Effects of Dimethyl Methylphosphonate, Aluminum Hydroxide and Ammonium Polyphosphate on the Flame Retardancy and Thermal Properties of Unsaturated Polyester Resin

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Abstract. The flame-retardant unsaturated polyester resin with dimethyl methylphosphonate (DMMP), aluminum hydroxide (ATH) and ammonium polyphosphate (APP) were prepared and found to exhibit a high flame-retardant efficiency and low cost. The different dosages of flame retardant effect on the flame retardant were evaluated based on limiting oxygen index (LOI) measurements, vertical burning test (UL94), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). A LOI value of 29.8% and a UL-94 vertical burning V-0 rating was achieved for UPR with 10phr DMMP, 15phr ATH and 9phr APP. In the presence of DMMP, ATH and APP, the dense char structure were produced in the combustion process of UPR.

1. Introduction

The most commonly used thermosetting resins unsaturated polyester resins (UPR) are prepared by the reaction of aliphatic diols with unsaturated and saturated diacids [1]. Due to low cost, electrical insulation, easy processing, and mechanical properties, the products of UPR are widely used in our daily life. However, typical UPR are highly flammable, and produce high smoke during combustion, will damage the human body and environment. These issues have promoted the research on the flame retardancy of UPR [2]. Meanwhile, environmentally friendly retardant UPR is the optimal choice.

Recently, new retardants are being used as fire resistance agents. In particular, halogen-free flame retardants, such as layered double hydroxide (LDH), aluminum hydroxide (ATH), ammonium polyphosphate (APP), expanded graphite, montmorillonite, and organophosphorus compounds, have garnered attention due to easy accessibility and simple synthetic schemes [3, 4].

ATH imposes excellent smoke suppression on UPR in the combustion process. However, The flame-retardant efficiency of ATH is wick and usually requires higher loading to achieve an excellent flame-retardant effect [5]. APP is an effective intumescent flame retardant. Its efficiency is usually attributed to increased char formation by condensed-phase reaction[6]. ATH and APP are commonly incorporated into UPR as a single effective flame retardant. Dimethyl methylphosphonate (DMMP) is
one of the most efficient halogen-free flame retardant [7]. However, due to it is a liquid flame retardant, it will migrate to the substrate surface when added in large dosages. In this work, 10phr of DMMP (where phr is parts per 100g of UPR) and different dosages of APP and ATH were mixed into the UPR. In this paper, the flame-retardant behaviour of UPR containing DMMP, ATH and APP were characterized. The purpose of this work was to maximize the flame retardancy of UPR with the lowest additive amount and optimal proportion.

2. Experimental

2.1. Materials

Unsaturated polyester resin was purchased from Changzhou Feiteng Chemical Co. Ltd. DMMP and ATH (particle size of 1 μm) was supplied by Aladdin Industrial Corporation (Shanghai, China). APP with the polymerization degree of 1,500 and the particle size of 15μm, was obtained from Adamas Reagent Co. Ltd (Shanghai, China). Benzyol peroxide (BPO) as the catalyst for curing reaction was produced by Shanghai Linfeng Chemical Reagent Co. Ltd (Shanghai, China).

2.2. Preparation of ATH/DMMP/UPR and ATH/APP/DMMP/UPR samples

The samples were prepared by mixing UPR with 10phrDMMP and different dosages of APP and ATH. Table 1 lists the formulations of UPR and flame retardant UPR composites. First, 100phrUPR and 10phrDMMP were poured into a beaker and stirred for 20min. Next, different dosages of ATH and APP were added into the mixture, the mixture was stirred for 40min. Then, 2phrBPO was added and used to initiate the curing reaction, which was followed by a further stirred. Finally, all the samples were poured into the mold and cured at 80℃ for 2h, followed by cured at 110℃ for 3h.

Table 1. The formulation of UPR and flame-retardant UPR composites.

| Samples                        | UPR (phr) | BPO (phr) | DMMP (phr) | ATH (phr) | APP (phr) | Retardant (wt%) | LOI (%) | UL-94 |
|--------------------------------|-----------|-----------|------------|-----------|-----------|-----------------|---------|-------|
| UPR                            | 98        | 2         | 0          | 0         | 0         | 19.8            |         | No rating |
| 5phrATH/10phrDMMP/UPR          | 98        | 2         | 10         | 5         | 0         | 13.0            | 24.8    | V-2    |
| 10phrATH/10phrDMMP/UPR         | 98        | 2         | 10         | 10        | 0         | 16.7            | 24.9    | V-2    |
| 15phrATH/10phrDMMP/UPR         | 98        | 2         | 10         | 15        | 0         | 20.0            | 25.5    | V-1    |
| 20phrATH/10phrDMMP/UPR         | 98        | 2         | 10         | 20        | 0         | 23.1            | 25.6    | V-1    |
| 25phrATH/10phrDMMP/UPR         | 98        | 2         | 10         | 25        | 0         | 25.9            | 25.8    | V-1    |
| 3phrAPP/15phrATH/10phrDMMP/UPR | 98        | 2         | 10         | 15        | 3         | 21.9            | 26.7    | V-1    |
| 6phrAPP/15phrATH/10phrDMMP/UPR | 98        | 2         | 10         | 15        | 6         | 23.7            | 27.8    | V-1    |
| 9phrAPP/15phrATH/10phrDMMP/UPR | 98        | 2         | 10         | 15        | 9         | 25.4            | 29.8    | V-0    |
| 12phrAPP/15phrATH/10phrDMMP/UPR| 98        | 2         | 10         | 15        | 12        | 27.0            | 30.1    | V-0    |
| 15phrAPP/15phrATH/10phrDMMP/UPR| 98        | 2         | 10         | 15        | 15        | 28.6            | 27.5    | V-0    |

2.3. Measurements and characterization

The limiting oxygen index (LOI) were measured according to ISO 4589-2 using a HC-2 oxygen index instrument (HC-2 type, Jiangning Analytical Instruments Co., Ltd., China), and the dimensions were 120×10×4mm. The LU-94 were performed on the vertical burning instrument (CFZ-2 type, China Jiangning Analytical Instruments Co., Ltd.), and the size of specimens was 130×13×3mm on the basis of ISO 1210. Thermogravimetric analysis (TGA) was tested using an SDT Q600 thermal analyzer at a heating rate of 10℃ min⁻¹ under N₂ atmosphere at temperatures ranging from 50℃ to 800℃. The micromorphology of residual char was obtained using a Hitachi s4800 scanning electron microscope by low-temperature fracturing under high vacuum and voltage of 20kV.
3. Results and discussion

3.1. Flame retardancy
LOI and UL-94 tests are widely used to assess the flammability of polymer products. The LOI and UL-94 test results for the samples are shown in Table 1. As shown in Figure 1, the LOI value of ATH/DMMP composites increased from 24.8% to 25.8%. When the amount of ATH was added to 15phr, the increase of ATH did not affect the LOI of the composites obviously. The LOI of the other five APP/ATH/DMMP composites increased from 26.7% to 30.1%. It was verified that the combination of APP/ATH/DMMP could apparently improve the LOI of UPR matrix.

As could be seen in Table 1, the 5phrATH/10phrDMMP/UPR reached the V-2 rating. The UL-94 results for 15phrATH/10phrDMMP/UPR had reached V-1 rating when the amount of ATH was increased to 15phr. For the other groups, the UL-94 of 9phrAPP/15phrATH/10phrDMMP/UPR achieved V-0 rating. The results showed that APP/ATH/DMMP/UPR system had good synergistic effect.

3.2. Thermal properties
Thermogravimetric analysis was used to evaluate the thermal decomposition of the polymer under nitrogen atmosphere. Fig. 1 showed the TGA and DTG curves for pure UPR and its composites. In addition, the curves of 15phrATH/DMMP/UPR and various APP/ATH/DMMP/UPR composites were shown in Fig. 2 with detailed TGA data shown in Table 2 and 3. The initial degradation temperature (T_{0.1}) is defined as the temperature at which the weight loss reaches 10%. The temperature at which the maximum rate of weight loss (T_{max}) of the sample was obtained.

The neat UPR showed two main stages of nitrogen degradation. The neat UPR began to degrade above 200°C. The first phase of weight loss was in the temperature range of 210-320°C, due to the water elimination reaction. After pyrolysis, another stage with a rapid weight loss temperature was in the range of 320-500°C. The weight of the carbon residue above 600°C was relatively small.

![Figure 1. TG (a) and DTG (b) curves of ATH/DMMP/UPR composites under nitrogen atmosphere.](image-url)
3.3. Thermal properties of ATH/DMMP/UPR composites

Fig. 1 shows the TG and DTG curves of ATH/DMMP/UPR composites in a nitrogen atmosphere. Compared to the neat UPR, the degradation temperatures of other five groups were shifted to an earlier time. Therefore, $T_{0.1}$ values had different degrees of decline, as shown in Table 2. As the temperature increased, a faster weight loss was obtained between 200 and 450°C. In this stage, the maximum mass loss rate of pure UPR exceeded other groups, and the lowest mass loss was found in 15phrATH/10phrDMMP group, indicated that the UPR composite decomposed slowly with ATH/DMMP. In addition, the char yield of UPR with ATH/DMMP at 800°C was 17.8 wt%, much higher than 5.5 wt% of pure UPR.

![TG and DTG curves of APP/ATH/DMMP/UPR composites](image)

**Figure 2.** TG (a) and DTG (b) curves of APP/ATH/DMMP/UPR composites under nitrogen atmosphere.

| Samples               | $T_{0.1}$ ($^{\circ}$C) | $T_{\text{max}}$ ($^{\circ}$C) | Char (500°C, wt%) | Char (800°C, wt%) |
|-----------------------|--------------------------|--------------------------------|-------------------|-------------------|
| UPR                   | N$_2$ 306, N$_2$ 409     | N$_2$ 409                      | 6.4               | 5.5               |
| 5phrATH/10phrDMMP     | N$_2$ 180, N$_2$ 412     | N$_2$ 412                      | 13.6              | 12.8              |
| 10phrATH/10phrDMMP    | N$_2$ 217, N$_2$ 409     | N$_2$ 409                      | 15.8              | 14.5              |
| 15phrATH/10phrDMMP    | N$_2$ 228, N$_2$ 408     | N$_2$ 408                      | 19.0              | 17.8              |
| 20phrATH/10phrDMMP    | N$_2$ 192, N$_2$ 406     | N$_2$ 406                      | 12.0              | 10.2              |
| 25phrATH/10phrDMMP    | N$_2$ 239, N$_2$ 405     | N$_2$ 405                      | 12.0              | 10.3              |

3.4. Thermal properties of APP/ATH/DMMP/UPR composites

The TG and DTG curves of APP/ATH/DMMP/UPR composites under a nitrogen atmosphere were presented in Fig. 2. The peak heat release rate of 9phrAPP/15phrATH/10phrDMMP/UPR compared to the other groups, was shifted to a lower temperature. Due to the initial pyrolysis of APP in the range of 350-400°C. In addition, the value of $T_{0.1}$ of each group was also reduced to 226-245°C, respectively, far below the value of 15phrATH/10phrDMMP/UPR. Meanwhile, the 9phrAPP/15phrATH/10phrDMMP/UPR samples had 22.0% carbon residue at 800°C, which was higher than 17.8% of 15phrATH/10phrDMMP/UPR.
Table 3. TGA data obtained for APP/ATH/DMMP/UPR composites.

| Samples                        | $T_{0.1}$ (°C.) | $T_{\text{max}}$ (°C.) | Char (500°C, wt%) | Char (800°C, wt%) |
|-------------------------------|-----------------|------------------------|-------------------|-------------------|
|                               | $N_2$           | $N_2$                  | $N_2$             | $N_2$             |
| 15phrATH/10phrDMMP            | 228             | 408                    | 19.0              | 17.8              |
| 15phrATH/3phrAPP/10phrDMMP    | 233             | 411                    | 19.8              | 18.6              |
| 15phrATH/6phrAPP/10phrDMMP    | 236             | 408                    | 22.9              | 21.2              |
| 15phrATH/9phrAPP/10phrDMMP    | 226             | 396                    | 26.1              | 25.9              |
| 15phrATH/12phrAPP/10phrDMMP   | 243             | 346                    | 28.4              | 26.0              |
| 15phrATH/15phrAPP/10phrDMMP   | 245             | 373                    | 30.3              | 27.7              |

3.5. Morphology of residual char

It is well-known that high quality char, as a barrier of protection, isolates oxygen, prevents the transfer of heat and cuts off the spread of flammable gases [8]. The morphology of the carbon was observed and the flame retardancy was evaluated by SEM as shown in Fig. 3.

Fig. 3. (a) shows a micrograph of the formation char for the pure UPR. A flaky carbon layer structure was observed on the surface. In addition, UPR surface could also be observed numerous random distribution of holes. Fig. 3. (b) depicts the residual carbon of 15phrATH/10phrDMMP/UPR. Compared with the carbon layer structure left by neat UPR, the neat ATH and DMMP made the carbon layer structure more compact, which could effectively prevent the diffusion of decomposition products during combustion. It may be due to the phosphoric acid produced by DMMP decomposition, resulting in the formation of aluminum-phosphate due to the reaction with ATH. Aluminum dihydrogen phosphate had strong chemical binding, impact and spalling resistance, high temperature resistance, prompting the coke residue became dense and compact. Fig. 3 (c) showed the residual charcoal of 9phrAPP/15phrATH/10phrDMMP/UPR. The SEM showed that at a certain temperature (usually about 350-400°C) burst resulted in rapid decomposition of APP. Residual char exhibited a pronounced swollen structure when 9phrAPP was mixed with 15phrATH/10phrDMMP/UPR composites in which the product resulting from DMMP cleavage bound well to APP. They were all effective in promoting the formation of more scaffolds and inducible debris.

![Figure 3](image_url)

**Figure 3.** SEM images of the char residual: (a) UPR, (b) 15phrATH/10phrDMMP/UPR, (c) 9phrAPP/15phrATH/10phrDMMP/UPR.

4. Conclusion

In this work, two flame retardant systems: ATH/DMMP and APP/ATH/DMMP were added to UPR. The LOI value of the 15phrATH/10phrDMMP composites could reach 25.5% and V-1 rating. Ultimately, while the 9phrAPP/15phrATH/10phrDMMP mixed into UPR, the LOI value increased to 29.8% and the result of UL-94 reached a V-0 rating. The system significantly reduced the rate of heat release and mass loss, the thermal properties had a good impact.
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