

# FLAME RETARDANT COATINGS FOR $\epsilon$ -CAPROLACTAM-BASED SELF-REINFORCED POLYAMIDE 6 COMPOSITES

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## Abstract

It is crucial to consider the potential for recycling raw materials to maintain sustainable development. Self-reinforced composites can be easily recycled through mechanical recycling, and their use is increasing. In our study, we examined the flame retardancy and mechanical recycling of self-reinforced polyamide 6 (PA6) composites. To prepare the composites, we injected a low-viscosity  $\epsilon$ -caprolactam (CL) monomer in the presence of an activator and initiator between five layers of polyamide 6.6 reinforcement pre-placed in the mould and then performed anionic ring-opening polymerisation in the mould. A flame retardant coating was formed on the surface of the composite through in-mould coating. A combination of flame retardants in the coating resulted in a synergistic effect, reducing the maximum heat release rate by up to 49%. In the mechanical recycling process, we added 50 mass% of the primary material to the milled self-reinforced composite yet still managed to reduce the maximum heat release rate by 25% compared to the reference.

## 1. Introduction

There is a growing demand for recyclable, environmentally friendly materials [1]. Self-reinforced composites (SPC) are becoming popular in meeting the requirements of the circular economy. These materials are beneficial because the reinforcement and the thermoplastic matrix come from the same family of materials, allowing both to be reused after mechanical recycling. This reduces the waste impact on the environment and eliminates the need for costly and energy-intensive technologies to separate the reinforcing fibre and the matrix during the recycling process, as would be the case for cross-linked matrix or non-self-reinforced composites with a thermoplastic matrix [2,3].

Thermoplastic resin transfer moulding is a method used to produce long fibre-reinforced thermoplastic matrix composites. In this process, a low-viscosity monomer is injected into the mould along with an activator and initiator while the reinforcement is already pre-placed. Polymerisation takes place in the mould within a few minutes, enabling short cycle times for mass production. One of the prominent examples of long fibre-reinforced thermoplastic composites is polyamide 6 (PA6) composite, which can be produced from caprolactam monomer [4,5]. In reactive polymer processing, such as in situ polymerisation of  $\epsilon$ -caprolactam, it is possible that the polymerisation process is disrupted by using various additives. Furthermore, when composites are created using liquid moulding techniques, challenges such as the filtration and uneven distribution of solid flame retardants arise, and the presence of fibre reinforcement might hinder the creation of a consistent protective layer. These issues can be circumvented by opting for liquid flame retardants and/or applying flame retardant coatings [6].

The high nitrogen content in polyamides may give the impression that they are self-extinguishing, but they melt easily when exposed to flames, leading to dripping and rapid fire spread. Safety regulations prohibit virgin PA6 in specific high-risk applications, so flame retardants must be added [7,8]. Many flame retardants interfere with the polymerisation reaction of CL. However, promising results have been achieved in the literature [9,10] using a phosphorus-containing hexaphenoxycyclotriphosphazene flame retardant with a heterocyclic structure. This compound has a hindered P atom, which minimises interference with the polymerisation reaction of CL. Additionally, the flammability of CL-based PA6 can be significantly reduced using red phosphorus, magnesium oxide, the polyhalogenated cyclopentadiene derivative (Dechlorane Plus), or a combination [11].

In our research, we created CL-based self-reinforced PA6 composites. The composites were coated with a flame retardant coating by in-mould coating. The flammability of the self-reinforced composites was investigated. Then, after mechanical recycling, new test specimens were created, and their flammability was also tested.

## **2. Materials and methods**

### **2.1. Materials**

To prepare the PA6 matrix through ring-opening in-situ polymerisation, we utilised AP-NYLON<sup>®</sup> type  $\epsilon$ -caprolactam monomer manufactured by the German company Brüggemann Chemical. We employed BRUGGOLLEN<sup>®</sup> C20P as an activator from Brüggemann Chemical and Dilactamate<sup>®</sup> from Katchem as an initiator. In addition, the flame retardants utilised included red phosphorus (RP, Clariant), magnesium oxide (MgO, Sigma Aldrich), EG ES100 type expandable graphite (EG, Graphit Kropfmühl), and Rabitle FP110 type hexaphenoxycyclotriphosphazene (HPCTP, Fushimi). The reinforcing material used for the self-reinforced composites is a satin woven polyamide 6.6 (PA6.6) fabric type CR-262 from the Spanish company Sati Envirotech. The fabric has a thickness of  $0.41 \pm 0.0615$  mm and an areal density of  $330 \pm 24.75$  g/m<sup>2</sup>. 50 mass% of Tarnamide T27 (T27, Grupa Azoty) type PA6 was added to the recycled samples.

### **2.2. Preparation of self-reinforced PA6 composites with flame retardant coatings**

An aluminium mould heated to 150°C was used for T-RTM modelling and in-mould coating application. The mould, measuring 100x100x2 mm<sup>3</sup>, contained five layers of PA6.6 reinforcement. The matrix composition included 87% CL, 3% C20P, and 10% DL. The CL and C20P were melted at 120°C and mixed before adding DL. The mixture was injected into the sealed mould using a syringe, where in-situ polymerisation occurred among the reinforcement material. The composite surface was coated in a 2.5 mm deep aluminium mould using the same procedure and ratios of monomer, activator, and initiator, along with flame retardants selected based on prior studies [12].

### **2.3. Recycling of self-reinforced PA6 composites with flame retardant coating**

The samples were recycled and ground using an IKA A 11 basic analytical grinder. After grinding, a 50 mass% primer T27 type PA6 granulate without flame retardant was mixed with the grindings using a Brabender Lab-Station type internal mixer. The mixing was conducted at 205°C, below the melting temperature of polyamide 6 of 220°C, as high shear during mixing causes a high thermal expansion in the system. New test specimens were produced from the homogeneous material obtained from the mixing using a 30 T hydraulic press. The press was heated to 220°C. The mould was gradually closed, taking into account the melting of the material, and when it was completely closed, it was kept at 0 bar for 5 minutes, then at 100 bar for 5 minutes and at 200 bar also for 5 minutes.

### **2.4. Methods**

UL-94 flammability tests were conducted following ISO 9772 and ISO 9773. The rate of flame spread is measurable through the horizontal setup (H-type), while the flammability rating can be assessed using the vertical setup (V-type). The test samples measured 120x10x3 mm<sup>3</sup>.

Limiting oxygen index tests (LOI) were conducted in line with the ISO 4589-1 and ISO 4589-2 standards. The LOI represents the lowest volume of oxygen in a flowing oxygen-nitrogen mixture

necessary to sustain the combustion of a test sample at a given flow rate. The dimensions of the test samples were 120x10x3 mm<sup>3</sup>.

A mass loss cone calorimeter (MLC, Fire Testing Technologies Inc.) was utilised to assess the combustion properties of the samples. During the evaluation, the samples were subjected to a heat flux of 50 kW/m<sup>2</sup>, adhering to the ISO 13927 standard. The composite sample measured 100x100x2 mm<sup>3</sup>, while the coated composites had dimensions of 100x100x2.5 mm<sup>3</sup>.

### 3. Results

#### 3.1. LOI and UL-94 tests

The results of the LOI and UL-94 testing of the primary material and recycled material samples are summarised in Table 1.

**Table 1.** The results of the LOI and UL-94 testing of the primary materials and recycled materials.

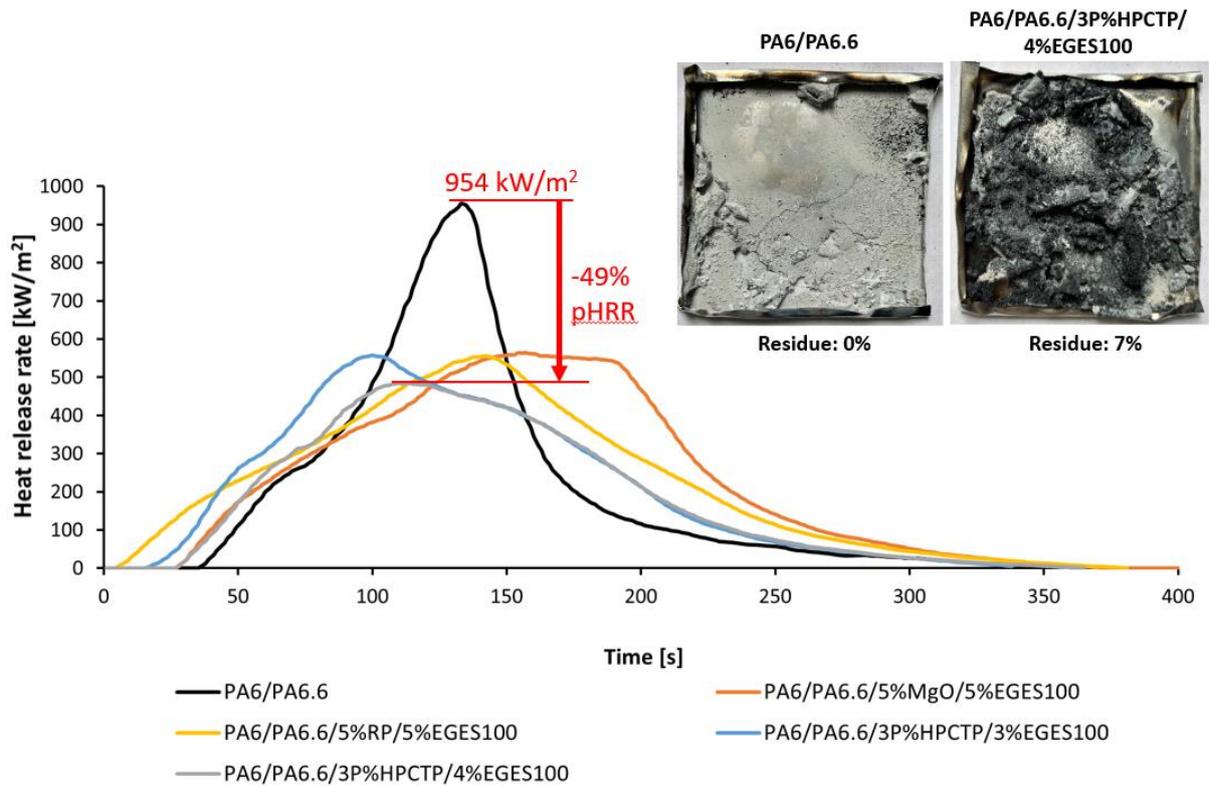
Specimen	Primer SPC		Recycled SPC	
	UL-94 rating	LOI (V%)	UL-94 rating	LOI (V%)
PA6/PA6.6	HB	21	HB	21
PA6/PA6.6/5%MgO/5%EG	HB	24	HB	22
PA6/PA6.6/5%RP/5%EG	V-0	26	V-2	24
PA6/PA6.6/3P%HPCTP/3%EG	HB	25	V-2	24
PA6/PA6.6/3P%HPCTP/4%EG	HB	25	HB	21

The efficacy of flame retardants in elevating the oxygen index of composites derived from primary raw materials is noteworthy. It has been observed that incorporating phosphorus red (PR) and expandable graphite (EG) into the compositions can result in an oxygen index reaching up to 26%. Within the field of recycled composites, formulations containing red phosphorus and formulations containing hexafenoxycyclotriphosphazene (HPCTP) and 3% expandable graphite showed the most favourable oxygen index of 24%. Conversely, the composite encompassing HPCTP and 4% expandable graphite manifested the same LOI as the reference recycled SPC.

Compared to the primary and recycled composite specimens, a diminution in the LOI values of flame-retarded samples was noticeable. This reduction can also be explained by the fact that the recycled samples were mixed with a 50 mass% primary feedstock, thus adding flammable material to the sample. For the UL-94 tests, only the sample containing RP and EG achieved a V-0 self-extinguishing classification for the primary materials, the other samples achieved HB classification. For the recycled samples, the PA6/PA6.6/5%RP/5%EG and PA6/PA6.6/3P%HPCTP/3%EG samples achieved a V-2 classification.

#### 3.2. Mass loss calorimetry

The results of the MLC test for primary material are given in Table 2, and for recycled samples in Table 3. The heat release rate curves of the original self-reinforced PA6 composites are shown in Figure 1, while the heat release rate curves compared to the recycled samples are shown in Figure 2.



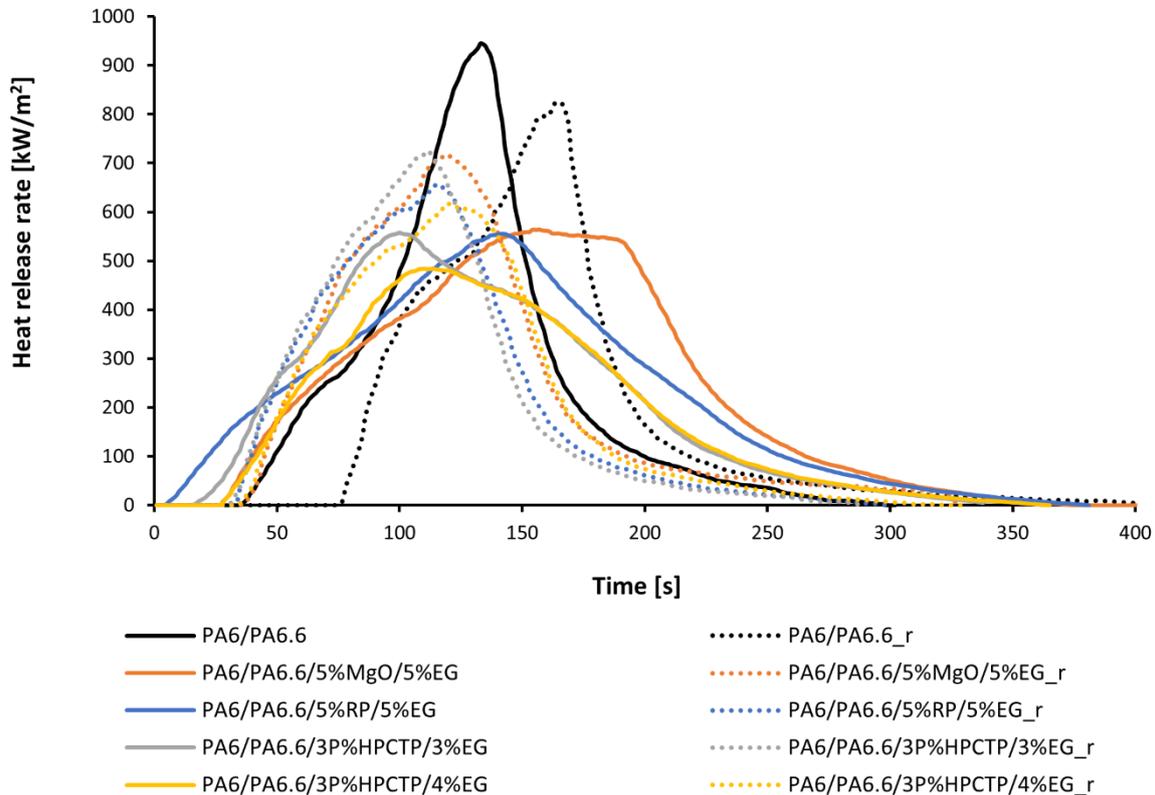
**Figure 1.** The heat release rate of reference and flame retarded self-reinforced polyamide 6 composites with coatings containing red phosphorus (RP), magnesium oxide (MgO), hexaphenoxycyclotriphosphazene (HPCTP) and expandable graphite (EG).

**Table 2.** The results of the MLC of the self-reinforced PA6 composites with flame retardant coatings.

Specimen	TTI (s)	pHRR (kW/m <sup>2</sup> )	time to pHRR (s)	THR (MJ/m <sup>2</sup> )	Residue (%)
PA6/PA6.6	36	942.4	135	67.3	0
PA6/PA6.6/5%MgO/5%EG	28	562.7	159	87.6	1
PA6/PA6.6/5%RP/5%EG	5	554.2	144	81.7	1
PA6/PA6.6/3P%HPCTP/3%EG	16	554.8	102	72.9	2
PA6/PA6.6/3P%HPCTP/4%EG	26	482.8	112	66.9	7

The flame retardant coatings have significantly reduced the maximum heat release rates: Compared to the peak heat release rate (pHRR) of the reference PA6 sample (955 kW/m<sup>2</sup>), the pHRR was reduced by at least 400 kW/m<sup>2</sup> in all cases. The pHRR of the PA6/PA6.6/3P% HPCTP/4% EG sample was 484 kW/m<sup>2</sup>, 49% lower than the reference. The maximum heat release time was shifted towards higher values for samples containing MgO and RP than the reference, while HPCTP reduced the pHRR time. For the total heat release (THR), compared to the reference sample (72 MJ/m<sup>2</sup>), only the PA6/PA6.6/3P% HPCTP/4%EG sample showed a decrease in total heat release (67 MJ/m<sup>2</sup>), while the sample containing MgO and EG showed an increase in THR of 18%. The time required for ignition decreased for all coatings, contrary to the expected results. In addition, the characteristic mechanism of action of the gas phase flame retardants may also explain the earlier ignition. Typically, the thermal degradation of phosphorus-containing flame retardants is initiated earlier, and phosphorus radicals are formed in the gas phase, which inhibits combustion. This way, the sample ignites sooner but has a better overall resistance to fire. The PA6/PA6.6/5% PR/5% EG sample ignited fastest (5 s). 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 having a residual mass value 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.



**Figure 2.** The heat release rate of primer and recycled polyamide 6 composites.

**Table 3.** The results of the MLC of the recycled self-reinforced PA6 composites.

Specimen	TTI (s)	pHRR (kW/m <sup>2</sup> )	time to pHRR (s)	THR (MJ/m <sup>2</sup> )	Residue (%)
PA6/PA6.6_r	76	823.4	167	65.6	0
PA6/PA6.6/5%MgO/5%EG_r	36	716.1	121	69.0	1
PA6/PA6.6/5%RP/5%EG_r	33	654.5	118	60.5	1
PA6/PA6.6/3P%HPCTP/3%EG_r	31	722.8	113	60.9	1
PA6/PA6.6/3P%HPCTP/4%EG_r	35	615.5	121	62.0	1

The data indicates that the presence of the flame retardant did not have a significant impact on the total heat release of the recycled samples, with the exception of the sample containing MgO. The other samples showed a minimal decrease, with the best result achieved by the sample containing RP and EG at 60.5 MJ/m<sup>2</sup>, representing a 7.7% decrease compared to the reference of 65.6 MJ/m<sup>2</sup>. The sample containing HPCTP and 4% EG achieved the lowest pHRR value at 615.5 kW/m<sup>2</sup>, 25.2% lower than the reference of 823.4 kW/m<sup>2</sup>. The flame retarded samples reached their maximum heat release earlier, and the flame retardants reduced the ignition time in all cases but to a nearly similar extent for all formulations. The sample containing HPCTP and 3% EG achieved the lowest TTI value at 31 s, representing a 59.2% decrease compared to the reference time of 76 s. However, in terms of residual mass, almost none (about 1%) of the tested samples remained after combustion. Expandable graphite

starts to act at temperatures above 200 °C. Therefore, it can be concluded that the graphite has started to expand during recycling and that the residual mass has not increased.

#### 4. Conclusions

Our research involved the development of self-reinforced polyamide 6 composites using anionic ring-opening polymerisation. To make the composites flame retardant, we applied a flame retardant coating to the surface of the composite through in-mould coating. The flame retardant coatings significantly reduced pHRR, with up to a 49% decrease in PA6/PA6.6/3P%HPCTP/4%EG samples and increased residual mass in all cases. A key benefit of self-reinforced composites is their ease of mechanical recycling. Even with 50 mass% of the primary material added during the recycling process, the pHRR was still reduced compared to the reference, with a reduction of up to 25% for sample PA6/PA6.6/3P%HPCTP/4%EG\_r. Despite the premature activation of EG during reprocessing and the addition of 50 mass% primary non-flame-retarded PA6, the heat release of the samples was still decreased.

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