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Research on the Synthesis and Application of a Weather-resistant Piperazine Pyrophosphate Flame Retardant Compound.

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Abstract

In this paper, we formulate an intumescent flame-retardant system (FR-NP) using piperazine pyrophosphate (PPAP) and melamine polyphosphate (MPP) as the principal components, in conjunction with a self-manufactured surface modifier. The flame-retardant performance, mechanical properties and weather resistance of this system in polypropylene (PP) were investigated. Our experimental findings suggest that incorporating 24% FR-NP into polypropylene yields a V-0 flame-retardant rating. In weathering tests, no white spot precipitation was observed in dark-coloured polypropylene materials.

Keywords

Piperazine Pyrophosphate; Polypropylene; Flame Retardant; Weathering Resistance.

1. Introduction

Polypropylene (PP) is a white, waxy polymer that is produced through the polymerisation of propylene. It is characterised by its semi-transparent appearance and offers distinct advantages, including low density, cost efficiency, and exceptional overall performance. Consequently, it finds extensive application in various domains, including household appliances, plastic pipes, construction, and the automotive industry [1]. However, polypropylene has a melting point of 189 °C, a heat deflection temperature of 105 °C, relatively poor rigidity, and a high dimensional shrinkage rate. Furthermore, polypropylene has a low limiting oxygen index (17.4 -18.5), burns rapidly, releases a significant amount of heat, and produces molten droplets, rendering it highly flammable. In order to enhance safety and practicality, it is necessary to implement flame retardant modification in addition to meeting mechanical performance requirements [2].

In the domain of flame retardancy for polypropylene materials, intumescent flame retardancy represents the most prevalent technique. Halogen-free intumescent flame retardants (IFR) offer a range of advantageous properties, including low smoke emission, non-toxicity, halogen-free composition, and the capacity to form a char layer that effectively prevents polymer melt droplets. These properties meet the current industry requirements for smoke suppression, low toxicity, and high efficiency in the flame retardancy field. Piperazine pyrophosphate is an intumescent flame retardant that combines acid, carbon, and gas sources, featuring high char formation efficiency, good thermal stability, and low hygroscopicity [3]. However, due to its low pH, high water solubility, and hygroscopic nature, piperazine pyrophosphate can cause corrosion of screws, easy precipitation, and caking during storage [4-6]. Furthermore, within the context of the extrusion moulding process of polypropylene (PP) materials, the presence of piperazine pyrophosphate, characterised by its low melt index, has been observed to result in inadequate dispersion. This, in turn, gives rise to defects such as pitting, white spots, and an unstable flame-retardant performance in the extruded sheets. A plethora

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of experiments have been conducted to enhance the utilisation of pyrophosphate in polypropylene (PP) materials through blending and modification techniques [7-8]. However, while the simple blending of melamine phosphate reduces the amount of flame retardant added and improves flame retardancy, the high water solubility and migration issues persist due to the simple physical mixing process. This limitation is particularly pertinent in the context of dark-coloured substrates, where migration issues are more pronounced [9-10].

In addressing the issue of weatherability, the present study focuses on piperazine pyrophosphate and melamine polyphosphate as the primary research subjects. The incorporation of a custom-made surface modifier into the composite system resulted in the synthesis of a pyrophosphate-based flame retardant with high flame retardancy and weather resistance. In the present study, the flame retardant was subjected to a combination process with polypropylene, resulting in the formation of flame-retardant samples. The weather resistance and flame retardancy of the samples were subsequently assessed through rigorous testing and evaluation procedures.

2. Experimental

2.1 Materials

Polypropylene (PP): K8003, supplied by China Balin Petrochemical Co., Ltd. in industrial grade; pyrophosphate, piperazine, melamine polyphosphate. Sichuan Jingshida Technology Co., Ltd. has developed an industrial-grade, self-made surface modifier, designated XJH-9H.

2.2 Synthesis of Weather Resistant Piperazine Pyrophosphate Complexed Flame Retardant (FR-NP)

Pyrimidine pyrophosphate (PAPP), melamine polyphosphate (MPP), and a self-made surface modifier (XJH-9H) were added to a reactor at room temperature in a specific ratio. Subsequently, the system temperature was heated to 240 °C within a nitrogen atmosphere, and the reaction was stirred for 2 hours. Then, the system was cooled to room temperature, which resulted in the acquisition of the final product, yielding a yield of 98 %.

2.3 Synthesis of FR-NP/PP Flame Retardant Composite Materials

In order to investigate the weather resistance of a pyrophosphate-based flame retardant in polypropylene, a black masterbatch was added. The blended flame retardant (FR-NP), black masterbatch, and polypropylene K8003 were subjected to a high-speed mixing process in order to ensure uniform blending. The mixture was then extruded into pellets using a twin-screw extruder and injection moulded using an injection moulding machine. Subsequent to this, a series of tests were conducted to ascertain the flammability, mechanical properties and weather resistance of the material.

3. Characterization

UL-94 Horizontal and Vertical Burning Test: The product has been tested in accordance with GB/T 2408-2021, with sample dimensions of 125 mm × 13 mm × 1.5 mm.

TG Test: The experiment was conducted in an N_2 atmosphere at a heating rate of 10 °C/min, reaching a final temperature of 450 °C.

Mechanical Properties Test: The specimens were prepared in accordance with the prevailing standards set out in GB/T 1040-2006, and subsequent testing was conducted utilising a WDW3020 universal materials testing machine.

Cone calorimetry analysis: Testing was conducted in accordance with ISO 5660 standards, with sample dimensions of 100 mm × 100 mm × 3 mm and a heat radiation power of 50 $kW \cdot m^2$.

High temperature and high humidity testing (double 85): Tested in accordance with GB/T 2423.3-2016 using a constant temperature and humidity testing machine. Sample dimensions: 100 mm × 100 mm × 3 mm and 125 mm × 13 mm × 1.5 mm.

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4. Results and Discussion

4.1 Test Results and Analysis of Various Indicators for FR-NP

As demonstrated in **Table 1**, the nitrogen content of the weather-resistant composite flame retardant is 19.23 %, and the phosphorus content is 18.11 %, which is higher than the nitrogen content of ordinary intumescent flame retardants. The pH of the system is 4.29 (10 g/L), which is higher than the pH of piperazine pyrophosphate (3.61), It indicates that the weakly acidic system is beneficial for reducing the corrosion of the screw. Furthermore, the whiteness level has been determined to be 95.48.

Table 1. Weather-resistant compound flame retardant index test data

N %	P %	pH	Moisture [%]	Whiteness
19.23	18.11	4.29	0.14	95.48

4.2 Infrared Structural Characterisation of FR-NP and Analysis of the Results

Infrared spectroscopy analysis reveals the antisymmetric stretching vibration doublet of N-H in $-NH_2$ at 3464 cm^{-1} and 3391 cm^{-1} in **Fig. 1**. Furthermore, the stretching vibration peak and the bending vibration peak of NH_3^+ appear at 3121 cm^{-1} and 1518 cm^{-1}, respectively. The absorption peak of C-C is observed at 1266 cm^{-1}, while the stretching vibration peak of P=O is seen at 1138 cm^{-1}. The stretching vibration peaks of P-O are found at 1167 cm^{-1} and 1067 cm^{-1}, and the stretching vibration peak of P-OH appears at 974 cm^{-1}. The stretching vibration peak of P-O-P is detected at 882 cm^{-1}. The characteristic peaks of the triazine ring are identified as follows: the C=N stretching vibration peak at 1673 cm^{-1}, the C-N stretching vibration peak at 1455 cm^{-1}, and the triazine ring bending vibration peak at 779 cm^{-1}. The positions of these infrared characteristic peaks indicate that FR-NP possesses the infrared characteristic peaks of the basic functional groups of the target product.

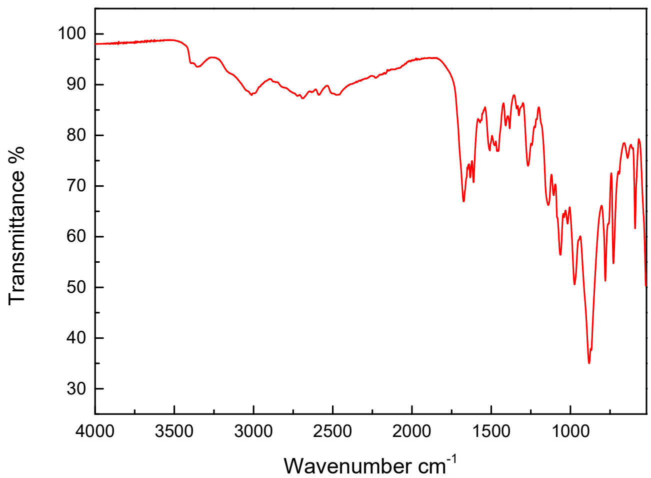

Fig. 1 Infrared spectra

4.3 Thermal Stability Analysis of FR-NP

To meet the processing requirements of plastics, flame retardants must be thermally stable. We therefore evaluated the thermal stability of the modified composite through thermogravimetric analysis. As illustrated in **Fig. 2**, the temperatures at which the composite loses 0.5 %, 1.0 % and 2.0 % of its weight are 258.9 °C, 265.3 °C and 273.6 °C, respectively. Once the composite has lost 10% of its weight, the temperature exceeds 300 °C. This indicates that the flame retardant exhibits good thermal stability in polypropylene (PP).

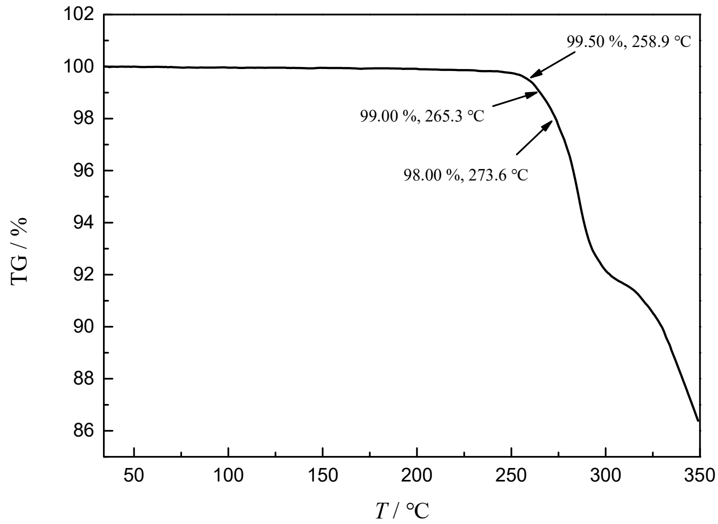

Fig. 2 TG curve of piperazine pyrophosphate compound flame retardant

4.4 Flame Retardant Testing and Analysis of FR-NP

In order to conduct a more in-depth investigation into the effect of flame-retardant dosage on polypropylene materials, the impact of varying flame-retardant dosages on the flame retardancy and mechanical properties of polypropylene materials was examined. The results of the UL-94 vertical burning test demonstrate a direct correlation between the amount of flame-retardant FR-NP and the LOI value, with an increase in the former resulting in a concomitant increase in the latter. It has been demonstrated that, upon the incorporation of flame-retardant FR-NP at the addition of 24 wt %, the burning grade attains V-0 classification, accompanied by an LOI value of 31.40. This finding suggests that flame retardant FR-NP demonstrates high flame-retardant performance in polypropylene materials.

Table 2. Test data of flame retardant properties and mechanical properties of PP and its composites

Samples	UL-94	LOI [%]	Tensile strength [Mpa]	Flexural strength [Mpa]	Notched impact strength[KJ/m^2]	Elongation at break [%]
PP	No grade	17.50	29.332	48.633	10.601	208.422
PP / 10 % FR-NP	No grade	23.22	26.413	45.345	9.921	192.334
PP / 15 % FR-NP	V-2	25.07	24.256	39.617	9.445	164.508
PP / 20 % FR-NP	V-1	27.21	20.543	32.509	8.913	128.240
PP / 24 % FR-NP	V-0	31.40	19.611	26.646	7.596	115.110

As shown in **Table 2**, the mechanical properties of the flame-retardant polypropylene (PP) system decline significantly overall compared to the pure system. While the addition of flame retardants greatly enhances the flame retardance of polypropylene, their rigid molecular structure may affect the crystallisation behaviour and molecular chain movement of the matrix. This can result in reductions in tensile strength, flexural strength, elongation at break and impact strength.

4.5 Cone Calorimetric Analysis of PP/FR-NP

The results of conical calorimetric analysis of PP and flame-retardant PP composites are shown in **Table 3,** and the curves of heat release rate (HRR) and total heat release (THR) are shown in **Fig 3.**

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Table 3. Cone calorimetry analysis parameters of PP and its composites

Samples	TTI/s	pHRR/kw.m^2	THR/MJ.m^2
PP	12	1346.46	154.298
PP/FR-NP	6	195.567	124.213

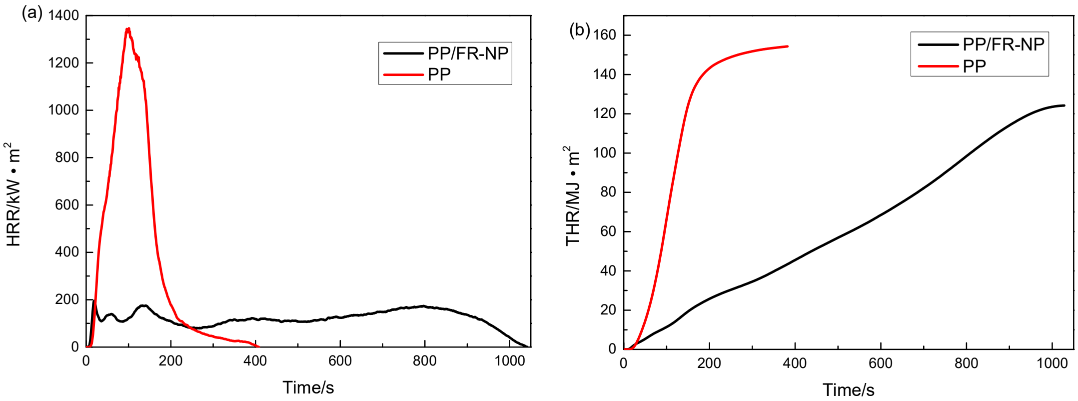

Fig. 3 (a) Heat release rate HRR (b) Total heat release THR

The time to ignition (TTI) is defined as the sustained ignition time required to achieve flaming combustion on the surface of the material. In comparison with PP, the TTI of the flame-retarded PP composites is significantly earlier due to the earlier decomposition of FR-NP when heated by the addition of FR-NP, consequently resulting in a shorter ignition time. In comparison with PP, the pHRR and THR of flame-retardant PP composites were reduced by 85 % and 19 %, respectively. The fundamental rationale for this phenomenon pertains to the formation of a layer of intumescent charcoal, which is produced by the intumescent flame retardant. This layer functions as an insulator, hindering the transmission of heat and oxygen and thereby curtailing the release of combustible gases during the combustion process. This carbon layer has been shown to impede several critical elements of combustion, including heat, oxygen, and fuel, thereby significantly reducing the intensity of combustion, the rate of flame propagation, and the total heat release.

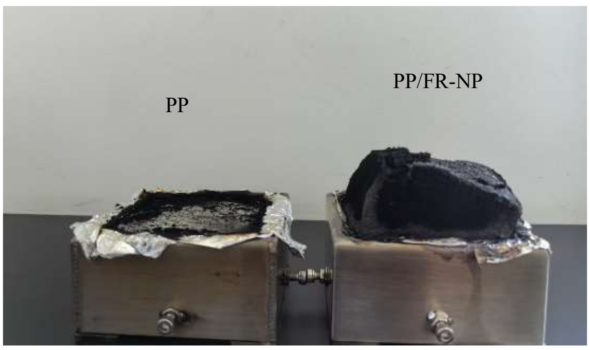

Fig. 4 Comparison of cone calorimeter combustion

In cone calorimeter combustion tests, it was observed that the char layer height formed after the combustion of polypropylene (PP) samples with added intumescent flame retardant (FR-NP) was significantly higher than that of ordinary PP (**Fig. 4**). The char layer has increased significantly, which can be attributed to the intumescent flame retardant successfully performing its 'intumescent charring'

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function in PP. This phenomenon can be considered the core manifestation and direct evidence of the successful action of the intumescent flame-retardant mechanism.

4.6 Weathering Test Results and Analysis of PP/FR-NP

As shown in **Table 4**, flame-retardant polypropylene materials demonstrate exceptional stability under the stringent conditions of the double 85 test (temperature 85 °C, relative humidity 85 %), exhibiting no alteration in flame-retardant rating. In mechanical tests, the tensile strength, elongation at break, flexural strength, and notched impact strength exhibited only marginal alterations following prolonged exposure to elevated temperatures and humidity levels associated with thermal ageing. This phenomenon is attributed to the penetration of moisture into the interface between the polypropylene (PP) matrix and the flame retardant, resulting in a weakening of their bond strength and a reduction in stress transfer efficiency. Furthermore, elevated temperatures have been shown to promote the oxidative degradation of PP molecular chains, while moisture has been observed to act as a plasticiser, accelerating chain segment slippage and reducing the material's load-bearing capacity. Despite alterations in mechanical properties, the flame-retardant performance of the material remains unaltered, signifying its relative stability under conditions of elevated temperature and humidity.

Table 4. Weather resistance test data of flame retardant polypropylene PP

Test \ Time	0 h	500 h	1000 h	1500 h	2000 h
UL-94	V-0	V-0	V-0	V-0	V-0
Tensile strength /MPa	19.611	19.180	18.709	19.231	17.694
Elongation at break [%]	115.110	97.620	106.349	99.732	99.597
Yield strength [Mpa]	26.646	33.542	31.296	32.986	32.010
Notched impact strength [KJ/m^2]	7.596	6.386	6.223	5.633	6.493

(a) (b)

Fig. 5 2000 h (double 85): a: Unmodified PPAP and MPP blend. b: Modified FR-NP

By subjecting both unmodified and modified flame-retardant materials to long-term ageing tests under conditions of high temperature and humidity for a period of up to 2,000 hours, it was observed that the surface of the unmodified material exhibited a significant amount of white spots, while the surface of the modified material remained smooth and clean, with no powdery or crystalline deposits (**Fig. 5**). This finding indicates that the composite flame-retardant agent exhibits remarkable anti-precipitation properties. The following three aspects will be analysed in order to provide a comprehensive understanding of the specific mechanisms that underpin this phenomenon: It has been demonstrated that by reducing the interfacial energy of the flame retardant, the molecular structure of the composite flame retardant (FR-NP) exhibits good affinity with the non-polar polypropylene

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(PP) matrix. Furthermore, it has been established that the particles of the composite flame retardant (FR-NP) undergo special surface treatment, enhancing chemical bonding or physical anchoring with PP. Finally, it has been determined that the formation of a stable network structure between different flame-retardant components inhibits the migration of small molecules. This composite flame-retardant polypropylene has been shown to demonstrate zero flame-retardant precipitation and structural stability under the stringent double 85 ageing conditions, thus providing comprehensive evidence that this flame-retardant system is a highly stable solution suitable for outdoor high-temperature and high-humidity environments.

5. Summary

In summary, the present study employed piperazine pyrophosphate (PAPP), melamine polyphosphate (MPP), and a custom-made surface modifier to develop an efficient intumescent flame-retardant system (FR-NP), which was successfully applied to dark-coloured polypropylene (PP) materials. The experimental findings suggest that this flame-retardant system not only substantially enhances the material's flame-retardant performance, achieving the UL-94 V-0 standard, but also preserves its exceptional mechanical properties, meeting the requirements for practical applications. It is noteworthy that the flame-retardant system demonstrates exceptional weather resistance when applied to black PP materials. I In comparison with conventional piperazine pyrophosphate and melamine phosphate blends, the FR-NP system incorporates a custom-made surface modifier to form a novel, highly efficient intumescent flame retardant. The modifier plays a catalytic role in the system, reducing the surface energy of the flame retardant and enhancing the system's dispersibility. This, in turn, enhances the compatibility between the powder flame retardant and the base PP material, thereby imparting self-lubricating properties to the blended flame retardant. This results in superior weather resistance. This study proposes a technically viable solution for the development of high-weatherability black flame-retardant PP materials. Future research endeavours may further refine the flame-retardant surface modification technology, thereby enhancing its long-term stability in complex environments and promoting its large-scale application in high-end fields.

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