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ARTICLE

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Highly efficient flame retardant and smoke suppression mechanism of polypropylene nanocomposites based on clay and allylamine polyphosphate

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1 | INTRODUCTION

Abstract

Fire-retarded polymer nanocomposites (FRPN) based on polypropylene with clay and allylamine polyphosphate (PP/clay-AAPP) were designed and prepared by melt mixing. Their morphological, thermal and fire-safety properties were investigated by TEM, SEM, EDS, TG, UL-94, LOI, cone-calorimeter test and TG-FTIR. The results exhibited that the LOI of PP/2 wt%clay-20wt%AAPP nanocomposites was 29.5% with V-0 rating level in UL-94 vertical testing. Significant enhancements in fire safety performance were also observed for fire-retarded PP nanocomposites from cone-calorimeter test decreasing heat release as well as smoke and toxic gases. PP/clay-AAPP nanocomposites not only provided relatively stable char layer during polymer burning, but also exhibited better fire safety performance due to the exfoliation of clay platelets. It displayed that incorporation of clay and AAPP were very efficient in increasing the fire safety of PP composites.

K E Y W O R D S

applications, clay, composites, degradation, flame retardance

automotives,³ wires,⁴ cables,⁵ etc. However, the high combustibility of PP is regarded as an important limiting factor for many applications.^{6,7} Thus, the use of fire-retardant (FR) is necessary to satisfied fire safety standards. At first,

Polypropylene (PP), as staple commodity polymers, is extensively used in electronic cases,¹ building materials,² many applications.^{6,7} Thus, the use of fire-retardant (FR) is necessary to satisfied fire safety standards. At first,

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. © 2022 The Authors. *Journal of Applied Polymer Science* published by Wiley Periodicals LLC. halogenated fire retardants (H-FR) are developed because of their high fire safety. However, some of H-FR are completely forbidden by many countries because of environmental issues.^{8,9} Up to now, phosphorus-containing fire retardants (P-FR) as halogen-free FR are the most promising candidates. Among them, ammonium polyphosphate (APP) containing of rich nitrogen element (N) and phosphorus element (P) is a very important P-FR in both industrial and academic field.^{6,10} When PP with APP composites are ignited, APP is degraded to ammonia (NH₃) and polyphosphoric acid firstly. To form phosphate ester, these polyphosphoric acid and hydroxyl group then would be reacted. After degradation of phosphate ester, the charring residue would be formed to against the heat and oxygen transfer.^{6,10,11} Since the formation of charring layer during burning PP with APP composites is not stable, fire safety efficiency of alone APP is too low. Thus, it is necessary to combine other technology to gain the good fire safety efficiency of APP.

To increase the stability of charring residue, researchers mainly have done two aspects of work. The first is the organic stable charring agents (e.g. pentaerythritol, phosphate and 1,3,5-triazine derivatives, etc.)^{11,12} were added as intumescent flame retardant (IFR). Recently, modified APP by piperazine^{13,14} and ethanolamine^{15,16} were developed via a simple step, which enhance the stability of char residue and fire safety efficiency of APP. However, there is still some room for improvement that is the required more than 35 wt.% modified APP loading in PP is too high to satisfied fire safety standards.^{14–16} The second aspect is inorganic charring (in particular nanofiller) as the synergist is used to enhance the fire safety of APP system.^{6,17} For example, clay is introduced into APP system due to their low cost, natural existence, high interfacial reactivity, large specific surface area, and nanoscale layered structure.^{18–21} During the claypolymer burning, the inorganic clay platelets can increase the stable char layer, enhance degradation temperature, prevent or delay mass and heat transfer. Wang et al investigated²² synergistic effect between clay and flame retardant for fire safety PP. Chen et al prepared²³ the clay aerogel with alginate for fire safety polyurethane. Fu et al used²⁴ clay into the cell wall of fire safety wood. Lai et al suggested²⁵ that modified phosphorus-containing clay (Pclay) via resorcinol bis(diphenyl phosphate), and the results showed that the fire safety of PP was effectively improved by only 2.0 wt% of P-clay. In clay-APP system, on one hand, APP as an eco-friendly and safe fire-retardant acts both as the gas and acid agent. On the other hand, only small amount of clay (≤ 5 wt%) is incorporated in the polymer matrix, which greatly decreases melt dripping, reduces heat release, and changes the carbonization.^{13,26-29} However, the fire safety of PP with APP-clay system is still not too high. Due to missing charring agent, a stable char from the APP-clay system cannot be formed during the combustion processes. In addition, the dispensability of hydrophilic

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In our previous work,³⁰ a novel IFR allylamine polyphosphate (AAPP) was well developed by simple cation exchange. The multifunctional AAPP not only had acid source (phosphorus element), gas source (nitrogen element), and carbon source (carbon element), but also had allyl group (carbon-carbon double bond) for grafting with polymer. Thermal stability of PP with AAPP composite was improved by environment-friendly electron beam treatment.^{30,31} To enhance the fire safety, fire-retarded polymer nanocomposites based on polypropylene with clay and allylamine polyphosphate (PP/clay-AAPP) were prepared by melt mixing. In this work contrary to traditional clay-APP system, some of APP was changed by AAPP. Under the total loading of filler was 22 wt%, PP/clav-APP nanocomposites were designed and investigated by melt blend. Their morphological, thermal, and fire-retardant properties were systematically investigated. Moreover, the related fire safety mechanism of PP/clay-AAPP system was explored in detail.

2 | EXPERIMENTAL AND CHARACTERIZATION

2.1 | Materials

Clay was bought from BYK Co., Ltd (Clay 30B, Germany); APP was purchased from Budenheim (Germany); Ethanol and allylamine were obtained from Sigma-Aldrich Company (Germany); PP was bought from Borealis Company (HD 120MO, Finland).

2.2 | Synthesis of AAPP

APP (100 g) and allylamine (60 g) were put in a threeneck flask in the mixed solvent of water and alcohol (9:1, 1000 mL) with a stirrer at 60°C under a N₂ atmosphere. Next, reaction between APP and allylamine were via cation interchange. After that, the mixture was reduced pressure distillation via rotary evaporator. The white samples were washed with ethanol and dried in a drying oven. ¹H-NMR ((500 MHz, D₂O): 5.72(m), 5.26(m), 3.45 (m)). ³¹P-NMR ((500 MHz, D₂O) (-24.1).³⁰

2.3 | Preparation of fire retarded PP

The samples (Table 1) were mixed melt blending (Brabender, KETSE 20/40 EC). The temperature of extruder was set up from 180 to 190° C. Then, the pellets

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TABLE 1 Formulation of PP/clay- APP and PP/clay-AAPP systems	Sample	PP (wt%)	APP (wt%)	AAPP (wt%)	clay (wt%)
	Pure PP	100	0	0	0
	PP/22 wt%APP	78	22	0	0
	PP/1wt%clay-21wt%APP	78	21	0	1
	PP/2 wt%clay-20 wt%APP	78	20	0	2
	PP/22 wt%AAPP	78	0	22	0
	PP/1wt%clay-21wt%AAPP	78	0	21	1
	PP/2wt%clay-20wt%AAPP	78	0	20	2

with the processing temperature at about 210° C were prepared using the Arburg injection molding machine (320°C) to prepare the suitable samples for fire safety properties tests.

2.4 | Characterization of samples

NMR data of AAPP and APP using D_2O as a solvent were carried out on a Bruker 500 MHz (Germany) instrument.

Transmission electron microscopy (TEM) images were performed on the Carl Zeiss Microscopy(Germany) apparatus at 200 kV.

X-ray powder diffraction (XRD) tests were obtained using D8ADVANCE (Bruker, Germany) with Cu-K α radiation ($\lambda = 0.1541$ nm) from 5° to 10° at 40 kV and 30 mA.

Thermogravimetric (TG) analysis was conducted on a Q5000 thermal analyzer (USA) from 35 to 800° C in N₂ at a liner heating rate of 10 K/min.

SEM images for fire retarded PP nanocomposites were carried out NovaNanoSEM450 (USA) to study morphological nanocomposites. The energy dispersive X-ray analysis (EDS) of fire retarded PP nanocomposites was obtained using OXFORD X-MaxN (USA).

UL-94 testing with dimensions $130 \times 13 \times 3.2 \text{ mm}^3$ was conducted on a FTT vertical burning (UK) following the ASTM D3801-2010.

LOI testing with dimensions $130 \times 6.5 \times 3 \text{ mm}^3$ was carried out with a FTT oxygen index meter (UK) following the ASTM D2863-2012.

Cone-calorimeter (CC) test samples with dimensions $100 \times 100 \times 3 \text{ mm}^3$ was performed on a FTT cone calorimeter (UK) measurement (50 kW/m²) following the ISO 5660-1.

SEM images for char residues was carried out Carl Zeiss SMT (Germany) microscope model to study morphological residues after CC test.

TG-FTIR measurements were carried out with a Q5000 TG (USA) linked with FTIR Nicolet 380 (USA)) at a heating rate of 10 K/min from 35 to 800° C in N₂.

Tensile measurements (TS) were performed on Zwick (8195.05, Germany) at a speed of 10 mm/min.

3 | RESULTS AND DISCUSSION

3.1 | Morphological fire retarded PP nanocomposites

The TEM images of PP/2wt%clay-20wt%APP and PP/2wt%clay-20wt%AAPP nanocomposites displayed the direct the information of dispersion of the clay platelets in the PP matrix in Figure 1. As shown in Figure 1a, most of the clay platelets showing reunited structures were dispersed in PP/APP system. However, from Figure 1b, the image of PP/2wt%clay-20wt%AAPP nanocomposite displayed most of the clay platelets were closely exfoliated. Thus, it was obvious that the dispersion of clay in PP/AAPP system was better than in the PP/APP system. In order to study crystallinity of PP/2wt%clay-20wt%APP and PP/2wt%clay-20wt%AAPP nanocomposites, the XRD results were shown in Figure 2. From Figure 2a, the XRD diffraction peaks of neat PP were at 14.1°, 15.5°, 17.0°, 18.6°, 21.3°, 22.0°, 26.2°, and 29.3° which displayed semicrystalline materials. The XRD diffraction peaks of PP/2wt%clay-20wt% APP nanocomposites were 14.1°, 15.5°, 17.7°, 18.0°, 21.2°, 22.2°, 26.2°, 27.6°, 29.2°, and 30.5°. Meanwhile, the XRD diffraction peaks of PP/2wt%clay-20wt%AAPP nanocomposites were 14.6°, 17.2°, 18.8°, 21.2°, 22.1°, and 25.6 °. Consequently, PP/2wt%clay-20wt%AAPP nanocomposites had still a crystalline structure but, as expected, less pronounced and different compared to PP/2wt%clay-20wt%APP nanocomposites. To deeply investigate dispersion of the clay platelets in the in PP/APP and PP/AAPP system, the XRD results from 5° to 10° were shown in Figure 2b. It was observed that the d001 peak of clay was disappeared, which demonstrated the relative exfoliated structure of clay platelets both PP/clay-APP systems and PP/clay-AAPP systems.

To further explore the microstructure of clay and flame retardant in PP, SEM and EDS graphs were shown in Figure 3. Many flame retardant APP and AAPP particles were observed in the PP matrix from SEM. It was seen in Figure 3a2 and b2 that there were large agglomerates in PP/2wt%clay-20wt%APP and PP/2wt%clay-20wt%

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FIGURE 1 TEM images of PP/2wt% clay-20wt%APP (a) and PP/2wt%clay-20wt%AAPP (b) systems



FIGURE 2 XRD plots of neat PP, PP/2wt%clay-20wt%APP and PP/2wt%clay-20wt%AAPP systems [Color figure can be viewed at wileyonlinelibrary.com]

AAPP nanocomposites, which illustrated some of flame retardant APP and AAPP with high loading (20 wt%) were relatively rough distributed since there was phosphorus element in APP and AAPP.^{27,30,32} From Figure 3a4 and b4, the silicon map of PP/2wt%clay-20wt %APP and PP/2wt%clay-20wt%AAPP nanocomposites displayed most of the clay platelets were relative uniform dispersion. Combining TEM, XRD, SEM, and EDS, the PP/clay-AAPP composites had a good dispersion state.

3.2 | Burning behavior

3.2.1 | UL-94 vertical testing and LOI test

To study the influence of clay on fire safety of PP composites, the UL-94 vertical testing and LOI testing results of pure PP and its composites were presented in Figure 4. PP with 22 wt% APP system had a low LOI value of 20.4. In further composites, under the total loading of filler was 22 wt%, some APP was changed using the clay. The LOI results of PP/1wt%clay-21wt% APP, PP/2wt%clay-20wt%APP systems amounted 20.4, 20.6, respectively. It is obvious that all PP/clay-APP systems exhibited no classified UL-94 vertical testing with not any self-extinguishing phenomenon. However, with 22 wt% amount of AAPP in PP, the LOI results of PP composites reached 29.2. At loading of 1 wt%, 2 wt% clay in PP/AAPP systems, LOI values of PP/1wt%clay-21wt%AAPP and PP/2wt%clay-20wt%AAPP amounted 28.4 and 29.6. Moreover, PP/2wt%clay-20wt%AAPP system achieved V-0 rating level in UL-94 vertical testing without melt dripping after fire ignition. The experimental results clearly exhibited that clay-AAPP system was better fire safety for PP in comparison with clay-APP system. According to UL-94 vertical testing and LOI results, fire safety of PP/AAPP system with only addition of 2 wt% clay was significantly increased in anti-melt dripping.

3.2.2 | Cone-calorimeter test

The cone-calorimeter (CC) test is a reliable and useful bench-scale method for combustible polymer to evaluate the intensity, spreading, and developing of fire.^{17,33} The heat release rate (HRR) data of pure PP and its composites were exhibited in Figure 5. The peak value of HRR (PHRR) of combustible pure PP rapidly reached 841 kW/m² after ignition. When 22 wt% APP was put in PP, the PHRR results of PP/22wt%APP system was 534 kW/m². After combining both clay and APP, the PHRR results of PP/1wt%clay-21wt%APP, PP/2wt%clay-20wt%APP systems were 453 (reduce 15%) and 363 (reduce 32%) kW/m². Nevertheless, the PHRR results of PP/22wt% AAPP system was 369 kW/m². Obviously, the AAPP

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FIGURE 3 The morphology of PP/2wt%clay-20wt%APP (a) and PP/2wt%clay-20wt%AAPP (b) systems as obtained by SEM and EDS via mapping of carbon (a1, b1), phosphorus (a2, b2), nitogen (a3, b3), silicon (a4, b4), oxygen (a5, b5), and all these elements (a6, b6) [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 4 UL-94 vertical testing and LOI test of pure PP and its composites [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 5 HRR images of pure PP and its composites [Color figure can be viewed at wileyonlinelibrary.com]

system had better fire safety in comparison with APP system. Further, the PHRR values of PP/1wt%clay-21wt% AAPP, PP/2wt%clay-20wt%AAPP systems were 390 (raise 5%) and 340 (reduce 8%) kW/m². Thus, it can be said that only 2 wt% of clay results in efficacious synergistic effect fire safety of PP/AAPP systems. Total heat release (THR) results of pure PP, PP/clay-APP and PP/clay-AAPP systems were exhibited in Figure 6. The THR results of PP/22wt%APP and PP/22wt %AAPP systems amounted to 147 MJ/m², 123 MJ/m², respectively. When the clay was introduced to APP and AAPP system, THR results of PP/1wt%clay-21wt%APP and PP/2wt%clay-20wt%APP were 140 (reduce 5%) MJ/m^2 and 121 (reduce 17%) MJ/m^2 . On the contrary, the THR results of PP/1wt%clay-21wt%AAPP and PP/2wt %clay-20wt%AAPP systems significantly reduced to127 (raise 3%) MJ/m^2 and 92 (reduce 27%) MJ/m^2 , respectively. Thus, the lower THR results of PP/2wt%clay-20wt %AAPP systems indicated that some of PP were not completely combusted and protected due to only addition of 2.0 wt% of clay, which led to significantly synergistic effect on the fire-safety of PP/AAPP system.^{20,30,31,34}

The toxic gases and smoke results of pure PP, PP/clay-APP, and PP/clay-AAPP systems were exhibited in Figure 7. The peaks SPR (smoke production rate) of PP/22wt%APP, PP/1wt%clay-21wt%APP, and PP/2wt% clay-20wt%APP were 0.08 m²/s, 0.06 m²/s, and 0.05 m²/s, respectively. However, when APP was replaced by AAPP, the peaks SPR of PP/22wt%AAPP, PP/1wt%clay-21wt% AAPP and PP/2wt%clav-20wt %AAPP reduced to $0.06 \text{ m}^2/\text{s}$, $0.05 \text{ m}^2/\text{s}$, and $0.04 \text{ m}^2/\text{s}$. Therefore, the SPR of PP/2wt%clay-20wt%AAPP system had remarkably reduced in comparison with that of PP/22wt%APP system. From Figure 7b, the lowest TSP (total smoke production) result was observed for the PP/2wt%clay-20wt% AAPP system. Further, according to Figure 7c, the peaks of CO₂ (carbon dioxide production) of PP/22wt%APP, PP/1wt%clay-21wt%APP, and PP/2wt%clay-20wt%APP were 0.28 g/s, 0.24 g/s and 0.20 g/s. Moreover, the relevant results of PP/22wt%AAPP, PP/1wt%clay-21wt% AAPP, and PP/2wt%clay-20wt%AAPP were 0.21 g/s, 0.19 g/s and 0.18 g/s, respectively. From Figure 7d, the peaks CO (carbon monoxide production) of PP/22wt% AAPP, PP/1wt%clay-21wt%AAPP, and PP/2wt%clay-20wt%AAPP reduced to 0.006 g/s, 0.004 g/s, and 0.003 g/s. Therefore, the combined AAPP with only 2.0 wt% of clay reduced the smoke release (e.g., SPR and



FIGURE 6 THR images of pure PP and its composites [Color figure can be viewed at wileyonlinelibrary.com]

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TSR) and toxic gases (e.g., CO_2 and CO) of fire-retarded PP composites.^{6,35}

3.3 | Possible fire retardant mechanism

The FTIR of PP/2wt%clay-20wt%APP (a) and PP/2wt% clay-20wt%AAPP (b) systems at various temperature were exhibited in Figure 8. The main pyrolysis products of neat PP/clay-APP and PP/clay-AAPP system were water (from 3623 to 3540 cm^{-1}), hydrocarbons (from 3012 to 2872 cm^{-1}), aldehyde (from 2757 to 2692 cm⁻¹), carbon dioxide (from 2634 to 2381 cm⁻¹), carbon monoxide $(2173 \text{ and } 2118 \text{ cm}^{-1})$, carbonyl compounds (1756 cm^{-1}) , or other compounds. Moreover, in comparison of PP without clay system in Figure S1, the concentration of the flammable pyrolysis products was reduced during PP/2wt%clay-20wt%APP and PP/2wt%clay-20wt%AAPP compounds burning. When clay was introduced, APP and AAPP can react with clay to form a ceramic-like structure at above 300°C.^{36,37} The decomposition of clay layer may further improve the char yield.³⁸ Moreover, during PP with flame retardant burning, an ablative reassembling of the clay layers may occur on the surface of the burning PP/2wt%clay-20wt%AAPP compounds nanocomposite creating a physical protective barrier.³⁹ The clay layer as a physical barrier limit the oxygen and heat to the substrate.

To study the effect of clay and AAPP on fire-safety property, the thermal degradation curves of AAPP and APP in N₂ were exhibited in Figure S2. When the temperature was below 300°C, APP was nearly no degradation. The mass then was lost from 97% to 81% from 310 to 500° C due to the release of vapor and ammonia. Nevertheless, the decomposition of AAPP with modification of organic material was about 210°C. The char residues of AAPP at 800°C was 7.4 wt.%, increasing the residual after burning due to charring-agent in AAPP.

For introducing AAPP to PP, the degradation results of PP composites under N₂ were shown in Figure S3. The first degradation of PP/AAPP system was 250°C for forming water vapor and ammonia. The second degradation of PP/AAPP system was from 250 to 450 °C. The maximum mass loss rate (T_{max}) of PP/AAPP system was lower than that of pure PP due to the formation of carbon residues. The last degradation of PP/AAPP system was from 450 to 600 °C. The more and stable char residue was obtained because of the composite contained more C and N sources during the combustion.²⁷

The effect of morphological char residues on the firesafety of PP/clay-APP and PP/clay-AAPP systems were exhibited by digital photos and SEM in Figure 9. From Figure 9a, the surface of PP/clay-APP system char layer was 7 of 10 WILEY_Applied Polymer



FIGURE 7 SPR (a), TSP (b), CO₂ (c) and CO (d) curves of pure PP and its composites [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 8 TG-FTIR images of PP/2wt%clay-20wt%APP (a) and PP/2wt%clay-20wt%AAPP (b) systems [Color figure can be viewed at wileyonlinelibrary.com]

holes and vesicular pores that was poor quality barrier for transmission of heat and mass. Seen from Figure 8d, the char layer after cone-calorimeter test of PP/clay-AAPP system was more strong and compact for preventing molten PP and combustible gases towards the fire.^{34,35} In the case of PP/clay-AAPP system (Figure 9b, c), loose and no closed intumescent charring residue was formed. However, the morphological char residues of PP/2wt%clay-20wt%AAPP system was closed honeycomb, dense and continuous (Figure 9e, f), which in the condensed-phase effectively insulated heat and gas transfer to inside, PP/2wt%clay-20wt %AAPP system achieved V-0 rating level in UL-94 vertical testing, as discussed above.

According to the results of digital photographs, SEM, EDS, TG-FTIR, and TEM, the fire-retardant mechanism of PP/clay-AAPP system was described as follows: PP/clay-AAPP system was degraded, with the release of NH₃ and H₂O at the beginning. Then, AAPP and PP were degraded and cross-linked which led to formed stable char residues because of the C=C of AAPP. Consequently, an excellent fire safety performance with P–N–C, P–O–C structures was obtained in the carbon residues.^{15,30,40-42} The second fire safety mechanism was

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on clay platelets in the PP/AAPP system. The combined AAPP with only 2.0 wt% of clay with high quality intumescent carbonaceous char residues and stable silicon layers not only reduced the heat release rate, retarded fire spread, prevented the transmission of heat and fuel, but also provided anti-dripping features, self-extinguishing as well as a ceramic-like performance under the PP composites combustion. In particular, PP/clay-AAPP system showed a better fire safety







Digital photographs

SEM images for outer surface

SEM images for inner surface

FIGURE 9 Digital photographs after cone-calorimeter test for the char residues of PP/2wt%clay-20wt%APP system (a), PP/2wt%clay-20wt%AAPP system (d), SEM images after cone-calorimeter test for the outer surface of PP/2wt%clay-20wt%APP system (b) and PP/2 wt% clay-20wt%AAPP system (e); SEM images after cone-calorimeter test for the inner surface of PP/2wt%clay-20wt%APP system (c) and PP/2wt %clay-20wt%AAPP system (f) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Tensile properties ofPP/clay-APP and PP/clay-AAPPsystems	Samples	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
	Pure PP	23.5 ± 0.8	984.7 ± 7.9	743.0 ± 21.3
	PP/22 wt%APP	23.0 ± 0.6	1157 ± 10.3	88.5 ± 7.1
	PP/2 wt%clay-20 wt%APP	23.2 ± 1.2	1162 ± 8.4	80.2 ± 5.2
	PP/22 wt%AAPP	23.8 ± 0.3	1056 ± 6.5	78.5 ± 7.6
	PP/2wt%clay-20wt%AAPP	22.6 ± 1.3	1142 ± 5.6	62.3 ± 10.4

performance than P PP/clay-AAPP system due to the exfoliated clay platelets. The possible fire safety mechanism was exhibited in Figure 10.

3.4 | Tensile properties

Tensile properties PP/clay-APP and PP/clay-AAPP systems were showed in Table 2 and Figure S4. Compare with pure PP, the Young's modulus of PP/clay-APP and PP/clay-AAPP systems were increased. It was seen that tensile properties of PP/clay-APP was sight better than PP/clay-AAPP systems. However, since the low interface compatibility between PP and APP or AAPP (high loading),^{10,30,43,44} elongation at break of PP/clay-APP and PP/clay-AAPP systems were reduced significantly. For PP with AAPP and clay system, AAPP has not only acid source, a foaming agent, but also a carbon source and allyl group. In the next step, The PP/clay-AAPP systems will be treated by electron beam processing in further to improve thermal fire safety and tensile properties.

4 | CONCLUSIONS

In order to enhance the fire safety of traditional clay-APP system, novel fire-retarded polymer nanocomposites based on polypropylene with clay and allylamine polyphosphate (PP/clay-AAPP) were explored. The results exhibited that the LOI of PP/2wt%clay-20wt% AAPP nanocomposites was 29.5% with V-0 rating in UL 94 test. Significant enhancements in fire safety performance were also observed for fire-retarded PP nanocomposites from cone-calorimeter testing decreasing heat release (e.g., HRR and THR) as well as smoke (e.g., SPR and TSP) and toxic gases (e.g., CO₂ and COP). PP/clay-AAPP nanocomposites not only provided relatively stable char layer during polymer burning, but also exhibited better fire safety property due to the good dispersion of clay platelets. All results demonstrate that greatly synergistic effect on the fire safety of PP/clay-AAPP system.

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AUTHOR CONTRIBUTIONS

dan xiao: Conceptualization (lead); data curation (lead); funding acquisition (lead); investigation (lead); writing – original draft (equal); writing – review and editing (equal). **Uwe Gohs:** Supervision (equal); writing – review and editing (lead). **Udo Wagenknecht:** Funding acquisition (supporting); supervision (equal); writing – review and editing (equal). **Brigitte Voit:** Supervision (equal); writing – review and editing (equal). **De-Yi Wang:** Supervision (equal); writing – review and editing (equal). **Meng-Ting Zheng:** Investigation (supporting); methodology (supporting).

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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REFERENCES

- [1] H. Maddah, J. Appl. Polym. Sci. 2016, 6, 1.
- [2] M. B. Abu Bakar, Z. A. Mohd Ishak, R. Mat Taib, H. D. Rozman, S. Mohamad Jani, J. Appl. Polym. Sci. 2010, 116, 2714.
- [3] W. Hufenbach, R. Böhm, M. Thieme, A. Winkler, E. Mäder, J. Rausch, M. Schade, *Mater. Design.* 2011, 32, 1468.
- [4] W. Brostow, S. Lohse, X. Lu, A. T. Osmanson, *Emergent Mater.* 2019, 2, 23.
- [5] J. Zha, H. Yan, W. Li, Z. Dang, Appl. Phys. Lett. 2016, 109, 222902.
- [6] J. Alongi, Z. Han, S. Bourbigot, Prog. Polym. Sci. 2015, 51, 28.

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- [7] Z. Huang, B. Ruan, J. Wu, N. Ma, T. Jiang, F. Tsai, J. Appl. Polym. Sci. 2021, 138, e50413.
- [8] W. He, G. Li, X. Ma, H. Wang, J. Huang, M. Xu, C. Huang, J. Hazard. Mater. 2006, 136, 502.
- [9] Š. Vojta, J. Bečanová, L. Melymuk, K. Komprdová, J. Kohoutek, P. Kukučka, J. Klánová, *Chemosphere* 2017, 168, 457.
- [10] K. Lim, S. Bee, L. Sin, T. Tee, C. Ratnam, D. Hui, Part B-Eng. 2016, 84, 155.
- [11] S. Ding, P. Liu, S. Zhang, Y. Ding, F. Wang, C. Gao, M. Yang, J. Appl. Polym. Sci. 2020, 137, 49001. https://doi.org/10.1002/ app.49001
- [12] Z. Xu, Z. Chu, L. Yan, H. Chen, H. Jia, W. Tang, Polym. Compos. 2019, 40, 712.
- [13] Y. Tan, Z. Shao, X. Chen, J. Long, L. Chen, Y. Wang, ACS Appl. Mater. Inter 2015, 7, 17919.
- [14] Y. Tan, Z. Shao, L. Yu, J. Long, M. Qi, L. Chen, Y. Wang, ACS Appl. Mater. Inter 2016, 7, 3003.
- [15] Z. Shao, C. Deng, Y. Tan, L. Yu, M. Chen, L. Chen, J. Mater. Chem. A 2014, 2, 13955.
- [16] Y. Guan, J. Huang, J. Yang, Z. Shao, Y. Wang, Ind. Eng. Chem. Res. 2015, 54, 3524.
- [17] X. Wang, E. Kalali, J. Wan, D. Wang, Prog. Polym. Sci. 2017, 69, 22.
- [18] S. Ray, M. Okamoto, Prog. Polym. Sci. 2003, 28, 1539.
- [19] Y. Deng, Z. Zhang, X. Li, Y. Yang, J. Appl. Polym. Sci. 2014, 131, 40704.
- [20] Q. Kong, T. Wu, H. Zhang, Y. Zhang, M. Zhang, T. Si, L. Yang, J. Zhang, *Appl. Clay Sci.* 2017, 146, 230.
- [21] C. Lu, X. Gao, D. Yao, C. Cao, Y. Luo, Polym. Degrad. Stabil. 2018, 153, 75.
- [22] Y. Liu, J. Wang, C. Deng, D. Wang, Y. Song, Y. Wang, Polym. Advan. Technol. 2010, 21, 789.
- [23] H. Chen, P. Shen, M. Chen, H. Zhao, D. Schiraldi, ACS Appl. Mater. Inter 2016, 8, 32557.
- [24] Q. Fu, L. Medina, Y. Li, F. Carosio, A. Hajian, L. Berglund, ACS Appl. Mater. Inter 2017, 9, 36154.
- [25] X. Lai, X. Zeng, H. Li, F. Liao, C. Yin, H. Zhang, J. Macromol. Sci. B 2012, 51, 1186.
- [26] Y. Hu, X. Wang, J. Li, Ind. Eng. Chem. Res. 2016, 55, 5892.
- [27] D. Xiao, Z. Li, X. Zhao, U. Gohs, U. Wagenknecht, B. Voit, D. Wang, *Appl. Clay Sci.* 2017, 143, 192.
- [28] F. Xin, C. Guo, Y. Chen, H. Zhang, L. Qian, RSC Adv. 2017, 7, 47324.

Applied Polymer_WILEY 10 of 10

- [29] Y. Yu, Z. Chen, Q. Zhang, M. Jiang, Z. Zhong, T. Chen, J. Jiang, Polym. Advan. Technol. 2019, 30, 998.
- [30] D. Xiao, Z. Li, U. Gohs, U. Wagenknecht, B. Voit, D. Wang, Polym. Chem. 2017, 8, 6309.
- [31] D. Xiao, U. Gohs, U. Wagenknecht, B. Voit, D. Y. Wang, *Thermochim. Acta* 2022, 708, 179083.
- [32] J. Zhou, L. Yang, X. Wang, Q. Fu, Q. Sun, Z. Zhang, J. Appl. Polym. Sci. 2013, 129, 36. https://doi.org/10.1002/APP.38661
- [33] V. Babrauskas, R. D. Peacock, Fire Safety J. 1992, 18, 255.
- [34] D. Wang, A. Leuteritz, Y. Wang, U. Wagenknecht, G. Heinrich, Polym. Degrad. Stabil. 2010, 95, 2474.
- [35] H. Qi, S. Liu, X. Chen, C. Shen, S. Gao, J. Appl. Polym. Sci. 2020, 137, 49047.
- [36] S. Bourbigot, M. Le Bras, F. Dabrowski, J. W. Gilman, T. Kashiwagi, *Fire Mater.* 2000, 24, 201.
- [37] F. Dabrowski, M. Le Bras, L. Cartier, S. Bourbigot, J. Fire Sci. 2001, 19, 219.
- [38] Y. Hu, Y. Tang, L. Song, Polym. Adv. Technol. 2006, 17, 235.
- [39] M. Zanetti, T. Kashiwagi, L. Falqui, G. Camino, *Chem. Mater.* 2002, 14, 881.
- [40] C. Ke, J. Li, K. Fang, Q. Zhu, J. Zhu, Q. Yan, Y. Wang, Polym. Degrad. Stabil. 2010, 95, 763.
- [41] Y. Yan, L. Chen, R. Jian, S. Kong, Y. Wang, Polym. Degrad. Stabil. 2012, 97, 1423.
- [42] Y. Xu, L. Qu, Y. Liu, P. Zhu, Carbohyd. Polym. 2021, 260, 117827.
- [43] H. Lin, H. Yan, B. Liu, L. Wei, B. Xu, Polym. Degrad. Stabil. 2011, 96, 1382.
- [44] Z. Qin, D. Li, W. Zhang, R. Yang, Polym. Degrad. Stabil. 2015, 119, 139.

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