

Flame Retardancy via in-Mould Coating and Durability of Flame Retardants After Mechanical Recycling in all-polyamide Composites Prepared by In Situ Polymerisation

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Sustainable development requires that the structural materials can be easily recycled. The advantage of all-polyamide composites (APCs) is that the matrix and the reinforcing material come from the same material family and can be easily mechanically recycled. In the research, polyamide 6.6 (PA6.6) reinforced polyamide 6 (PA6) composites by anionic ring-opening polymerisation are prepared and created a flame retardant coating on their surface by in-mould coating. The thermal stability of the created flame retarded APCs is investigated by thermogravimetric analysis (TGA), and the flammability is tested by UL-94 test, limiting oxygen index (LOI) and mass loss type cone calorimetry (MLC). The coatings reduced the peak heat release rate (pHRR) by up to 49% and increased the residual mass after combustion. The flame retarded APCs are mechanically recycled with the addition of 50 mass% primary material, and their thermal properties and flammability are investigated. The most effective formulations fully preserved their ability to reduce pHRR, demonstrating the durability of flame retardant properties through multiple life cycles. In the case of the sample containing 3% phosphorus from hexaphenoxycyclotriphosphazene (HPCTP) and 4% expandable graphite (EG), the pHRR after recycling is reduced by 35% compared to primary APC without flame retardants.

1. Introduction

The increasing popularity of continuous fibre-reinforced composites (CFRCs) in various engineering applications can be attributed to their exceptional mechanical properties. These composites boast high strength-to-weight ratios, excellent fatigue resistance, and superior impact performance. As a result, CFRCs are well-suited for use in the automotive, aerospace, and construction industries, with a growing demand for lightweight, durable, and high-performance materials. Notably, the superior strength-to-weight ratio of CFRCs enables significant weight reduction in structural components without compromising their mechanical integrity. This feature is essential for enhancing fuel efficiency and reducing emissions in the transportation sector.^[1,2]

Polyamide 6 (PA6) is one of the many matrices utilised in CFRCs. It has gained considerable attention due to its well-balanced mechanical properties, chemical resistance, and thermal stability.^[3,4] As a thermoplastic polymer, PA6 offers a unique combination of toughness, flexibility, and ease of processing, making it an ideal matrix material for

CFRCs. Its ability to maintain mechanical performance across various temperatures and its resistance to multiple chemicals enhance its suitability for demanding environments, which makes PA6-based composites particularly valuable in automotive applications.^[5]

PA6 is commonly produced through anionic ring-opening polymerisation (AROP) of ϵ -caprolactam.^[6] The low viscosity (5 mPa·s at 100 °C) of the monomer system makes it suitable as a matrix material for long fibre-reinforced polymer composites by thermoplastic resin transfer moulding (T-RTM).^[7] The polymerisation process typically involves using an initiator, such as an alkali metal compound or organometallic compound, and an activator (such as an acylactam or organophosphorus compound), which facilitates the ring-opening of caprolactam and the subsequent polymerisation.^[8] The process of anionic polymerisation of PA6 follows a complex three-step mechanism.

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Initially, the initiator undergoes dissociation to generate the necessary anionic species that can commence the polymerisation process. Subsequently, the activator combines with the initiator to amplify the reactivity of the anionic species. Finally, polymerisation takes place as monomer units are added to the growing anion, with the anion being regenerated with the addition of each new monomer.^[9] The great advantage of anionic ring-opening polymerisation is that the reaction takes place within minutes (3–5 min).^[10] However, the AROP of ϵ -caprolactam comes with challenges, as it is highly sensitive to impurities, moisture, and reaction conditions.^[11,12] These factors can lead to incomplete polymerisation, low molecular weight, and poor mechanical properties of the resulting PA6.

To overcome these challenges, precise control of the polymerisation parameters is essential. Factors such as temperature, reaction time, initiator and activator concentrations, and the presence of stabilisers must be carefully optimised to ensure the successful synthesis of high-quality PA6. The polymerisation typically proceeds via a nucleophilic attack on the carbonyl carbon of caprolactam, followed by the propagation of the polymer chain.^[13] The resulting PA6 exhibits a semi-crystalline structure, with a balance of amorphous and crystalline regions contributing to its mechanical and thermal properties.

All-polyamide composites (APCs) represent a unique class of materials where both the reinforcement and matrix are made from the same polymer family, such as polyamide 6 and polyamide 6.6 (PA6.6). This homogeneity offers several advantages, including improved recyclability, mechanical properties, and favourable density-strength correlation.^[14] Besides T-RTM, APCs made from PA6 can be processed through techniques such as hot compaction, where oriented PA6 fibres are compacted under heat and pressure to form a composite material with superior tensile strength and stiffness compared to conventional PA6.^[15,16] Due to the chemical similarity between PA6 and PA6.6, good interface bonding can be achieved between the matrix and the reinforcement, and a nucleation effect of the fibre interface on the crystallisation of the matrix can be observed in the all-polyamide composites.^[17]

One of the critical benefits of APCs is their potential for mechanical recycling. Since both the matrix and reinforcement are made from the same polymer family, APCs can be easily recycled without complex separation processes.^[18] The recycled matrix retains a significant portion of its original mechanical properties, making it suitable for secondary applications. This feature aligns with the growing emphasis on sustainability and the circular economy in material science.^[19]

Polymer composites have a significant drawback in that they are highly flammable, which can be a major concern in structural composite applications. This is especially true for thermoplastic polymers that are less stable and prone to dripping, making it essential to have proper flame retardancy.^[20–22] However, there are several issues that can arise during the flame retardancy of composites. For example, in carbon fibre-reinforced composites, the high thermal conductivity of the reinforcing material can make the composites easier to ignite. Additionally, the reinforcing material can filter out solid flame retardants and prevent the formation of a protective layer. These problems can be addressed by applying a flame retardant coating on the surface of the composite.^[23] In addition to traditional coating technologies

such as spraying and brushing, in-mould coating, created in a closed mould, presents itself as an option.^[24] Our recent review article discussed the challenges and solutions related to the flame retardancy of caprolactam-based PA6.^[25]

In our previous studies,^[26,27] we investigated the effect of expandable graphite, hexaphenoxycyclotriphosphazene, red phosphorus and magnesium oxide flame retardants on the thermal and flammability properties of PA6 produced by anionic ring-opening polymerisation. The best formulations were selected and further research was carried out with them. These formulations provide the basis for the present publication. The aim of this work is to create polyamide 6.6 reinforced polyamide 6 composites by anionic ring-opening polymerisation. In the course of our research, we created a flame retardant coating on the surface of the all-polyamide composites and investigated the flammability of the samples. Furthermore, we investigated the remaining flame retardancy after mechanical recycling of the flame retarded all-polyamide composites.

2. Experimental Section

2.1. Materials

The monomer used to produce the PA6 matrix by ring-opening polymerisation was *AP-NYLON Caprolactam* type ϵ -caprolactam (CL), manufactured by the Brüggemann GmbH & Co. KG (Heilbronn, Germany) company. *Bruggolen C20P* type hexamethylene-1,6-dicarbonyl caprolactam (C20), also supplied by Brüggemann GmbH & Co. KG (Heilbronn, Germany), was used as an activator and *Dilactamate* type sodium dicaprolactamate-bis-(2-methoxyethoxy)-aluminate (DL), supplied by Katchem (Prague, Czech Republic), was used as an initiator. Before application, both CL and C20 were kept in a vacuum at 40 °C. The chemical structures of the monomer, the activator and the initiator are shown in **Figure 1**. The flame retardants used are summarised in **Table 1**.

It was quantified that the HPCTP in the samples using phosphorus percentage (P%) rather than mass percentage (mass%). One P% corresponds to 7.56 g of HPCTP per 100 g of material. For the expandable graphite used, the expansion is 100 cm³ g⁻¹. To ensure a correct temperature window during processing, PA6.6 was used as reinforcing material. The reinforcing material for the all-polyamide composites was a satin woven polyamide 6.6 (PA6.6) fabric, designated as CR-262, from Sati Envirotech (Barcelona, Spain). The fabric features a thickness of 0.41 ± 0.0615 mm and an areal density of 330 ± 24.75 g m⁻². A process often used in industry was to add a primary material to the recycled material during the recycling process. For easier reprocessing, 50% *Tarnamid T27* type (T27) primary raw material was mixed with the all-polyamide composite, produced by Grupa Azoty (Tarnów, Poland). T27 has a melting point of 221 °C and a density of 1.14 g cm⁻³.

2.2. Preparation of the all-Polyamide Composites

An aluminium mould, preheated to 150 °C, was used for the T-RTM process. The mould, with dimensions of 100 × 100 ×

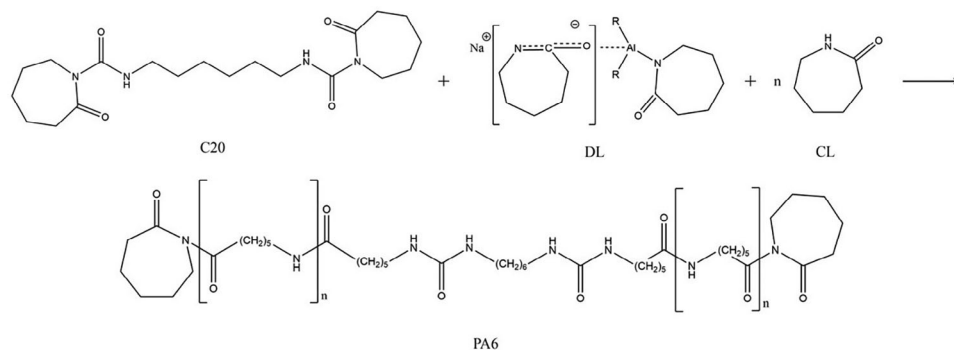


Figure 1. Chemical structure of ϵ -caprolactam, C20 activator, DL initiator and PA6.

2 mm³, contained five layers of PA6.6 reinforcement. The matrix formulation comprised 87% CL, 3% C20P, and 10% DL. The CL and C20P were liquefied at 120 °C and homogenised before DL was added. Subsequently, the resulting mixture was injected into the sealed mould using a syringe, inducing an in situ polymerisation process within the reinforcement material. The method of producing APCs is shown in **Figure 2**.

2.3. Preparation of the Flame Retardant Coatings on the Surface of the APCs

A flame retardant coating based on PA6 was created by in-mould coating on the surface of the APCs. A tool with a cavity of 100 × 100 × 2.5 mm³ for the coating were used. The first step in the coating preparation procedure was to insert the previously prepared APC into the mould and then preheat it at 150 °C after moulding. CL and C20 were mixed with flame retardants to create the coating and melted at 120 °C using a heated magnetic stirrer. In our previous research,^[26] it was investigated that the effect of different flame retardants on the thermal and flammability properties of polyamide 6. The flame retardants and compositions used in this paper were chosen on this basis, and they are listed in **Table 2**. Once the system was melted, DL was added and injected into the mould using a heat-resistant glass syringe, and polymerisation occurred in the mould. The prepared APC with flame retardant coating was left to cool at room temperature. The method of producing flame retardant coating on the surface of APCs is shown in **Figure 3**.

Since the flame retardant coating was only on one surface of the composite, the results may be distorted by the uneven spread of flame in the UL-94 and limiting oxygen index tests. For this reason, only the coatings alone were tested by these

methods, for which 120 × 10 × 3 mm³ test specimens were fabricated.

2.4. Mechanical Recycling of the APCs

The APCs were recycled by cutting the samples into roughly 20 × 20 mm pieces and grinding them in an IKA A 11 basic type (IKA-Werke, Germany) analytical grinder using liquid nitrogen. Then, in order to facilitate the processability, 50 mass% T27 primer PA6 were added using a Brabender Lab-Station type (Brabender GmbH & Co., Germany) internal mixer at 205 °C. The shearing effect of the mixing was sufficient to melt the material and obtain a homogeneous mixture. New test specimens were prepared using a T30 hydraulic press (Metal Fluid Engineering s.r.l., Italy). The following parameters were applied during pressing: 0 bar for 5 min, 100 bar for 5 min and 200 bar for 5 mins. The machine has a 60 mm diameter piston, so the 140 × 140 mm specimens were pressed with a surface pressure of 28 bar. The method of the recycling of the APCs is shown in **Figure 4**.

2.5. Characterisation

2.5.1. Thermogravimetric Analysis (TGA)

The thermal stability and monomer conversion of the samples were tested using a TA Instruments Q500 (New Castle, DE, USA) thermogravimetric analyser (TGA). The mass of the samples was between 15–20 mg. The test was carried out with a 30 ml min⁻¹ flow rate in a nitrogen atmosphere. The heating rate was 20 °C min⁻¹, and the temperature range was between 30–600 °C. When taking samples of APCs, equal cross-sectional slices were cut from the sample so that the sampling was representative and reproducible.

Table 1. Flame retardants and their properties.

Flame retardant	Main component	Manufacturer/Distributor	Brand name	P content [%]	Appearance
RP	Red phosphorus	Clariant	Exolit RP607	>95	Red powder
MgO	Magnesium oxide	Sigma Aldrich	Magnesium oxide	–	White powder
EG	Expandable graphite	Graphit Kropfmühl	ES 100 C10	–	Black powder
HPCTP	Hexaphenoxy-cyclotriphosphazene	Fushimi/ NRC	Rabitle FP110	13.4	White powder

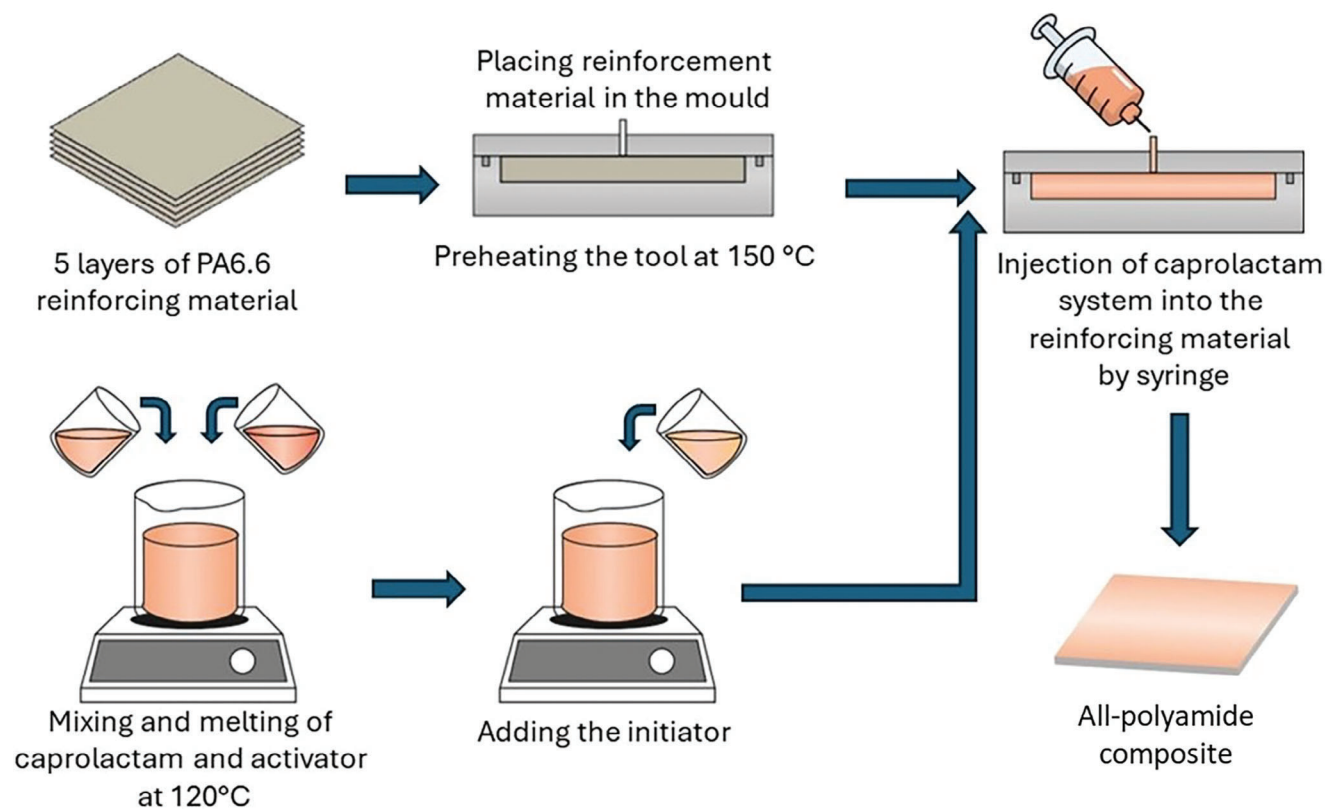


Figure 2. Flowchart for the production of all-polyamide composites.

2.5.2. UL-94 Flammability Test

During UL-94 flammability testing (designated as ISO 9772 and ISO 9773), the flame spread rate was assessed in the horizontal arrangement (H-type), while the flammability classification was evaluated in the vertical arrangement (V-type). The classifications available in the test and their criteria were listed in **Table 3**. The sample size was $120 \times 10 \times 3$ mm.

2.5.3. Limiting Oxygen Index (LOI)

The oxygen index tests (LOI) were conducted following standards ISO 4589-1 and ISO 4589-2. The oxygen index represents the minimum volume percentage of oxygen in an oxygen-nitrogen gas mixture flowing at a specific velocity in the test sample that sustains combustion. The sample size was $120 \times 10 \times 3$ mm.

Table 2. Flame retardant content of prepared coatings.

Sample	EG [mass%]	MgO [mass%]	RP [mass%]	HPCTP [P%]
PA6/5%RP/5%EG	5	–	5	–
PA6/5%MgO/5%EG	5	5	–	–
PA6/3P%HPCTP/3%EG	3	–	–	3
PA6/3P%HPCTP/4%EG	4	–	–	3

2.5.4. Mass Loss Type Cone Calorimetry (MLC)

The complex combustion characteristics of the samples were determined using mass loss type cone calorimetry (MLC) from Fire Testing Technology (East Grinstead, UK). The samples, with a surface area of 100×100 mm², were exposed to a heat flux of 50 kW m^{-2} . A spark ignition unit assisted in the ignition of the specimen surfaces. Various parameters were determined, including time to ignition (TTI), total heat release (THR), peak heat release rate (pHRR), time to pHRR, total burn time, and residual mass. The reference sample thickness was 2 mm, while the thickness of coated APCs and rAPCs was 2.5 mm.

2.5.5. Dynamic Mechanical Analysis (DMA)

Using a TA Q800 device of TA Instruments (New Castle, DE, USA), $60 \times 10 \times 2$ mm specimens were tested in a three-point bending setup (with 50 mm support) at a loading frequency of 1 Hz and a relative deflection of 0.1%, at a heating rate of 3 °C min^{-1} in the temperature range 25–200 °C. Deformation excitation was applied during the measurement. The software of the measuring instrument (TA Instruments Universal Analysis 2000 version 4.7A) was used to obtain the temperature dependence of the storage modulus of the composites and to determine the glass transition temperature (T_g) of the samples from the temperature values at the peaks of the $\tan\delta$ curves.

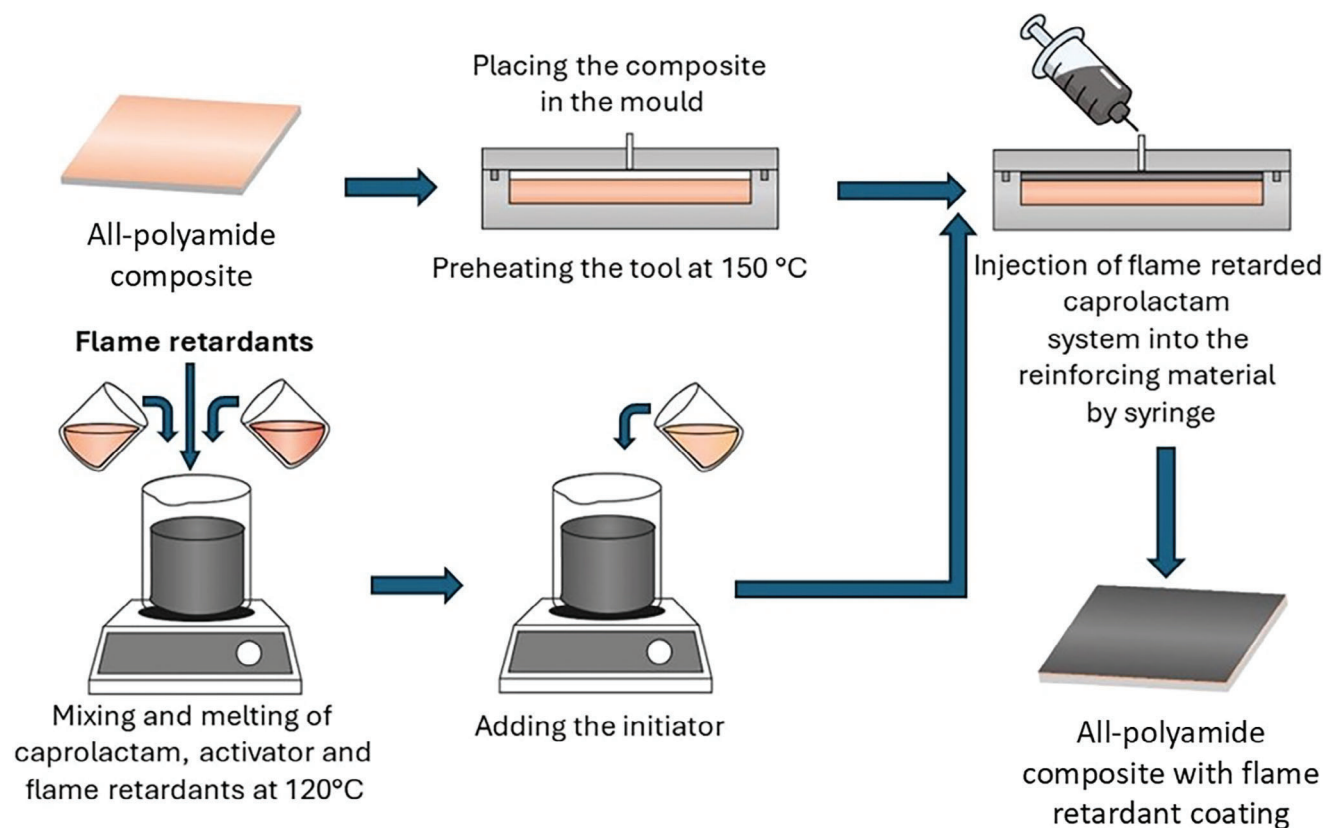


Figure 3. Flowchart for producing a flame retardant coating on the surface of the all-polyamide composites.

3. Results and Discussion

In this study, we investigated the thermal stability and flammability of APCs with flame-retardant coatings. After mechanical recycling, the thermal stability and flammability changes were analysed. The chosen flame retardant compositions were determined based on our previous article.^[26,27]

3.1. All Polyamide Composites

3.1.1. Thermal Stability of all-Polyamide Composites

First, the thermal stability of the samples was tested by TGA. The results obtained are presented in **Table 4**.

The temperature at 5% mass loss ($T_{-5\%}$) of the reference APC was 329 °C. Except for the sample containing RP and EG (332 °C), this value was reduced by the effect of the flame retardants. This reduction may be explained by the fact that the used flame retardants exert their effect at lower temperatures, thus shifting the $T_{-5\%}$ toward lower values. However, for the temperature at 50% mass loss ($T_{-50\%}$), it is observed that the temperature value increased for all the flame retarded samples compared to the reference (389 °C). Also, in this case, the sample containing RP and EG had the highest $T_{-50\%}$ of 407 °C. The maximum mass loss rate of the APC reference was 1.7%/°C, which decreased except for the sample containing MgO and EG (1.9%/°C). The temperature belonging to the maximum mass loss rate was shifted to-

ward higher temperatures in all cases compared to the reference (380 °C) and could be up to 10 °C higher than the reference due to the combined application of RP and EG. Even though the APC reference did not contain any additives, there was still a residual mass of 3.6%. The residual mass increased in all cases except for the sample containing HPCTP and 3% EG. The anionic ring-opening polymerisation of caprolactam is considered adequate when the monomer conversion is above 96%. The monomer conversion of the coated and reference SPCs was between 98.0–98.7%.

3.1.2. Flame Retardancy of all-Polyamide Composites

Because the flame retardant coating was applied only to the top surface of the composite, flame spread would not be uniform during the UL-94 and LOI tests. Therefore, we tested the coating materials themselves using UL-94 and LOI methods, while the flame retarded APCs were evaluated using MLC tests. The results of the UL-94 and LOI tests are shown in **Table 5** and the results of the MLC test are shown in **Figure 5** and **Table 6**.

The sample containing RP and EG achieved a V-0 self-extinguishing UL-94 classification, while the other samples were classified as HB. The LOI of the reference sample without flame retardant was 21%. This value increased with the effect of flame retardants and could be as high as 26% (PA6/5%RP/5%EG).

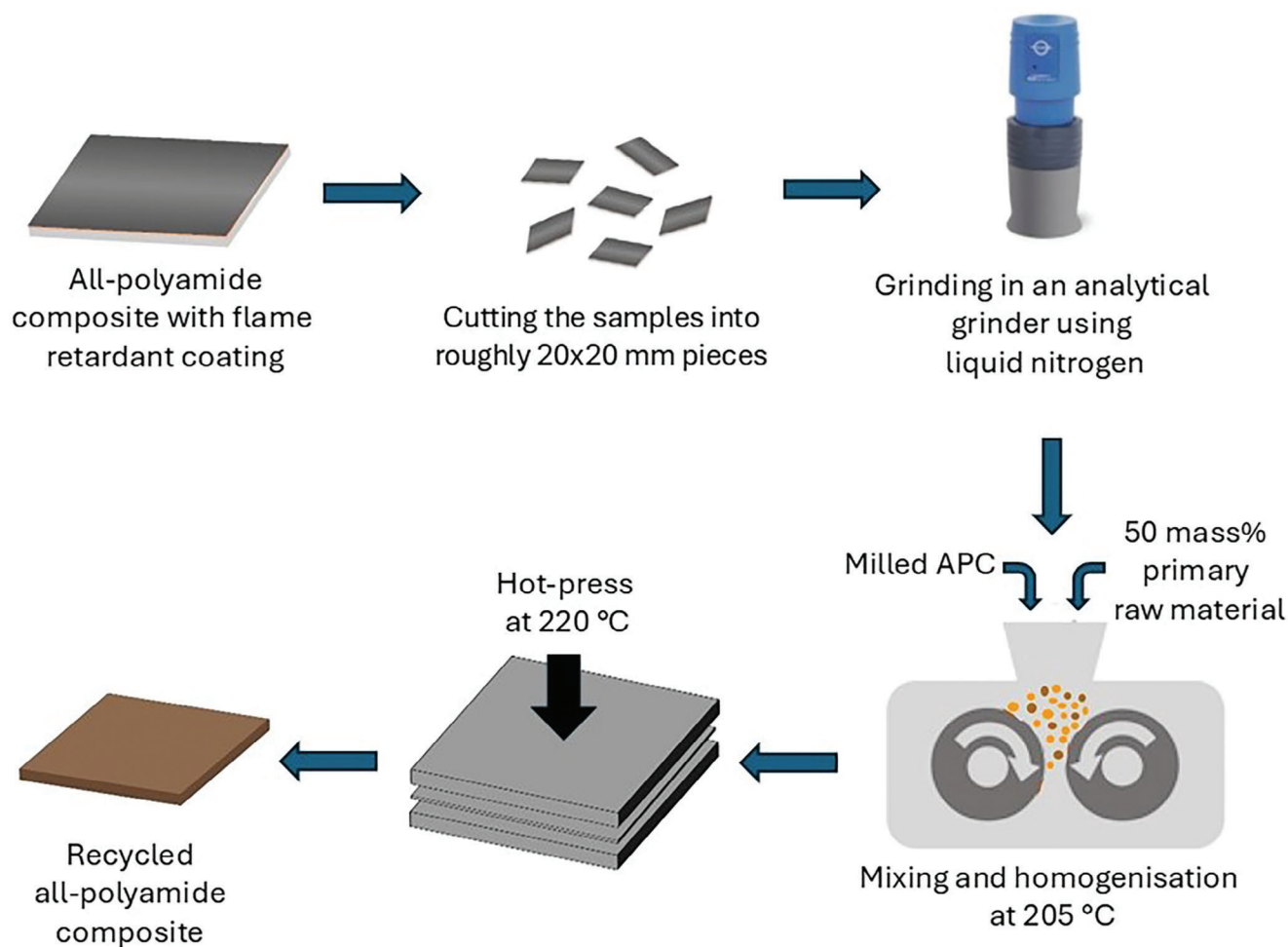


Figure 4. Flowchart for recycling the all-polyamide composites.

The time to ignition has decreased for all coated samples which may be explained by the characteristic mechanism of action of the gas phase flame retardants. Typically, the thermal degradation of phosphorus-containing flame retardants starts earlier, and phosphorus radicals are formed in the gas phase, inhibiting combustion. Thus, although the sample ignites sooner, its overall

Table 3. Ratings and criteria for UL-94 test.

Rating	Test criteria
HB	On the horizontal specimen, slow-burning; burning rate <math>< 40 \text{ mm min}^{-1}</math> for 3 mm thick samples
V-2	On the vertical specimen, the burn time should not exceed 30 s, and the test specimen should not burn to the end, but the cotton wool may ignite.
V-1	On the vertical specimen, the burn time must not exceed 30 s, the test piece must not burn to the end, and the cotton must not ignite.
V-0	On the vertical specimen, the burn time must not exceed 10 s, the test piece must not burn to the end, and the cotton must not ignite.

flame retardancy is improved. The APC/5% RP/5% EG ES100 sample ignited fastest (5 s). The flame retardant coatings have significantly reduced the pHRR values. Compared to the pHRR of the reference PA6 sample (955 kW m^{-2}), the pHRR was reduced by at least 390 kW m^{-2} in all cases, and the pHRR of the APC/3P%HPCTP/4%EG sample was 483 kW m^{-2} , which is 49% lower than the reference. The time to the pHRR was shifted toward higher values compared to the reference by 9 s and 24 s for samples containing RP and MgO, respectively, while HPCTP reduced the pHRR time by 33 and 23 s. Concerning the THR, only APC/3P%HPCTP/4%EG reached the same value as the reference, the other samples increased the THR by at least 7 MJ m^{-2} . The amount of solid residue remaining after combustion was increased in all cases compared to the reference, but the samples containing MgO and RP had only 1% residual mass, even in the presence of EG acting in the solid phase. Samples containing HPCTP and EG had a higher residual mass, with 4% EG as high as 7%. It should be noted that the aluminium sample holders used in the study were sometimes burnt through, which may slightly distort the residual mass value.

The heat release rate curve serves as a comprehensive representation of the influence of flame retardants. By individually

Table 4. The TGA results of reference and flame retarded APC samples ($T_{-5\%}$: the temperature at 5% mass loss; $T_{-50\%}$: the temperature at 50% mass loss; dT_{Gmax} : maximum mass loss rate; $T_{dT_{Gmax}}$: temperature belonging to the maximum mass loss rate; Average standard deviation values: temperature measurements: ± 0.5 °C, mass measurements: $\pm 1\%$).

Sample	$T_{-5\%}$ [°C]	$T_{-50\%}$ [°C]	dT_{Gmax} [%/°C]	$T_{dT_{Gmax}}$ [°C]	Residue at 600 °C [%]	Monomer conversion [%]
APC	329	389	1.7	380	3.6	98.3
APC/5%RP/5%EG	332	407	1.4	390	3.7	98.5
APC/5%MgO/5%EG	270	393	1.9	389	4.5	98.0
APC/3P%HPCTP/3%EG	316	402	1.4	388	3.4	98.7
APC/3P%HPCTP/4%EG	284	395	1.5	381	4.2	98.5

examining the impact of each flame retardant and assessing the residual material in the composite after combustion (**Figure 6**), it is possible to infer the distinct mechanisms of action of the flame retardants. Literature^[28] suggests a synergistic effect can be attained when combining MgO with various flame retardants which were leveraged here by using MgO together with EG, which led to a significant reduction of pHRR. Phosphorus-containing flame retardants have also been utilised with expandable graphite in various materials,^[29–32] as their combined application can yield a synergistic effect. The phosphorus compounds function in both the solid and gas phases, while expandable

Table 5. The UL-94 and LOI results of reference PA6 and PA6-based flame retardant coatings itself.^[26] (Average standard deviation of the LOI: ± 1 vol.%).

Sample	UL-94 ranking	LOI [%]
PA6	HB	21
PA6/5%RP/5%EG	V-0	26
PA6/5%MgO/5%EG	HB	24
PA6/3P%HPCTP/3%EG	HB	25
PA6/3P%HPCTP/4%EG	HB	25

graphite operates in the solid phase. When utilised together, the expandable graphite generates a char layer with low thermal conductivity, safeguarding the material from subsequent fire. Additionally, as the temperature escalates, the phosphorus undergoes oxidation, forming diverse P-containing groups that can further react with the graphite in the char layer when exposed to oxygen and heat. This interaction impedes the development of cracks in the protective layer.

The maximum average rate of heat emission (MARHE) decreased with all flame retardant compositions, with the lowest value ($291 \text{ kW m}^{-2}\text{s}^{-1}$) obtained with the sample containing HPCTP and 4% EG. For this sample, MARHE decreased by 18% compared to the reference ($354 \text{ kW m}^{-2}\text{s}^{-1}$). The sample containing HPCTP and 4% EG also had the lowest value for effective heat of combustion (EHC), which was 25.3 MJ kg^{-1} .

3.1.3. Dynamic Mechanical Analysis of all-Polyamide Composites

The results of the DMA study are presented in **Table 7**. Storage modulus values were measured at room temperature (25 °C) and above T_g (80 °C). The value of T_g was determined from the peak of the $\tan\delta$ curve.

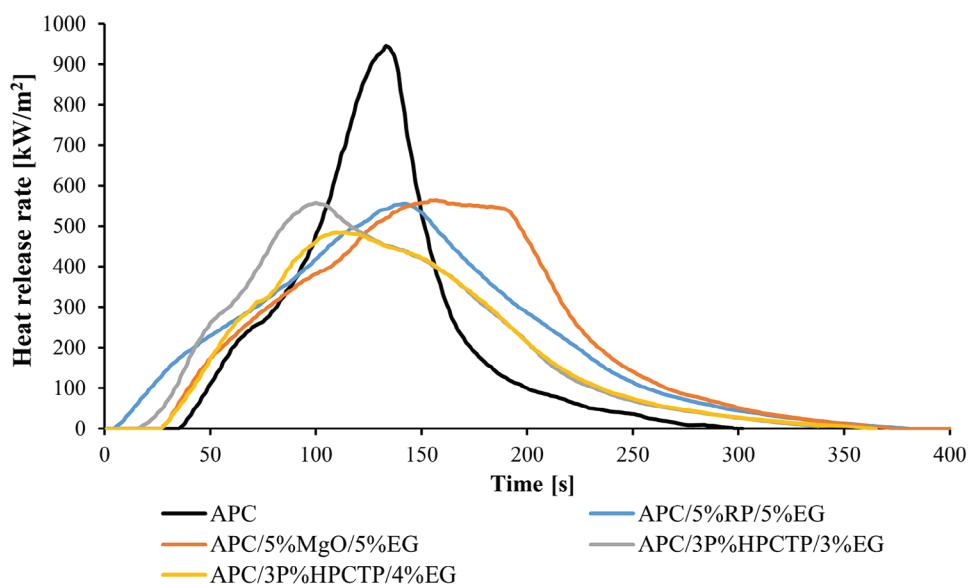


Figure 5. The heat release rate of reference and flame retarded APCs.

Table 6. The MLC results of reference and flame retarded APCs (TTI: time to ignition, pHRR: peak heat release rate, THR: total heat release, MARHE: maximum average rate of heat emission, EHC: effective heat of combustion, Average standard deviation of the measured mass loss calorimeter values: TTI: ± 3 ; pHRR: ± 30 ; time to pHRR: ± 5 ; residue: ± 2).

Sample	TTI [s]	pHRR [kW m ⁻²]	t _{pHRR} [s]	THR [MJ m ⁻²]	Residue [%]	MARHE [kW m ⁻² s ⁻¹]	EHC [MJ kg ⁻¹]
APC	36	955	135	67	0	354	28.4
APC/5%RP/5%EG	5	554	144	82	1	337	32.5
APC/5%MgO/5%EG	28	563	159	88	1	343	33.4
APC/3P%HPCTP/3%EG	16	555	102	73	3	334	30.0
APC/3P%HPCTP/4%EG	26	483	112	67	7	291	25.3

The reference APC had a storage modulus of 1565 and 665 MPa at 25 and 80 °C, respectively. At 25 °C, only the APC/3P%HPCTP/3%EG sample had a higher storage modulus

Table 7. The DMA results of reference and flame retarded all-polyamide composites.

Sample	Storage modulus at 25 °C [MPa]	Storage modulus at 80 °C [MPa]	T _g [°C]
APC	1565	665	58
APC/5%RP/5%EG	1432	668	69
APC/5%MgO/5%EG	1493	698	62
APC/3P%HPCTP/3%EG	1798	742	66
APC/3P%HPCTP/4%EG	1349	462	57

(1798 MPa), than the reference. At 80 °C, all samples except the APC/3P%HPCTP/4%EG sample had a higher storage modulus than the reference. With the exception of the APC/3P%HPCTP/4%EG sample, T_g increased with the addition of the flame retardants and reached values above 60 °C. The APC/5%RP/5%EG sample had the highest T_g, 11 °C higher than the reference APC.

3.2. PA6 samples from the Recycling of all-Polyamide Composites

After mechanical recycling, we intended to assess the durability of the applied flame retardants as well. During recycling, APCs alone are difficult to process, so primary PA6, T27 had to be added. This resulted in halving the flame retardant content in the

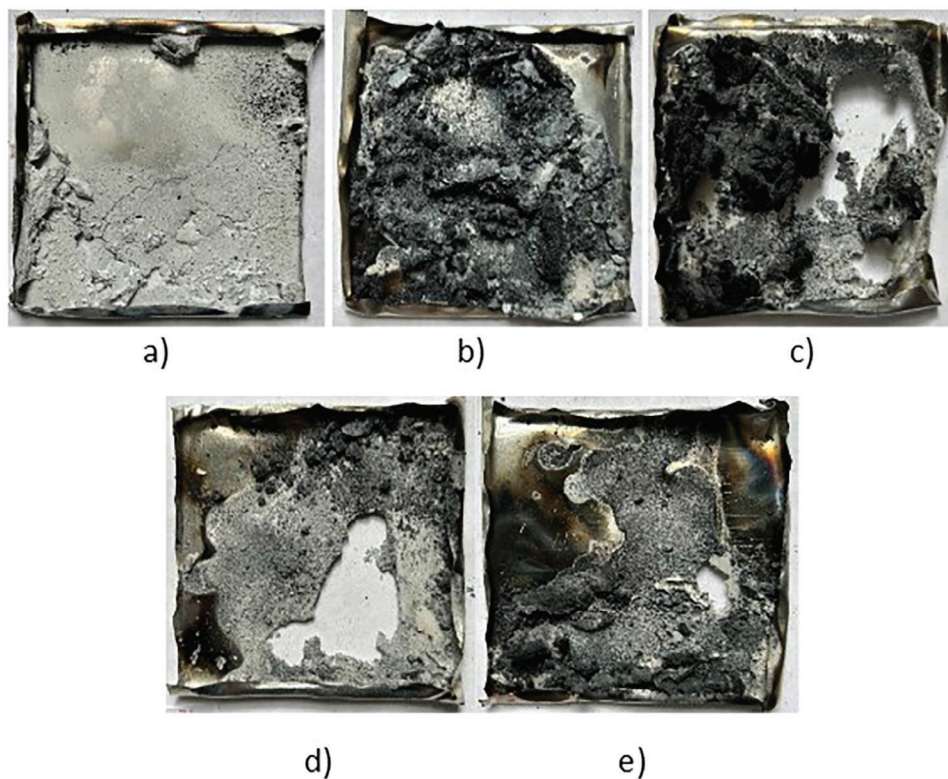


Figure 6. The residue of reference and flame retarded APCs after burning, where a) is sample APC, b) is sample APC/5%RP/5%EG, c) is sample APC/5%MgO/5%EG, d) is sample APC/3P%HPCTP/3%EG, e) is sample APC/3P%HPCTP/4%EG.

Table 8. The TGA results of reference and flame retarded recycled PA6 samples ($T_{.5\%}$: the temperature at 5% mass loss; $T_{.50\%}$: the temperature at 50% mass loss; dT_{Gmax} : maximum mass loss rate; $T_{dT_{Gmax}}$: temperature belonging to the maximum mass loss rate; Average standard deviation values: temperature measurements: ± 0.5 °C, mass measurements: $\pm 1\%$).

Sample	$T_{.5\%}$ [°C]	$T_{.50\%}$ [°C]	dT_{Gmax} [%/°C]	$T_{dT_{Gmax}}$ [°C]	Residue at 600 °C [%]
rAPC	379	442	1.6	449	3.1
rAPC/5%RP/5%EG	356	398	1.7	399	3.7
rAPC/5%MgO/5%EG	353	389	2.2	384	3.5
rAPC/3P%HPCTP/3%EG	347	409	1.7	412	2.7
rAPC/3P%HPCTP/4%EG	342	435	1.1	438	1.3
T27	391	455	2.2	463	1.1

recycled samples, which was taken into account when evaluating the results.

3.2.1. Thermal Stability of Recycled PA6 Samples

The TGA results for the reference and flame retarded samples are summarised in **Table 8**.

The $T_{.5\%}$ and $T_{.50\%}$ of the reference recycled sample (379 and 442 °C, respectively) were somewhat reduced by the flame retardants. HPCTP samples had lower $T_{.5\%}$ temperatures than samples containing RP or MgO, but the opposite was true for $T_{.50\%}$. The maximum mass loss rate of the reference recycled sample was close to 450 °C, but the flame retardants also reduced this value. By comparing the values with the APCs, it was observed that the $T_{.5\%}$ values were higher for the recycled samples. This may be explained by the high $T_{.5\%}$ temperature of T27 (391 °C), thus shifting the temperatures toward higher values. The rAPC sample had 53 °C higher $T_{.50\%}$, which can be also explained by the addition of T27. In contrast, the $T_{.50\%}$ of the flame retarded rAPCs was lower than the $T_{.50\%}$ values of the APCs. For the temperatures corresponding to the maximum mass loss, only the rAPC/5%MgO/5%EG sample had a lower value compared to the primary APCs, the reverse being true for the other cases. The residue amounts indicate that the expandable graphite likely expanded during recycling to some extent, resulting in less residue after decomposition compared to before recycling.

3.2.2. Flame Retardancy of Recycled PA6 Samples

The flammability of the recycled samples was determined using UL-94, LOI and MLC tests. The results of the UL-94 and LOI tests of the rAPCs are shown in **Table 9** and the results of the MLC test are shown in **Figure 7** and **Table 10**.

In the UL-94 test, in addition to the T27 sample, two flame retarded samples achieved a V-2 classification (rAPC/5%RP/5%EG, rAPC/3P%HPCTP/3%EG). In most cases, UL-94 classification results are the same for primary and recycled samples. One exception is the sample containing 3P% HPCTP and 3% EG, where the recycled sample was classified better (V-2) than the primary sample (HB). The addition of 50% T27 may have caused this because it also has a V-2 classification. As for the burning of

Table 9. The UL-94 and LOI results of reference and flame retarded recycled PA6 samples. (Average standard deviation of the LOI: ± 1 vol%).

Sample	UL-94 ranking	LOI [%]
rAPC	HB	21
rAPC/5%RP/5%EG	V-2	24
rAPC/5%MgO/5%EG	HB	22
rAPC/3P%HPCTP/3%EG	V-2	24
rAPC/3P%HPCTP/4%EG	HB	21
T27	V-2	26

the samples, little smoke was produced, but all compositions dripped.

Of the recycled samples, the sample containing RP and the sample containing HPCTP and 3% EG had the most favourable oxygen index value of 24%. The presence of MgO also increased the LOI value by 1% compared to the reference (21%), reaching 22%. In contrast, the sample containing HPCTP and 4% EG achieved the same value as the reference. The T27 sample achieved an LOI of 26%, which is higher than the flame retarded samples.

When comparing the results of the recycled samples with the primary samples, it can be seen that the LOI for the reference did not change. A 1–2% decrease in LOI is observed after recycling for most samples containing flame retardants. The only sample with a significant reduction after recycling was the rAPC/3P%HPCTP/4%EG. The primary sample had an LOI of 25%, whereas the LOI of the recycled sample was only 21%.

In the recycled flame retarded samples, the ignition time was reduced compared to rAPC reference, the TTI was affected to a nearly similar extent for all flame-retardant formulations. The sample containing HPCTP and 3% EG achieved the lowest TTI value (31 s), with a 59.2% decrease compared to the reference time of 76 s. The lowest pHRR value was reached by the sample containing HPCTP and 4% EG, which was 616 kW m⁻², 25.2% lower than in the case of the recycled reference rAPC sample (823 kW m⁻²) and 35.5% lower than in the case of the primary reference APC sample (955 kW m⁻²). Regarding time to pHRR, the flame retarded samples reached their maximum heat release earlier. The data show that the presence of the flame retardant did not significantly affect the THR of the recycled samples, except the sample containing MgO, the other samples showed a minimal decrease, the best result being achieved by the sample containing RP and EG with 61 MJ m⁻², a 7.7% decrease compared to the reference of 66 MJ m⁻². In terms of residual mass, however, the result differs from that of the coated samples because almost none ($\approx 1\%$) of the recycled samples tested remained after combustion, which can be seen in the images of the samples after MLC analysis (**Figure 8**). The two recycled compositions with best flame retardancy are those containing RP and EG and, having similar results to the coated samples with HPCTP and 4% EG.

Upon comparing the APC reference with the rAPC sample without flame retardants, it is evident that the rAPC ignites later and exhibits lower maximum heat release. This behaviour can be attributed to the different heat release characteristics of the

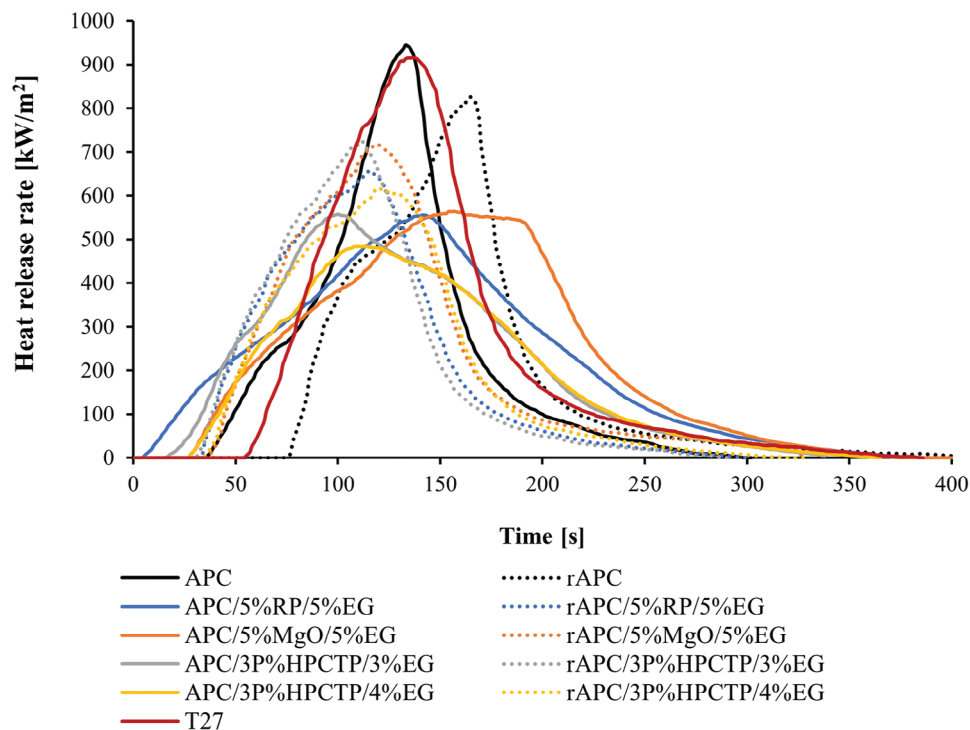


Figure 7. The heat release rate of reference and flame retarded recycled PA6 samples. The MLC curves of the primary samples are the same as the curves shown in Figure 5.

added T27 primary PA6 material (50 mass%) compared to the caprolactam-based PA6 system and PA6.6 reinforcing material. Furthermore, the ignition of T27 was observed later than that of the APC sample, with the maximum heat release being almost identical for both samples. Additionally, it was noted that the peak heat release rate of the recycled samples containing flame retardant is higher than that of the primary flame retarded samples, as due to the addition of 50% non-flame retarded T27 their flame retardant content is half of the virgin APC compositions. In the rAPC/5%RP/5%EG and rSRC/3P%HPCTP/4%EG recycled samples the decrease of pHRR compared to the decrease in primary SRC samples was approximately proportional to the decrease of the flame retardant ratio due to the addition of 50 mass% T27 (25.2% vs 48.7 in the case of 3P%HPCTP/4%EG samples, and 20.4 vs 42.0% in the case of rAPC/5%RP/5%EG sample).

In the case of two less efficient formulations (5%MgO/5%EG and 3P%HPCTP/3%EG) the decrease in pHRR was somewhat less than proportional (13.0% vs 41.0%, and 12.2% vs 41.9%), but they still kept $\approx 60\%$ of their efficiency after one recycling process.

For MARHE, it is observed that in all cases, the flame retarded samples achieved a higher value than the reference rAPC. Comparing the primary and recycled samples, it is observed that the primary samples have a lower MARHE value in all cases except for the flame retarded samples containing HPCTP and 4% EG. The increase after recycling is due to the addition of 50 mass% of PA6 without flame retardant to the primary material during recycling. Looking at T27 separately, the MARHE value is $384 \text{ kW m}^{-2}\text{s}^{-1}$, which is almost $100 \text{ kW m}^{-2}\text{s}^{-1}$ higher than in the case of rAPC.

Table 10. The MLC results of reference and flame retarded recycled PA6 samples (TTI: time to ignition, pHRR: peak heat release rate, THR: total heat release, MARHE: maximum average rate of heat emission, EHC: effective heat of combustion, Average standard deviation of the measured mass loss calorimeter values: TTI: ± 3 ; pHRR: ± 30 ; time to pHRR: ± 5 ; residue: ± 2).

Sample	TTI [s]	pHRR [kW m^{-2}]	t_{pHRR} [s]	THR [MJ m^{-2}]	Residue [%]	MARHE [$\text{kW m}^{-2}\text{s}^{-1}$]	EHC [MJ kg^{-1}]
rAPC	76	823	167	66	0	293	29.9
rAPC/5%RP/5%EG	33	655	118	61	1	348	25.1
rAPC/5%MgO/5%EG	36	716	121	69	1	362	29.4
rAPC/3P%HPCTP/3%EG	31	723	113	61	1	366	26.9
rAPC/3P%HPCTP/4%EG	35	616	121	62	1	333	25.9
T27	54	918	139	81	0	384	35.5

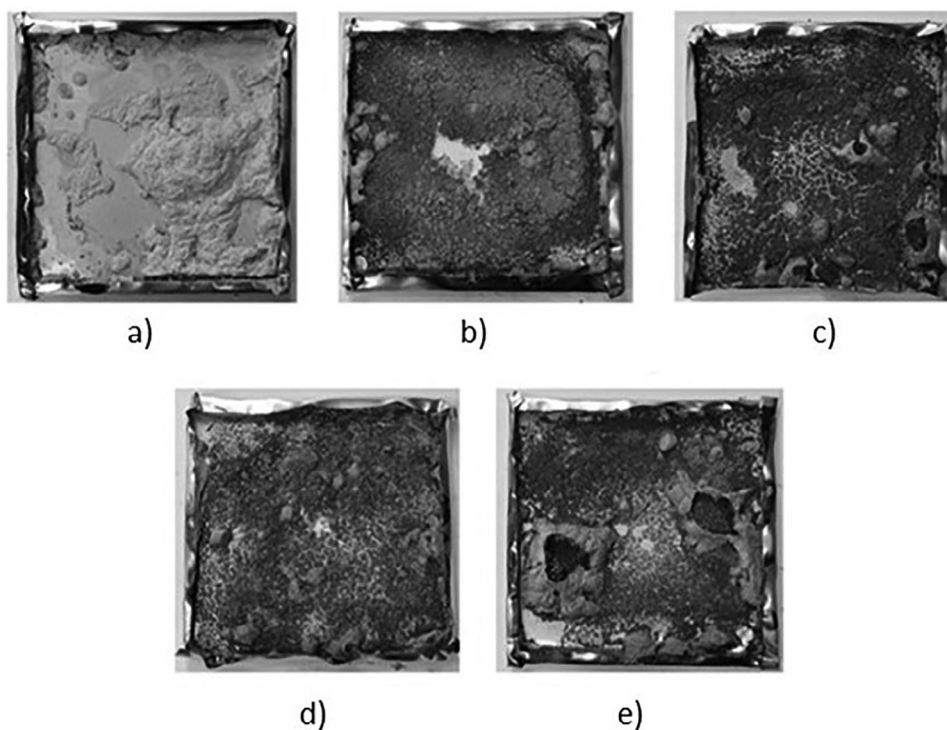


Figure 8. The residue of reference and flame retarded recycled samples after burning, where a) is sample rAPC, b) is sample rAPC/5%RP/5%EG, c) is sample rAPC/5%MgO/5%EG, d) is sample rAPC/3P%HPCTP/3%EG, e) is sample rAPC/3P%HPCTP/4%EG.

3.2.3. Dynamic Mechanical Analysis of Recycled PA6 Samples

The results of the DMA study are presented in **Table 11**. Storage modulus values were measured at room temperature (25 °C) and above T_g (80 °C). The value of T_g was determined from the peak of the $\tan\delta$ curve.

In terms of storage modulus, the recycled sample without flame retardants achieved the highest values for both 25 °C (2716 MPa) and 80 °C (1033 MPa) and also had the highest T_g (63 °C). Comparing the results with the APCs (Table 7), it can be seen that the storage modulus at 25 and 80 °C increased with recycling. This could be explained by the fact that higher pressure can be achieved with the hydraulic press than in the case of the specimens produced by a syringe. As a result, the specimens may have fewer voids. In contrast, the T_g in the recycled samples was mostly lower than in the APCs. There is one exception where the T_g of the recycled specimen is higher,

and that is the all-polyamide composite without flame retardant. The decrease in the glass transition temperature can be explained by the fact that the graphite may have expanded during recycling.

4. Conclusion

This study demonstrated that all-polyamide composites (APCs) prepared via anionic ring-opening polymerisation with flame retardant in-mould coatings offer improved flame retardancy and recyclability. The flame retardant coatings led to a substantial reduction in peak heat release rate (pHRR), with as much as a 49% decrease observed in the composite comprising 3P% hexaphenoxycyclotriphosphazene (HPCTP) and 4% expandable graphite (EG). Additionally, there was an overall increase in residual mass across all cases.

A notable advantage of these all-polyamide composites is their relative ease of mechanical recycling compared to composites reinforced with other fibres and thermoset composites. In accordance with current industry practice, it may be worthwhile mixing primary material with the recyclates to improve the processability. Care should also be taken when designing the original formulations to ensure that the flame retardants used are as stable as possible at the reprocessing temperature, which is a challenge for PA6 due to its high melting point.^[33] In the present case, EG may have started to expand slightly, but the composition was still processable. Even with the addition of 50 mass% non-flame retarded primary material during the recycling process, a significant decrease in pHRR was achieved in comparison both to the primary and recycled reference. In the case of less effective

Table 11. The DMA results of recycled PA6 samples.

Sample	Storage modulus at 25 °C [MPa]	Storage modulus at 80 °C [MPa]	T_g [°C]
rAPC	2716	1033	63
rAPC/5%RP/5%EG	1895	774	49
rAPC/5%MgO/5%EG	1921	779	50
rAPC/3P%HPCTP/3%EG	1741	711	51
rAPC/3P%HPCTP/4%EG	1913	746	51

formulations, the flame retardants kept their efficiency in $\approx 60\%$, while the most effective ones fully retained their ability to reduce pHRR. Sample rAPC/3P%HPCTP/4%EG, for instance, exhibited a reduction of up to 25%, which means that a proportional decrease in pHRR was achieved with the use of flame retarded recycled material. This demonstrates the durability of the flame retardant properties through multiple life cycles, contributing to sustainable material use and waste reduction.

Our findings underscore the potential of all-polyamide composites with flame-retardant coatings as a promising avenue for enhancing fire safety while facilitating mechanical recycling.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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all-polyamide composites, flame retardancy, in situ polymerisation, mechanical recycling, polyamide 6 composite

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