Multifunctional Flame-Retardant Coatings on Carbon Fiber-Reinforced PA6 Composites Prepared by Anionic Ring-Opening Polymerization

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1. Abstract

Due to the increasingly widespread use of carbon-fiber-reinforced polymer composites, it is important to develop solutions that enhance their fire-retardant properties without significantly compromising their other functional characteristics. In this study, we investigated the thermal stability, electrical conductivity, and flame-retardant performance of flame-retardant coatings containing hexaphenoxycyclotriphosphazene (HPCTP) and different amounts of expandable graphite (EG) on carbon fiber-reinforced polyamide 6 (PA6/CF) composites. As the concentration of expandable graphite increased, the coatings exhibited increased char formation and enhanced electrical conductivity, indicating the formation of a conductive network of graphite particles and the strengthening of the protective effect of the condensed phase. Flammability tests of the coated composites confirmed that the protective layer effectively reduces the intensity of combustion, as evidenced by decreases in the peak heat release rate and the fire growth rate index, and by the formation of a larger amount of burning residue. Based on the results, the combination of HPCTP and EG resulted in a multifunctional coating system that simultaneously improves the electrical and flame-retardant performance of PA6/CF composites.

2. Introduction

Fiber-reinforced polymer composites are becoming increasingly important in the automotive and aerospace industries due to their favorable mechanical properties, low density, and corrosion resistance. Polyamide 6 (PA6) composites prepared by anionic ring-opening polymerization (AROP) are increasingly important, as the low-viscosity ε-caprolactam monomer enables efficient impregnation of continuous fiber reinforcements. The composites prepared in this way exhibit excellent mechanical properties, while the thermoplastic matrix offers better recyclability than that of conventional cross-linked composites.

However, the use of PA6-based composites is limited by their low electrical conductivity and flammability. The concentration of free charge carriers in these polymers is extremely low, causing them to behave as electrical insulators [1]. This can lead to localized damage in the event of a lightning strike or electrical discharge. Although the copper mesh solutions currently in use improve conductivity, they increase the weight of the structure, can adversely affect structural integrity, and make recycling more difficult [2].

Expandable graphite (EG) is a potential alternative to increase the electrical conductivity and flame resistance of composites. When exposed to heat, it forms an expanded carbon layer, containing "work-like" formulations that inhibit heat and mass transfer, thereby reducing the intensity of the combustion. Expandable graphite can be used on its own to flame-retard polyamides, but a synergistic effect can be achieved when combined with phosphorus-based flame retardants [3], [4], [5]. Among phosphorus-based flame retardants, hexaphenoxycyclotriphosphazene (HPCTP) is a particularly promising additive for PA6 systems, as it is highly soluble in molten ε-caprolactam. As a result, the flame retardant can be uniformly distributed throughout the polymerization system, thereby promoting effective flame retardancy and facilitating its use in anionic ring-opening polymerization [6], [7].

In this study, we investigated flame-retardant coating containing HPCTP and EG at different concentrations. We applied the coating on the surface of carbon fiber-reinforced PA6 composites prepared by anionic ring-opening polymerization. The thermal stability of the coatings was measured by thermogravimetric analysis, and their electrical conductivity was determined, while the fire-retardant performance of the coated composites was evaluated using cone calorimeter tests.

3. Materials and methods

3.1. Materials

For the preparation of polyamide 6 via anionic ring-opening polymerization, AP-NYLON Caprolactam type ε-caprolactam (CL, L. Brüggemann GmbH & Co. KG, Heilbronn, Germany) was used as the monomer. As activator, hexamethylene-1,6-dicarbamoyl caprolactam, marketed as Bruggolen C20P (C20, L. Brüggemann GmbH & Co. KG, Heilbronn, Germany), was used, and sodium dicaprolactamato-bis-(2-methoxyethoxo)-aluminate, by brand name Dilactamate (DL, Katchem, Prague, Czech Republic), was used as the initiator. We used unidirectional PX 35 UD 300 type carbon fiber reinforcement (CF, Zoltek, Nyergesújfalu, Hungary) as the composite reinforcement. The reinforcement had an areal density of 300 g/m². As flame retardants, we used Rabitle FP110-type hexaphenoxycyclotriphosphazene (HPCTP, Fushimi Pharmaceutical Co., Ltd., Japan) and GHL PX 92/-1 HT 270-type expandable graphite (EG, Georg H. LUH GmbH, Germany). HPCTP is a flame retardant available in the form of white powder with a phosphorus content of 13.4%. For phosphorus-containing flame retardants, the amount of additive is often specified as a phosphorus percentage [P%] rather than a weight percentage [%], since the P content is correlated with the flame-retardant effect. For this reason, we express the HPCTP content as P% and, based on our previous research, have chosen a concentration of 3P%, corresponding to 22.8% by weight. EG is a condensed-phase flame retardant that expands when heated, forming "worm-like" structures. The expansion rate is 40 ml/g, and the initial decomposition temperature is 270 °C. For EG, the amounts tested ranged from 1 to 5 wt%.

3.2. *Preparation of flame retarded PA6*

The TGA and electrical conductivity measurements were performed on the coating layer alone, not on the coated composite samples. The reason for this was that the aim of the tests was to determine the thermal and electrical properties of the coating itself, while excluding the influence of the composite. For these measurements, we prepared samples containing only the coating components, without reinforcing materials.

To prepare the PA6-based coatings, we used 87% CL, 3% C20 activator, and 10% DL initiator. Anionic ring-opening polymerization is extremely sensitive to moisture, so the raw materials were stored in a Faithful DZ-3BCI type vacuum drying oven (Faithful, Huanghua, China), and we dried the flame retardants at 80 °C for 4 hours before use in a UT6-type (Heraeus Holding GmbH, Hanau, Germany) drying oven. The first step in the preparation was to clean the aluminum mold with a 100 mm x 100 mm x 2 mm cavity with methanol, then spray it with Lusin Alro LL 261 (Chem-Trend L. D., Howell, USA) mold release agent, and finally close the mold. We placed the closed mold in a 150 °C drying oven. The mold was tilted at 15° to allow air inside the mold to escape more easily. Next, we mixed the monomer, the activator, and the flame retardant using an MR Hei-TEC type (Heidolph, Germany) heated magnetic stirrer and melted them at 120 °C. After adding the initiator, the mixture was injected into the aluminum mold preheated in a 150 °C oven using a 1025 TLL 25 ml SYR heat-resistant glass syringe (Hamilton Company, Reno, Nevada), and then the mold was removed from the oven after 15 minutes.

3.3. Preparation of PA6 composite with flame-retardant coating

To prepare the composites, we used a mold cavity measuring 100 mm × 100 mm × 2 mm to simulate the thermoplastic resin transfer molding (T-RTM) process on a small scale. After cleaning the mold with methanol, we sprayed it with a mold release agent. Five layers of unidirectional PX 35 UD 300 CF reinforcement were placed into the mold in a $[0]_5$ layup. We placed the closed mold containing the reinforcement material at a 15° angle in a preheated drying oven at 150 °C until the mold reached the appropriate temperature. To prepare the PA6 matrix, we used 87% CL, 3% activator, and 10% initiator. We melted the CL and C20 at 120 °C and mixed them using an MR Hei-TEC type magnetic stirrer. After adding the initiator, we injected the CL-system into the closed mold using a 1025 TLL 25 ml SYR heat-resistant glass syringe (Hamilton Company, Reno, USA) to ensure proper pressure. After 15 minutes, we removed the mold from the oven and let it cool to room temperature.

After disassembling the mold, we placed the finished composite into a mold cavity measuring 100 mm × 100 mm × 2.5 mm (after cleaning the mold and applying a release agent). We preheated the closed mold containing the composite at a 15° angle in a drying oven set to 150 °C. Using a magnetic stirrer, we melted and mixed the CL, C20, and flame retardants. After adding the initiator, we injected the flame-retardant CL system into the closed mold using a heat-resistant syringe. After 15 minutes, we removed the mold from the drying oven. A 0.5 mm thick coating was applied to one surface of the resulting coated composite.

3.4. Characterization

The thermal stability of the coatings was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q500 (New Castle, DE, USA) tester. Samples weighing 5–10 mg were analyzed at temperatures ranging from 30 to 600 °C in a nitrogen atmosphere with a flow rate of 30 ml/min, with a heating rate of 20 °C/min. The results were evaluated using the TA Universal Analysis software.

The electrical conductivity of the coatings was determined by four-point resistance measurement using an Agilent 34970A (Agilent Technologies, USA) digital multimeter data logger. During the measurement, resistance was measured using four probes spaced 20 mm apart, with the current applied through the outer probes and the voltage measured through the inner probes. The specific resistance of the sample was determined using Equation (1):

$$\rho = \frac{\pi w}{ln2} \cdot \frac{U}{I} \tag{1}$$

where ρ is the specific resistance of the sample [Ω·m], w is the thickness of the sample [m], U is the voltage [V], and I is the current [A].

The specific conductivity of the sample was determined using Equation (2):

$$\sigma = \frac{1}{\rho} \tag{22}$$

where σ is the specific electrical conductivity [S/m].

The flammability of the coated composites was determined by cone calorimetry using a TCC 918 Cone Calorimeter (NETZSCH TAURUS Instruments GmbH, Germany) in accordance with ISO 5660-1. The test specimens measured 100 mm × 100 mm × 2.5 mm; they were exposed to radiant heat at an intensity of 50 kW/m² and ignited using a spark igniter.

4. Results

4.1. Thermal stability of the coatings

In the case of coated composites, the measured results would be significantly influenced by the properties of the composite, thus reflecting the combined behavior of the coating and the composite in terms of thermal decomposition and residual mass. However, testing the coating independently allows for the direct examination of its thermal stability and residue-forming effects, and the results obtained provide a basis for interpreting the properties of the coated composite. For this reason, we independently examined the thermal stability of the coatings. The results of the TGA measurements of the reference PA6 and the PA6 samples containing HPCTP and different amounts of EG are presented in Figure 1 and Table 1.

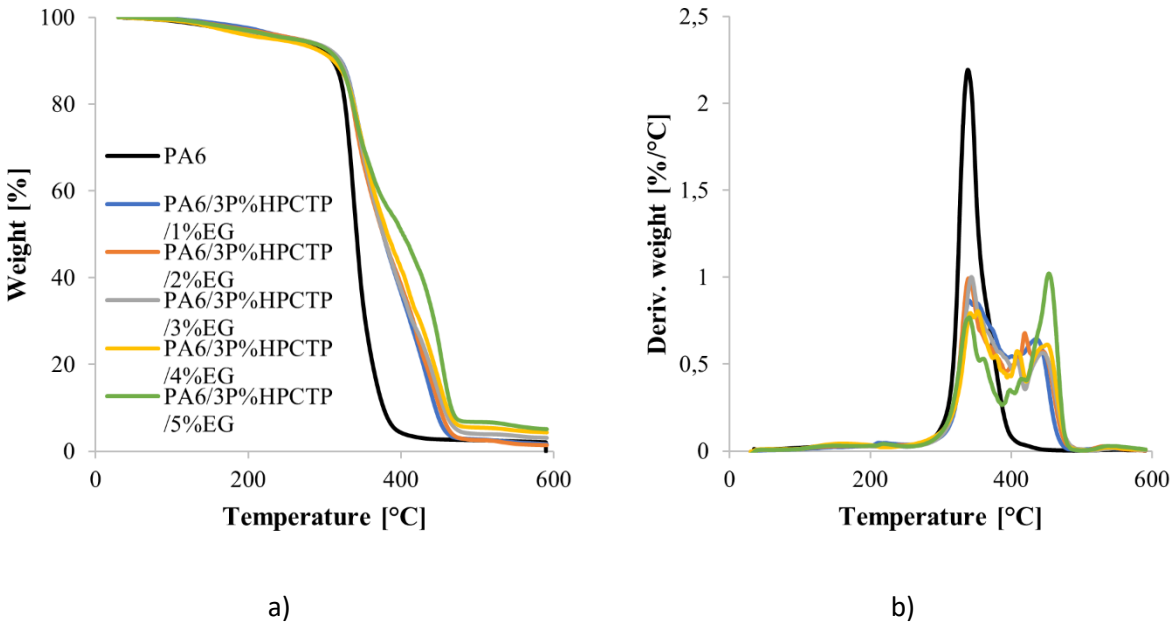

Figure 1. Results of the TGA measurement, showing (a) weight loss as a function of temperature, and (b) the derivative of weight as a function of temperature.

Table 1. The results of TGA for reference and flame retarded PA6 ($T_{-5\%}$: the temperature at 5% weight loss; $T_{-50\%}$: the temperature at 50% weight loss; dTG_{max}: maximum weight loss rate; T_{dTGmax}: temperature belonging to the maximum weight loss rate); Average standard deviation values: temperature measurements: ± 0.5 °C, weight measurements: ± 1%.

Material	$T_{-5\%}$ (°C)	$T_{-50\%}$ (°C)	dTG_{max} (%/°C)	T_{dTGmax} (°C)	Char yield at 600 °C (%)
PA6	241	341	2.00	338	2
PA6/3P%HPCTP/1%EG	263	377	0.87	340	1.6
PA6/3P%HPCTP/2%EG	265	376	0.99	334	1.4
PA6/3P%HPCTP/3%EG	262	377	1.00	343	3.1
PA6/3P%HPCTP/4%EG	235	382	0.81	353	4.3
PA6/3P%HPCTP/5%EG	260	401	1.02	454	5.1

For the reference PA6, the temperature corresponding to a 5% weight loss ($T_{-5\%}$) was 241 °C, whereas for most of the flame-retardant samples, this value increased to 260–265 °C. The increase in the $T_{-5\%}$ value suggests that the combination of HPCTP and expandable graphite mitigates early degradation processes. This may be related to the carbonization promoted by the phosphorus-containing component, as well as the heat- and mass-transport-inhibiting effect of the expandable graphite, which together increase the thermal stability of the system.

The temperature corresponding to a 5% weight loss ($T_{-50\%}$) for all flame-retardant samples was significantly higher than that of the reference PA6. While the $T_{-50\%}$ for reference PA6 was 341 °C, values ranging from 376 to 401 °C were measured for the flame-retardant PA6 samples. The highest value was measured in the sample containing 5 wt% expandable graphite, where $T_{-50\%}$ reached 401 °C.

The DTG curves (Figure 1b) provide further information on the degradation mechanism. The reference PA6 exhibited a single sharp degradation peak at 338 °C, accompanied by a maximum mass loss rate of 2.00 %/°C. In the systems containing the flame retardants, the maximum mass loss rate decreased significantly, ranging from 0.81 to 1.02 %/°C. The decrease in the degradation rate suggests that the flame-retardant system inhibits the rapid thermal degradation of the polymer. In addition, the DTG curves of the modified samples reveal multiple degradation stages, suggesting a more complex degradation mechanism. In particular, the composite containing 5 wt% EG exhibits a degradation peak at a higher temperature (454 °C), suggesting increased thermal stability of the resulting char.

The effectiveness of the flame-retardant system is well illustrated by the amount of char residue remaining at 600 °C. In the case of the reference PA6, only 2% char residue was formed, whereas increasing the EG content gradually increased the char residue to 5.1% at 5 wt% EG. The greater tendency toward residue formation suggests that HPCTP and expandable graphite promote the formation of a condensed-phase protective layer. Expandable graphite expands upon heating to form a physical barrier, while the decomposition products of phosphorus-containing HPCTP may promote carbonization and stabilize the protective layer as it forms.

4.2. Electrical conductivity of the coatings

To determine electrical conductivity, we prepared coating samples without reinforcing material. Although the conductivity measurements were taken at the coating surface, the presence of carbon fiber reinforcement could have influenced the resulting current paths and, consequently, the measured conductivity. Therefore, to determine the electrical properties of the coating, we examined samples that did not contain reinforcing material. The change in specific conductivity is shown in Figure 2, which illustrates the variation in conductivity with EG concentration at a 3P% HPCTP content.

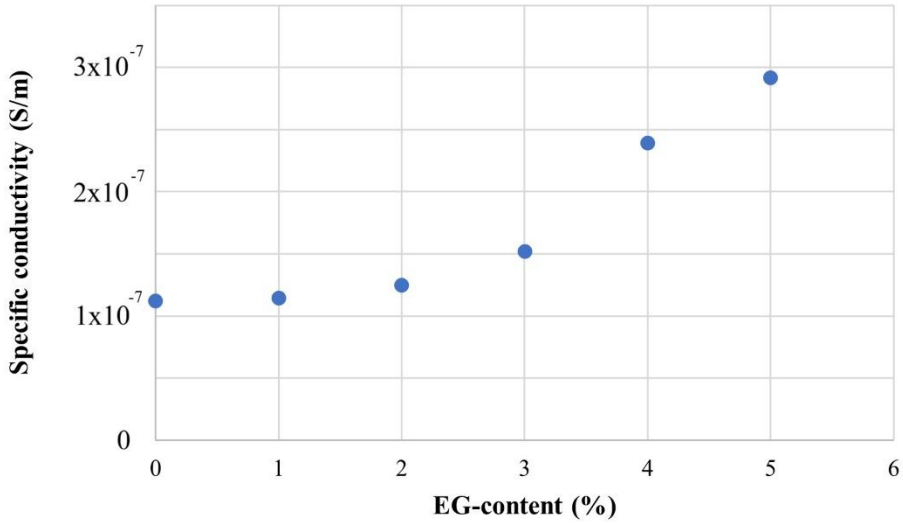

Figure 2. Results of the specific conductivity.

When examining the specific conductivity of the coatings, it is observed that conductivity increases steadily with increasing EG concentration. The conductivity of the reference sample was approximately 1.1×10^{-7} S/m. For samples containing 3P% HPCTP and 1 and 2 wt% EG, only a slight increase is observed, suggesting that in this concentration range, the connections between conductive particles are not yet sufficient to form a coherent conductive network.

As the EG content increases, the improvement in electrical conductivity becomes more significant. A noticeable improvement is already observed in the sample containing 3 wt% EG, while at 4 and 5 wt% EG, electrical conductivity increases to nearly twice and more than two and a half times that of the reference sample, respectively. This suggests that as the distance between graphite particles decreases, conductive pathways gradually form, facilitating the movement of charge carriers within the coating.

However, within the concentration range studied, no sharp percolation threshold is observed, leading to a sudden increase in conductivity. Instead, a gradual increase in conductivity is observed, suggesting that the system is near the percolation threshold but that a complete, three-dimensional conductive network has not yet formed. The relatively low conductivity values, on the order of 10^{-7} S/m, also indicate that the coatings remain essentially insulating, whereas the presence of expandable graphite measurably improves their electrical conductivity.

4.3. Flammability of the coated composites

The flammability of the coated composites was investigated using a cone calorimeter. The results obtained during the measurements are presented in Figure 3 and Table 2.

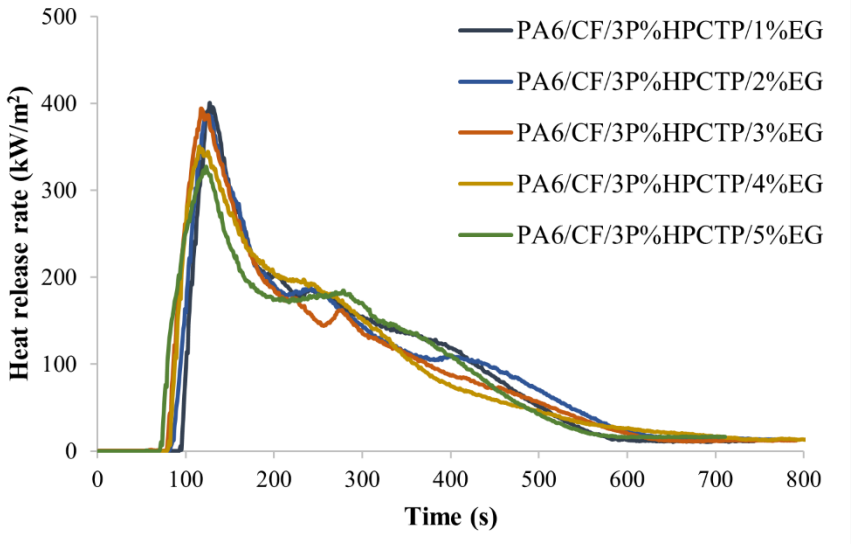

Figure 3. Results of the cone calorimetry.

Table 2. The results of cone calorimetry for coated PA6 composites (TTI: time to ignition, pHRR: peak heat release rate, THR: total heat release, TSP: total smoke production, FIGRA: fire growth rate index, COY: CO yield, CO2Y: CO_2 yield).

Material	TTI (s)	pHRR (kW/m^2)	THR (MJ/m^2)	TSP (m^2/m^2)	Residue (%)	FIGRA ($kW/m^{-1}s^{-1}$)	COY (g/g)	CO2Y (g/g)
PA6/CF/3P%HPCTP/1%EG	35	400	72	1400	38	4.6	0.04	1.89
PA6/CF/3P%HPCTP/2%EG	24	386	74	1378	36	4.1	0.03	1.88
PA6/CF/3P%HPCTP/3%EG	23	394	72	1373	37	4.3	0.05	1.82
PA6/CF/3P%HPCTP/4%EG	21	350	73	1209	36	3.8	0.04	1.84
PA6/CF/3P%HPCTP/5%EG	13	327	71	1318	39	3.1	0.04	1.87

The time to ignition (TTI) decreased gradually as the EG content increased, from 35 s for the sample coated with 3P% HPCTP and 1 wt% EG to 13 s for the sample containing 3P% HPCTP and 5 wt% EG. The peak heat release rate (pHRR) decreased with increasing EG content. The pHRR value of 400 kW/m^2 for PA6/CF/3P%HPCTP/1%EG decreased to 327 kW/m^2 with 3P% HPCTP and 5 wt% EG, representing a reduction of nearly 18%. It is clearly observable in the heat release curves that, for samples with higher EG content, the peak is lower, and the combustion process is more prolonged. This suggests that the expanded, carbonaceous protective layer formed by the expandable graphite under heat effectively limits heat and mass transfer between the polymer and the flame zone.

The total heat release (THR) values varied only slightly among the tested samples (71–74 MJ/m^2), suggesting that the total energy content of the combustible material remained essentially unchanged. Total smoke production (TSP) decreased significantly as the EG content increased. While the sample containing 3P% HPCTP and 1 wt% EG had a TSP value of 1400 m^2/m^2, the system containing 3P% HPCTP and 4 wt% EG measured 1209 m^2/m^2. The reduced smoke formation is likely due to the protective layer that forms, which mitigates the release of combustible and smoke-forming decomposition products. The COY and CO_2Y values showed only minor variation across the investigated formulations, suggesting that expandable graphite primarily influenced combustion intensity and heat release characteristics, with a less pronounced effect on the composition of the gaseous combustion products.

The residual weight was high for all coated composites, ranging from 36% to 39%. The highest residual value was observed in the sample PA6/CF/3P%HPCTP/5%EG (39%). This is consistent with the TGA results, which also showed an increased tendency toward charring with increasing EG content. The expanded “worm-like” formulation formed in expandable graphite under heat, together with the effect of HPCTP in the condensed phase, may contribute to the formation of a stable residue.

The fire growth rate index (FIGRA) decreased from 4.6 $kW/m^{-1}s^{-1}$ to 3.1 $kW/m^{-1}s^{-1}$ as the EG content was increased. Since FIGRA characterizes the rate of fire spread, a lower value indicates more favorable fire-resistant behavior. Based on the results, systems with higher EG content exhibit slower fire development, which confirms the effective functioning of the protective layer that forms.

5. Conclusion

In our work, we investigated the thermal, electrical, and flame-retardant properties of coating systems containing hexaphenoxy-cyclotriphosphazene (HPCTP) and expandable graphite (EG) at various concentrations. To determine the intrinsic properties of the coatings, thermogravimetric and conductivity tests were performed on model samples containing no reinforcing material, while flammability tests were conducted on coated PA6/CF composites.

The TGA results confirmed that increasing the concentration of expandable graphite improves the thermal stability of the coatings. The main degradation process occurred at higher temperatures, while the amount of residual carbon increased significantly. The higher residue formation indicates a greater tendency for the coatings to carbonize and a more favorable condensed-phase flame-retardant effect.

During electrical conductivity measurements, the conductivity of the coatings increased as the EG content increased. This suggests that increasingly efficient conductive connections are forming between the expandable graphite particles, which facilitate the movement of charge carriers within the coating structure.

Based on cone calorimeter results, expandable graphite improves the combustion behavior of the coated composites. As the EG content increased, the maximum heat release rate and the fire growth index decreased, while the amount of residue remaining after combustion increased. Total smoke emissions also decreased, supporting the favorable fire protection effect of the coating system.

Based on the results, the combination of HPCTP and EG yields an effective flame-retardant coating system. The combined use of these two components promotes the formation of a stable, heat-resistant protective layer that reduces combustion intensity and slows the spread of fire. Among the systems tested, the coating containing 3P% HPCTP and 5 wt% expandable graphite demonstrated the most favorable overall performance, providing the greatest thermal stability, the highest electrical conductivity, and the best fire protection.

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