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Phosphorus compounds improve flame retardancy of unsaturated polyesters

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Two novel phosphorus-containing reactive flame retardants were synthesized and incorporated into unsaturated polyester to enhance its thermal stability and flame retardancy.

Unsaturated polyester (UPR) is among the most commercially important thermosetting materials for fiber-reinforced composites,[1] employed in fields such as naval construction, offshore applications, water pipes, coatings, building construction, and the automotive industry.[2] UPR is widely used by virtue of its low cost coupled with good mechanical properties, thermal stability, and weather resistance. However, it has the drawback of high flammability and, when burnt, produces large quantities of smoke and toxic gases[3] due to its inherent chemical composition and molecular structure. Hence, it is necessary to incorporate either additive or reactive flame retardants to improve its thermal stability and flame retardancy.[4] (Additive flame retardants are simply mixed with the base material, whereas reactive ones are chemically bonded with it.)

In the past, a variety of additive flame retardants such as aluminum trihydroxide,[5] magnesium hydroxide,[6] and expandable graphite have been effectively incorporated into UPR to improve its flame retardancy. Penczek and coworkers synthesized flame-retardant UPR blended with expandable graphite and ammonium phosphate.[7] Shih and coworkers developed a series of flame-retardant UPRs by incorporating various flame retardants such as ammonium polyphosphate and triphenyl phosphate, along with expandable graphite.[8] Although additive flame retardants are cheap, they have certain disadvantages. Achieving effective flame retardancy requires high loadings, which can cause a rise in viscosity and may sometimes result in phase separation.[9] Therefore, reactive flame retardants are preferred, and are currently receiving great attention.

To further investigate these types of materials, in our study[10] we synthesized two phosphorus-containing reactive flame retardants, namely, triallyl phosphate (TAP) and diethylene glycol modified tetra-allyl phosphate (DTAP). We then incorporated these into commercial UPR

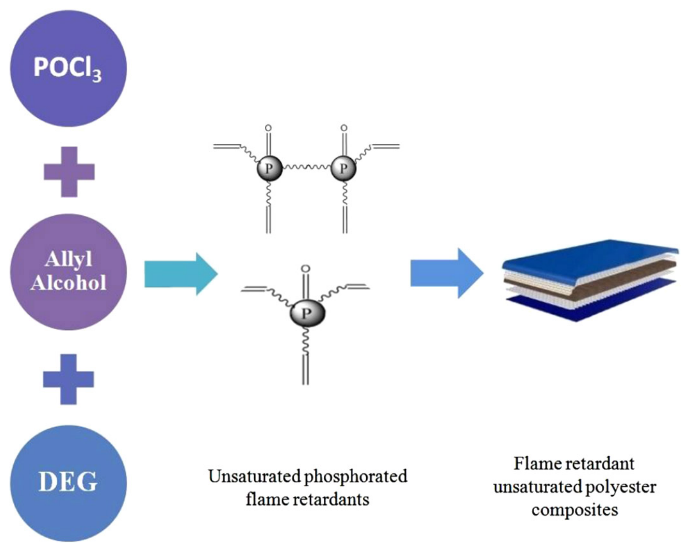

Figure 1. *Phosphoryl chloride ($POCl_3$), allyl alcohol, and diethylene glycol (DEG) were used to synthesize two novel, phosphorus-containing reactive flame retardants. These were then incorporated into unsaturated polyester to obtain composites with improved flame retardancy. P: Phosphorus.*

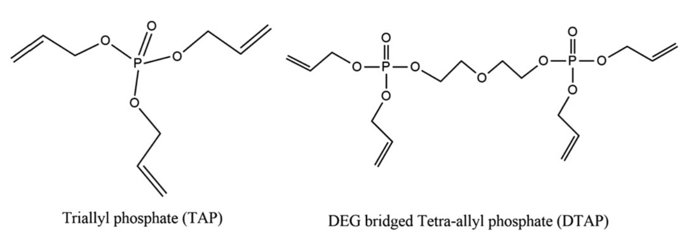

Figure 2. *Chemical structures of the two synthesized flame retardants: triallyl phosphate (TAP) and DEG-modified tetra-allyl phosphate (DTAP).*

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in varying amounts—5, 10, and 15 parts per hundred resin (phr)—to yield flame-retardant unsaturated polyester (FRUPR) composites. The overall process is illustrated in Figure 1, while the chemical structure of the two synthesized flame retardants is shown in Figure 2.

We then evaluated the FRUPR composites obtained in this way for their engineering performance, including their mechanical and thermal properties, as well as flame retardancy. We found that the tensile strength and hardness of the composites were enhanced by the addition of TAP and DTAP, whereas the flexural and impact strength were reduced. These changes can be ascribed to an increased crosslinking density of the composites, resulting from the double bonds in the structures of TAP and DTAP (see Figure 2). This behavior was confirmed by differential scanning calorimetry (DSC) analysis, which showed that there was a significant increase in the glass transition temperature with the addition of flame retardants, suggesting the formation of dense and cross-linked structure in FRUPR composites.

Thermo-gravimetric analysis (TGA) showed that the thermal stability and the flame-retardant properties improved with increasing concentration of flame retardant in the UPR. As can be seen from Table 1, beyond 10phr concentration of flame retardants, all the composites achieved a V-0 classification in the standard UL-94 flammability rating test. (The V-0 rating denotes lower flammability than V-1 or V-2.) We also found that an increase in phosphorus content in the composites led to a corresponding improvement in the limiting oxygen index (LOI) values. The LOI is the amount of ambient oxygen required for the material to sustain a flame. Since air comprises approximately 21% oxygen, materials with LOI greater than 21 will have a reduced tendency to propagate flame.

Table 1. *Flame-retardant properties of the unsaturated polyester (UPR) composites obtained by adding varying amounts (5, 10, and 15 parts per hundred resin) of the two synthesized flame retardants, TAP and DTAP. Higher flame-retardant concentrations correspond to a higher limiting oxygen index (ambient oxygen concentration required to sustain flaming combustion) and to better ratings in the standard UL-94 test for safety and flammability of plastics materials. V-0: Burning stops within 10 seconds, drips of non-inflamed particles allowed. V-1: Burning stops within 30 seconds, drips of non-inflamed particles allowed. V-2: Burning stops within 30 seconds, drips of flaming particles allowed.*

Composites	Limiting oxygen index	UL-94 testing
Commercial UPR	21	–
UPR-TAP-5	25	V-2
UPR-TAP-10	28	V-0
UPR-TAP-15	30	V-0
UPR-DTAP-5	27	V-1
UPR-DTAP-10	29	V-0
UPR-DTAP-15	32	V-0

In summary, our work shows that chemically modifying the UPR backbone with TAP and DTAP enhances the flame retardancy and thermal stability of the resultant composites. It also increases the hardness of the composites but reduces their flexibility. For engineering applications, composites should have a balance of hardness and flexibility. In our case, the composites containing 15phr of TAP or DTAP exhibited maximum flame-retardant properties (from LOI values) without hampering any of the mechanical properties. In future work, we propose to further improve the flame retardancy and thermal stability of such composites by modifying the phosphorus-based flame retardants with silicon and nitrogen compounds. Phosphorus is in fact known to exhibit synergistic effects, when combined with silicon and nitrogen, that can be expected to increase the overall flame retardancy of the system.

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Anagha Sabnis was born in 1975 and received her PhD in paint technology from the University Department of Chemical Technology (UDCT), University of Mumbai, in 2006. She worked for a large multinational company for two-and-a-half years before joining ICT (formerly UDCT) as assistant professor of paint technology. She has 29 international publications.

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References

1. M. A. Sawpan, K. L. Pickering, and A. Fernyhough, *Flexural properties of hemp fibre reinforced polylactide and unsaturated polyester composites*, **Compos. Part A 43**, pp. 519–526, 2012.
2. S. Nazare, B. K. Kandola, and A. R. Horrocks, *Flame-retardant unsaturated polyester resin incorporating nanoclays*, **Polym. Adv. Technol. 17**, pp. 294–303, 2006.
3. J. R. Ugal and R. B. Jima, *Study of the activity of some metal oxides and salts as flame retardants for unsaturated polyester resin*, **Second Sci. Conf. of Tikrit Univ. Sci. College**, pp. 38–42, 2012.
4. C. M. C. Pereira, M. Herrero, F. M. Labajos, A. T. Marques, and V. Rives, *Preparation and properties of new flame retardant unsaturated polyester nanocomposites based on layered double hydroxides*, **Polym. Degrad. Stabil. 94**, pp. 939–946, 2009.
5. T. D. Hapuarachchi and T. Peijs, *Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin*, **Express Polym. Lett. 11** (21), pp. 743–751, 2009.
6. T. Hao, Z. X. Bai, and L. X. Lu, *Effect of magnesium hydroxide on the flame retardant properties of unsaturated polyester resin*, **Procedia Eng. 52**, pp. 336–341, 2013.
7. P. Penczek and R. Ostrysz, *Expandable graphite as a fire retardant in unsaturated polyester resins*, **Proc. Flame Retardants 2000 Conf.**, 2000.
8. Y. F. Shih, Y. T. Wang, R. J. Jeng, and K. M. Wei, *Expandable graphite systems for phosphorus-containing unsaturated polyesters. I. Enhanced thermal properties and flame retardancy*, **Polym. Degrad. Stab. 86**, p. 339, 2004.
9. M. Frigione, A. Maffezzoli, P. Finocchiaro, and S. Failla, *Cure kinetics and properties of epoxy resins containing a phosphorous-based flame retardant*, **Adv. Polym. Technol. 22**, pp. 329–342, 2003.
10. K. Wazarkar, M. Kathalewar, and A. Sabnis, *Flammability behavior of unsaturated polyesters modified with novel phosphorous containing flame retardants*, **Polym. Compos.**, 2015. First published online: 25 August 2015. doi:10.1002/pc.23716