Environmentally Friendly Flame Retardant Systems for Unsaturated Polyester Resin

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Abstract. Melamine cyanurate (MCA) and triphenyl phosphate (TPP) were added in unsaturated polyester resin (UPR) and the combustion behaviour were investigated. Flame retardant and thermal stability were investigated through limiting oxygen index test (LOI), vertical burning test (UL-94) and thermogravimetric analysis (TGA). The scanning electron microscopy (SEM) and TGA analyses showed that the char yield was increased by the introduction of MCA and TPP system. Therefore, a profound flame retardant effect was obtained as MCA and TPP were added to UPR.

1. Introduction
Unsaturated polyester resin (UPR) is the most significant thermoset resin which has excellent mechanical performance, low density, good corrosion resistance, low cost and high strength-to-weight ratio [1, 2]. So it is extensively applied as coating to increase the corrosion resistance of steel components, chemical equipment, and automotive production. But, poor flame resistance of UPR hinders the practical application.

Phosphorus-containing flame retardants modified polymer is considered to be more environmentally friendly and have received outstanding attention [3, 4]. Among the phosphorus-containing flame retardants, triphenyl phosphate (TPP), as a novel kind of phosphorous-based flame retardants, and have attracted more attention because of the high reactivity and strong char forming effect in condensed phase [5]. Some studies indicated that a significant development of flame-retardant efficiency was observed when phosphorus and nitrogen elements existed simultaneously in the cure system of UPR [6, 7]. Thus, in this work, melamine cyanurate (MCA) and TPP was considered as a better flame retardant to UPR as an environmentally friendly flame retardant synergistic system [8]. The focus of this study lies on the influence of MCA and TPP on the pyrolysis analysis and the combustion properties of thermosets.

2. Experimental

2.1. Raw materials
Unsaturated polyester resin (commercial grade, type 191#) (UPR) was supplied by Changzhou Feiteng Chemical Co., Ltd. (Jiangsu, China). Triphenyl phosphate (TPP) was purchased from Aladdin...
Industrial Corporation (Shanghai, China). Melamine cyanurate (MCA) of chemical grade was supplied by Sichuan Fine Chemical Research and Design Institute (Sichuan, China). Benzoyl peroxide (BPO) as the catalyst for curing reaction was obtained from Linfeng Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used directly without further purification.

2.2. Sample preparation
TPP was heated to melt in the thermostatic water bath at 60 °C, and then UPR and MCA were added successively into the melting TPP. The mixture was stirred for one hour at room temperature. During stirring, the initiator BPO was dissolved into the mixture. The homogeneous mixture was poured into molds, pre-cured at 80 °C for 2 h, and post-cured at 110 °C for 3 h.

2.3. Measurements and characterization

2.3.1. Limiting oxygen index (LOI). The LOI of the samples was determined according the standard ISO 4589-2 at room temperature using an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., Ltd. China). The dimensions of the specimens were 120 mm×10 mm×4 mm. They were ignited using top surface ignition method.

2.3.2. Vertical burning test (UL-94). The UL-94 was measured on a vertical burning instrument (CFZ-2-type, Jiangning Analysis Instrument Company, China). According to the ISO 1210, the dimensions of the specimens used for the test were 130 mm×13 mm×3 mm.

2.3.3. Thermogravimetric analysis (TGA). Thermal stability of the samples were investigated by a thermal analyzer (Q600TGA, TA Instruments, USA). In each test, about 8 mg sample was weighed into an alumina crucible.

2.3.4. Morphology observation (SEM). The residual char after combustion was observed with a scanning electron microscopy (Hitachi S-4800N, Japan) by low temperature fracturing under high vacuum with a voltage of 20 kV.

3. Results and discussion

3.1. Combustion performance
The flame retardancy of the UPR composites were measured by LOI and UL-94 vertical burning tests. The LOI values and UL-94 tests were conducted and the relative data were shown in Table 1. UPR had a LOI value of 18.9% and shown no vertical rating in UL-94 test. The LOI value of the Sample 2 was only 24.4%, whereas the Sample 3 reached 25% with TPP content of 30 wt%, which indicated TPP was more effective in promoting flame retardance than MCA did, however, only UL-94 V-2 rating could be achieved. The higher LOI value was obtained with the Sample 4. LOI value increased drastically from 18.9% to 27.5% when 15 wt% MCA and 15 wt% TPP was jointly incorporated into UPR. The experimental resulted of UL-94 shown that the Sample 4 achieved a V-0 rating.

Table 1. Detailed data obtained from LOI and UL-94 measurements of UPR and its composites.

| Samples | Components (%) | Flame retardancy |   |   |
|---------|----------------|------------------|---|---|
|         | UPR  | MCA | TPP | LOI (%) | UL-94 | Ranking | Dripping |
| 1       | 100  |     |     | 18.9   | Fail  | No      |          |
| 2       | 70   | 30  |     | 24.4   | V-2   | No      |          |
| 3       | 70   |     | 30  | 25     | V-2   | No      |          |
| 4       | 70   | 15  | 15  | 27.5   | V-0   | No      |          |
3.2. Thermal degradation behavior

The thermal stability is very significant when a material is added with flame retardant, which mainly concerns the release of decomposition products and the formation of a char [9]. Fig. 1 shows the TG and DTG curves of UPR and its composites. The relative data are given in Table 2.

The thermal oxidative degradation process of UPR had three steps. The first step was in the temperature range of 250–300 °C corresponding to a loss of water by dehydration. The main degradation step ranging from 300 to 430 °C resulted from the chain scission of polystyrene and polyester fragments corresponding to a strong DTG peak at 394 °C. This led to the formation of a primary carbonaceous char, which degraded at high temperature around 540 °C of the third step.

Table 2. TGA data of UPR and its composites in both air and nitrogen atmosphere.

| Samples | T_{0.1} (°C) | T_{max} (°C) | Char (500 °C, wt %) | Char (800 °C, wt %) |
|---------|--------------|--------------|---------------------|---------------------|
|         | N₂           | Air          | N₂                  | Air                  |
| 1       | 306          | 309          | 410                 | 409                 | 6.3                   | 18.4                   | 5.4 | 1.7 |
| 2       | 325          | 323          | 390                 | 388                 | 10.5                  | 21.1                   | 8.8 | 0.5 |
| 3       | 254          | 252          | 414                 | 407                 | 9.1                   | 16.2                   | 8.7 | 1.5 |
| 4       | 255          | 251          | 375                 | 370                 | 11.5                  | 25.7                   | 8.6 | 2.4 |

Figure 1. TGA and DTG curves of the pure UPR and its composites in nitrogen atmosphere and air atmosphere.

Fig. 1(a) and (b) also shows TG and DTG curves of the UPR composites in air. The thermal oxidative degradation processes of the UPR composites had the similar three stages as the pure UPR. Before 317 °C, flame retardant coating underwent slow weight loss, which was due to the evaporation of polyphosphoric acid during combustion of TPP. The medium-term stage was the key region where
the pyrolysis decomposition occurred in the temperature range of 295–500 °C. From DTG curve, the temperature of maximum weight loss rate (T_{\text{max}}) of MCA indicated that it decomposed abundant acid source which could effectively form the char of the carbonization agent in MCA and TPP system.

When the samples were evaluated in nitrogen, their degradation behaviors displayed differently from those in air. It was obvious that replacing air by a non-oxidative atmosphere affected the thermal degradation behaviors of samples, as Fig. 1(c) and (d) illustrated. T_{\text{max}} of the Sample 3 was slightly higher than that of the Sample 2 and the Sample 4. It was found that the char residue at 500 °C for the Sample 2, the Sample 3 and the Sample 4 were 10 wt% 9 wt% and 11 wt%, respectively, slightly higher than the values of 5.4 wt% for pure UPR. The char yielded of the Sample 4 under nitrogen and air atmosphere were 8.6 and 2.4 wt%, respectively, and this demonstrated that the presence of oxygen had an accelerating effect on acid-catalyzed cross-linking actions in the polymer degradation. Both the LOI and UL-94 results indicated that the Sample 4 exhibited good flame-retardant effect on UPR.

3.3. Morphology of residual char

The morphology and structure of char residue observed by scanning electron microscopy (SEM) are shown in Fig. 2. As can be seen from Fig. 2(a) for UPR, loose and flaky char could be observed at the outer surface of UPR, with lots of large holes distributed on the surface. In comparison, char residue of the Sample 2 and 3 showed relatively compact but open porous structure (Fig. 2b, c). Such open porous structure presented disadvantage in isolating the gas and heat. Furthermore, char residue of the Sample 4 composite showed greatly different morphology in contrast to above UPR systems. One could see a honeycomb sealed structures with thick and dense char layer (Fig. 2d).

Figure 2. The morphology of the char layers of the pure UPR and its composites
4. Conclusion
The combination of MCA with TPP presented an evident synergistic effect for flame retardant UPR composites. The incorporation of 15 wt% MCA and 28.8 wt% TPP improved the properties of UPR, the composites could reach the LOI value of 27.5% and pass the UL-94 V-0 rating. TGA analysis indicated that the enhancement in synergistic effect should be related to the high char residual weight ratio. Meanwhile, SEM images of char residue results showed a honeycomb structure with compact surface.

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