Flame Retardant Properties and Mechanical Properties of Polypropylene with Halogen and Halogen-Free Flame Retardant System

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Abstract. In this study, to improve the flame retardancy properties of polypropylene, DBDPE/Sb₂O₃ and DBDPE/HBCD/Sb₂O₃ flame retardant systems were used for flame retardant PP, and a halogen-free flame retardant PP material was prepared using the one-component intumescent flame retardant PNP1D. Tensile tests, impact tests, ultimate oxygen index, UL94V-0 vertical combustion, thermogravimetric analysis, rheological analysis and scanning electron microscopy were used to study the flame retardant properties and mechanical properties of the flame retardant PP. The test results show that both the ultimate oxygen index of DBDPE/Sb₂O₃ compounded flame retardant PP and the ultimate oxygen index of PNP1D flame retardant PP are nearly double that of pure PP, passing the UL-94V-0 flame retardant standard. The thermal decomposition temperature range of DBDPE/Sb₂O₃ compounded system and the thermal decomposition temperature range of PNP1D flame retardant PP both completely cover the thermal decomposition temperature range of pure PP. The tensile and impact strength of the DBDPE/Sb₂O₃ flame retardant system with 10% SK-80 is 50% higher than that of the DBDPE/Sb₂O₃ flame retardant system without SK-80. The modified PP with 25% PNP1D is nearly 1 time higher than pure PP in terms of carbon formation and has an ideal flame retardant effect.

1. Introduction
Polypropylene (PP) is a versatile plastic that is used in a wide range of industries such as construction materials, household goods, automobiles and electrical and electronic appliances. As polymeric materials, they have many advantages that are incomparable to other materials, but one significant disadvantage limits their application: they are flammable materials, especially when used as construction materials and electronic and electrical materials, and are a serious potential fire hazard [1]. The main brominated flame retardants commonly used in the market for flame retardant modified polypropylene are decabromodiphenyl oxide (DBDPO) and tetrabutylammonium bromide (TBAB). TBAB have a lower melting point and can be more evenly dispersed in the matrix during processing, with less impact on the mechanical properties of the material. DBDPO has the advantage of high bromine content, high flame retardant efficiency, good compatibility with the substrate and not easy to precipitate, but when burning, polybrominated dibenzo-p-dioxin (PBDD) and polybrominated dibenzo-p-dibenzofuran (PBDF), which are harmful to the human body, is released. It has been shown that decabromodiphenyl ethane (DBDPE) and DBDPO have the same flame retardant mechanism, the
flame retardant effect is comparable and no toxic gas is generated by combustion, so it can be used as a substitute for DBDPO. Diantimony trioxide (Sb$_2$O$_3$) was chosen as a synergistic flame retardant for DBDPE to form a halogen-antimony compound flame retardant system[2,3].

When PP melt burns, it is easy to form molten droplets, and the bromine-antimony compounding flame retardant system mainly releases hydrogen bromide gas through decomposition and generates antimony bromide to achieve flame retardancy, neither of which can form a carbon layer to stop the droplets like intumescent flame retardants. The nano-sheeted kaolin (SK-80) was selected as a melt drip inhibitor, with a thickness of 5-10 nm. After melt blending, SK-80 is inserted into the matrix, which effectively improves the viscosity of the material and does not easily produce molten drops when the material burns, thus improving the flame retardant efficiency of the bromine-antimony compound flame retardant system.

The addition of thermally stabilised hexabromocyclododecane (HBCD) with a lower decomposition temperature makes up a high and low-temperature segmented flame retardant system to improve flame retardant efficiency and reduce the amount of flame retardant used [4]. The decomposition temperature of untreated HBCD is only 160°C, which cannot be used to flame retard PP, but the decomposition temperature of thermally stabilised HBCD can reach 220°C, which can withstand the processing temperature of PP. When DBDPE and HBCD are used together, HBCD will first decompose and flame retard, and then DBDPE will decompose and flame retard at a higher temperature. This improves the flame retardant efficiency and reduces the amount of flame retardant used.

Most bromine flame retardants can be harmful to the environment when burned, and in today's increasingly environmentally conscious world, people are beginning to turn their attention to halogen-free flame retardant modifications of polypropylene. In recent years, research on halogen-free flame retardant polypropylene has focused on the use of intumescent flame retardants (IFR) to modify polypropylene, which is mostly P-N synergistic flame retardant systems with the advantages of high efficiency, high thermal and light stability, low toxicity, low smoke, low corrosion and no environmental pollution [5-7]. PNP1D was selected for halogen-free flame retardant modification of PP. PNP1D is a new type of single-component intumescent flame retardant, combining acid, carbon and gas sources, of which the phosphate ester part is used as the acid source, the pentaerythritol part is a polyhydroxyl structure rich in carbon atoms, which is used as the carbon source of the intumescent flame retardant, and the melamine part is decomposed by heat to release ammonia gas to provide the gas needed for the expansion and foaming of the system, which is used as the gas source. Compared with the mixed type of intumescent flame retardant, PNP1D itself has a cyclic phosphate structure, which is more conducive to carbon formation, and its higher P and N content makes the flame retardant much more efficient than the mixed type of intumescent flame retardant and avoids the problem of easy precipitation of pentaerythritol in the mixed type of intumescent flame retardant.

![PNP1D structural formula](image_url)

**Figure 1. PNP1D structural formula**

In this work, halogen-containing and non-halogen flame retardants were used to modify polypropylene with flame retardants, in which DBDPE/Sb$_2$O$_3$ and DBDPE/HBCD/Sb$_2$O$_3$ were used instead of DBDPO and TBAB for the halogen-containing flame retardant system, and PNP1D, a single-component intumescent flame retardant, was used instead of the commonly used mixed...
intumescent flame retardant for the non-halogen flame retardant system, reducing the amount of flame retardant and improving the efficiency of the flame retardant.

2. Experimental

2.1. Materials
PP was purchased from Yanshan Petrochemical Co., Ltd. DBDPE was a commercial product of Albemarle Co. (USA). HBCD was provided by Legend Flame Retardant Technology Co., Ltd. (Lianyungang, China). Sb$_2$O$_3$ was obtained from Star Better Co., Ltd. (Beijing, China). PNP1D was purchased from Jieshi Flame Retardant Chemical Co., Ltd. (Hangzhou, China). SK-80 was supplied by Fenghong Chemical Materials Co. (Zhejiang, China).

2.2. Preparation of Halogen-contained Flame-retarded PP Spline
The flame retardants are weighed and mixed according to the required content of each sample, laid out on trays and dried in an electric blast oven at 80°C for 4 hours and then sealed. The polypropylene and other raw materials are weighed according to the required content of each sample and mixed with the dried additives in a high-speed mixer. The extrusion temperature is set at 185°C. The pellets are dried in an oven at 80°C for 8 hours and then injected into a standard strip using an injection moulding machine. The injection temperature is set at 180-190°C. The moulded strips are left to stand for 24 hours.

2.3. Preparation of Halogen-free Flame-retarded PP Spline
PNP1D is weighed and mixed according to the required content of each sample, laid out on trays and dried in an electric blast oven at 75°C for 4 hours and then sealed. The polypropylene and other raw materials are weighed according to the required content of each sample and mixed with the dried additives in a high-speed mixer. The extrusion temperature is set at 185°C. The pellets are dried in an oven at 80°C for 8 hours and then injected into a standard strip using an injection moulding machine. The injection temperature is set at 180-190°C. The moulded strips are left to stand for 24 hours.

2.4. Characterization
The tensile test of flame-retarded PP was carried out using a universal testing machine in accordance with GB/T1040-92 "Test Methods for Tensile Properties of Plastics". The impact test of materials was performed by a beam impact testing machine with GB/T1043-93 "Test method for impact strength of rigid plastic simple beams". Limiting oxygen index (LOI) values were measured using a horizontal and vertical tester with GB2406-93 "Oxygen Index Method of Test Methods for Combustion Properties of Plastics". Thermal gravimetric analysis (TGA) was carried out with a STA409C simultaneous analyzer. Measurement was conducted at a heating rate of 10°C·min⁻¹ from 50 to 650°C. Micromorphology was characterized with an Instron-1122 Environmental scanning electron microscope (SEM). The specimen face was notched impact sectioned with gold sprayed before observation. Vertical burning tests were conducted according to UL-94 standard. UL-94 vertical burning tests were performed by the horizontal and vertical tester with specimen dimensions of 125mm×13mm×3mm. Pre-treatment of spline is keeping spline at 23±2°C, RH50±5% for 48 hours. The rheological analysis is carried out by weighing and mixing the raw materials according to the recipe and then adding them to a preheated Harker kneader for melting and mixing. The machine is set to process at 180°C and the rotor speed is set at 60 rpm.

3. Results and Discussion

3.1. Effect of Halogen-contained Flame Retardant and SK-80 on Flame Retardancy and Mechanical Properties of PP
The flame retardant properties and mechanical properties of pure PP and DBDPE/Sb$_2$O$_3$/PP systems with different flame retardant ratios are compared in Table 1. As can be seen from Table 1, the ratio of DBDPE to Sb$_2$O$_3$ is 2.75:1, and the material can be made to meet UL-94V-0 flame retardant standards.
at a dosage of 30%. When the ratio of DBDPE to \( \text{Sb}_2\text{O}_3 \) is 2.5:1 or 3:1 neither V-0 can be achieved. It is also clear from Table 1 that the same specific gravity of DBDPE/\( \text{Sb}_2\text{O}_3 \) will not enable the material to achieve UL-94V-0 flame retardancy without the addition of SK-80.

**Table 1.** Flame Retardant and Mechanical Properties of DBDPE/\( \text{Sb}_2\text{O}_3 \)/PP Flame Retardant System

| Sample | PP | DBDPE | \( \text{Sb}_2\text{O}_3 \) | LOI | Tensile strength (MPa) | Impact strength (kJ·cm\(^{-2}\)) |
|--------|----|-------|-----------------|-----|-----------------------|-------------------------------|
| PPy0   | 100| —     | —               | 17.5| 21.98                 | 43.13                         |
| PPy1   | 56 | 24    | 8               | fail| —                     | —                             |
| PPy2   | 58 | 22    | 8               | pass| 31.6                  | 20.88                         |
| PPy3   | 60 | 20    | 8               | fail| —                     | —                             |
| PPy4   | 62 | 19    | 7               | fail| —                     | —                             |
| PPy    | 68 | 24    | 8               | fail| 20                    | 20.01                         |

**Table 2.** Effect of SK-80 on flame retardancy and mechanical properties of materials

| Samples | SK-80 | UL-94V-0 | LOI | Tensile strength (MPa) | Impact strength (kJ·cm\(^{-2}\)) |
|---------|-------|----------|-----|-----------------------|-------------------------------|
| PPy5    | 14    | pass     | 32.3| 19.43                 | 12.78                         |
| PPy2    | 12    | pass     | 31.9| 20.88                 | 13.13                         |
| PPy6    | 10    | pass     | 31.4| 20.27                 | 13.37                         |
| PPy7    | 8     | pass     | 30.5| 20.3                  | 11.62                         |
| PPy8    | 6     | pass     | 27.2| 19.91                 | 10.46                         |
| PPy9    | 4     | fail     | 20.6| 19.16                 | 9.57                          |

The amount of SK-80 was gradually reduced by fixing the content of the halogen-antimony system to determine the minimum amount of SK-80 that would enable the material to pass the UL-94V-0 flame retardant standard. Table 2 gives the effect of different SK-80 content on the flame retardancy and mechanical properties of the material. As can be seen from Table 2, SK-80 has a great influence on the flame retardant properties of the material. When its dosage is below 4%, the material cannot meet the UL-94V-0 flame retardant standard because it cannot effectively inhibit the molten droplets.

Figure 2 shows the effect of the amount of SK-80 on the oxygen index of the material according to Table 2. As shown in Figure 2, when the amount of SK-80 added is small, the increase in viscosity of the material melt is small and cannot effectively inhibit melt droplets, the oxygen index is low and the material does not reach UL-94V-0 grade. As the amount of SK-80 increases, it can be observed that the material no longer produces molten droplets when burning, which is shown in the graph as a rapid increase in the oxygen index. If the amount of SK-80 is increased further, the remaining SK-80 is equivalent to the inorganic filler present in the matrix and has less effect on the oxygen index.

![Figure 2](image-url)
Figure 3. Effect of SK-80 content on the notched impact strength and tensile strength of the material

On the other hand, SK-80, while acting as a melt drop suppressor, improves the mechanical properties of the material to a certain extent, especially the notched impact strength of the material. Figure 3 is a graphical representation of the effect of SK-80 content on the notched impact strength and tensile strength of the material according to Table 2. As can be seen from Figure 3, with the increase in the amount of SK-80, the notched impact strength of the material gradually increases, this is because SK-80 exists in the matrix in a nano-thick sheet structure when the material is impacted, it induces more silver patterns, part of the impact energy is partially absorbed by the silver patterns, at this time the material will not fracture, thus making the impact resistance and tensile properties of the material improved. However, if too much SK-80 is added, it will not be evenly distributed in the matrix and may agglomerate together in local areas. When the material is subjected to impact, the area where the agglomeration is located will produce stress concentration and cause the material to fracture, as shown in the graph, when the amount of SK-80 increases to a certain level, the mechanical properties of the material decreases, with the tensile properties decreasing more obviously.

Considering the flame retardant performance and mechanical properties, the dosage of SK-80 is better at 10%. The tensile strength and impact strength of the DBDPE/Sb₂O₃ flame retardant system with 10% SK-80 are 50% higher than those of the DBDPE/Sb₂O₃ flame retardant system without SK-80. In summary, PPY6 was determined to be the best formulation for the DBDPE/Sb₂O₃ flame retardant system with the content of PP:DBDPE:Sb₂O₃:SK-80=60:22:8:10.

Because DBDPE and HBCD are both brominated flame retardants with the same flame retardant mechanism, the addition of HBCD will not affect the use of Sb₂O₃ and SK-80, so fix the amount of Sb₂O₃ and SK-80 added as the amount in the formula PPY6, change the amount of HBCD and DBDPE added and the ratio to find the amount of flame retardant added that can make the material pass the V-0 flame retardant standard. Table 3 shows the flame retardant properties and mechanical properties of the DBDPE/HBCD/Sb₂O₃/PP system with different flame retardant ratios.

Table 3. Flame retardant and mechanical properties of DBDPE/HBCD/Sb₂O₃/PP flame retardant system

| Samples | DBDPE | HBCD | UL-94V-0 | LOI | Tensile strength (MPa) | Impact strength (kJ·cm⁻²) |
|---------|-------|------|----------|-----|------------------------|--------------------------|
| PPY14   | 12    | 8    | pass     | 28  | 15.51                  | 10.97                    |
| PPY15   | 10    | 10   | pass     | 33.2 | 15.36                  | 9.03                     |
| PPY16   | 8     | 12   | fail     | 24.6 | ---                    | ---                      |
| PPY17   | 9     | 9    | fail     | 25.5 | ---                    | ---                      |
| PPY18   | 9     | 8    | fail     | 23.5 | ---                    | ---                      |
As can be seen from Table 3, a dosage of 20 parts of DBDPE and HBCD at a ratio of 1:1 allows the material to pass the UL-94V-0 flame retardant standard. Recipe PPY14 can also pass UL-94V-0, but the oxygen index is too low. PPY15 was finally determined to be the best formulation of DBDPE/HBCD/Sb$_2$O$_3$ system for flame retardant modified PP with the following components: DBDPE(10%), HBCD(10%), Sb$_2$O$_3$(8%) and SK-80(10%). HBCD and DBDPE form a segmented flame retardant system, which effectively improves the flame retardant efficiency and reduces the amount of flame retardant. Compared with the DBDPE/Sb$_2$O$_3$ compounding system, the flame retardant dosage of the DBDPE/HBCD/Sb$_2$O$_3$ compounding system is reduced by 12.5%.

Comparing PPY6 and PPY15, although the amount of flame retardant in PPY15 is less than that of PPY6, the mechanical properties of the samples made from it are poorer, indicating that the compatibility of HBCD with PP is not as good as that of DBDPE with PP, and the stability of HBCD in PPY15 is not good and it is easy to decompose, so it is finally determined that the DBDPE/Sb$_2$O$_3$ system is more effective in flame retarding PP.

### 3.2. Analysis of Thermal Properties of Halogen-contained Flame Retardant PP

The flame retardant effect on the matrix depends on whether the thermal decomposition interval of the flame retardant matches the thermal decomposition interval of the polymer matrix. If the thermal stability of the flame retardant is much lower than that of the polymer, the flame retardant will be completely decomposed before the polymer decomposes, and the flame retardant will not work. If, on the other hand, the thermal stability of the flame retardant is much higher than that of the matrix, it may remain intact when it is required to act. Therefore, the thermal decomposition temperature range of the flame retardant should be relatively close to the thermal degradation temperature range of the substrate, and can generally cover the thermal degradation temperature region of the substrate to achieve the purpose of flame retardant. Figure 4 shows the thermal weight loss curves of pure PP and the flame retardant material made according to PPY6. The decomposition temperatures and residue amounts for pure PP and PPY6 are listed in Table 4 according to the Figure 4.

![Figure 4. Thermal properties curves for pure PP and PPY6](image)

**Table 4. Flame retardant and mechanical properties of DBDPE/HBCD/Sb$_2$O$_3$/PP flame retardant system**

| Sample | Thermal decomposition interval(°C) | Amount of residue(%) |
|--------|----------------------------------|---------------------|
| PPY0   | 298–410                          | 12.81               |
| PPY6   | 289–500                          | 7.88                |

As can be seen from the data in Figure 4 and Table 4, the initial decomposition temperature of pure PP is 298°C, while the initial decomposition temperature of PPY6 is 289°C. This indicates that when the PPY6 sample burns, the DBDPE has already started to decompose before the thermal degradation...
of the base material, preventing the burning from taking place. While pure PP ends its degradation at 410°C, the PPY6 sample does not stop degrading until 500°C. This indicates that there is still decomposition of the flame retardant until after the thermal degradation of the matrix is complete. The thermal decomposition temperature range of the flame retardant covers the thermal degradation temperature range of the matrix material very well. During the combustion of the matrix, there is a flame retardant that delays and prevents the combustion reaction by releasing hydrogen bromide gas to trap the reactive radicals and forming heat-absorbing insulation of the halide antimonide. The flame retardant plays a good role in the whole combustion process, and the flame retardant effect is ideal.

The residue at the end of combustion of the PPY6 sample is less than the residue of pure PP because during combustion the DBDPE in the PPY6 sample evaporates into the air and loses more mass than the same mass of PP.

3.3. Analysis of the Rheological Properties of Halogen-contained Flame Retardant PP

The addition of flame retardants to the base material affects the melt viscosity of the material, which in turn affects the rheological properties of the material. During processing, the change in torque of the blends reflects the change in their melt viscosity. Figure 5 shows the melt torque-time variation curves of pure PP and DBDPE/Sb$_2$O$_3$ compounded flame retardant PP made using a Harker rheometer. In Figure 5, PPY0 corresponds to the torque-time variation curve of pure PP, PPY corresponds to the torque-time variation curve of the material with only the bromine-antimony compounded flame retardant system without the addition of SK-80, and PPY6 corresponds to the torque-time variation curve of the material with the addition of SK-80 in addition to the bromine-antimony system. PPY6 corresponds to the torque-time variation curve for materials with SK-80 added in addition to the bromine-antimony system. The maximum torque and equilibrium torque for each curve are listed in Table 5.

![Figure 5. Torque-time variation curves of pure PP and bromine-antimony compounded flame retardant PP melts](image)

**Table 5. Melt torque change after bromine-antimony compounding of flame retardant PP**

| Sample     | PPY0 | PPY  | PPY6 |
|------------|------|------|------|
| Maximum torque(Nm) | 29.1 | 30.9 | 44   |
| Balancing torque(Nm)  | 3    | 4.3  | 6    |

It is easy to see from Figure 5 and Table 5 that the torque rises rapidly to a maximum value within one minute of the material being added to the Harker compactor, and then falls rapidly, gradually levelling off by about five minutes. The highest torque and equilibrium torque of pure bromine-
antimony compounded flame retardant PP increased slightly compared with pure PP, but the increase was not significant, which is because DBDPE is more compatible with PP and has little effect on its melt viscosity after blending with PP, Sb$_2$O$_3$ is an inorganic filler and has greater friction with the material during processing, making the melt viscosity of the material larger, but because its particle size is smaller and the amount added is not large, the melt viscosity of the material becomes larger. The maximum torque and balance torque of the material increase, but the change is not significant. Therefore, the DBDPE/Sb$_2$O$_3$ compounding system has little effect on the rheological properties of the material.

When SK-80 was added to the PP, it can be seen from Table 5 that both the maximum and equilibrium torque of the material increased significantly, with the maximum torque increasing by 51.2%, while the equilibrium torque doubled. This indicates that SK-80 significantly increased the melt viscosity of the material and reduced the fluidity of the material melt after entering the matrix through the melt co-mingled intercalation. This disrupts the processability of the material to some extent, but because SK-80 does not decompose when it burns, SK-80 can effectively inhibit the generation of molten droplets during combustion when the system burns, enhancing the flame retardant efficacy of the bromine-antimony compounded flame retardant system.

3.4. Analysis of the Distribution of Added Components in the Matrix for Halogenated Flame Retardant PP

Figure 6 shows SEM photographs of pure PP (a) and according to formulation PPY6 (b) and formulation PPY15 (c) with magnifications of 50x and 400x respectively. From the 400x SEM photographs, it can be seen that the additives are uniform respectively, where the largest particle is SK-80, which is distributed in the matrix in the form of flakes; followed by DBDPE, HBCD and antioxidant, and the smaller particle is Sb$_2$O$_3$. As the photos show, the additives are more uniformly dispersed and no agglomeration occurs, so the above experimental data can be seen as the performance of the whole material and not as a local effect.
3.5. Effect of Halogen-free Flame Retardant PNP1D on the Flame Retardancy and Mechanical Properties of PP

The flame retardant properties and mechanical properties of pure PP and PNP1D/PP systems with different flame retardant ratios are given in Table 6. According to Table 6, the dosage of PNP1D is the main factor affecting the flame retardant performance of the material, and the oxygen index of each sample with the dosage of PNP1D is shown in Fig. 7. As can be seen from Fig. 7, the minimum dosage of PNP1D to achieve the UL-94V-0 flame retardant standard is 23%, compared with the dosage of each component of the commonly used mixed intumescent flame retardants to achieve the UL-94V-0 flame retardant standard, which is: ammonium polyphosphate (24%) pentaerythritol (8%) melamine urethane (6%). The amount of PNP1D required to achieve UL-94V-0 is only 60% of that of the mixed intumescent flame retardant, and the flame retardant efficiency is greatly improved. As the amount of PNP1D increases, the material becomes more and more flame retardant and the oxygen index increases rapidly, almost linearly. This is because the more PNP1D is used, the easier it is to form an expanded carbon layer on the surface of the material during combustion. the increase in the amount of PNP1D is directly proportional to the speed of forming the carbon layer, which is also directly proportional to the flame retardant effect. According to Table 6, after adding flame retardants,
there is a large loss of mechanical properties of the material, mainly in the notched impact strength of the material. After the flame retardant modification, the notched impact strength of the material is only about 25% of that before the modification. For the five groups of samples that passed the UL-94V-0 flame retardant standard, considering their oxygen index and mechanical properties, PPW3 was determined to be the best formulation.

Table 6. Flame retardant properties and mechanical properties of PNP1D/PP systems with different flame retardant ratios

| Sample | PP | PNP1D | UL-94V-0 | LOI  | Tensile strength (MPa) | Impact strength (kJ·cm⁻²) |
|--------|----|-------|----------|------|------------------------|---------------------------|
| PPW0   | 100| —     | —        | 17.5 | 21.98                  | 43.13                     |
| PPW1   | 70 | 30    | pass     | 35.2 | 17.57                  | 7.25                      |
| PPW2   | 73 | 27    | pass     | 32.8 | 19.11                  | 9.03                      |
| PPW3   | 75 | 25    | pass     | 30.5 | 20.1                   | 10.48                     |
| PPW4   | 76 | 24    | pass     | 29.3 | 20.34                  | 11.05                     |
| PPW5   | 77 | 23    | pass     | 27.1 | 21.93                  | 11.37                     |
| PPS6   | 78 | 22    | fail     | 23.5 | —                      | —                         |

Figure 7. Effect of PNP1D dosage on the flame retardancy of the material

3.6. Analysis of the Thermal Properties of Halogen-Free Flame Retardant Materials

Figure 8 shows the thermal weight loss curves of pure PP and PNP1D flame retardant modified PP. The curves correspond to samples PPW1, PPW2 and PPW3, respectively, from which it can be seen that the thermal degradation temperature of pure PP ranges from 298 to 410°C, while the thermal decomposition temperature of PNP1D flame retardant modified PP is 265 to 470°C. The evaluation of the flame retardant's flame retardant performance mainly depends on whether its thermal decomposition temperature zone can effectively cover the thermal degradation temperature zone of the base material. The initial decomposition temperature of flame retardant modified PP is lower than the initial decomposition temperature of pure PP, so PNP1D starts to decompose before the thermal degradation of the base material to prevent combustion from taking place. When the matrix ends its thermal degradation (410°C), the decomposition of PNP1D is still going on up to 470°C. The thermal decomposition region of PNP1D covers the thermal degradation temperature range of the matrix material very well. Therefore, during the combustion process of the material, PNP1D has been playing a flame retardant role by forming a charcoal layer, heat insulation and oxygen barrier, and the flame retardant effect is ideal.

The flame retardant effect of PNP1D is mainly through the formation of an expanded porous carbon layer on the surface of the material under high heat, which prevents the gas from entering the gas phase and insulates and insulates the oxygen. In the TGA diagram, the amount of residue is the amount of carbon formation in the material, so the amount of residue in the TGA curve becomes an important means of characterising the flame retardant effect of PNP1D. The amount of residue after
combustion for pure PP and each flame retardant modified PP in the graph is listed in Table 7 according to Figure 8.

![Graph showing TGA curves](image)

**Figure 8.** Thermal properties curves for pure PP and PNP1D flame retardant modified PP

**Table 7.** Comparison of the thermal performance of pure PP and PNP1D flame retardant modified PP

| Sample   | PPW0 | PPW1 | PPW2 | PPW3 |
|----------|------|------|------|------|
| Residue(%) | 12.81 | 23.22 | 24.26 | 26.24 |
| LOI      | 17.5 | 30   | 32   | 35   |

As can be seen from Table 7, the addition of PNP1 causes a significant increase in the amount of residue left after the combustion of PP. This indicates that PNP1D forms a large amount of char layer on the surface of the material when it burns that can insulate and insulate against oxygen. After adding 25% PNP1D, the amount of char formation of the material almost doubles, and the amount of residue increases as the amount of PNP1D increases, when the amount of PNP1D is 25%, 27% and 30%, the burning residue is 23.22%, 24.26% and 26.24% respectively. At the same time, the oxygen index of the material increased significantly with the increase in the amount of combustion residue, which is a good indication that the formation and growth of the carbon layer has a significant improvement on the combustion performance of the material. The effect of the amount of PNP1D on the oxygen index is shown by the rapid increase in oxygen index with the increase in the amount of PNP1D.

3.7. **Analysis of the Rheological Properties of Halogen-Free Flame Retardant Materials**

The addition of flame retardant to the base material changes its rheological properties. Figure 9 shows the torque-time variation curves for pure PP and PP with 30% and 25% PNP1D addition respectively. The highest torque and equilibrium torque for each curve are shown in Table 8. It can be seen from Figure 9 and Table 8 that the maximum torque and equilibrium torque of the material increased after the addition of PNP1D to the matrix, and that the equilibrium torque of the flame retardant modified PP with 30% PNP1D was 77% higher than the equilibrium torque of pure PP at the end of the dense refining. This indicates that PNP1D has greater friction with the matrix material during processing, which makes the melt viscosity of the material increase. PNP1D has a greater impact on the rheological properties of the material, making the processing performance of the material decrease.
Figure 9. Torque-time variation curves of pure PP and PNP1D flame-retardant modified PP

Table 8. Melt torque change in PNP1D flame retardant modified PP

| Sample     | PP     | PPW3   | PPW1   |
|------------|--------|--------|--------|
| Maximum torque (Nm) | 29.1   | 32.6   | 39.5   |
| Balancing torque (Nm) | 3      | 5      | 5.3    |

3.8. Analysis of the Rheological Properties of Halogen-free Flame Retardant Materials

Figure 10 shows SEM photographs of the halogen-free flame retardant modified PP according to formulation PPW8 with magnifications of 50x and 600x respectively. As can be seen from the 600x SEM photographs, the additives are homogeneous separately, where the larger particles are the antioxidants and the smaller particles are PNP1D. As the additives are more evenly dispersed and no agglomeration occurs, the above experimental data can be seen as the performance of the whole material and not as a local effect.

Figure 10. Distribution of added components in the matrix for halogen-free flame retardant PP

4. Conclusions

The DBDPE/Sb$_2$O$_3$ compounded flame retardant system and the DBDPE/HBCD/Sb$_2$O$_3$ compounded flame retardant system flame retardant PP samples were determined by analysing the experimental results. The thermal decomposition temperature range of the DBDPE/Sb$_2$O$_3$ compounding system completely covers the thermal degradation range of pure PP, and the flame retardant can play a good role in the combustion process. The DBDPE/Sb$_2$O$_3$ compounding system has a slight influence on the rheological properties of the material. SK-80 significantly increases the melt viscosity of the material and has a great influence on the rheological properties of the material. The tensile strength and impact strength of the DBDPE/Sb$_2$O$_3$ flame retardant system with 10% SK-80 increased by 50% compared to the DBDPE/Sb$_2$O$_3$ flame retardant system without SK-80. Halogen-free flame retardant PP materials were prepared using the one-component intumescent flame retardant PNP1D. The ultimate oxygen index of PNP1D flame retardant PP was nearly doubled compared to that of pure PP and passed the
UL-94V-0 flame retardant standard. The thermal decomposition temperature range of the flame retardant modified PP completely covers the thermal degradation temperature range of pure PP, and PNP1D forms a large amount of carbon on the surface of the material when it burns, and the amount of carbon formation increases by nearly one time when 25% is added, making the flame retardant effect ideal. PNP1D has a major impact on the rheological properties of the material, increasing the melt viscosity and making the processing of the material difficult.

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