Synthesis of a new phosphorus-nitrogen flame retardant and its application to polypropylene

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Abstract: A new halogen-free phosphorus-nitrogen flame retardant (FR) was synthesized from triethylenetetramine, phosphorous acid, urea and other raw materials. Thermogravimetric (TG) analysis suggested that FR had good thermal stability, there was still 16.3% carbon residue at 800 °C. When the content of FR is 30%, the LOI of flame retardant composites (FR-PP) is improved from 18.0% to 25.4%, reaching the V-0 level of UL-94. SEM (Scanning electron microscope) and EDS (Energy dispersive spectrometer) results indicated that FR was successfully put on PP. The mechanical test showed that the tensile strength of FR-PP decreased from 20.8MPa to 13.1MPa, and the notched impact strength decreased from 34.5kJ/m² to 31.6kJ/m².

1. Introduction
Polypropylene (PP) has low density, non-toxic, easy processing and good chemical resistance. Because of its excellent mechanical properties, it is widely used in automobile and household electricity [1-3]. It is estimated that by 2022, the average growth rate of domestic PP production capacity will reach 8.54% [4]. However, PP is a flammable material with poor flame retardancy. The LOI is only 17.4%-18.5%, and the calorific value is high during combustion. At the same time, molten droplets are produced during combustion, which can easily lead to fire [5-6], the application of PP in flame retardant occasions is limited. Therefore, it is of great significance to develop PP flame retardant with high efficiency and environmental protection. There are many kinds of flame retardants that can be used for PP flame retardancy, among which there are many researches and some problems. The representative ones mainly include hydrated metal compounds, phosphorus series, nitrogen series, silicon series, intumescent flame retardants, etc [7-8]. Among them, the hydrated metal compound flame retardant belongs to inorganic environmental friendly flame retardant, but it has poor compatibility with PP, large dosage and low flame retardant efficiency [9]. When phosphorus, nitrogen, silicon and other halogen-free flame retardants are used alone, they generally have poor compatibility with the substrate and poor flame retardant effect [10]. Therefore, scientists use the theory of coordination to design the molecular combination of several flame retardant elements, forming a new type of dual or multi-element flame retardant structure, resulting in synergistic flame retardant effect [11-12]. The intumescent flame retardant containing 2 kinds of flame retardant elements, nitrogen and phosphorus, can form a carbon foam layer on the surface of the flame retardant at high temperature. It can play the role of heat insulation, oxygen isolation and smoke suppression, and has good flame retardancy [13-15].

A novel halogen-free phosphorus nitrogen synergistic flame retardant FR was synthesized by three-step method. The FR has high yield, good thermal stability and good compatibility with PP. In the experiment of FR application of PP, the synergistic FR effect of phosphorus-nitrogen is remarkable,
and it plays a flame retardant effect in both condensed phase and gas phase.

2. Experiment

2.1 Main materials and reagents

| Name of raw material | Specifications       | Manufacturer                          |
|----------------------|----------------------|---------------------------------------|
| PP                   | Industrial grade     | On the market                         |
| Triethylenetetramine| Analytically pure    | Tianjin Damao Chemical Reagent Factory|
| Formaldehyde         | Analytically pure    | Liaoning Quanrui Reagent Co., Ltd     |
| Phosphorous acid     | Analytically pure    | Tianjin Damao Chemical Reagent Factory|
| Urea                 | Analytically pure    | Tianjin Damao Chemical Reagent Factory|

2.2 Synthesis of FR:
FR synthesis: As shown in Scheme 1, 0.10 mol triethylenetetramine, 0.70 mol formaldehyde, 0.80 mol phosphorous acid and 25.00 ml distilled water were added into a four mouthed flask, 150.00 ml of 5% KMnO4 solution to oxidize the formaldehyde released during the reaction, reacted at 95 ℃ for 2.0 h, and after cooling, the intermediate triethylenetetramine phosphate (TEP) solution is poured into the beaker. 0.7 mol urea and TEP reacted at 130 ℃ for 1 h to obtain light yellow semi-solid FR with a yield of 75.8%.

2.3 Synthesis of FR-PP
At first, PP and FR with different mass concentrations were evenly mixed in a high-speed mixer, and then the mixed raw materials were extruded in an extruder. Finally, the FR-PP was dried at 80 ℃ for 8h, and injection molded into standard samples for mechanical and flame-retardant properties testing.

2.4 Performance test and characterization
Vertical combustion performance test: according to GB/T 2408-2008.
LOI test: according to GB/T 2406.2-2009.
TG analysis: heating rate 10 ℃/min, N2 atmosphere, flow rate 20 ml/min, the sample mass is 4-6mg.
SEM-EDS test: after spraying gold on the surface for 1 min, the surface morphology and element composition of the samples were observed under the working voltage of 20 kV.
Impact strength test: refer to GB/T 1843-2008.
Tensile property test: refer to GB/T 1040-2006.

3. Results and discussion

3.1 SEM and EDS analysis

The impact fracture surface morphology of PP and FR-PP is shown in Fig. 3. In Fig. 3(a), the PP surface is relatively smooth, indicating that the material is brittle fracture. In Fig. 3(b), FR-PP shows obvious plastic deformation morphology, which indicates that FR-PP undergoes severe shear and torsion during high speed impact, and the phosphorus-nitrogen combination improves the impact toughness of PP. EDS showed that the P content of FR-PP was improved to 15.3%, indicating that FR particles were successfully treated into PP.

3.2 TG analysis

TG and DTG analysis results of FR in nitrogen atmosphere are shown in Fig. 2. The initial degradation temperature (T5%) of FR is 113.5 ℃, which is caused by water evaporation and oligomer decomposition. In the stage of 113.5-200.0 ℃, P-O, C-C and N-C bonds are broken successively, and the decomposition rate is fast. The temperature (Tmax) corresponding to the maximum thermal decomposition rate is 161.0 ℃. The maximum thermal degradation rate (Rmax) was 0.77%/℃; At 200.0-500.0 ℃, FR mainly decomposed; At 500.0-800.0 ℃, FR further decomposes into N2 and NH3, and decomposes slowly. There is still 16.3% carbon residue at 800 ℃, which shows that FR has good thermal stability.

![Fig.1 SEM of PP (a) and FR-PP (b)]

![Fig.2 TG(a) and DTG(b) curves of FR](a)
3.3 Flame retardancy analysis

The effect of FR on the flame retardancy of PP was studied by LOI and vertical combustion test. It can be seen from Fig. 3 and Table 2 that the LOI of PP is only 18.0%, which can not pass the UL-94 flame retardant rating test, and the melting drop phenomenon occurs. However, with the increase of FR content, the LOI value of FR-PP increases significantly from 18.0% to 26.5%, which has excellent flame retardancy. When the content of FR is 30%, the after-flame time and after-glow time of FR-PP are 5.6s and 3.2s, respectively. There is no melting and dripping phenomenon, reaching the V-0 level of UL-94, and the corresponding LOI value is 25.4%. The flame retardant mechanism of FR in PP can be divided into two aspects: phosphoric acid is degraded in the condensed phase, which promotes the degradation of the material, forms a large number of dense and continuous expanded carbon layers, and inhibits the continuous combustion of the material; In the gas phase, the amount of hydrocarbon released from combustible gas is significantly reduced, and the release time is obviously delayed, which reduces the concentration of combustible gas.

![Fig.3 LOI curve of FR](image)

| FR content (%) | After-flame time(s) | After-glow time(s) | UL-94 | Is there anything dripping |
|----------------|---------------------|-------------------|-------|--------------------------|
| 0              | -                   | -                 | NR    | Yes                      |
| 10             | 8.9                 | 7.6               | V-1   | Yes                      |
| 20             | 7.1                 | 6.2               | V-0   | NO                       |
| 30             | 5.6                 | 3.2               | V-0   | NO                       |
| 40             | 2.0                 | 1.6               | V-0   | NO                       |

3.4 Mechanical property analysis

It can be seen from Fig. 4 that the tensile strength of PP is 20.8MPa. After flame retardant modification of PP, the tensile strength of FR-PP decreases to a certain extent. When the content of FR is 30%, the tensile strength decreases from 20.8MPa to 13.1MPa. This is because the introduction of flame retardant system destroys the crystallinity of FR-PP, followed by the uneven dispersion of flame retardant system in FR-PP, A phenomenon similar to island effect is formed, which makes the tensile strength decrease. The notched impact strength of FR-PP decreases from 34.5kJ/m² to 31.6kJ/m², which is 8.4% lower than that of PP. However, When the content of FR is 40%, the notched impact strength of FR-PP decreases obviously, which is 17.1% lower than that of PP, this is due to the agglomeration of a large number of FR in PP and the stress concentration phenomenon, which leads to the decrease of impact strength of FR-PP. Therefore, the optimum content of FR is 30%. It can be seen from the above analysis that the mechanical properties of FR-PP are reduced to a certain extent after the introduction of flame retardant system, and the impact strength of notch is more obvious. If the surface modification of flame retardant system is carried out to improve the hydrophilicity of flame retardant and the dispersion of flame retardant in the system, It can improve the effect of flame retardant system on the mechanical properties of materials.
4. Conclusion

The effects of FR on the flame retardancy and mechanical properties of PP were investigated, and the flame retardancy mechanism of FR in PP was analyzed.

(1) The LOI of PP is 18%. When the content of FR is 30%, the LOI of FR-PP is 41.1% higher than that of PP. The melting drop is effectively prevented. The UL-94 grade is also increased from V-2 to V-0. The flame retardant effect is very obvious, and the amount of flame retardant is less.

(2) FR has a certain influence on the tensile strength and notched impact strength of PP, but has a relatively greater influence on the impact strength.

(3) FR has stable chemical properties, high decomposition temperature and high compatibility with PP, which can adapt to high temperature processing of PP. The raw materials are cheap and easy to obtain, the synthesis process is simple, and it is easier to realize industrial production, so it has a good prospect of application and development.

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