

## DEVELOPMENT OF FLAME RETARDANT COATINGS FOR $\epsilon$ -CAPROLACTAM-BASED POLYAMIDE 6 COMPOSITES

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**Abstract:** *The use of long fibre reinforced thermoplastic composites is increasing due to their short cycle times and ease of recycling. A major representative of thermoplastic matrices is the  $\epsilon$ -caprolactam-based polyamide 6 (PA6). Due to the strict safety regulations of the automotive industry, PA6 composites need to be flame retarded. The flame retardant (FR) can be added to the matrix or used as a coating. The use of coatings ensures that flame retardants do not alter the properties of the composites, prevent the solid additives from being filtered out by the reinforcing materials, and prevent delamination caused by intumescent flame retardants. We developed  $\epsilon$ -caprolactam-based flame retardant coatings suitable for in-mould coating carbon fibre reinforced PA6 composites during thermoplastic resin transfer moulding (T-RTM).*

**Keywords:** flame retardancy; in situ polymerisation;  $\epsilon$ -caprolactam; polyamide 6

### 1. Introduction

Due to short cycle times and easy recycling, thermoplastic matrix composites are becoming increasingly important in many technical fields, particularly in the automotive industry [1]. PA6 is one of the most commonly used matrix materials to produce long fibre reinforced thermoplastic composites. PA6 can be produced from  $\epsilon$ -caprolactam monomer by anionic ring-opening polymerisation in the presence of an activator and initiator [2]. One of the most promising methods for their production is thermoplastic resin transfer moulding (T-RTM) technology based on in-situ polymerisation, where the polymerisation of the monomer impregnated in the reinforcing materials takes place in the mould. A significant drawback of PA6 is its flammability, as it melts easily in flames, and melt droplets can cause rapid fire spread. The strict fire safety requirements make the flame retardancy of PA6 [3].

There are two basic options for polymer flame retardancy: additive and reactive flame retardancy. In additive flame retardancy, the flame retardant additive can be mixed directly into the unmodified polymer, while in reactive flame retardancy, flame retardant monomers are incorporated into the polymer main chain. Of the methods mentioned above, additive flame retardancy is the most commonly used method for PA6. The disadvantage of this process is that flame retardants that are not soluble in  $\epsilon$ -caprolactam may be filtered out by the reinforcing materials. In addition, additives can affect the mechanical properties and viscosity of the matrix, which can cause problems during processing. The use of caprolactam-soluble flame retardants or flame retardant coatings may solve these problems [4].

Höhne et al. [5] used caprolactam soluble hexaphenoxycyclotriphosphazene (HPCTP) for carbon fibre reinforced polyamide 6 composites. The authors found that the PA6 composite flame

retarded with HPCTP meets the requirements of FAR 25.853 for aerospace applications and achieves a self-extinguishing V-0 rating in UL-94 testing.

HPCTP can also be effectively used in glass fibre reinforced PA6 composites. A V-0 rating and a high oxygen index value can be achieved in UL-94 tests. During the initial stage of thermal decomposition, HPCTP releases mainly non-combustible gases (NH<sub>3</sub>, H<sub>2</sub>O, and CO<sub>2</sub>). In addition to the gas-phase flame retardant effect, a solid-phase effect is also observed in forming a foamed carbon layer [6].

Alfonso et al. [7] achieved a synergistic effect for the combustion inhibition of PA6 by combining red phosphorus with magnesium oxide (MgO) or a polyhalogenated cyclopentadiene derivative (Dechlorane Plus - DP). In the case of MgO, the synergistic effect was explained by the ability of MgO to increase the rate of phosphoric acid formation, which leads to a higher rate of char formation on the surface. In the case of DP, it forms phosphorus-containing radicals from the thermal decomposition of hydrochlorinated hydrocarbons. The authors also found that many flame retardants commonly used for PA6 flame retardancy inhibit the polymerisation reaction of  $\epsilon$ -caprolactam and thus cannot be used for its flame retardancy.

Our research investigated the development of flame retardant coatings for carbon fibre reinforced polyamide 6 composites. The flame retardants used were red phosphorus (RP), magnesium oxide (MgO), and expandable graphite. The effect of the flame retardants on crystallinity, glass transition temperature, thermal stability, and fire performance was investigated.

## **2. Materials and methods**

### **2.1 Materials**

To prepare the PA6 matrix, we used AP-NYLON Caprolactam (CL, Brüggemann Chemical) as the monomer. BRUGGOLEN C20P (C20P, Brüggemann Chemical) was used as the activator and Dilactamate (DL, Katchem) as the initiator. Magnesium oxide (MgO, Sigma Aldrich), red phosphorus (RP, Clariant), and two types of expandable graphite (EG ES100 and EG ES350, Graphit Kropfmühl) were used as flame retardants. The difference between the two expandable graphites is their particle size and foaming rate: for the ES100 type, the particle size is in 75% < 150  $\mu\text{m}$ , and the change in volume during foaming is 100  $\text{cm}^3/\text{g}$ , while for the ES350 type, the particle size is in 80% > 300  $\mu\text{m}$ , while the expansion rate is 350  $\text{cm}^3/\text{g}$ . We used PX 35 UD 300 carbon fibre from Zoltek to prepare the composites.

### **2.2 Preparation of coating materials**

Reference and flame retardant coatings were tested on their own. The reference PA6 was prepared using 87% CL, 3% activator, and 10% initiator. 10% flame retardant was used to produce flame retarded PA6. The materials were stored in a vacuum oven, and the flame retardants were dried at 80 °C for 4 hours before use. The monomer and activator, and in the case of flame retarded samples, the flame retardant, were mixed and melted at 120 °C using a heated magnetic stirrer. After adding the initiator, specimens were prepared in an aluminium mould at 150 °C.

### 2.3 Preparation of composites with coating

An aluminium mould at 150 °C was used to model T-RTM and in-mould coating. In the mould with the dimensions of 100x100x2 mm<sup>3</sup>, 5 layers of unidirectional carbon reinforcement were pre-placed in [0]<sub>5</sub> layer order. We used 87% CL, 3% C20P and 10% DL for the matrix. The CL and the C20P were mixed and melted at 120 °C. Then, after adding DL, the system got into the closed mould using a syringe, and in-situ polymerisation was carried out between the reinforcing material. The coating was applied to the composite surface in a 2.5 mm deep aluminium mould. The coating was applied using the same method and monomer/activator/initiator ratio with 10% flame retardant.

### 2.4 Methods

Differential scanning calorimetric measurement (DSC) was performed with a TA Instruments Q2000 device. 2-5 mg samples were analysed in 50 ml/min nitrogen flow. We used heat/cool/heat cycles in a temperature range of 25-250 °C with heating and cooling rates of 10 °C/min.

The thermal stability of the samples was tested using a TA Instruments Q500 TGA device. The test was carried out on 2-5 mg samples under 30 ml/min nitrogen flow. The samples were heated in a temperature range of 30-600 °C with a heating rate of 20 °C/min.

We performed UL-94 flammability test according to ISO 9772 and ISO 9773. The flame spread rate can be determined from the horizontal arrangement (H-type), and the flammability classification can be determined from the vertical arrangement (V-type). The dimensions of the samples were 120x15x4 mm<sup>3</sup>.

The oxygen index tests (LOI) were performed according to ISO 4589-1 and ISO 4589-2 standards. LOI is defined as the minimum oxygen content by volume of an oxygen-nitrogen gas mixture flowing at a specified velocity in the test sample that is still burning. The size of the samples was 120x15x4 mm<sup>3</sup>.

To determine the complex combustion characteristics of the samples, we used a mass loss type cone calorimeter (MLC, Fire Testing Technologies Inc.). In the test, we exposed samples to a heat flux of 50 kW/m<sup>2</sup> based on the ISO 13927 standard. The dimensions of the coating samples were 100x100x4 mm<sup>3</sup>, and the dimensions of the coated composites were 100x100x2.5 mm<sup>3</sup>.

## 3. Results and discussion

Firstly we characterised the coating materials according to thermal and fire behaviour. Then we investigated the coated composites focusing on fire performance.

### 3.1 The effect of FRs on the glass transition temperature and crystallinity (DSC)

The effect of the flame retardants on the glass transition temperature and the crystallinity was investigated by differential scanning calorimetry. The results are given in Table 1.

The crystalline fraction was calculated from the enthalpy of the first heating curve using the following equation:

$$X_c = \frac{\Delta H_{m1}}{\Delta H_{100\%}(1-\alpha)} \cdot 100 \quad (1)$$

where  $\Delta H_{100\%}=188$  J/g is the theoretical value of the enthalpy of crystallization for 100% crystalline PA6,  $\alpha$  [-] is the filler fraction.

Based on the DSC measurements, the added additives had no significant effect on the glass transition temperature of PA6. In general, the  $T_g$  and  $X_c$  values obtained agreed with those reported in the literature. However, the residual CL in the system may distort the results due to inadequate polymerisation. The CL sublimates at 60 °C, which, in the best case, only occurs in an endothermic peak, but the baseline may be shifted in some cases.

*Table 1: DSC results of reference and flame retarded PA6 samples ( $T_g$ : glass transition temperature;  $\Delta H_{m1,2}$ : enthalpy of crystallisation for the first and second heating;  $\Delta H_c$ : enthalpy of crystallisation;  $X_c$ : crystalline fraction.*

Sample	$T_g$ [°C]	$\Delta H_{m1}$ [J/g]	$\Delta H_{m2}$ [J/g]	$\Delta H_c$ [J/g]	$X_c$ [%]
PA6	49	78.6	40.5	45.9	42
PA6/10%RP	51	59.4	28.6	32.9	35
PA6/10%MgO	44	73.2	43.7	42.6	43
PA6/10%EGES100	46	66.7	36.2	32.9	39
PA6/10%EGES350	45	104.2	31.1	29.3	62
PA6/5%RP/5%MgO	49	103.6	37.0	37.1	61
PA6/5%RP/5%EGES100	50	80.7	35.2	35.6	48
PA6/5%RP/5%EGES350	47	80.1	50.1	50.2	47
PA6/5%MgO/5%EGES100	46	95.0	47.0	46.3	56
PA6/5%MgO/5%EGES350	49	127.9	28.3	26.9	76

### 3.2 The effect of FRs on thermal stability (TGA)

The thermal stability of the samples was tested using TGA. The results are presented in Table 2.

The temperature associated with 5 and 50% mass loss was shifted towards higher values than the reference PA6. The improvement in thermal stability was also reflected in an increase in the residual mass, which is favourable from an application point of view. The samples containing expandable graphite performed exceptionally well: although their decomposition usually started below 200 °C, the temperature for 50% mass loss was above 400 °C in all cases, except the samples containing MgO as well, and the maximum decomposition rate occurred at the highest temperatures. For samples containing 5% RP and expandable graphite, the graphite with a larger particle size (EG ES350) led to a higher residual mass due to the larger expansion of the graphite. Similar observations were made for samples containing MgO and expandable graphite.

*Table 2: TGA results of reference and flame retarded PA6 samples ( $T_{-5\%}$ : the temperature at 5% mass loss;  $T_{-50\%}$ : the temperature at 50% mass loss;  $dTG_{max}$ : maximum mass loss rate;  $T_{dTGmax}$ : temperature belonging to the maximum mass loss rate).*

Sample	$T_{-5\%}$ [°C]	$T_{-50\%}$ [°C]	$dTG_{max}$ [%/°C]	$T_{dTGmax}$ [°C]	Char yield at 600 °C [%]
PA6	104	324	0.8	139	3.4
PA6/10%RP	332	439	1.5	432	35.0
PA6/10%MgO	155	391	1.2	412	16.3
PA6/10%EGES100	243	446	1.0	437	38.6
PA6/10%EGES350	152	435	1.0	439	27.1
PA6/5%RP/5%MgO	123	383	0.9	435	7.4
PA6/5%RP/5%EGES100	120	407	1.0	436	9.1
PA6/5%RP/5%EGES350	214	425	1.0	442	11.4
PA6/5%MgO/5%EGES100	192	354	1.2	341	6.2
PA6/5%MgO/5%EGES350	111	354	0.7	370	15.4

### 3.3 Fire performance of PA6 coating materials

The flammability of reference and flame retardant coating materials was analysed by LOI, UL-94, and MLC. The results of the UL-94 and LOI measurements are shown in Table 3.

*Table 3: UL-94 and LOI results of reference and flame retardant coating materials.*

Sample	UL-94 ranking	LOI [%]
PA6	HB	21
PA6/10%RP	HB	26
PA6/10%MgO	HB	21
PA6/10%EGES100	HB	25
PA6/10%EGES350	V-1	25
PA6/5%RP/5%MgO	V-2	25
PA6/5%RP/5%EGES100	V-0	26
PA6/5%RP/5%EGES350	V-1	25
PA6/5%MgO/5%EGES100	HB	24
PA6/5%MgO/5%EGES350	HB	24

The oxygen index of the samples containing flame retardant was higher than that of the reference, except for the sample containing pure MgO. Although the oxygen index of the individual compositions is not an outstandingly high value, it can be seen that the UL-94 classification of the samples containing expandable graphite is significantly better than the reference. The PA6/5%RP/5%EGES100 sample has the highest oxygen index (26%) and is the only sample to achieve a V-0 self-extinguishing rating in the UL-94 test.

The complex combustion properties of the samples were investigated using MLC. The results compared to the reference PA6 without flame retardant are shown in Figure 1.

The flame retardants significantly reduced the peak heat release rate (pHRR): the best performing sample (PA6/10%EGES350) had a maximum heat release of only 253 kW/m<sup>2</sup> compared to the reference value of 729 kW/m<sup>2</sup>. For samples containing red phosphorus, the ignition time was in all cases shorter than the ignition time of the reference, which can be explained mainly by the gas phase mechanism of the additive. In general, the residual mass of the sample was higher than the reference due to the flame retardant additives. While the reference sample was almost completely burnt, the sample with high graphite additives retained almost one-third of its mass. Neither red phosphorus nor magnesium oxide provided outstanding results when used alone, but their combination with the two types of expandable graphite showed favourable flame retardancy. A significant shift characterised the graphite samples in the times to ignition and peak heat release rate, which in all cases can be explained by the intense foaming of the additives. The intense foaming caused the sample to ignite and reach the peak heat release rate only much later during combustion. The time course of the heat release also illustrates the intensive foaming: These samples foamed into the cone calorimeter, which caused the heat release curve to have an incomplete decay.

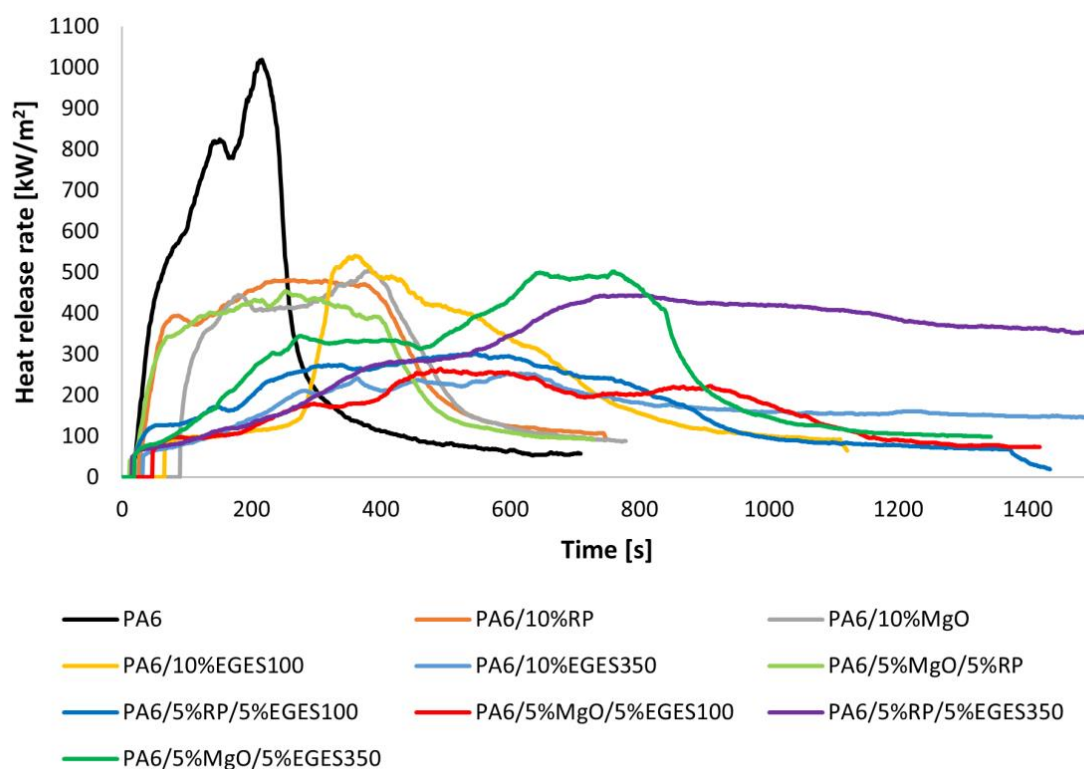


Figure 1. Heat release rate of reference and flame retardant coating materials

Based on preliminary testing of the coatings, the following samples were used as coatings for carbon fibre reinforced PA6 composites: PA6/10%EGES350, PA6/5%RP/5%EGES350, PA6/5%MgO/5%EGES100, PA6/5%RP/5%EGES100.

### 3.4 Fire performance of coated CF/PA6 composites

The MLC results for the reference and flame retardant coated PA6 composite samples are shown in Figure 2.

Compared to the reference composite without flame retardant (347 kW/m<sup>2</sup>), only sample PA6/CF/5%RP/5%EGES100 had a lower heat release (274 kW/m<sup>2</sup>). In all cases, the residual mass was increased due to the flame retardants, but the samples ignited sooner than the reference except for PA6/CF/5%RP/5%EGES100. The poorer fire performance of these samples may be explained by the significant sedimentation observed in samples with EG ES350, and a noteworthy amount of the flame retardant remained in the inlet.

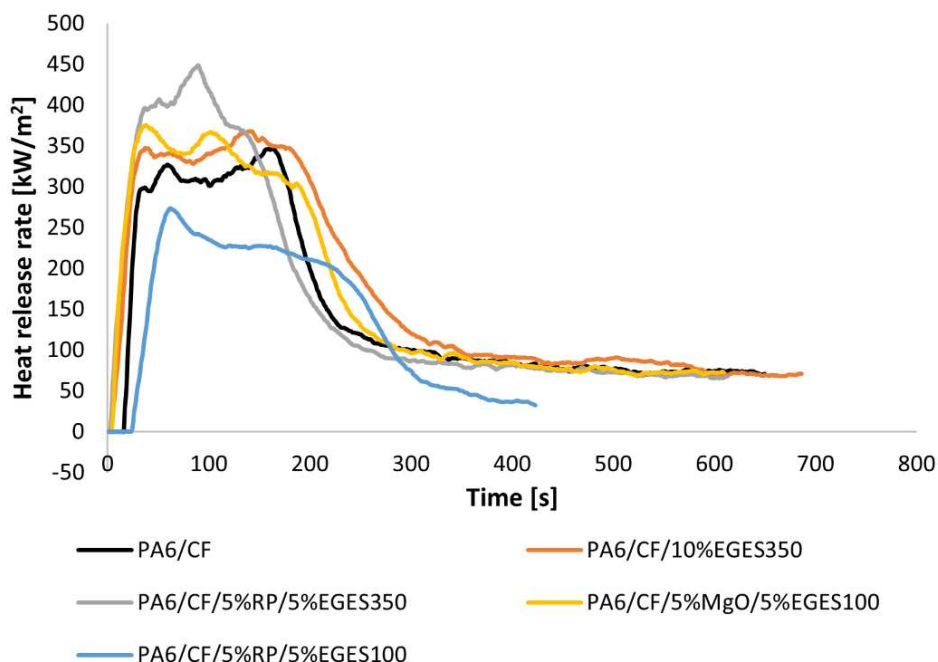


Figure 2. The heat release rate of reference and flame retardant coated carbon fibre reinforced polyamide 6 composites

## 4. Conclusions

In our work, we first investigated the effect of different flame retardants on the crystallinity, glass transition temperature, thermal stability, and flammability of the PA6 matrix. Red phosphorus, magnesium oxide, and expandable graphite with small and large particle sizes were used as flame retardants. They did not considerably affect the glass transition temperature and crystallinity, but they improved the thermal stability compared to the reference. Neither red phosphorus nor magnesium oxide showed outstanding results when used as sole additives, but their combination with expandable graphite is favourable in terms of flame retardancy. The best formulations were applied to coat carbon fibre reinforced polyamide 6 composites. T-RTM and in-mould coating were modelled by preparing the composites and coatings. The composite

coated with 5% red phosphorus and 5% small grain expandable graphite showed the best fire performance.

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