

Study on the Properties of Ammonium Polyphosphate (APP) Flame Retardant Polypropylene (PP)

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Abstract: Ammonium polyphosphate/polypropylene (APP/PP) flame retardant composites were prepared by melt blending extrusion. The impact properties, tensile properties and melt flow rate (MFR) of the composites were tested and characterized, and their mechanical properties and flame retardancy were compared. The effects of APP content on the melt flow rate, thermodynamic behavior, crystallization behavior and mechanical properties of flame retardant composites were discussed. The results showed that the addition of flame retardant APP significantly reduced the flammability of PP, and APP had the role of catalytic carbonization and anti-melting drop in the combustion process of composite materials; With the increase of the addition amount, the thermodynamic stability of the composite increases, and the MFR decreases first and then increases; When APP content (mass fraction) is greater than 20%, APP has heterogeneous nucleation effect on the crystallization of PP, which not only affects the mechanical properties of the composite, but at the same time, the interfacial bonding between APP and PP matrix is also improved. At the same time, the interfacial bonding between APP and PP matrix is also improved.

1. Introduction

1.1 Background of the Topic and Significance of the Study

Fire lights up the world and human civilization; however, even today, fire disasters still cause incalculable damage to human life and property every year. 2020, more than 2.5 million fire disasters occurred in China, causing 000 deaths, 1,183 injuries and more than 775 billion yuan in direct property damage [1]. Under such severe conditions, all industries have imposed strict flame retardant requirements on the materials they use[2]. Polymer materials, as inseparable basic materials for civil equipment, industrial facilities and medical applications[3] Most of them are highly flammable due to their organic chemical structure. When heated, as in Figure 1 When heated, as shown in Figure 1, polymeric materials undergo thermal decomposition, "a process in which a large number of chemical substances are changed by heat", resulting in the formation of combustible gaseous fuel vapours which burn on top of the polymeric material in the presence of heat and oxygen[4]. The combustion of the gaseous fuel vapour generates a large amount of heat, some of which is fed back into the polymer material, leading to further decomposition of the polymer material and the continuous generation of combustible gaseous fuel vapour. On this basis, flame retardancy can be achieved in either or both of the gaseous and condensing phases. In the gas phase, flame retardancy is mainly achieved by trapping combustion radicals, diluting combustible or co-firing gases[5]. In the condensed phase, flame retardancy is mainly achieved by heat absorption/reduction, drip promotion and barrier protection[6]. A number of flame retardant methods have been proposed based on these mechanisms and have achieved satisfactory results.

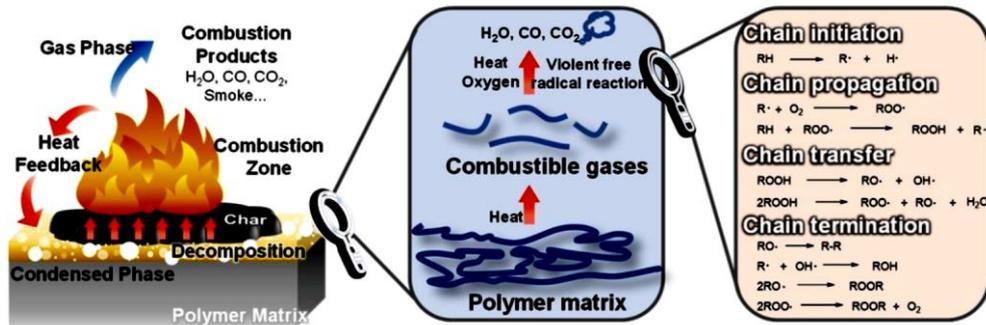


Fig. 1 Combustion process of polymeric materials.

Methods to improve the flame retardancy of polymeric materials are usually based on flame retardant modification of the native polymer matrix or the polymer surface. Flame retardants are added to the polymer matrix by physical mixing (Fig. 2a)[7] , incorporation of flame retardant monomer units into the polymer chain (Figure 2b) [8] and the construction of a flame retardant layer on the polymer surface (Fig. 2c). 2c) are the basic flame retardant methods for polymeric materials. Flame retardant modification of polymeric materials dates back to ancient Greece, when alum solutions were first applied to the surface of wooden bunkers (mainly made of cellulose, a natural polymeric material) to improve their flame retardant properties. Over the next few centuries, a number of practical flame retardant methods were developed which addressed, to varying degrees, the flame retardancy of polymers. With the rapid development of modern society, the requirements for flame retardancy are increasing, making conventional flame retardant methods inadequate for some practical applications. In this context, a number of advanced flame retardant methods have been developed in recent years, aimed at solving the problems of conventional flame retardant methods or providing new strategies for the design of flame retardant polymeric materials.

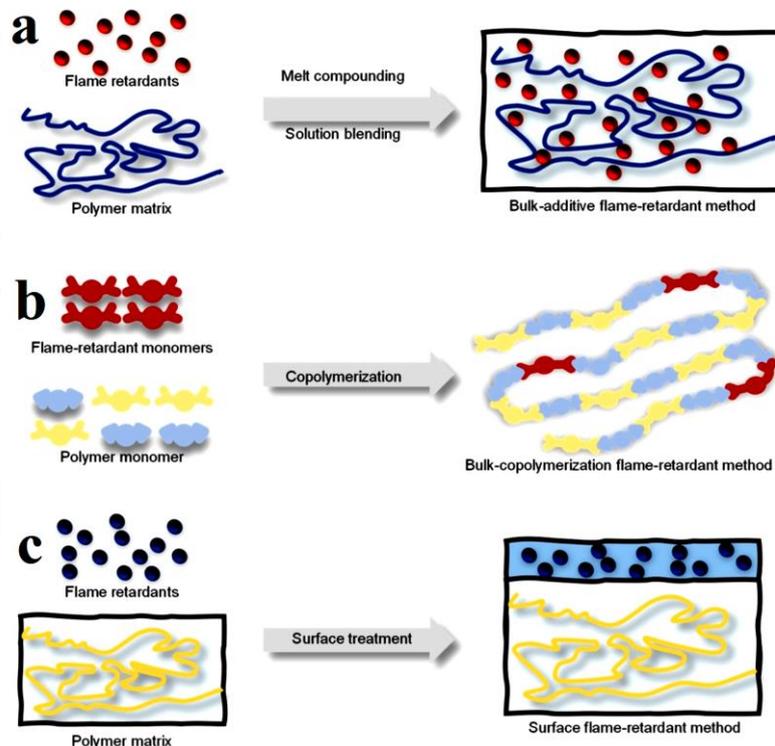


Fig. 2 Ontological additives (a) Ontological copolymerisation (b) Surface treatment (c) Schematic representation of flame retardant methods.

With development of society development, some halogen-based flame retardants have been phased out due to environmental considerations, thus promoting the development of halogen-free flame retardants in recent years.[9] Among all the halogen-free flame retardants, phosphorus-

containing flame retardants are the most popular because of their high performance. Of all the halogen-free flame retardants, phosphorus-containing flame retardants are the most popular because of their toxicity. Therefore, they are probably one of the most promising flame retardant materials.[10]. When an external heat source reaches a specific combustion temperature, the reaction of degraded combustibles sustains the combustion of the polymer in the presence of oxygen or air. The combustion process of some polymers is caused by the involvement of highly reactive hydrogen (H·) and hydroxyl radicals (OH·), which are the two key in the presence of flame free radicals. The combustion of the polymer itself also generates a significant amount of heat of combustion, providing thermal feedback to the underlying polymer to promote combustion [11]. This system is understood as a fire triangle, although it has now been modified into a fire tetrahedron consisting of four key contributors Tetrahedron: fuel, oxygen, heat and the chain reaction (Figure 3).

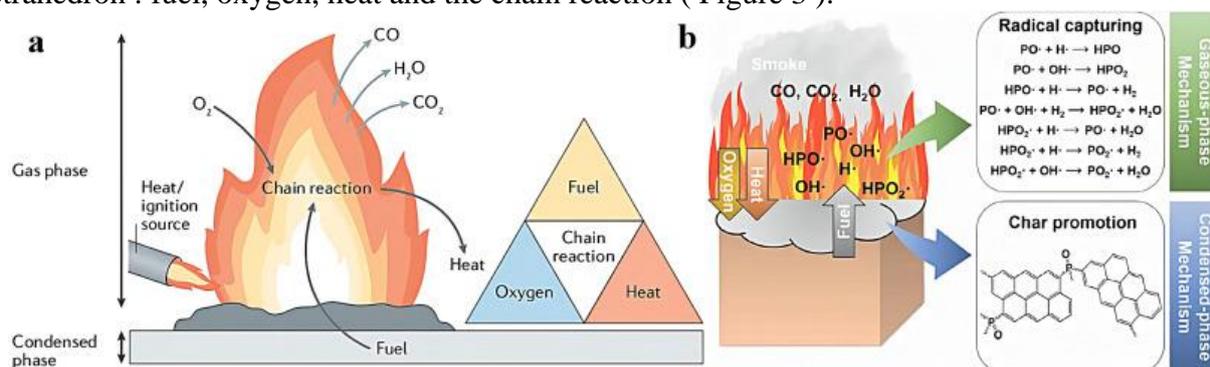


Fig. 3 (a) Schematic diagram of the combustion mechanism of polymer materials.[5] (a) Schematic diagram of the combustion mechanism of polymer materials. (b) Flame retardant mechanism of FRS containing phosphorus.[12, 13] (b) Flame retardant mechanism of phosphorus-containing FRS.

In order to achieve good flame retardancy in PP, it is necessary to understand the flame retardant mechanisms of different flame retardants, as well as the structural characteristics of PP itself and the possible effects of the addition of flame retardants on its structural properties. PP is a highly crystalline polymer and our study investigated the effect of ammonium polyphosphate (APP) addition on the combustion state, melt flow rate, mechanical properties and thermal stability.

1.2 Needs and Trends in Flame Retardant Polypropylene

Polypropylene (PP) is one of five general-purpose plastics with good heat resistance, electrical insulation, high transparency and ratio of light weight, high impact strength, chemical resistance, easy to shape and process at the same time, can be injection, extrusion and hollow molding using a variety of methods to form a variety of products with high efficiency. In addition, due to the low price of raw materials and abundant resources in recent 20 years, it has developed rapidly and is widely used in chemical fibres, construction, light industry, home appliances, packaging and other industrial fields. In recent years, polypropylene has been further promoted worldwide thanks to the continuous development of its production technology and application areas and the rapid development of the grease industry. In the future, the application areas of polypropylene resin, especially the demand for cars and bags will have a high growth packaging and consumer market. But PP flame retardant poor, easy to burn, oxygen index of only 17 to 19%, burning calorific value, it is easy to produce a large number of molten droplets, which can easily cause a fire[14]. At the same time, with the continuous development of polypropylene applications and applications more and more use brings more and more fire hazards, thus giving polypropylene materials flame retardant property which is very important and necessary.

Polymers are complex and diverse in composition, often containing nitrogen, oxygen, halogens, phosphorus and sulphur in addition to the main components of carbon and hydrogen. These substances can easily form toxic gases and substances during combustion, such as N₂, HCN, etc., which are harmful to humans. As combustion in fire is usually incomplete combustion, polymers in the combustion process will burn to produce carbon monoxide, and the amount of carbon monoxide

produced during the combustion of polypropylene is comparable to that of wood, regarding the bottleneck in the development of polypropylene materials, it is vital to improve the flame retardant property of polypropylene materials. Adding polypropylene flame retardants are the main flame retardants, compared with other flame retardants, halogen flame retardants in polypropylene use the least, the effect is significant, but plastic products containing halogen flame retardants in the burning will produce a lot of smoke and toxic and corrosive gases[15] However, plastic products containing halogenated flame retardants produce large amounts of smoke and toxic and corrosive gases on burning. As the use of halogen-containing flame retardant materials is gradually restricted, this has led to the active search for new halogen-free, low smoke, low toxicity, environmentally friendly and efficient flame retardant systems for polypropylene. Intumescent flame retardant polypropylene materials are attracting attention because of the synergy and synergistic effect between phosphorus and nitrogen elements, making this type of flame retardant with good flame retardant properties and low smoke generation and toxic gas production, which is considered to be one of the main development directions for future flame retardant materials.

1.3 Mechanisms of Thermal Decomposition and Flame Retardant Reactions of Ammonium Polyphosphate

The most widely sold and available non-halogenated alternatives are based on phosphorus compounds. Common examples of this type of flame retardant include elemental red phosphorus, and phosphine, phosphonium oxide, phosphonium compounds, phosphonates phosphonium compounds Phosphite Hypophosphonates and phosphates. These compounds act in the condensed phase mainly by altering the pyrolytic path of the polymeric material and reducing the amount of gaseous combustibles (dehydration and char formation are the main modes of action).[16] For example, most phosphorus-containing compounds have a significant impact on the pyrolysis of polymeric materials. For example, most phosphorus-containing compounds are converted during pyrolysis to phosphoric acid Phosphoric acid is produced by eliminating water condensation to produce pyrophosphates and polyphosphate salt structures. They catalyse the dehydration of polymer end chains (and any reactive groups) and trigger the formation of char. The water released dilutes the oxidising gas phase. In some cases, phosphorus-based flame retardants volatilise into the gas phase to form reactive radicals (PO_2^- , PO^- and HPO^-) and act as scavengers of H- and OH- radicals.[17]. Some preliminary studies on the toxicity of phosphorus-based compounds also indicate that these FRs are neurotoxic when decomposed in the environment; in addition, stress corrosion cracking of various parts can occur when they volatilise and condense.

In the condensed phase, P-containing FRs promote the formation of carbon by the formation of carbon play a role. Specifically, at high temperatures they generate phosphate species during polymer combustion, which can be used by dehydration reactions to promote PP carbonisation of the matrix[18]. For example, APP, DOPO phosphates and phosphine hydroxides, etc. Compounds act synergistically as flame retardants in the condensing and gas phases.[19]. Thus, the material's flame retardancy is enhanced.

1.4 Research Ideas and Research Content

In this paper, PP and APP were used as raw materials to synthesize APP/PP composites with different mass ratios of APP additions, and the effects of APP additions on APP/PP composite flame retardant materials were investigated by combustion performance tests, impact performance tests, tensile performance tests and melt flow properties tests.

The main research content of this paper is as follows: this paper uses PP and APP as the main raw materials to prepare a filled flame retardant polypropylene composite material using a twin-screw extruder melt blending. The mechanical properties of the PP/APP composite system were studied and the flame retardancy was investigated using the vertical combustion method.

2. Effect of APP Addition on APP/PP Composite Flame Retardant Material

2.1 Analysis of the Current State of Research

As the most important thermoplastic polymer material, PP has been widely used due to its excellent overall performance [20]. However, its high combustibility makes it a significant fire hazard. Therefore, its flame-retardant performance has always been a research hot spot. Since phosphorus intumescent flame retardants have low toxicity, less smoke and great flame retardant effect, it has been widely noticed and used in recent years [20]. Therein, APP is the acid source in the intumescent flame retardant (IFR) flame retardant. It decomposes into inorganic acid as a dehydrating agent when heated. When the combustion temperature continues to rise, the dehydrating agent induces the carbon source to form an ester compound, and then dehydrates to form a carbon layer. The resulting carbon forms a foam-structured carbon layer that expands when the gas source releases non-combustible gases. In addition, the protective foam layer has the ability to prevent the diffusion of combustible gases, not only from escaping from pyrolysis, but also from PP with flame retardant performance. The P-containing compounds in PP can be inorganic P-containing compounds, organic P-containing compounds or a combination of inorganic and organic P-containing compounds. P-containing materials typically act in the condensing phase to promote surface coking of carbon which forms a physical barrier and further inhibits polymer re-decomposition and combustion.[20]. Different P-based substances are added to PP to make it flame retardant[5]. Table 1 shows the names and percentage content of APP FR in PP.

Table 1 Proportions of phosphorus-containing FRs, together with cone calorimetric (CCT) parameters (TTI, PHRR, THR), LOI and UL-94 values. names and percentages of FRs are listed separately. wt% represents the negative load weight of the flame retardant, whereas it represents the additive-free system or pure PP.

P-Containing FRs*	Wt%	TTI (s)	PHRR (kW.m-2)	THR (MJ.m-2)	LOI (%)	UL-94	Ref.
APP	20	40.0	787	92.0	20.5	NR	[21]
APP	20	31.0	424	38.6	21	NR	[22]
APP	25	-	411 ± 14	73.2 ± 3.8	20.7 ± 0.2	NR	[23]
APP	25	20	1455	148.0	21.9	V-2	[24]
APP	25	21	-	107	21.7	NR	[25]
APP	25	19 ± 1	526 ± 17	180 ± 1	19.6	NR	[26]
APP	30	57 ± 1	373.4	127.1	-	NR	[27]
APP	30	30	432	114	22.0	NR	[28]

2.2 Experimental Details

2.2.1 Raw Materials

Polypropylene (PP): P-340; ammonium polyphosphate: APP, with the general formula $(\text{NH}_4)_3\text{P}_3\text{O}_{10}$, as shown in Figure 4, which has a phosphorus mass fraction of 21% to 33% and a nitrogen mass fraction of about 14%, and a molecular structure formula as shown in Figure 6.

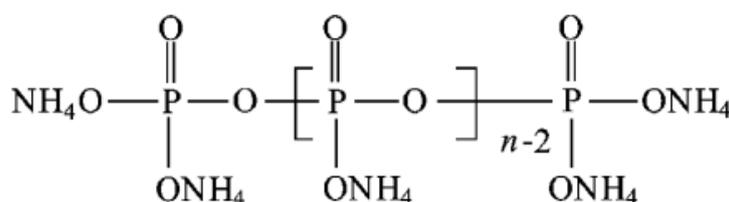


Fig. 4 Molecular structure of APP.

2.2.2 Apparatus and Equipment

High-speed mixer, twin-screw extruder, injection machine, tensile tester, impact tester, melt flow rate meter.

2.2.3 APP/PP Composite Formulation

PP and powdered APP were first mixed in a certain mass ratio, then melt extruded by a twin-screw extruder, pelletized and injected into a standard sample strip. The temperature of each section (head) of the injection moulding machine was 190, 200, 210, 210, 200 °C, and the pelletizing was carried out at a controlled speed of 350 r/min. The pellets were dried at 80 °C for 4 h and then injected at 210 °C to prepare the sample strips for the experimental test.

Table 2 Sample numbers for PP and APP/PP

Sample number	PP/g	APP/g	APP to composite mass ratio %
PP	100	0	0
A10P	90	10	10
A15P	85	15	15
A25P	75	25	25
A30P	70	30	30

2.3 Results and Discussion

2.3.1 Burning Performance Tests

In order to observe the changes in the combustion performance of the composites after the addition of flame retardants more directly, samples of pure PP and APP/PP composites A10P, A15P, A25P and A30P with the same specifications were taken and directly ignited under air to observe their combustion status; the flaming time of each group was also measured separately, as shown in Table 2. The flameless burning time was not observed in all samples, and the total flaming time was calculated as shown in Figure 7. The flame retardant performance was significantly improved.

The increasing amount of APP can generate a charcoal foam layer on the surface of PP, which acts as a barrier to prevent heat transfer and oxygen dispersion from the gas and solid phases, effectively delaying the thermal degradation of PP and preventing the production of volatile combustible components, thus achieving the purpose of flame retardation.[29] The flame retardation is achieved by preventing the production of volatile combustible components. The expansion into carbon reduces the release of combustible gases and smoke, which reduces the molten droplet behaviour of polymer combustion and to a certain extent prevents the spread of flame.[30] This reduces the molten droplet behaviour of the polymer and prevents flame propagation to some extent. With the increasing APP, the burning time of A20P decreases, but the melt-drop phenomenon of flame-retardant PP improves during the burning process, as shown in Figure 5.

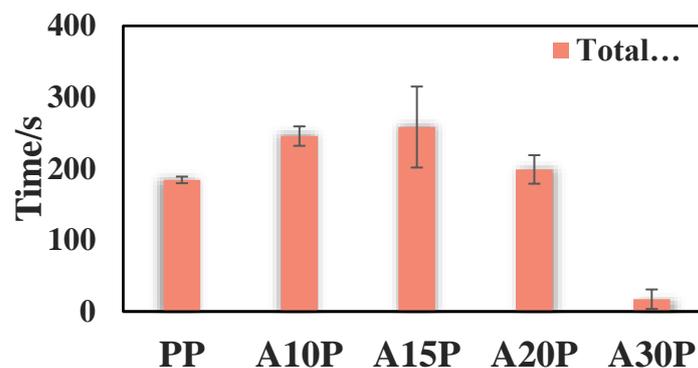


Fig. 5 Total flaming time of PP and APP/PP composites.

2.3.2 Impact Performance Tests

The impact test is an experiment to study the resistance of a material to dynamic loading. Unlike the action of static loading, the material shows another response to the action of dynamic loading because of the rapid loading speed, which causes a sudden increase in stress within the material and the rate of deformation which affects the institutional properties of the material. Often materials with very good plastic properties under static load will exhibit brittle properties under impact loading.

The work of impact (J) per unit cross-sectional area (m²) consumed by a specimen during a single impact test is given in J/m².

$$a = W / (h \times d)$$

where a is the impact strength, W denotes the impact loss energy (J), h denotes the remaining width of the notch (m) and d denotes the thickness of the sample strip (m).

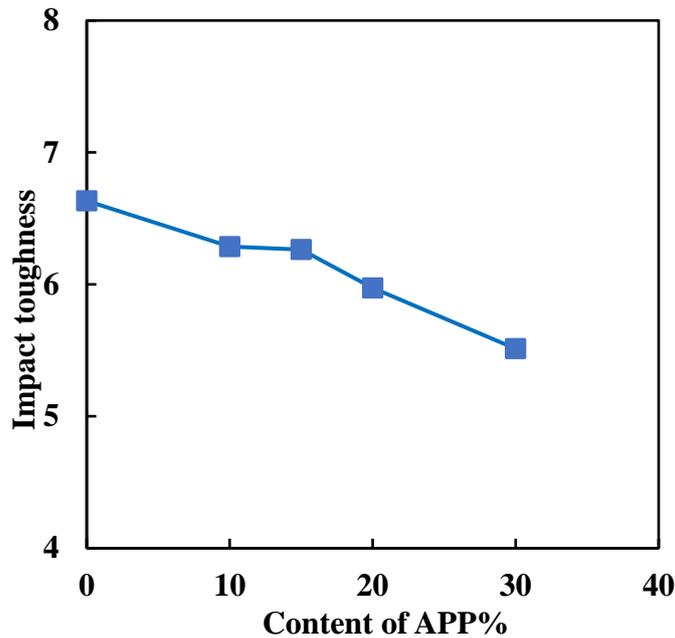


Fig. 6 Impact toughness of PP and APP/PP composites.

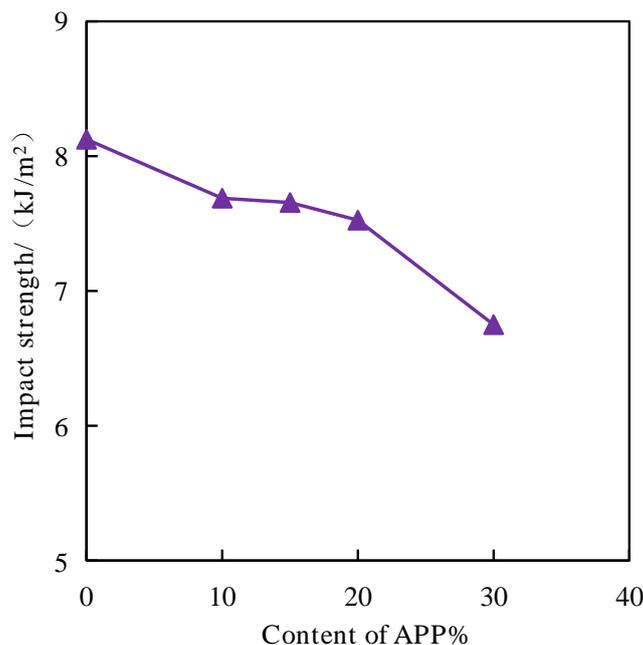


Fig. 7 Impact strength of PP and APP/PP composites.

The relationship between the ammonium polyphosphate content and the impact strength was

investigated during the experiments, and the results are shown in Figure 7. Under the same experimental conditions, the impact strength of the composites decreased as the APP content increased, and the introduction of ammonium polyphosphate in the polypropylene molecular chain reduced the regularity and crystallinity of the PP molecular chain, resulting in a decrease in the impact strength of the simply supported beam.[31] The impact strength of the simple beam decreases. As shown in Figure 6, we can see that the increase of APP content makes the product less crystalline, and the crystallization can make the product high rigidity and low toughness; good toughness and low rigidity will lead to the material's poor high pressure tolerance, so the material requires a balance of rigidity and toughness, and cannot be added too much APP.[32] Therefore, the material requires a balance of stiffness and toughness, and cannot add too much APP. The content of ammonium polyphosphate in the composite material affects the internal structure of the material and the interface, with the increase of APP content, the density of micro-voids increases and the tensile yield stress decreases.[33] The tensile yield stress decreases. As the amount of APP increases, the notched impact strength of the composites gradually deteriorates, mainly because the molecular chain segments are relatively short, brittle, poor deformation ability, and can not effectively absorb the impact energy when impacted, so it leads to poor notched impact of the composites.

2.3.3 Tensile Properties Testing

The tensile test is a mechanical property test in which a standard tensile specimen is pulled to fracture at a specified tensile speed under the constant action of a static axial tensile force, and the force and elongation are recorded continuously during the tensile process to derive its strength and plasticity criteria.

In order to analyse the effect of the addition of APP on the mechanical properties of the material, samples of PP and APP/PP composites were tested for tensile properties. The tensile strengths obtained from the experiments are shown in Figure 8 and the tensile fracture forces are shown in Figure 9.

Compared to pure PP, the tensile strength of APP/PP composites are all reduced to varying degrees because APP flame retardants are inorganic particles, and when they are melt-blended with the polymer matrix, interfacial compatibility problems will inevitably occur, so the plasticity of the resulting composites will be reduced[34] The plasticity of the resulting composite will be reduced. From Figure 8, it can be seen that with the addition of flame retardant, the tensile properties of the material first decreased. But the tensile fracture force of Figure 9 should be noted. When the amount of APP flame retardant reached a certain value, that is, $\geq 20\%$, the tensile fracture force of the composite suddenly changed. This may be because with the addition of flame retardant, APP particles have heterogeneous nucleation effect on polypropylene matrix. Therefore, the interfacial interaction between flame retardant and polymer matrix is enhanced [35]. This may be due to the enhanced interfacial interaction between flame retardant and polymer matrix.

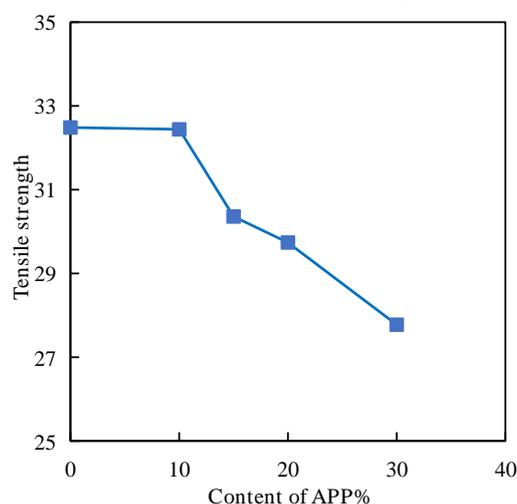


Fig. 8 Tensile strength of PP and APP/PP composites

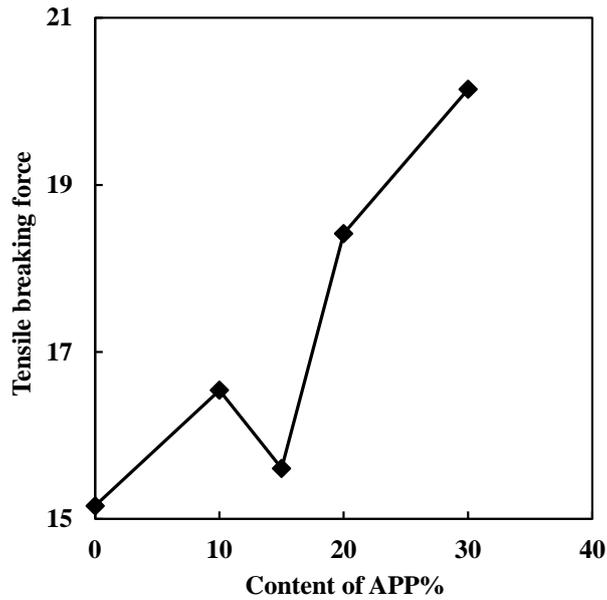


Fig. 9 Tensile fracture forces of PP and APP/PP composites.

2.3.4 Melt Flow Properties Test

Figure 10 shows the effect of the addition of the flame retardant APP on the melt flow rate (MFR) of PP. It can be seen from the figure that as the amount of APP increases, the curve of MFR value first gradually decreases, and then gradually increases after reaching a certain degree; when the amount of APP added (mass fraction) is 20%, the MFR value is the smallest; when the content of APP is higher than 20%, the melt flow rate will increase. This is because APP is a rigid particle, not easy to deform, its flow resistance is greater than the PP molecular chain; the more APP content, the greater the friction between the PP molecular chain and APP particles, the viscosity of the melt will increase, so the MFR value of the material will gradually decrease.[36, 37]. This is because with the increase of APP, the heterogeneous nucleation effect of APP on PP is obvious, APP is covered by PP in the form of crystal nuclei, the friction between APP particles and PP molecular chains is reduced, and its interfacial bonding is enhanced, so the viscosity of the system is reduced and the MFR value is increased.[38].

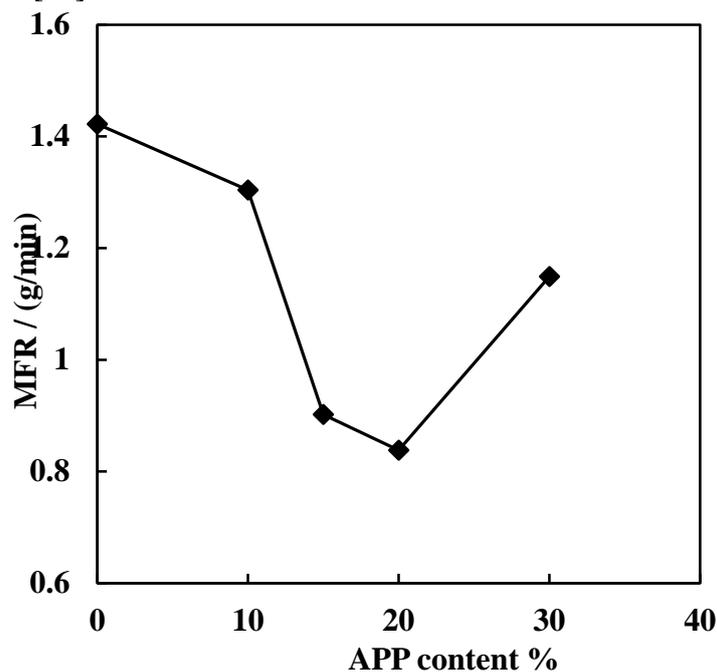


Fig. 10 Curves of MFR values for PP and APP/PP composites.

3. Conclusion

In this paper, APP powder and PP powder were used as raw materials to synthesize different APP/PP composite flame retardant materials at different APP powder additions, and their burning conditions were analysed by vertical combustion method, impact performance tests and tensile performance tests were used to understand the properties of the materials, and finally the melt flow rates were used to compare the composites with different mass ratios. The main findings were found to be as follows.

The flame retardant composite material obtained after the blending of APP flame retardant with PP matrix has improved flame retardant performance. APP will be thermally decomposed during the combustion process and has the effect of catalytic carbon formation and anti-melt drop dripping on the surface of PP matrix.

The addition of APP has a heterogeneous nucleation effect on the PP matrix, which becomes more obvious when the addition amount (mass fraction) reaches 20%, which affects the melt flow and mechanical properties of the composite and improves the interfacial bonding between APP particles and the PP matrix.

With the increase of APP addition, when the addition amount (mass fraction) reaches 20%, the melt flow rate of APP/PP composites changes from the initial decrease to a gradual increase; the mechanical properties of APP/PP composites keep decreasing.

According to the research in this paper, it is further confirmed that the flame retardant composites obtained by blending APP flame retardant with PP matrix can improve their flame retardant properties with the increase of APP content, but the improvement is not obvious; the research in this paper is still inadequate, and further experiments are needed to improve the APP/PP composites, so that the flame retardant properties can be significantly improved and the mechanical properties can be improved at the same time.

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