalMatch	Italy	100			No	Yes	[47]
Melamine cyanurate	n.a.	n.a.	–	Melamine cyanurate		n.a.	No	[21]
Ammonium polyphosphate	n.a.	n.a.	31–32	Ammonium polyphosphate		n.a.	No	[21]
Tin dichloride	n.a.	n.a.	–	Tin dichloride		n.a.	No	[21]
Velsicol 935	Velsicol Chemical LLC	USA	–	Halogenated hydrocarbons		n.a.	No	[21]
DE 83 R	n.a.	n.a.	–	Decabromodiphenyl oxide		n.a.	No	[48]
Dechlorane plus	Hooker Chemical (now: Occidental Chemical Company)	USA	–	Bis(hexachlorocyclopentadieno)cyclooctane		n.a.	Yes	[49]
Antimony trioxide	n.a.	n.a.	–	Antimony trioxide		n.a.	Yes	[21]
Magnesium oxide	Carlo Erba	Spain	–	Magnesium oxide		n.a.	Yes	[50]
PHED	commercially n.a.	–	11.6	6, 6'-(1-phenylethane ^o 1,2-diyl)bis(dibenzo [c,e] [1,2]-		Yes	Yes	[31,32]

Table 6 (continued)

Flame retardant	Manufacturer	Country	P content	Main component	Main component formula	Soluble in molten ϵ -caprolactam	Polymerisable	Ref.
ED	commercially n.a.	-	12,7	6,6'-(Ethane-1,2-diylbis(azanediyl))bis(dibenzo[c,e][1,2]oxaphosphinine-6-oxide)		Yes	Yes	[32]
NED	commercially n.a.	-	10,6	6,6'-(1-(2-Naphthyl)ethane-1,2-diyl)bis(dibenzo[c,e][1,2]-oxaphosphinine-6-oxide)		Yes	Yes	[32]
PTCDA	Sanghai Aladdin Company	China	-	Perylene-3,4,9,10-tetracarboxylic dianhydride		Yes	Yes	[51]
DPDPO	commercially n.a.	-	9,6	2,3-dicarboxypropyl diphenyl phosphine oxide		Yes	Yes	[34]

Thermoplastic polymers are not suitable for vacuum injection due to their high viscosity. An alternative solution is reactive processing, whereby a low viscosity monomer is introduced into the reinforcing material, and the matrix is polymerised in situ. The use of a vacuum eliminates the need for high pressure [53].

Pillay et al. [54] produced carbon fibre reinforced PA6 by vacuum-assisted resin transfer moulding (VARTM). They used a heated aluminium mould on which four layers of carbon fabric were sandwiched between two Teflon sheets, and finally, the mould was sealed with a vacuum bag. The electron microscopy studies showed that the fibres were properly impregnated due to the low viscosity of the caprolactam. The matrix material is visible in the cross-section and is evenly distributed along the length of the fibres. Monomer conversion is an important consideration in the VARTM process, as low conversion results in a product with poor mechanical properties. During extraction, it was found that the conversion of monomer to polymer ranges from 97.5 to 98.5%.

In their study, Rijswijk et al. [55] described that the two most important parameters during vacuum injection are polymerisation temperature and infusion pressure. At high temperatures, polymerisation occurs faster, which reduces the infusion time available. The infusion pressure must be adjusted so that the pressure inside the mould never falls below the vapour pressure of the caprolactam. This prevents the boiling of the caprolactam, which would result in air bubbles. They determined the processing window of a polyamide containing 0.4% activator and 1.2% initiator. At 10% conversion, the viscosity exceeded 1 Pa·s, which is the practical upper limit for vacuum infusion. Moreover, conversion of at least 95% is required for mould opening. Therefore, they produced composites at 160 °C with an infusion pressure of 250 mbar. They also compared the mechanical properties of glass fibre reinforced anionic PA6 composites produced by vacuum infusion with those of glass fibre reinforced hydrolytic PA6 composites produced by hot pressing. They found that the flexural strength and flexural modulus of the two composites investigated are nearly identical. However, scanning electron microscopy studies revealed that the fibre-matrix interface of the anionic PA6 composite is not satisfactory, presumably due to incomplete polymerisation, but they found that the mechanical properties could be improved by the sizing of a fibre compatible with the matrix.

Ben et al. [56] compared the properties of carbon and glass fibre reinforced polyamide composites produced by VARTM with the properties of composites made from hot-pressed PA sheets. They investigated the effect of mould temperature on polymerisation time and average molecular mass. The average molecular mass reached a maximum at 160 °C and polymerisation time decreased with increasing temperature. Furthermore, the crystalline fraction was also investigated as a function of mould temperature. It was first tested immediately after injection and again after cooling and solidification. The highest crystalline fraction was obtained during the first heating at 140 °C, as crystallisation was faster at lower temperatures. In contrast, the values obtained during hot forming were almost identical for the first and second heating. Considering the residual monomer content and water absorption, they found the ideal mould temperature between 140 and 160 °C. Also, in this temperature range, flexural strength and modulus were the highest for all samples. Compared to the hot-formed specimens, carbon fibre reinforcement can achieve higher flexural strength with the VARTM process, but there was no significant difference when glass fibres were used.

Li et al. [57] had similar results about the effect of manufacturing temperature on the mechanical properties and polymerisation kinetics of carbon fibre reinforced vacuum injected polyamide composites. As in the previous study, the lowest residual monomer content and water absorption were found between 140 and 160 °C. The flexural strength and modulus were highest at 140 °C, with sig-

nificantly increased values for carbon fibre reinforced composites compared to unreinforced PA6. For carbon fibre reinforced composites, impact strength was highest at 120 °C and 200 °C, which the authors attributed to the residual monomer content. The viscosity of the ϵ -caprolactam matrix increases as polymerisation proceeds (Fig. 6). From this, a critical processing time can be determined when the flow front stops. This time is independent of the shape and size of the part. It was found that between 140 and 200 °C, the critical time is around 20 s.

3.1.2. Thermoplastic resin transfer moulding

The production of long-fibre reinforced crosslinked matrix components used to require much manual labour. The process is time-consuming and, therefore, not suitable for mass production. In resin transfer moulding (RTM), the reinforcing material is pre-placed in the mould and impregnated with the matrix material using pressure or vacuum. The technology no longer requires as much manual work as hand lamination, but cycle time and, for most resins, crosslinking time is long. In addition, the recycling of crosslinked matrix composites on an industrial scale is still in its infancy [58]. T-RTM has been developed to overcome these problems. The technology is based on RTM, used for crosslinked matrix composites, but in this case, thermoplastic reactive polymers are used. In reactive processing, the polymers are processed in monomeric and/or oligomeric state and polymerised at the end with the addition of an initiator and activator. Due to their low molecular mass, monomers and oligomers have a viscosity similar to water and can easily impregnate the dry reinforcing material. A chemical change occurs during reactive processing, but the result is a thermoplastic polymer without crosslinks. Several reactive thermoplastic polymers are currently available for in situ polymerisation. The most promising is PA6, as it can be produced by reactive processing from a low-viscosity monomer at the lowest temperature [59–61].

The T-RTM equipment typically consists of a dosing system, a mould and a clamping unit. A schematic drawing is shown in Fig. 7.

In the first step of the T-RTM process, the reinforcing material is cut to the appropriate shape. The reinforcement can be multi-layered, and the direction of the fibres in each layer can be different. The reinforcing materials are placed in a closed mould. As with RTM, a double-sided, heatable mould is used, typically aluminium or steel. When the mould is closed, after a nitrogen flush, the monomer of PA6, ϵ -caprolactam, is introduced into the mould, which is polymerised by adding an appropriate activator and initiator. The novelty of the T-RTM technology is that the reaction is initiated in the mould after impregnation and takes 2–3 min. The injection pressure is in the range of a few bars, similar to RTM. After the melt has entered the mould, a hydraulic cylinder provides additional pressure to ensure complete filling [61,62].

As for T-RTM production lines, renowned manufacturers, such as KraussMaffei and Engel already offer complex, fully automated solutions. The production line shapes and pre-forms the reinforcing material and then produces the composite product in the mould. The process can achieve high reinforcement fibre content, and the finished product requires no post-processing [60]. An example of automotive components produced by T-RTM is the B-pillar made from PA6 reinforced with glass fibre, created in cooperation between Volkswagen and KraussMaffei. In cars, the B-pillar is located behind the front doors and connects the body and the roof. The composite reduces the weight of the component by 36% compared to conventional steel. Another example is the roof panel of the Roding Roadster R1. The polyamide composite, produced by T-RTM, is reinforced with glass and carbon fibre and contains steel inserts [61,63].

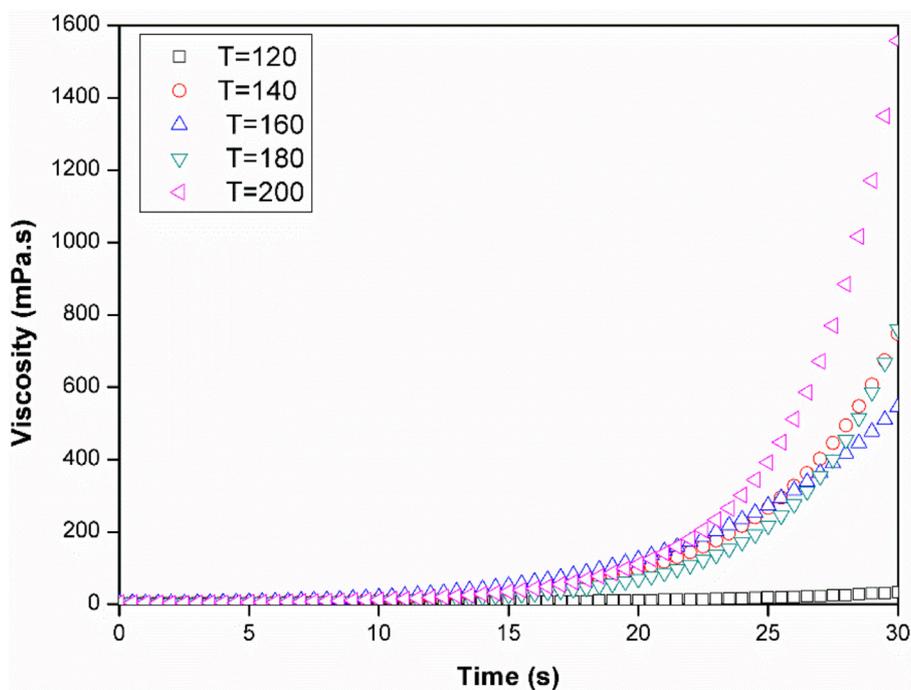


Fig. 6. Change in viscosity in the first 30 s at different temperatures [57].

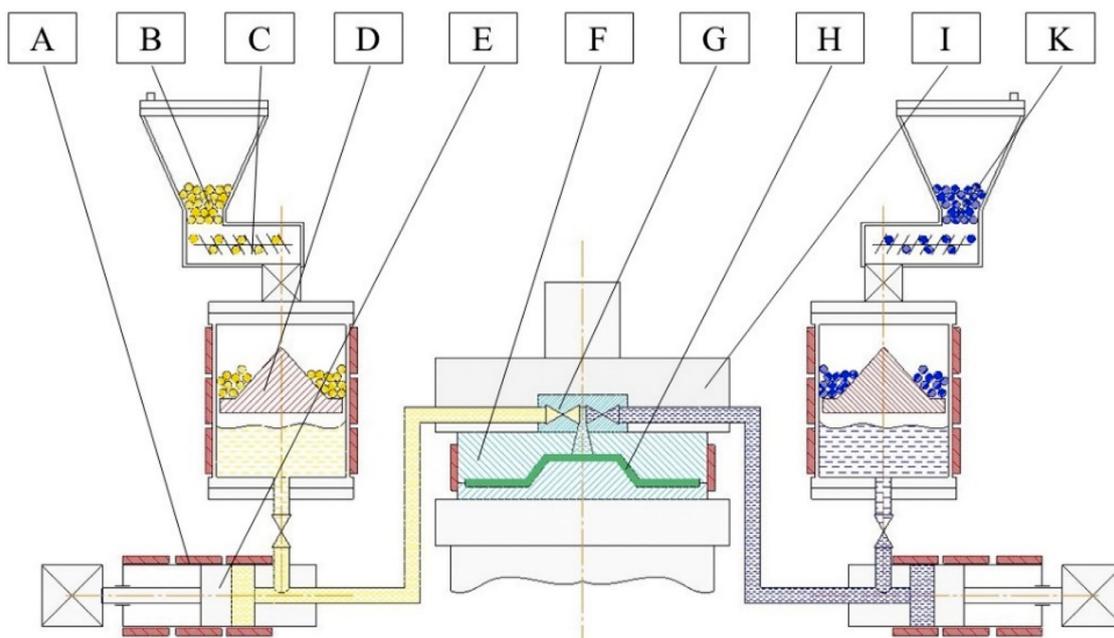


Fig. 7. Schematic diagram of the T-RTM process (A: heating, B: ϵ -caprolactam + initiator, C: feeding system, D: melting unit, E: feeding pump, F: mould, G: mixing head, H: product, I: tool clamping unit, K: ϵ -caprolactam + activator [59].

Lee et al. [64] investigated carbon fibre reinforced PA6 composites prepared by T-RTM. They proposed optimal processing parameters for the fabrication of products with good mechanical properties and maximum productivity. They applied surface flame treatment to the carbon fibres to remove moisture and improve the interfacial adhesion between the matrix and the fibres. Moisture in the reinforcing material affected the properties of the matrix, and reduced interfacial bond strength. However, the surface treatment increased tensile modulus by 18.5% and tensile strength by 15%. A dielectric measurement method was used to monitor the viscosity change and polymerisation rate. As the polymerisation temperature increased, polymerisation time decreased, taking less

than 4 min at 160 °C. However, above the crystallisation temperature of PA6 (170 °C), polymerisation time increased to 8 min. At 200 °C, polymerisation occurred rapidly, but crystallisation did not take place. These results indicate that temperatures above the crystallisation temperature are not suitable for T-RTM.

Höhne et al. [20] prepared flame retarded carbon fibre reinforced PA6 composites using T-RTM. In separate dosing units, ϵ -caprolactam with initiator, and flame retardant and ϵ -caprolactam with activator was melted at 110 °C. The melts were then mixed in a 1:1 ratio and injected into the mould from one side. The polymerisation was carried out at 150 °C for 360 s.

3.2. Coating technologies

An efficient method to reduce the flammability of composites without considerably affecting their mechanical properties is the application of a flame retardant coating. Coatings must have a good quality surface and uniform thickness. In the following, brushing, spraying, and in-mould coating (IMC) technologies will be presented. In the case of long-fibre reinforced ϵ -caprolactam-based composites prepared by T-RTM, IMC is of particular interest because, with IMC, an ϵ -caprolactam-based flame retardant coating can be deposited on the surface of the composite practically during the production of the composite. Considering adhesion, it is highly advantageous that the matrix material is the base material of the coating at the same time.

3.2.1. Brushing

One possible way to apply coatings is by brushing, which can be done with a brush or roller. Brushing is the easiest way to apply coatings. A significant advantage of this method is its low volatile organic compound (VOC) emission, short coating times and minimal tool requirements. The brushed coating is usually applied in two layers. The method's effectiveness is greatly influenced by the viscosity of the coating, the speed of application and the number of brush strokes. The technique also has drawbacks: the brush strokes are visible on the surface in many cases, and separation can occur with colourants. Another major disadvantage of this method is that it is impossible to achieve uniform layer thickness [65,66]. Yuhazri et al. [66] found that the optimum thickness of a brush-applied coating on glass fibre reinforced polyester is between 0.3 and 0.4 mm. They achieved the best mechanical properties within this range. They also determined that the most common failure mode was coating breakage. Brushing can also be performed with a roller. This method is usually used for larger surface area products because it is much faster. However, some coatings cannot be applied with a roller, only with a brush [7,65].

3.2.2. Spraying

A better solution than brushing may be spraying. It is a more productive technology and has lower VOC emissions. The advantage of the technology is that it can be applied to more complex geometries and fast. During spraying, the gun should be held perpendicular to the surface, at a distance of about 0.5 m, depending on the size of the nozzle and the material used. The sprayed droplets should be as large as possible, and the pressure should be low to minimise the emission of volatile organic compounds (especially styrene). Spraying can achieve more uniform coating thickness with faster coating times [7,66]. The viscosity of the coating material should be lower than in the case of brushing; a diluent can be used to achieve the correct viscosity [65].

3.2.3. In-mould coating

Coatings applied by brushing and spraying are applied to an open mould, which increases the level of volatile organic compounds. For health and environmental reasons, in-mould coating (IMC) is becoming increasingly common [67]. While the styrene level for in-mould coating is between 0.23 and 0.37 ppm, the styrene level for open mould coating is two orders of magnitude higher [68]. The in-mould coating is most commonly used for compression moulding, injection moulding and resin infusion under double flexible tooling (RIDFT). The most commonly used IMC techniques are:

- The small opening of the mould to allow space for coating injection,
- Use of a third mould tool to provide space for coating injection,
- Removable spacer to determine the volume of coating,

- Use of fabric to ensure that the coating does not penetrate the reinforcement,
- Use of a release layer to separate the coating from the laminated resin [7,69].

Gombos et al. [67] extensively investigated two promising IMC processes. One of these is in-mould gel-coating (IMGC), where a separator layer creates a void into which the coating can be injected. Thanks to the barrier layer, the matrix and the coating do not mix. This technique allows the entire manufacturing process to take place in a closed mould, thus reducing VOC emissions and controlling the thickness of the coating. The concept can be applied to all liquid composite moulding (LCM) technologies, in particular to resin transfer moulding (RTM) and resin infusion under flexible tooling (RIFT). The other technology is in-mould surfacing (IMS), where a removable, reusable silicone layer is used in the mould. After composite production, the mould is opened, and the silicone layer is removed. After the mould is closed, the coating can be injected. The advantages and disadvantages of the two technologies are shown in Table 7.

4. Characterisation methods of ϵ -caprolactam-based polyamide 6 systems

Although more and more research is focused on the in situ polymerisation of ϵ -caprolactam in the presence of additives, e.g. flame retardants, the characterisation of the modified polymers is often incomplete [2]. This chapter summarises the most important characterisation methods of ϵ -caprolactam-based PA6 matrix and composite systems, including the flame retardancy tests.

4.1. Characterisation of ϵ -caprolactam-based polyamide 6 matrix systems

During the anionic polymerisation of ϵ -caprolactam, the monomer may remain in the polymer, negatively affecting the mechanical properties of the matrix. Rijswijk et al. [70] investigated anionic polyamide composites. They extracted the prepared composite samples overnight in demineralised water, and then dried the samples. Since the monomer is soluble in water and the polyamide is not, the mass loss can indicate the mass of the residual monomer. However, in addition to the monomer, low molecular mass oligomers are also soluble in water, which may distort the residual monomer's mass. In composites, the next step is to determine the mass of the reinforcing material. The researchers used a thermal cleaning process at 565 °C, and then measured the mass of the residual composite after cooling. The degree of conversion (DOC) was determined with Eq. (2):

$$DOC = 100 - \frac{m_{mon}}{m_{tot} - m_f} \cdot 100 \quad (2)$$

where m_{mon} is the mass of the residual monomer, m_{tot} is the mass of the sample before extraction, and m_f is the mass of the fibre.

Höhne et al. [20] investigated flame retardant PA6 produced by in situ polymerisation of ϵ -caprolactam. The residual monomer content was determined by high performance liquid chromatography (HPLC) after extraction with water.

Thermogravimetric analysis (TGA) can also measure monomer conversion. Vicard et al. [71] used the mass loss derivative to determine the amount of residual monomer. The mass loss can be observed in two different ranges. The first mass loss is between 100 and 225 °C and is related to ϵ -caprolactam and water evaporation. However, the amount of water is negligible since the samples were stored in a drying oven before the test. The other range is related to the decomposition of PA6 between 245 and 260 °C. The degree of conversion (X_p^∞) for the final mass can be calculated

Table 7
Advantages and disadvantages of in-mould gel-coating (IMGC) and in-mould surfacing (IMS) [67].

Technology	Advantages	Disadvantages
IMGC	Controlled process, adjustable layer thickness	Improper operation of the separator layer at consolidation pressure may inhibit the flow of coating
	Fast	Questionable surface quality due to penetration of the separator layer
	Low styrene emission Allows the use of incompatible laminates and coatings	Difficult to apply a separator layer for more complex products Moisture may seep through the fabric
	Possibility of simultaneous injection of coating and matrix	Sharp corners of the mould may puncture the fabric Expensive
IMS	Controlled process, adjustable layer thickness	Styrene emission when the mould is opened
	Fast	Restricted use of materials
	Coating thickness can be adjusted with the silicone layer	Silicone layer handling and the resulting workload
	Minimal styrene emission (only when silicone is removed)	Lower surface adhesion due to silicone
	The silicone layer can be reused	Additional costs Limited durability of the silicon layer due to repeated use

from the ratio of the residual mass of ε -caprolactam ($m_{\varepsilon-CL}$) to the total mass (m_0) according to Eq. (3).

$$X_p^\infty = 1 - \frac{m_{\varepsilon-CL}}{m_0} \quad (3)$$

PA6 is a semi-crystalline polymer, which owes its mechanical properties mainly to its ability to form crystals. The higher the crystalline fraction, the better the chemical resistance, the lower the water absorption and toughness and the higher the modulus of PA6 are [23]. The crystalline fraction can be determined with Eq. (4).

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1 - \varphi)} \quad (4)$$

where ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallisation, ΔH_f is the melting enthalpy of a theoretically 100% crystalline sample, and φ is the filler content of the sample [72].

Rijswijk et al. [70] first dried the disc-shaped samples at 50 °C overnight to determine their crystalline fraction. At the beginning of the DSC test, they held the PA6 composite samples at 25 °C for 2 min and then heated them to 240 °C at 10 °C/min. Then they determined the fibre content of the samples using TGA, and corrected the crystalline fraction by the degree of monomer conversion. This is described by Eq. (5).

$$X = \frac{\Delta H_m}{\Delta H_{100}} \cdot \frac{m_{disc}}{m_{disc} - m_f} \cdot \frac{1}{\frac{DOC}{100}} \cdot 100, \quad (5)$$

where ΔH_m is the enthalpy of melting, ΔH_{100} is the melting enthalpy of a theoretically 100% crystalline sample, m_{disc} is the mass of the disc-shaped sample, m_f is fibre content, and DOC is the degree of conversion.

Dielectric measurements can be used to monitor in situ polymerisation in real-time. Polymerisation and solidification are related to dipoles in the matrix and ionic motion. Dielectric measurement measures the dissipation factor (D), which is the energy loss due to dipole ordering and ionic motion in the direction of the alternating field. The dissipation factor is proportional to dynamic viscosity, which converges to a constant value as polymerisation time progresses [64]. Dielectric measurements on polymers have developed significantly in recent years because dielectric measurements can be coupled with rheological tests. Dielectric relaxation spectroscopy (DRS) is a method that combines dielectric and rheological tests. DRS is highly sensitive to small changes in material properties such as segmental motions, molecular relaxation,

chemical reactions and dipole changes. Therefore, it can detect local movements associated with chemical reactions in ion mobility changes. It complements rheological tests well by identifying transitions in the electrical properties of materials [73].

4.2. Characterisation of ε -caprolactam-based polyamide 6 composite systems

In fibre reinforced composites, voids can often occur during production, which can be a point of failure and contribute to crack propagation. They also have a significant impact on mechanical properties. A higher void content generally leads to reduced fatigue resistance, easy penetration of water into the voids, and changes in strength. It also affects the variance of the mechanical properties. In addition to the bulk density of the voids, other microstructural characteristics such as their spatial distribution and aspect ratio should also be investigated. The void content of fibre reinforced polymers can be modelled or determined according to ASTM D2734 [74–77]. For void content (6), first, the density of the matrix, the reinforcing material and the composite must be measured separately. Matrix content is then recorded, and the theoretical density of the composite is calculated and compared to the measured density of the composite. According to the standard, a good composite has a void content of less than 1% [77].

$$V = 100 \cdot \frac{T_d - M_d}{T_d} \quad (6)$$

where V is void content, T_d is the theoretical density of the composite, and M_d is the measured density of the composite.

Thanks to advances in 3D imaging techniques, such as X-ray computed tomography (CT), non-destructive testing can be used to identify cavities and defects in composites. Voids can be determined using the mean area method based on the volume integration obtained from 3D X-ray CT images evaluated by digital image processing of orthographic snapshots [77].

The volume fractions and spatial distribution of cavities in the composite can be studied by digital microscopy (DM). DM is a convergence of microscope automation, digital image acquisition, processing and analysis. The acquired images can be automatically processed, and features of interest can be isolated [78].

It is essential to determine fibre content to characterise the mechanical properties and calculate the processing parameters. According to Bücheler [79], the test method depends on the type of reinforcing fibre. For glass fibre, TGA is recommended according to the standards, whereas for carbon fibre, the fibre content can be calculated after determining the difference of the mass before and

after matrix extraction with sulphuric acid. Gong et al. [80] investigated a self-reinforced ϵ -caprolactam-based PA6 composite and calculated the fibre content using Eq. (7).

$$\phi_f = \frac{n \cdot \rho_s \cdot S_c}{m_c} \cdot 100, \quad (7)$$

where ϕ_f is the fibre content, n is the number of layers of reinforcing material, S is the area density of the single-layer PA6 fabric, S_c is the area of the self-reinforced PA6 composite, and m_c is the mass of the self-reinforced PA6.

Höhne et al. [20] determined the fibre content of flame retardant PA6 by TGA. For measurements, the samples were pyrolysed for 50 min at 650 °C in a nitrogen atmosphere.

Several properties of composites can be investigated by microscopy, such as polymer distribution around the fibres, layer thickness, layer structure, fibre volume content, fibre-matrix interaction and the distribution of solid additives e.g. flame retardants [81]. Pillay et al. [54] investigated the extent to which the impregnation of carbon fibre reinforced PA6 composites were adequate, and the fibres were impregnated with the matrix. Then they examined the composites by optical and scanning electron microscopy. They stated that proper impregnation at the fibre level is due to the capillary effect, which is a function of the viscosity of the matrix. In the in situ polymerisation of polyamide, the low viscosity monomer caused the fibres to be uniformly surrounded by the matrix. Botezatu et al. [82] investigated the surface of glass fibre reinforced polyamide composites by scanning electron microscopy to observe the damage processes. In the case of a 30% glass fibre reinforced PA6 composite, most of the glass fibre was pulled out under load. No matrix remained on the fibre surface, indicating weak adhesion between the fibres and the matrix.

4.3. Flammability tests of ϵ -caprolactam-based polyamide 6 systems

Various tests can be used to characterise and rate the flammability of polymers. One of the most commonly used tests is the UL-94 test, performed according to ISO 9772 or ISO 9773. The test can determine the burning rate from the horizontal arrangement (H-type) and the UL-94 classification of the tested material from the vertical arrangement (V-type). A sample of 125±5 mm length and 40 mm² cross-section is used for the test. The sample is marked at a distance of 25 mm and 100 mm from the point of ignition for the horizontal arrangement. The burning rate (8) can be determined from the burning distance between the two marks and burning time [83].

$$v = 60 \cdot \frac{L}{t} \quad (8)$$

where v [mm/min] is the burning rate, L [mm] is the burning distance between the two marks, and t [s] is burning time. A sample can be classified as HB (high burning) if one of the following criteria is met:

- the maximum burning rate is 40 mm/min for a specimen with 3–13 mm thickness,
- the maximum burning rate is 75 mm/min for a specimen less than 3 mm thick,
- self-extinguishment occurs before the mark at 100 mm [83].

In a vertical arrangement, samples can be classified as V-0, V-1 and V-2 according to Table 8.

The limiting oxygen index (LOI) can be used to quantify the flammability of polymers. The LOI defines the minimum percentage of oxygen at which the test sample is still burning. The test is described in ASTM D2863, ISO 4589-1 and ISO 4589-2 standards. The oxygen index is the oxygen content at which the sample burns for more than 3 min after an ignition time of 30 s or has a flame

Table 8

UL-94 classification of the tested samples [83].

Conditions	V-0	V-1	V-2
Combustion time after ignition	≤ 10 s	≤ 30 s	≤ 30 s
Combustion time after second ignition	≤ 30 s	≤ 60 s	≤ 60 s
Total burning time	≤ 50 s	≤ 250 s	≤ 250 s
Can the cotton bud ignite?	No	No	Yes
Can the specimen burn to the clamping?	No	No	No

spread of more than 50 mm [84]. Although the LOI test is widely used, Weil [85] et al. argue that the measurement method does not reflect the combustion conditions of the sample under test in a real fire. Their research indicated that in real fires, the downward spread of the flame is of little significance. The heat transfer and burning rate characteristics under downward flame spread conditions are different from those under upward flame spread conditions. In addition, the oxygen concentration used in the LOI test is generally higher than the typical oxygen content of the air.

One of the most comprehensive tests for measuring the flammability of polymers is the cone calorimetry test. The test can continuously measure the heat release rate of the tested sample. The maximum heat release rate and the corresponding time, the mass loss and the ignition time can be determined. The great advantage of the test is that it is a good representation of most real fires. The sample can be tested in both horizontal and vertical arrangements. However, the horizontal arrangement is usually used because, in this case, the convective component of heat transfer is almost negligible [84].

6. Summary

The use of ϵ -caprolactam-based polyamide (PA6) is becoming more widespread but is limited by the flammability of the polyamide. Polyamides melt easily in flames, which can cause dripping and rapid fire spread. However, only a few studies have been carried on the flame retardancy of PA6 produced by anionic in situ polymerisation of ϵ -caprolactam, and the choice of flame retardants that do not hinder the polymerisation is limited. Based on the reviewed articles, the most promising results have been achieved with phosphorus-containing bulkier heterocyclic structures, particularly hexaphenoxycyclotriphosphazene, where the access to P atom is sterically hindered, and therefore they do not significantly interfere with the polymerisation reaction of ϵ -caprolactam. Regarding the composite processing requirements, optimally, the flame retardant should be soluble in ϵ -caprolactam and thus not be filtered out by fibre reinforcement. The correlation between the flame retardant structure and polymerisation reaction inhibition needs further investigations to develop targeted flame retardants for this purpose. An area for further development could be the combination of flame retardants acting dominantly in the gas phase and the solid phase. This way, the synergistic effects due to the combined phase effect could be potentially exploited with a lower amount of each flame retardant that would not yet hinder the polymerisation.

For the production of flame retardant PA6 systems, low viscosity ϵ -caprolactam is impregnated into the reinforcing materials mainly by vacuum injection or thermoplastic resin transfer moulding (T-RTM), and the polymerisation occurs in situ in the mould. In situ polymerisation can be challenging due to several factors: choosing the proper ratio of activator and initiator and the proper mould temperature is essential for proper conversion. The literature suggests that the optimal mould temperature is between 140 and 160 °C. Furthermore, moisture, additives, in particular, flame retardants, and contaminants can hinder polymerisation. Moisture can be eliminated using a nitrogen atmosphere, or the less mois-

ture sensitive Dilactamate® initiator can be applied in the case of hygroscopic additives.

In composites, flame retardancy is typically achieved by adding a flame retardant additive to the composite matrix. It is also possible to use flame retardant coatings for adequate flame retardancy without changing the properties of the composite structure. Coatings can be applied by brushing or spraying. These technologies have the disadvantage of high VOC emissions and difficulty achieving uniform layer thickness. For this reason, in-mould coating (IMC) is becoming increasingly common. Applying in situ polymerised ϵ -caprolactam-based flame retardant coatings with IMC during T-RTM ensures good adhesion between the PA6 composite and the coating due to the same matrix. In addition, it allows high flame retardant loadings in the coating without the reinforcement affecting the mode of action; therefore, it represents a possible logical step forward in the flame retardancy of ϵ -caprolactam-based composites.

Declaration of Competing Interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Zsófia Kovács: Conceptualization, Writing – original draft, Writing – review & editing. **Ákos Pomázi:** Conceptualization, Writing – review & editing. **Andrea Toldy:** Conceptualization, Writing – review & editing, Supervision, Project administration.

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Supplementary materials

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