Plastics Research Online

10.2417/spepro.006597

Highly effective flame-retardant system for unsaturated polyester resin

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In a novel approach, ammonium polyphosphate and aluminum hypophosphite are incorporated into unsaturated polyester composites to enhance their flame retardancy.

Unsaturated polyester (UP) resins are employed extensively as the matrix material in fiber-reinforced composites. In addition, UP resins are used as a substitute for traditional materials in many modern engineering applications because of their excellent processability, low cost, and prominent mechanical properties.[1] In the process of curing UPs, styrene is used as both a diluent and a cross-link agent. Styrene, however, has a high intrinsic flammability. Coupled with the high styrene content required for UP curing, it means that UPs are associated with strong fire risks and its applications are thus greatly limited.[2]

In attempts to reduce the fire risk of UPs, a wide variety of flame retardants have been explored. For example, halogen-containing compounds are the most common flame retardants used with UP.[3] During the combustion of these halogen-containing compounds, however, highly toxic and corrosive fumes are released. The use of such materials as flame retardants has thus been restricted in some application areas. As alternative flame retardants, phosphorus-containing materials have recently been gathering more interest.[4]

It is well known that by combining a gas-phase mechanism and a condensed-phase mechanism, flame retardancy performance can be improved.[2,3] Indeed, the phosphorus-containing compound ammonium polyphosphate (APP) acts mainly in the condensed phase and is a highly effective flame retardant for many polymers. In contrast, aluminum hypophosphite (AHP) acts predominantly in the gas phase. In our work,[5] we have thus studied a new approach—in which we incorporate APP and AHP into a UP matrix in different ratios—for enhancing the flame-retardant efficiency of polymers.

We investigated the flammability of our UP/APP/AHP composites through a series of limiting oxygen index (LOI) and UL 94 tests (see Table 1). Our results show that the pure UP sample is highly flammable, exhibiting a relatively low LOI and no UL 94 rating. The LOI values of

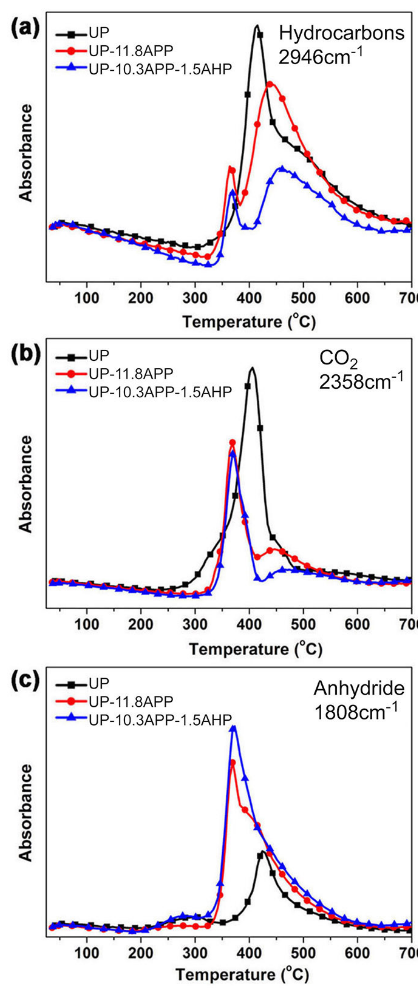

Figure 1. *IR absorbance, as a function of time, of pyrolysis products from a pure unsaturated polyester (UP) sample, and from UP composites (see Table 1) containing ammonium polyphosphate (APP) and aluminum hypophosphite (AHP). Results are shown for (a) hydrocarbons, (b) carbon dioxide (CO_2) and (c) anhydride.*

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Table 1. Compositions and measures of flame retardancy for the UP, UP/APP, and UP/APP/AHP composites. UL 94: A plastics flammability standard. NR: No rating. V-0 and V-1: Burning stops within 10 and 30 seconds, respectively. LOI: Limiting oxygen index.

Sample	Composition (wt%)			UL 94	LOI
	UP	APP	AHP		
UP	100	0	/	NR	23.0
UP-17.6APP	82.4	17.6	/	V-0	34.0
UP-14.7APP	85.3	14.7	/	V-1	32.5
UP-11.8APP	88.2	11.8	/	NR	31.5
UP-11.2APP-0.6AHP	88.2	11.2	0.6	NR	30.0
UP-10.9APP-0.9AHP	88.2	10.9	0.9	NR	30.5
UP-10.3APP-1.5AHP	88.2	10.3	1.5	V-0	31.0
UP-9.4APP-2.4AHP	88.2	9.4	2.4	V-1	30.0

the UP/APP composites increase with the addition of APP, but a high APP content is required. To reduce the loading of APP in the samples, without degrading the flame retardancy, we introduced AHP into the UP/APP system. As shown in Table 1, we find that the UP/APP/AHP composites exhibit significantly better flame retardancy than the UP and the UP/APP composites, i.e., we obtain a UL 94 V-0 classification (burning stops within 10 seconds) and increased LOI values (by up to 34.8%). Our results therefore indicate that the combination of APP and AHP can be used to achieve better flame retardancy than APP alone.

In our study we also used thermogravimetric analysis and IR spectrometry to examine the flame retardancy mechanisms. The absorbance intensity of hydrocarbons, carbon dioxide (CO_2), and anhydride for our UP/APP/AHP composites is illustrated in Figure 1. The measured signals show that the pyrolysis products of the UP-11.8APP (i.e., containing 11.8wt% APP) and the UP-10.3APP-1.5AHP (i.e., containing 10.3 and 1.5wt% APP and AHP, respectively) samples are released earlier than those of the pure UP sample. For the UP-11.8APP and UP-10.3APP-1.5AHP samples it is also evident—see Figure 1(a) and (b)—that the release of CO_2 and hydrocarbons is significantly lower than for neat UP, which reveals that more carbon is left in the condensed phase.

As a result of incomplete combustion, the release of small molecular gases (e.g., CO_2 and hydrocarbons) from our samples is suppressed. We find—see Figure 1(c)—that more anhydrides evaporated into the ambient atmosphere when APP, or APP and AHP, were incorporated into the composites. This is because the APP and APP/AHP catalyzed the dehydration of UP to form a char layer. With our results we have thus demonstrated that the presence of APP and APP/AHP can inhibit the release of combustible gases from a polymer matrix during combustion.

In summary, we have investigated a new approach to enhance the flame retardancy of polymer materials. We have conducted a series of tests to examine the flame retardancy of composites that contain different ratios of unsaturated polyester resin, ammonium polyphosphate, and aluminum hypophosphite. We find that the introduction of APP and AHP into the UP matrix gives rise to enhanced flame retardancy. We believe that our combination of condensed-phase (APP) and gas-phase (AHP) flame retardants plays a key role in the improved flame-retardance efficiency of the polymers. Our work demonstrates a new and effective methodology for improving the flame retardancy of UP, but should also stimulate further efforts in the study of highly effective flame-retardant polymer systems. The next step of our research is to investigate how the incorporation of flame retardants into a UP matrix affects the mechanical and optical properties of the system.

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