Effect of a novel intumescent flame retardant on the flame retardancy of unsaturated polyester resins

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Abstract. Modified montmorillonite containing phytic acid (PA-MMT) has been prepared by acid treatment. PA-MMT and Melamine Pyrophosphate (MPP) were introduced into unsaturated polyester resins (UPR) and the combustion behaviour were investigated by limiting oxygen index (LOI) measurements, vertical burning test (UL94), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM). Besides, the flame retardant mechanism of PA-MMT/MPP was proposed according to the results of combustion behavior and char analysis.

1. Introduction

Unsaturated polyester resin (UPR) is one of the most important thermoset resin which is widely applied in many fields due to its excellent mechanical performance, processing advantages, good corrosion resistance, low cost and high strength-to-weight ratio. However, poor flame resistance of UPR impedes their wider utilization [1]. Intumescent flame retardants (IFR) have attracted more and more attention because of highly flame retardant effective. Melamine Pyrophosphate (MPP), as an environment friendly and nitrogen-based flame retardant, including acid source, charring agent and blowing agent. When being exposed burning, MPP can generate a swollen multicellular charred layer, as a physical barrier to prevents heat transmit and cut off combustible gas [2]. Montmorillonite (MMT) was extensively used to combine with other flame retardant because it can improve the dispersion of other flame retardant in the polymers matrix [3]. Besides, some studies indicated that a significant synergistic effect of flame-retardany was observed when MMT and IFR incorporated simultaneously in polymer. Thus, in this work, modified MMT with PA has been proposed, and then the PA-MMT was incorporated with MPP as an environmentally friendly flame retardant synergistic system to improve the thermal stability and flame-retardant properties of UPR [4].

2. Experimental

2.1. Raw materials

Unsaturated polyester resin (commercial grade, type 191#) was provided by Changzhou Feiteng Chemical Co., Ltd. (Jiangsu, China). Melamine Pyrophosphate (MPP) was purchased from Sichuan Fine Chemical Research and Design Institute (Sichuan, China). Phytic acid (PA) was purchased from

Aladdin Industrial Corporation (Shanghai, China). Montmorillonite (MMT) was provided by Klamar Chemical Reagent Co. Ltd., Co. Ltd (Shanghai, China).Benzoyl peroxide (BPO) was obtained from Linfeng Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Sample preparation

A total of 10 g of MMT was dispersed into 180 ml of deionized water and stirred for 1 h at room temperature, and 20 ml of a PA solution (70 wt%) was added and stirred for another 1 h. The products were then collected by vacuum filtration and dried in an oven at 80 ^{o}C for 12 h. The product was smashed via a universal pulverizer and PA-MMT was obtained.

The UPR composites samples were prepared by different dosages of MPP and PA-MMT. Table 1 lists the formulations of UPR and flame retardant UPR composites. MPP and PA-MMT were incorporated into UPR and stirred for 1 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 ^{o}C for 2 h, and post-cured at 110 ^{o}C for 3 h.

Table 1. The formulation of UPR composites.

Composition	Samples	UPR	IFR	IFRs	MMT	PA-MMT
K1	UPR	100	-	-	-	-
K2	UPR/MPP	80	20	-	-	-
K3	UPR/MPP/MMT	80	-	18.5	1.5	-
K4	UPR/MPP/PA-MMT	80	-	18.5	-	1.5

2.3. Measurements and characterization

The limiting oxygen index (LOI) test was determined according the standard ISO 4589-2 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. The vertical burning test (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. Thermal stability of the samples was investigated by a thermal analyzer (Q600, TA Instruments, and USA). The residual char after combustion was observed with a scanning electron microscopy (Hitachi TM3000, Japan) under high vacuum with a voltage of 20 kV.

3. Results and discussion

3.1. SEM images of MMT and PA-MMT

The surface morphologies of the particles of MMT and PA-MMT are shown in Fig.1. The particles sizes of MMT was uneven, and the average size was bigger than that of PA-MMT. The average chip thickness of MMT is less than 25 nm, but the layer spacing between the chip is small, forming a larger particles. While PA incorporated into MMT, the layer spacing increase and uneasy to aggregate together. Therefore, the dispersion of PA-MMT in UPR matrix is better than MMT, contribute to increase the flame retardant of UPR composites.

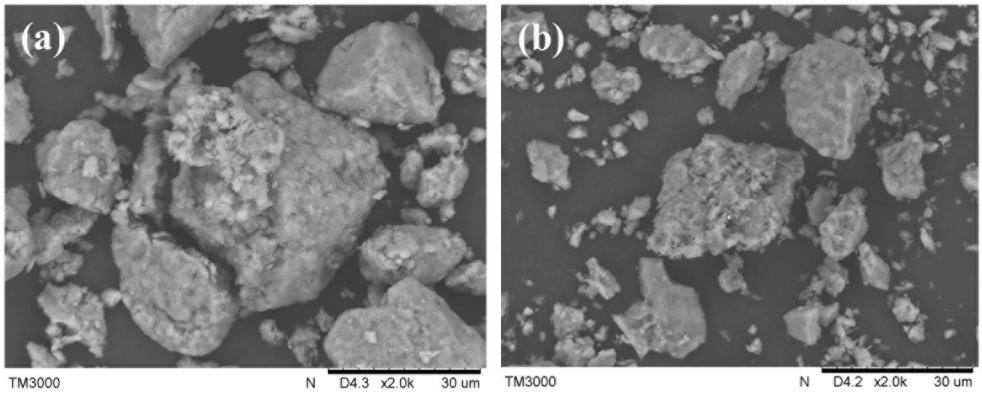

Fig. 1 The morphology of the char layers of the pure UPR and its composites

3.2. Combustion performance

The LOI values and UL-94 testing results of the UPR composites are listed in Table 2. Neat UPR is highly combustibility that which presents no rating in the UL-94 test and the LOI value is only 19.5%. With 20 wt% MPP was incorporated into UPR, the LOI value of K2 was only 25.3%, whereas the K3 reached 27.1% with 1.5wt% MPP was replaced by the same dosage of MMT. It was largely ascribed to the existence of MMT improve the distribution of MPP in the UPR matrix. From K3 and K4, it was interesting to note that the substitution of MMT with equal PA-MMT resulted in an obviously increase in the LOI value, from 27.1% to 28.8%. This result indicated that the flame retardant of PA-MMT is better than MMT.

Table 2. Detailed data obtained from LOI and UL-94 measurements of UPR and its composites.

Composition	Samples		UL-94	
		LOI (%)	Ranking	Dripping
K1	UPR	19.5	NR	No
K2	UPR/MPP	25.3	V-1	No
K3	UPR/MPP/MMT	27.1	V-1	No
K4	UPR/MPP/PA-MMT	28.8	V-0	No

3.3. Thermal degradation behavior

The thermal stability is very significant when a material is added with flame retardant, which mainly assessed by the thermogravimetic analysis (TGA) under nitrogen atmosphere. The TGA and derivative thermo gravimetric (DTG) curves are presented in Fig.2, and detailed data are given in Table 3. The UPR and its composites display two degradation steps in nitrogen atmosphere. The first step is in the temperature range of 210-280oC ascribe to the loss of water by dehydration. In this step, little mass loss was observed. The temperature at 10wt% weight loss ($T_{0.1}$) of K1, K2, K3 and K4 were 306 ^{o}C, 261 ^{o}C, 266 ^{o}C and 269 ^{o}C. This result corresponding to MPP/MMT and MPP/PA-MMT pyrolysis in a low temperature. With the temperature increase, the thermal oxidative degradation of UPR and its composites entering the second stages. This stage mainly range from 280-450 ^{o}C, and an obvious peak founded on DTG curves due to the lager mass loss in this stages.

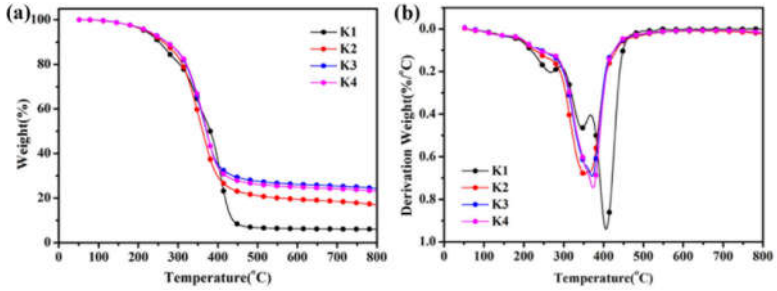

Fig. 2 (a) TG and (b) DTG curves of UPR and its composites in nitrogen atmosphere

The temperature of the maximum weight loss rate (T_{max}) of K1, K2, K3 and K4 were 409 ºC, 354 ºC, 375 ºC and 372 ºC. This result ascribe to the formation of intermediate phosphorus species from MPP could react with UPR molecules to form residues. Besides, Tmax of K3 and K4 are higher than K2 can account for the thermal stability of MMT and PA-MMT are better than MPP. It is found that the char residue of K2 at 800 ºC is 16.9%, higher than the values of 5.4% for neat UPR. The char residue increased from 16.9% to 24.1% when the MMT combine with MPP. However, while MMT was replaced by the same dosage of IPA-MMT, the char residue of K4 was reduce to 23.1%, ascribe the PA-MMT produces phosphoric acid in the process of decomposition, which promote carbon layer further decomposition.

Table 3. TGA data of UPR and its composites in nitrogen atmosphere.

Composition	$T_{0.1}$ (ºC)	T_{max} (ºC)	Char (500 ºC, wt%)	Char (800 ºC, wt%)
K1	306	409	6.34	5.47
K2	261	354	21.06	16.98
K3	266	375	27.37	24.15
K4	269	372	26.17	23.01

3.4. Morphology of residual char

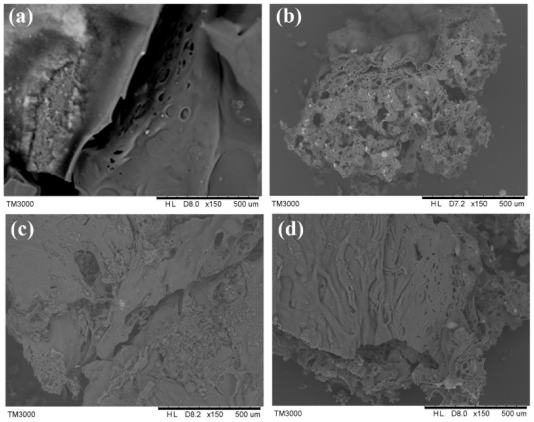

Fig. 3 The morphology of the char layers of the pure UPR and its composites

It is well known that high-quality char, as insulating barrier during combustion process could isolate oxygen, prevents heat transmit and cut off combustible gas [6]. From the Fig. 3(a), the residue char of neat UPR was form with numerous holes, and was present lamellar structure, thus it will not insulate oxygen and heat very well. In the Fig. 3(b), swell and cellular residual char structure could be

observed, which could be ascribe to the catalytic carbonization effect of polyphosphates released from MPP and the release of gas products from MPP. However, the char structure of K2 was not compact enough. With the MMT combined with MPP, it made char layer become more compact. Beside, while MMT was replaced by IPA-MMT, Structures of P–N–P, P–N–C, C–O–P, and C=C were generated and promote the structure of char become more integrity and dense.

4. Conclusion

PA-MMT was successfully prepared and then was combined with MPP presented an evident synergistic effect for flame retardant UPR. The result showed that a small dosages of PA-MMT (1.5 wt %) incorporated with MPP (18.5 wt %) could promoted the LOI value of UPR/MPP/PA-MMT composites increased from 19.5% to 28.8% and passed UL-94 V-0 rating. The TGA test indicated that PA-MMT and MPP could improve the thermal stability of UPR composites. Meanwhile, the residual char of UPR/MPP/PA-MMT showed much more integrity and dense.

Acknowledgments

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