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The Synthesis and Flame Retardance of a High Phosphorus-containing Unsaturated Polyester Resin

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A high phosphorus-containing unsaturated polyester resin (P-UPR) was synthesized by a one-step or two-step method with dimethyl methylphosphonate (DMMP) as a reactive flame retardant. Phosphorus content in the cured P-UPR could be increased to 3.0 wt %, and a low amount of 15.0 wt % DMMP used in the reactants allowed P-UPR to achieve a UL94 V-0 rate. The incorporation of phosphorus into the UPR chain was confirmed by ^{31}P NMR. The condensed phase flame-retardant mechanism of P-UPR was investigated by TG, SEM/EDS, and TG-FTIR.

Unsaturated polyester resin (UPR) is one of the most important thermosetting materials. Just as epoxy, the major drawback of UPR is its flammability.[1] High flammability of any polymeric system brings out a considerable hazard. Two methods have been used to make polymers flame-retardant and safe: the introduction of flame-retardant elements into the polyester structure using reactive flame retardants[2] and the blending of nonreactive flame retardants with polymers.[3] Since the blending method brings problems of compatibility, the goal of current research is to develop and employ reactive flame retardants to enhance the flame resistance of polymers.[4]

Phosphorus-containing flame retardants, which give off less toxic combustion products, are particularly effective in materials with oxygen-containing polymer and have become an important replacement for halogen flame retardants which form highly toxic and potentially carcinogenic halogenated furans and dioxins during burning.[5] In resent years, phosphorus-containing flame retardants have been successfully applied to epoxy, urethane, and saturated polyester.[6] However, very little research on phosphorus-containing reactive flame retardant UPR has been reported. Ma[7] and co-workers synthesized phosphorus-containing flame retardant, SPDPC, and applied it to the synthesis of UPR. Unfortunately, two reactive chlorine atoms are present in SPDPC and are partly incorporated into the UPR chain. It was reported in a U.S. patent that one phosphorus-containing flame retardant was used in the synthesis of flame retardant UPR. Japanese patents also have presented new solutions to obtain flame retardant UPR.[8] Although the desired UPRs were obtained, too much flame retardant was employed because the flame retardants in these patents had a phosphorus content no more than 15.0 wt %. The application of too much flame retardants will raise the cost and increase the probability of weakening some properties of UPR, such as mechanical and electrical properties. According to previous experience, the higher phosphorus content the final polymer configuration possesses, the higher flame resistance the polymer will obtain.[4,6] How can the phosphorus content be effectively increased in UPR?

Dimethyl methylphosphonate (DMMP) has the highest phophorus content among commonly used organic phosphorus flame retardants. In this letter, it is, therefore, chosen as a reactive flame retardant for the synthesis of high phosphorus-containing UPR (P-UPR) to improve flame resistance. P-UPR was based on maleic anhydride (MA), phthalic anhydride (PA), DMMP, ethylene glycol (EG), and 1,2-propanediol (PG). Phosphorus was incorporated into the chain of P-UPR with the ester-exchange reaction between DMMP and EG or PG.

P-UPR was synthesized by a one-step or two-step method. The one-step procedure was as follows: A mixture of 100 g of MA, PA, PG, EG, and DMMP (molar ratio = 2:1:3:2:1) was introduced in a four-neck round-bottom flask fitted with a condenser, mechanical stirrer operated at approximately 300 rpm, and a nitrogen gas inlet to facilitate the removal of water and oxygen from the system. After N_2 bubbling for 5 min, 0.11 g of dibutyltin oxide (DBO) was added into the flask. The reactions were carried out by heating the reactants from room temperature to 140 °C, under a N_2 atmosphere for 1.5 h. Then the temperature was held at 160 °C for 12 h. The pressure of the reaction system was gradually reduced to 100 mmHg over the course of 30 min, and then the temperature was raised to 180 °C for the required period of time with simultaneous removal of all volatiles by distillation. Finally, the pressure was returned to normal atmospheric pressure, and the polymer was dissolved in 40.0 wt % styrene, which acted as a solvent and a crosslinker for P-UPR. Dicumyl peroxide (as initiator) and hydroquinone (as free radical inhibitor) were subsequently added.

In the two-step procedure, 16.12 g of DMMP, 18.60 g of EG, 0.11 g of DBO, and 0.22 g of *p*-toluenesulfonic acid were introduced to a four-neck round-bottom flask. The reaction was carried out with stirring under a N_2 atmosphere at 120 °C for 10 h. After the end of this first step, MA, PA, and PG were added to the cooled reaction system. The followed steps were carried as the one-step method mentioned above.

In Table 1, P-UPR synthesized by the one-step or two-step method has transparent appearance before and after curing, and the flame retardance reaches UL94 V-0. But the mixture of UPR and DMMP has bubbles after curing and obtains flame retardancy of UL94 V-1. The high degree of flame resistance implies that DMMP reacted with diol and that phosphorus was incorporated into the UPR chain. ^{31}P NMR spectra of DMMP and the purified P-UPR synthesized by the one-step method confirm the conclusion in Figure 1.

In Table 2, since the phosphorus content in DMMP is as high as 25.0 wt %, the phosphorus content in the cured P-UPR can reach 3.0 wt % with 20.0 wt % DMMP taking part in the reaction. High phosphorus content leads to formation of more

Table 1. Effect of preparation methods on P-UPR

Preparation methods	Appearance of UPR before curing	Appearance of UPR after curing	Phosphorus content in cured UPR/wt %	UL94
One-step	Transparent	Transparent	2.25	V-0
Two-step	Transparent	Transparent	2.25	V-0
Blending	Transparent	Transparent with bubbly	3.75	V-1

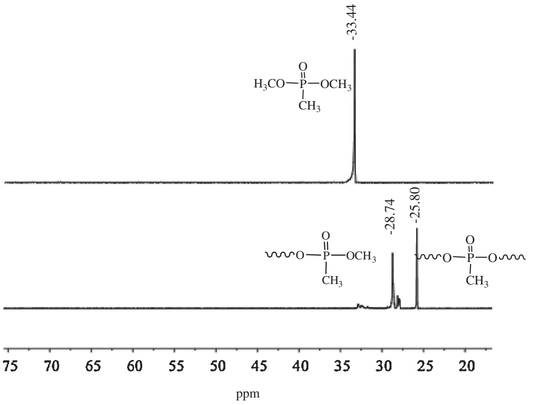

Figure 1. ^{31}P NMR spectra of DMMP and the purified P-UPR synthesized by the one-step method.

Table 2. Effect of DMMP content on P-UPR prepared by the one-step method

No.	DMMP content /wt %	Appearance of UPR before curing	Appearance of UPR after curing	Phosphorus content in cured P-UPR/wt %	UL94
P-UPR1	10.0	Transparent	Transparent	1.50	V-1
P-UPR2	15.0	Transparent	Transparent	2.25	V-0
P-UPR3	20.0	Transparent	Transparent	3.00	V-0

char yield at high temperature shown in Figure 2, and the char yield at 800 °C increases from 3.7 to 11.8 wt % with increasing phosphorus content from 0 to 3.0 wt %. 15.0 wt % DMMP in the reactants can allow P-UPR2 to achieve a V-0 rate in the UL94 test. Compared to our previous research,[8d] only a half the amount of flame retardants can meet UL94 V-0 rate.

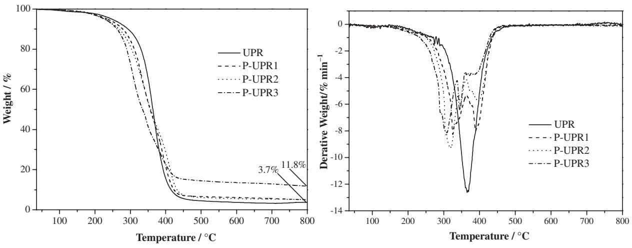

Figure 2. TG and DTG curves of P-UPR in N_2.

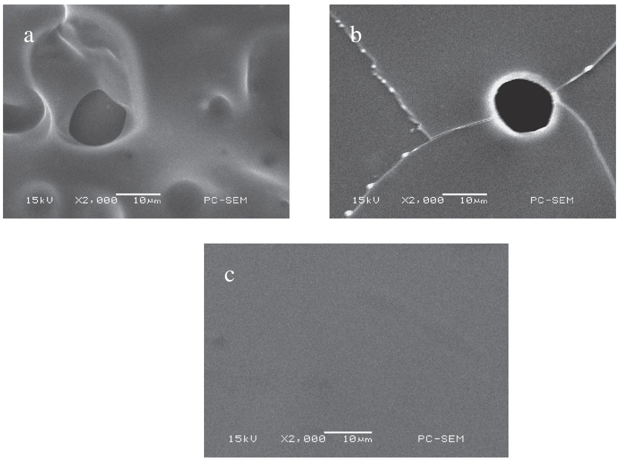

Figure 3. SEM microphotographs of burned P-UPR with different DMMP content: a) P-UPR1, b) P-UPR2, and c) P-UPR3.

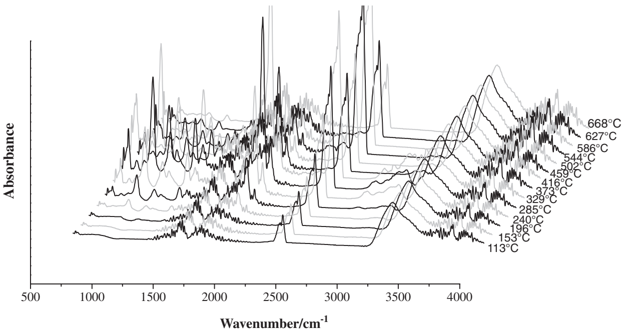

Figure 4. TG-FTIR stack plots of degraded P-UPR2 under air.

In order to further investigate how a phosphorus moiety in P-UPR improves flame resistance, a NAVA SEM/EDS system was used to examine the variations of char residues on the surface of different burned resins. In Figure 3, clear differences in the morphology of three char residues have been observed. Higher phosphorus content induces more whole char residue. P-UPR1 forms a layer of continuously consolidated char with some small pores (Figure 3a). In Figure 3b, there are cleavages and one round hole on the surface of the char residue. In P-UPR3, the formation of a compact whole carbon layer demonstrates that phosphorus plays an important role in flame resistance.[6] During burning, phosphorus in polymers is converted to phosphoric acid and polyphosphoric acid, which esterifies and dehydrates the pyrolyzing polymer, and then a phosphorus-rich carbonaceous layer simultaneously forms to inhibit pyrolysis reactions. This protective layer plays a crucial effect in flame resistance. Therefore, the high flame resistance of P-UPR works by condensed phase mechanism.

The results of TG-FTIR also confirm this mechanism. In Figure 4, the characteristic absorption peaks of phosphorus-containing compounds do not appear. The EDS of P-UPR2 showed that before and after burning the phosphorus content on the surface increased from 3.7% to 13.0%, also confirming the condensed phase mechanism.

In summary, a UL94 V-0 rate unsaturated polyester resin (P-UPR) with high phosphorus content was synthesized by a one-step or two-step method with a low amount of 15.0 wt % dimethyl methylphosphonate (DMMP) as a reactive flame retardant. This method of effectively increasing the phosphorus content of polymer could be also applied in other polymer systems.

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References

1 P. Penczek, P. Czub, J. Pielichowski, *Adv. Polym. Sci.* **2005**, *184*, 1; S. Vlad, S. Oprea, A. Stanciu, C. Ciobanu, V. Bulacovschi, *Eur. Polym. J.* **2000**, *36*, 1495; H. Kimura, M. Iwama, S. Sasaki, M. Takeishi, *Chem. Lett.* **1999**, 737.
2 M. P. Luda, A. I. Balabanovich, A. Hornung, G. Camino, *Polym. Adv. Technol.* **2003**, *14*, 741.
3 C. M. C. Pereira, M. Herrero, F. M. Labajos, A. T. Marques, V. Rives, *Polym. Degrad. Stab.* **2009**, *94*, 939; S. Nazaré, B. K. Kandola, A. R. Horrocks, *Polym. Adv. Technol.* **2006**, *17*, 294.
4 R. M. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, M. Ciesielski, M. Döring, *J. Mater. Sci.* **2006**, *41*, 341; S.-Y. Lu, I. Hamerton, *Prog. Polym. Sci.* **2002**, *27*, 1661.
5 S. Hörold, *Polym. Degrad. Stab.* **1999**, *64*, 427.
6 Y.-L. Chang, Y.-Z. Wang, D.-M. Ban, B. Yang, G.-M. Zhao, *Macromol. Mater. Eng.* **2004**, *289*, 703; H. Ai, K. Xu, H. Liu, M. C. Chen, *Polym. Eng. Sci.* **2009**, *49*, 1879; H. B. Liang, Z. G. Huang, W. F. Shi, *J. Appl. Polym. Sci.* **2006**, *99*, 3130; D. Yu, W. Q. Liu, Y. F. Liu, *Polym. Compos.* **2010**, *31*, 334.
7 Z. L. Ma, W. G. Zhao, Y. F. Liu, J. Shi, *J. Appl. Polym. Sci.* **1997**, *63*, 1511.
8 a) J. Termine, N. A. Favstritsky, K. G. Taylor, U. S. Patent 5346938, **1994**. b) O. Hiroya, U. Toshiaki, T. Hiroshi, Jpn. Patent 2001002769, **2001**. c) A. Takeshi, H. Yoshifusa, Jpn. Patent 2003183370, **2003**. d) C. Zhang, J. Y. Huang, S. M. Liu, J. Q. Zhao, *Polym. Adv. Technol.* **2010**, in press.