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Organo-Phosphorus Flame Retardants for Unsaturated Polyester Derived from Recycled Poly(ethylene terephthalate)

DongQuy Hoang[*,1,2], **ThuHien Nguyen**[1], **Haiyan An**[2], **and Jinhwan Kim**[*,2]

[1]*Faculty of Materials Science, University of Science, Vietnam National University, Ho Chi Minh City, Vietnam*
[2]*Department of Polymer Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi 16419, Korea*

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Abstract: In an attempt to suppress the flammability of unsaturated polyesters (RUP) derived from recycled poly(ethylene terephthalate) (PET) and investigate the relationship between flame retardant (FR) chemical structures and their flame retardancy, RUP was incorporated with four organo-phosphorus FRs; triphenyl phosphate (TPP), aluminum hydrogen phosphonate (AHP), diammonium hydrogen phosphate (DAP), and aluminum diethyl phosphinate (OP). The effects of adding FR with regard to the thermal stability of RUP/FR mixtures were investigated *via* thermogravimetric analysis (TGA). The chemical structure of FR and its mixtures with RUP were determined *via* FTIR and X-ray photoelectron spectroscopy (XPS). The morphology of the residual char was investigated using a field emission scanning electron microscope (FE-SEM). Flame retardancies were evaluated by a UL-94 vertical test and limiting oxygen index (LOI) measurements. The results indicated that the presence of FR significantly improved the flame retardancy and thermal stability of RUP. LOI values increased from 20 to 28 and V-0 ratings were obtained with an 8 wt% FR loading for DAP and with a 10 wt% FR loading for OP. In contrast, no ratings were recorded for the mixture containing 30 wt% of TPP or AHP. These findings clearly indicate that the efficiency of a phosphorus-based FR depends on the quantity of phosphorus elements within the FR itself, although interactions of the FR with the target polymer should also be accounted for when determining its effectiveness as a FR.

Keywords: unsaturated polyester, recycled PET, flame retardant, organo-phosphorus compound, thermal stability.

Introduction

Unsaturated polyester resin (UP) is one of the most widely used thermoset possessing excellent processability and outstanding cross-linking tendencies in addition to good mechanical properties and resistance to oil, moisture, and acids when cured.[1,2] Many researchers have reported that considerable quantities of poly(ethylene terephthalate) (PET) waste can be recycled to UP by various methods.[3-7] Among the technologically feasible recycling techniques that follow principles of sustainable development, the most acceptable method is chemical recycling, primarily because it can lead to the formation of monomers/oligomers from which the polymer was made. Chemical recycling methods are generally based on the breaking of ester bonds present in PET *via* chemical reagents such as alcohol, amine, water, *etc*. Glycolysis, as reviewed by many authors,[8-10] is based on the chemical reaction of PET with ethylene glycol, diethylene glycol, propylene glycol, and/or triethylene glycol. From glycolyzed oligomers, UP can be prepared to meet the property requirements of thermoset materials suitable for consumer's needs and cost savings.

The major drawback of UP materials is that they are highly flammable and large quantities of heavy smoke are generated when they are burned. The incorporation of flame retardants to reduce the combustibility of polymers and reduce smoke or toxic fume generation has become an important part of the development and practical application of polymers. There are two common ways to make UP materials flame retardant: through the introduction of halogen moieties into the polyester structure or by blending the flame retardants with the UP resin. Typical additive-type flame retardants for UP can be classified with two categories: inorganic and halogen.[1,2,11-14] One of the most widely used inorganic flame retardants is aluminum trihydroxide (ATH). However, the use of this hydroxide is limited in that large quantities must be added to acquire sufficient flame retardancy. Other flame retardants (FRs) which are known to be effective toward flame retardancy are halogen-containing compounds such as decabromodiphenyl oxide, tetrabromobisphenol, *etc*. Methods to employ halogen-containing compounds can lead to environmental concerns. Therefore, phosphorus-based compounds that are halogen-free have been accepted as one of the most promising candidates to replace halogen-based FRs.[15-22]

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*Corresponding Authors. E-mails: jhkim@skku.edu or htdquy@hcmus.edu.vn

The most widely employed halogen-free flame retardants for UP materials are ammonium polyphosphate (APP) and melamine pyrophosphate.[23,24] A significant reduction in the flame spread index was achieved through the combination of a polyhydroxy compound, polyphosphate, melamine, cyanuric acid, melamine salt, *e.g*., melamine cyanurate, and a polyacrylate monomer.[25] The effect of ATH in combination with APP has been investigated.[26] No significant synergistic effects in the UL-94 and limiting oxygen index (LOI) tests were found. A phosphorus and silicon-containing liquid monomer (9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide-vinyltrimethoxysilane (DOPO-VTS)) was also examined.[27] LOI and microscale combustion calorimetry results confirmed that DOPO-VTS imparted excellent flame retardancy to UP. The thermogravimetric analysis (TGA) results indicated that glass-fiber reinforced UP materials containing FR possessed greater thermal stability and residual char yields than those of pure UP materials at high temperatures. It was also reported that the combination of APP and TPP could form an effective intumescent residue for UP.[28] However, high loadings of more than 50 wt% were needed to obtain an UL-94 V-0 rating. Recently, Wang *et al.*[29] investigated the flammability, thermal stability, heat resistance, and mechanical properties of UP resins using aluminum diethylphosphinate (Exolit OP), which will henceforth be referred to as OP. They reported that OP improved the flame retardancy of UP, with the LOI increasing from 21 to 29.5 with an increased OP loading and UP/OP (25 wt%), passing the V-0 classification, indicating that OP could be used as an effective flame retardant for UP.

Nevertheless, all the aforementioned studies were obtained for UP materials yielded from virgin chemical mixtures. No publications have been reported in the literature, having investigated the flame retardancy of UP materials derived from recycled PET. In this study, UP materials derived from recycled PET, which will henceforth be referred to as RUP, have been treated with four different organo-phosphorus FRs: triphenyl phosphate (TPP), aluminum hydrogen phosphonate (AHP), diammonium hydrogen phosphate (DAP), and aluminum diethyl phosphinate (OP), for the following reasons. It is well known that the efficiency of phosphorus-based FRs depends not only on the quantity of phosphorus elements within the FR itself but also on the relative quantity of phosphorus volatiles generated during decomposition. Herein, a series of organo-phosphorus FR compounds having high phosphorus content were employed with the goal of suppressing the flammability of RUP materials and to investigate the relationship between FR chemical structures and their effectiveness toward flame retardancy.

Experimental

Materials. Triphenyl phosphate (TPP) was purchased from Aldrich. Aluminum diethyl phosphinate (OP-Exolit OP 1240) was obtained from Clariant. Diammonium hydrogen phosphate (DAP) was purchased from Guangdong Guanghua Chemical Factory Co., Ltd. Methyl ethyl ketone peroxide was obtained from Keum Jung Akzo Nobel Peroxide Co., Ltd. Aluminum trinitrate nonahydrate, anhydride maleic, ethylene glycol, styrene monomer, and zinc acetate dehydrate were purchased from Xilong Chemical Co., Ltd. Acid phosphorous was supplied from the Shang Hai Jinshan Tingxin Chemical Reagent Company.

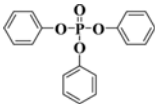
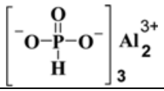
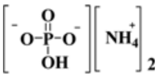
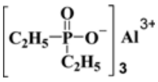
Waste PET bottles were cut to 5×10 mm^2, rinsed with water, and dried for 24 h in an oven at 60 °C. RUP materials were prepared by reacting glycolyzed products with maleic anhydride, styrene monomer, and methyl ethyl ketone peroxide as described by prior studies.[4-8] Aluminum hydrogen phosphonate (AHP) was synthesized in our laboratory by reacting acid phosphorous with aluminum trinitrate nonahydrate.

The chemical structures, generic names, and abbreviations of the FRs employed in this study are presented in Table I.

Measurements and Sample Preparation.

Spectroscopic Analysis: Infrared spectra (IR) were obtained with a Nicolet 380 FTIR spectrometer. X-Ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS HSi spectrometer using a monochromatized AlK_{α} X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms (40 eV energy). The anode voltage and current were set to 15 kV and 10 mA, respectively.

Table I. Structures and Characteristics of FRs Employed in this Study

FR	Generic Name	Abbreviated Name	P Content (wt%)
	Triphenyl Phosphate	TPP	9.51
 $\left[{}^{-}O-P(=O)(H)-O^{-}\right]_3 Al^{3+}_2$	Aluminum Hydrogen Phosphonate	AHP	10.54
 $\left[{}^{-}O-P(=O)(OH)-O^{-}\right]\left[NH_4^{+}\right]_2$	Diammonium Hydrogen Phosphate	DAP	23.48
 $\left[C_2H_5-P(=O)(C_2H_5)-O^{-}\right]_3 Al^{3+}$	Aluminium Diethyl Phosphinate	OP	23.81

Field Emission Scanning Electron Microscope (FE-SEM): Char morphologies were investigated for the outer surface of residues *via* FE-SEM (JEOL JSM-7401F).

Thermogravimetric Analysis: TGA was performed under a nitrogen and air atmospheres at a heating rate of 5, 10, 20, and 40 °C/min using a TGA 2050 thermogravimetric analyzer.

Sample Preparation for the UL-94 and LOI Tests: A mixture of a flame retardant with RUP at a designated composition was processed in a mold, cured at room temperature for 1 h, post-cured at 60 °C for 10 h, and 80 °C for 24 h to obtain the test bars.

UL-94 Measurement: Fire retardancy performance was evaluated according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bars that were 127 mm in length, 12.7 mm in width, and 3.0 mm thick.

LOI Measurement: LOI measurements were performed on an LOI testing device (Qualitest, USA). The test specimens had dimensions of 100×10×3 mm^3 according to ASTMD 2863.

Results and Discussion

Thermal Decomposition Behavior. The thermal decomposition behavior of RUP, FRs, and RUP/FR mixtures was investigated with a thermal gravimetric analyzer (TGA) under both nitrogen and air atmospheres. The obtained TGA results are presented in Figure 1. Detailed TGA data, including the initial decomposition temperature (T_{onset}), the temperature at which 10% mass loss (T_{10}) occurred, and the fraction of charred residue remaining at 600 °C can be seen in Table II. The results shown in Figure 1(a) reveal that the initial decomposition temperatures of AHP, OP, DAP, and TPP under nitrogen began at about 120, 340, 150, and 180 °C, respectively. The char yields of AHP, OP, DAP, and TPP at 600 °C were 73.4, 30.9, 2.3, and 0.2%, respectively. Only one primary decomposition around 294-470 °C resulting from the chain scission of polystyrene and polyester segments was observed for the thermal decomposition of RUP. Further decomposition led to the formation of primary carbonaceous char (12.7% under nitrogen and 14.5% under air at 500 °C). Neat RUP volatilized almost completely at 600 °C under air, leaving very little in the form of charred residue (1.1%).

The TGA spectrum of RUP/TPP featured two main pyrolysis steps with a char yield of near zero (Figures 1(b) and 1(c)). It was important to note that the starting mass loss temperature of TPP was much lower when compared to that of RUP. This implied that TPP evaporated prior to the decomposition of RUP. Therefore, TPP was expected to be ineffective toward preventing the decomposition of RUP. It could be seen that the RUP/AHP and RUP/DAP mixtures displayed a major mass loss *via* one main step decomposition under nitrogen but through two decomposition steps under air. The second decomposition step observed under air was believed to be related to residual char formation during interaction with oxygen. It was noted that the RUP/AHP mixture left the highest amount of residual char (Table II).

It has been reported[30-32] that at 432-873 K, DAP decomposes to ammonia, water, and phosphoric acid. The acid can be further dehydrated, producing pyrophosphoric acid and forming P_4O_{10} (or P_2O_5) at a very slow rate, which has a melting temperature of 842 K and a boiling point of 864 K. The formation of a viscous fluidic layer from this compound could function as a barrier coating for thermal and oxygen transport. The TGA

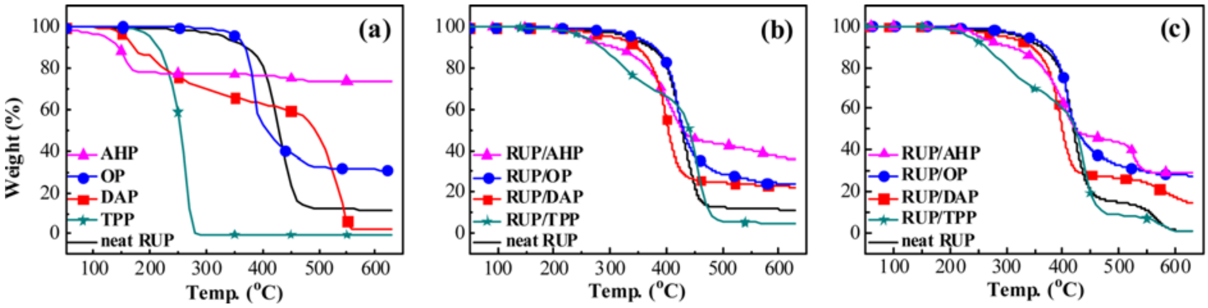


Figure 1. TGA thermograms of RUP and FRs under nitrogen (a) and of various RUP/FR mixtures under nitrogen (b) and air (c).

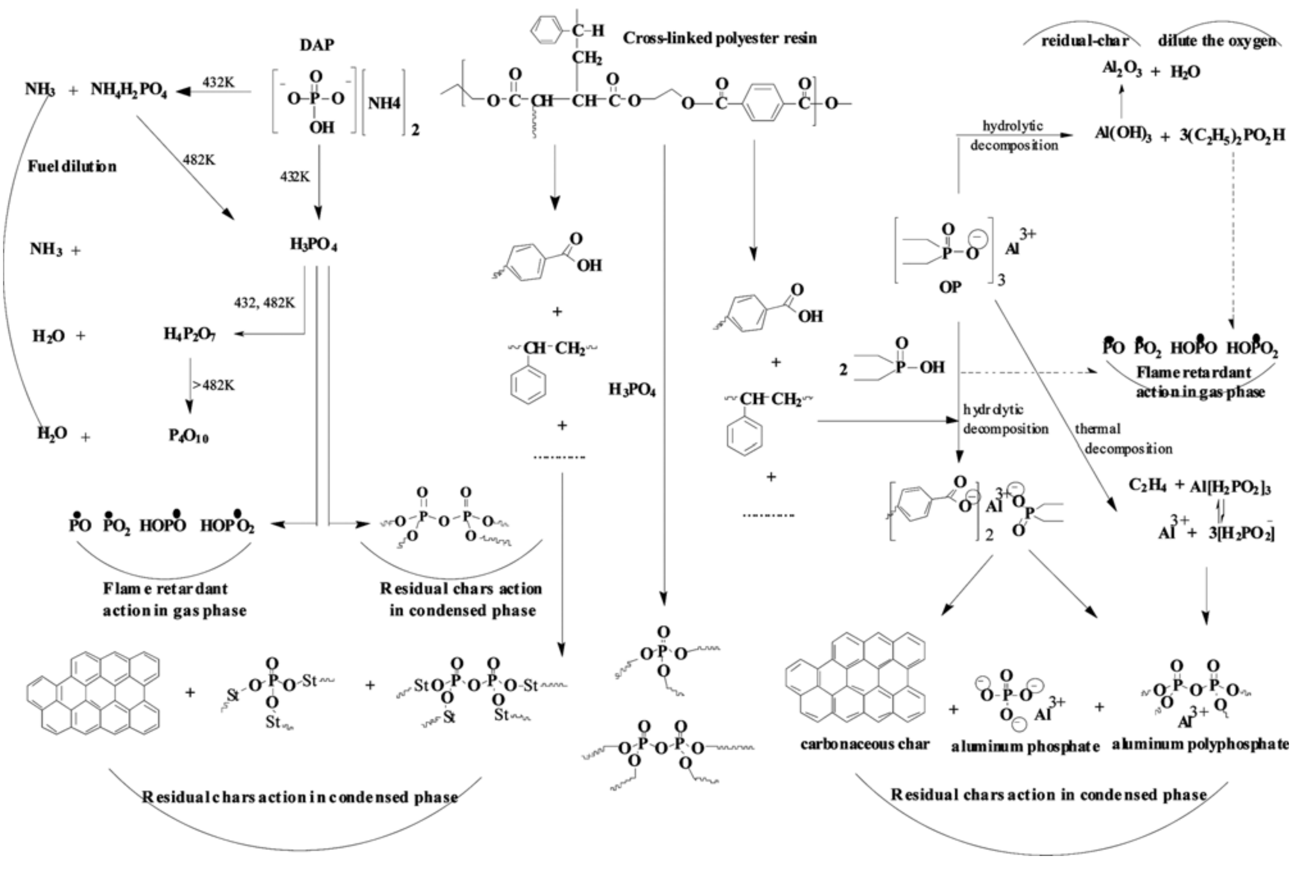
Table II. Summary of Thermal Stability Parameters from the TGA Results Presented in Figure 1

Samples	RUP/FR (wt/wt)	T_{onset} (°C)		T_{10} (°C)		Residue at 600 °C (%)	
		N_2	Air	N_2	Air	N_2	Air
Neat RUP		309	294	373	363	11.5	1.1
RUP/TPP$_{30}$	70/30	230	214	285	260	5.2	1.2
RUP/AHP$_{30}$	70/30	233	232	309	306	37.2	29.2
RUP/DAP$_8$	92/8	265	258	349	346	23.3	16.7
RUP/OP$_{10}$	90/10	313	304	380	372	24.6	27.9

results clearly showed that the RUP/DAP possessed less thermal stability than RUP at the early stages of decomposition. Volatilization of DAP induced flame inhibition simply due to fuel dilution effects, although more complicated effects could be made possible due to interactive reactions between the decomposed DAP and RUP generated during the early stages of decomposition. The formation of residual char, protecting the mixture from further decomposition, profoundly contributed toward fuel inhibition. This plausible decomposition scheme is presented in Scheme I. This assertion could be accepted when observing that the char yield of RUP/DAP at 450-650 °C was much higher than that of RUP and the thermal stability parameters of RUP/DAP were significantly improved compared to RUP/TPP and RUP/AHP mixtures (Table II).

OP decomposed at relatively high temperatures and its decomposition temperature coincided with that of RUP. RUP/OP mixtures featured one primary decomposition from 304 to 470 °C under air and from 313 to 477 °C under nitrogen, with the decomposition of RUP occurring simultaneously at this temperature range. It was noted that the RUP/OP mixture exhibited a lower mass loss of the main decomposition, with large amounts of charred residue forming above 430 °C compared to RUP. These results could be explained as follows: the added OP decomposed concurrently with RUP and the pyrolysis products of OP such as phosphoric acid and/or phosphorus-containing moieties would self-condense or react with other volatiles generated from the decomposing RUP, thus resulting in the formation of stable charred residue, which would further reduce the generation of volatilized products. This plausible decomposition scheme is also presented in Scheme I. OP was expected to act both in the gas phase through the release of diethylphosphinic acid and in the condensed phase through the formation of aluminum phosphate at higher temperatures.[33-35]

In order to more clearly understand the effects of FR addition on the thermal degradation behavior of mixtures, experimentally observed TGA data was compared with TGA values calculated by adopting the additive rule. The calculated data was composed by combining the TGA data of the components comprising the mixture. The obtained results can be seen in Figure 2. The quantity of experimentally-observed char residues was lower during the early stages of decomposition and higher at later stages than the calculated values for all three mixtures, indicating that the FRs decomposed earlier than RUP, producing phosphoric, phosphinic, and subsequent pyro- and poly-acids which reacted with the fragments generated from the decomposition of RUP, consequently forming a stable char *via* crosslinking.



Scheme I. Plausible schemes for the main decomposition of RUP and DAP, RUP (left side) and OP (right side) and interaction between them (the decomposition mechanism of DAP is cited from the literatures[29-31] and OP is cited from the literatures.[32-34]).

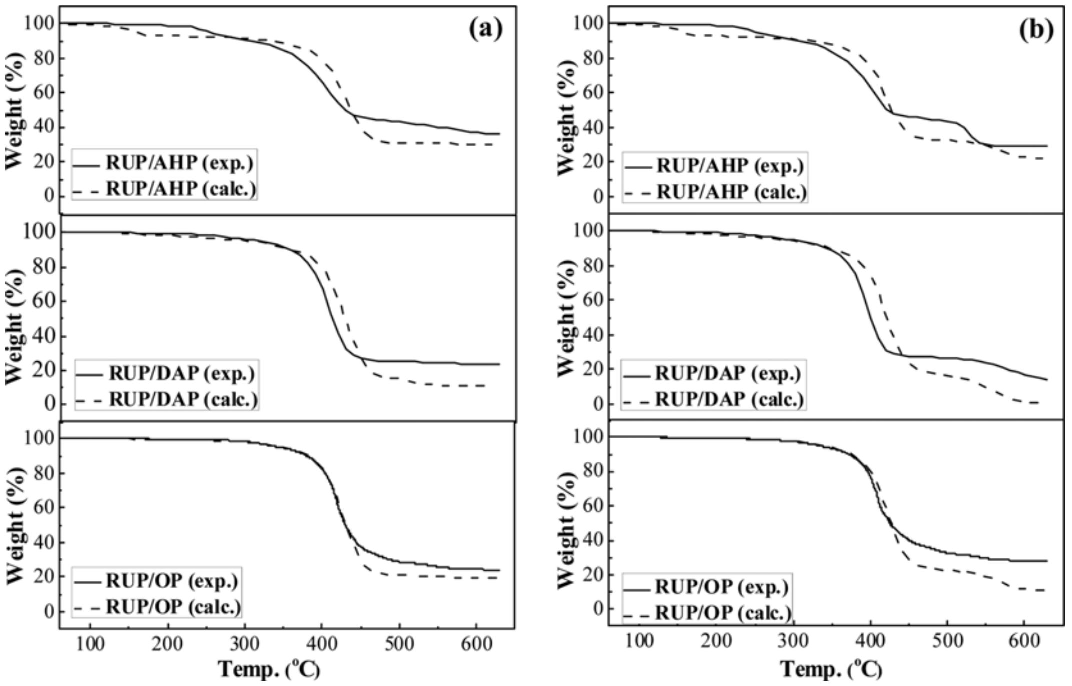


Figure 2. Comparison between experimentally determined TGA results and calculated values by adapting the additive rule for RUP/FR mixtures under nitrogen (a) and air (b).

The kinetic parameters of thermal degradation could be used to evaluate the thermal stability. The activation energy (E) was calculated using dynamic TGA experiments measured at various heating rates by adopting a modified Ozawa's method as follows:[36,37]

$$\frac{d(\log r)}{d(1/T)} = -0.4567\frac{E}{R}$$

where r was the heating rate, T corresponded to the temperature yielding the same heat loss at a different heating rate, E was the activation energy of the decomposition reaction, and R was the gas constant. According to the above equation, the activation energy could then be determined from a plot of log r *vs.* $1/T$ at a given mass loss. TGA experiments of RUP/OP and RUP/DAP at four different heating rates of 5, 10, 20, and 40 °C/min were carried out and the experimental results and kinetic parameters obtained therein are listed in Figure 3 and Table III. It was determined that the E values of the RUP/DAP mixture were lower than those of RUP at a low mass loss and higher at a high mass loss. This suggested that the presence of DAP accelerated the thermal decomposition of RUP at the earlier stages of decomposition and then was hindered due to the formation of char at the later stages of decomposition. The same trends were found for the RUP/OP mixtures. The E values of the RUP/OP mixtures were slightly lower than those of neat RUP at a low mass loss but were significantly higher at a high mass loss. OP decomposed at the same temperature range where the decomposition of neat RUP occurred, leaving a very large quantity of residual char to resist the further pyrolysis of RUP. Therefore, the presence of OP significantly increased the thermal stability of RUP.

Flame Retardancy and Mode of Action. UP commonly consists of a mixture of various components. When UP is processed, the main reaction is radical polymerization between unsaturated polyester chains and styrene monomers. During the reaction, styrene plays a versatile role, acting as both a diluent and cross-linking agent. However, the intrinsic flammability of styrene as well as its high content (35-40 wt%) in uncured UP mixture can generate a large fire risk in the cured UP product.[38] It was difficult to find effective non-halogen alternatives of single component FRs for UP materials comprising highly flammable styrene units. Therefore, the incorporation of char-forming agents in addition to phosphorus FRs operating in the gas phase were inevitable in order to achieve sufficient flame retardancy. Moreover, typical UP materials which were not derived from recycled PET contained a considerable amount of aliphatic constituents. However, RUP from recycled PET had a large aromatic component and was thermally more stable. As a result, RUP passed the UL-94 HB test while normal UP materials were unable to satisfy this test.

In the scope of our investigation, a series of phosphorus-based FRs were employed in an attempt to find a single component organo-phosphorus FR for RUP. FRs were added in 5-30 wt% loading amounts to the RUP materials and their flammability was evaluated *via* the UL-94 vertical test method and LOI values. The designated compositions and test results can be seen in Table IV. Neat RUP materials in the absence of any FRs were highly flammable with a low LOI value of 20%.

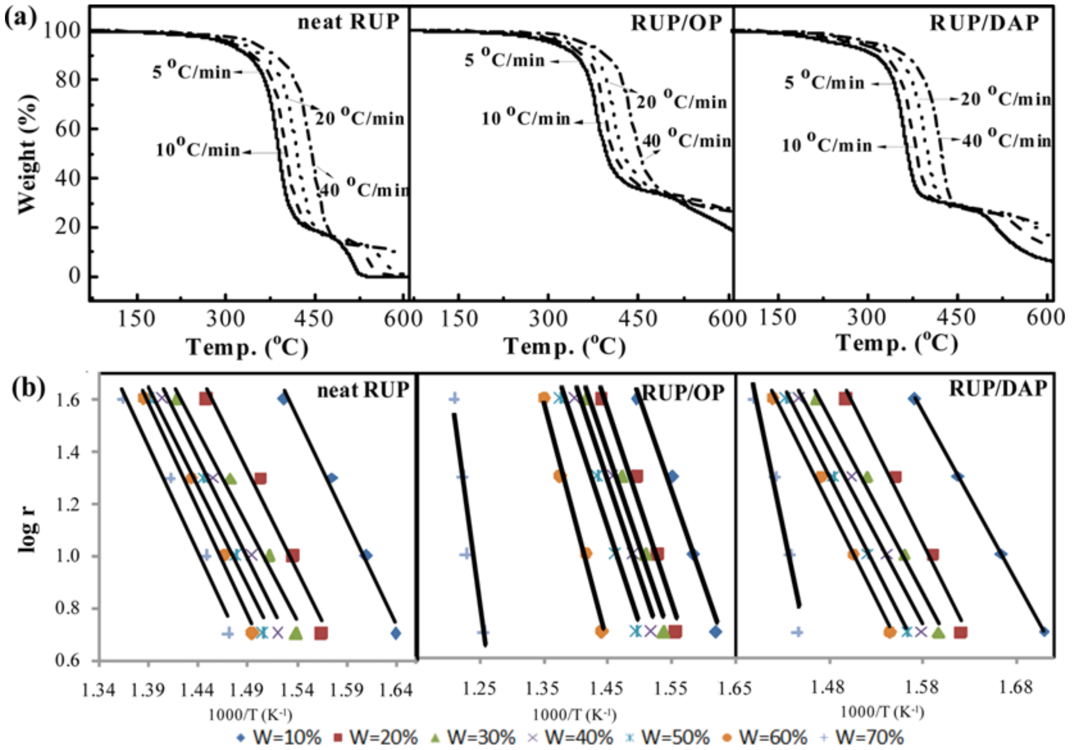


Figure 3. (a) TGA thermograms of RUP and two RUP/FR mixtures under air at different heating rates and (b) the log r *vs.* $1/T$ for neat RUP and two RUP/FR mixtures at various mass losses (W: mass loss).

Table III. Calculated Activation Energy of RUP and Two Different RUP/FR Mixtures under Air

Mass Loss	Activation Energy (kJ/mol)		
	Neat RUP	RUP/OP	RUP/DAP
0.1	145.2	130.6	119.5
0.2	140.0	136.2	132.9
0.3	133.1	131.5	125.1
0.4	139.0	135.7	125.2
0.5	140.4	136.6	129.4
0.6	148.3	170.8	131.6
0.7	148.6	337.9	317.8

The flame propagated in the test specimens up to the clamp, so no rating was recorded for the UL-94V test. A V-1 rating was achieved when 7.5 wt% of FRs were added to both DAP and OP. V-0 ratings could be obtained with FR loadings as low as 8 wt% for DAP and 10 wt% for OP. No ratings were recorded for mixtures containing 30 wt% TPP or 30 wt% AHP. LOI values were found to be significantly increased from 20 to 28 with the addition of 8 wt% DAP and 10 wt% OP.

The efficiency of phosphorus-based FRs depended not only on the phosphorus volatiles generated during decomposition in the case of a gas phase mode of action but also upon the quantity of phosphorus remaining in the charred residue in the case of a condensed phase mode of action. The P content of TPP, AHP, DAP, and OP was 9.51, 10.54, 23.48, and 23.81 wt%,

Table IV. UL-94 and LOI Results for RUP and Various RUP/FR Mixtures

FR	wt% of P in FR	Samples	RUP/FR (wt/wt)	wt% of P in RUP/FR	UL-94 Rating	LOI
		Neat RUP			No rating	20
TPP	9.51	RUP/TPP_{30}	70.0/30.0	2.85	No rating (1st step: 1 s, 2nd step: burn)	
AHP	10.54	RUP/AHP_{30}	70.0/30.0	3.16	No rating	
DAP	23.48	RUP/DAP_5	95.0/5.0		No rating	28
		RUP/$DAP_{7.5}$	92.5/7.5		V-1	
		RUP/DAP_8	92.0/8.0	1.88	V-0	
OP	23.81	RUP/OP_5	95.0/5.0		No rating	28
		RUP/$OP_{7.5}$	92.5/7.5		V-1	
		RUP/OP_{10}	90.0/10.0	2.38	V-0	

respectively. Both the LOI and UL-94 results indicated that DAP and OP exhibited good FR efficiency on the RUP materials. The UL-94V results presented in Table IV demonstrated that DAP and OP exhibited better flame retardant characteristics among the four FRs employed in this study. However, the results were quite surprising when considering the elemental P content within the formulations. Mixtures with DAP and OP contained a reduced P content compared to the mixtures with TPP and AHP but exhibited better FR performance. Principally, the FR effect was governed by the FR P content within the formulation. The experimental results in this study clearly implied that the FR chemical structure itself and the flame retarding mechanism between the FR and matrix polymer should be carefully considered. In order to provide a reasoning for this assertion, the thermal decomposition behavior discussed in the previous section should also be accounted for.

During combustion, TPP was vaporized to the gas phase, yielding active radicals such as $PO_2^{\bullet}$, $PO^{\bullet}$, and $HPO^{\bullet}$. These radicals acted as scavengers for $H^{\bullet}$ and $OH^{\bullet}$ radicals and thus suppressed flames during the combustion process.[39,40] RUP/TPP mixtures could not pass the UL-94 test even at a 30 wt% addition. The P content in the mixture was high (2.85 wt%). This was because TPP evaporated prematurely and had almost no opportunity to act as a radical scavenger or cross linker to the pyrolytic products of RUP.

AHP left the highest amount of charred residue among the four tested FRs in this study. The amount of charred residues was higher for the RUP/AHP mixture than that of the RUP/DAP and RUP/OP mixtures (Figure 1). No rating for the UL-94 test was observed at a 30 wt% loading of AHP, although V-0 ratings were observed for DAP and OP containing mixtures with lower loading amounts. These results indicated that the char layer that formed during the decomposition of AHP with RUP was not abundant enough to construct an efficient insulating protective layer, preventing the transfer of combustible gases to the surface of the compound. It was noted that RUP was a non-charrable polymer based on the TGA results in Figure 1. Therefore, it was concluded that effective flame retardancy was very difficult to achieve with RUP when using FRs in the condensed phase. The reason why UL-94 V-0 ratings were observed for mixtures with DAP and OP even though the loading amount was very low was that the RUP/DAP and RUP/OP mixtures after pyrolysis yielded significantly high amounts of char compared to neat RUP materials. However, the quantity of elemental P in the formulations was far lower than that of the RUP/AHP mixtures at which the highest amount of element P and charred residue was observed. With this regard, the only possible explanation would be that the flame retardant properties of DAP and OP were based primarily on contributions from gas phase modes of action. It was speculated that contributions from the char layer in the condensed phase were partially responsible for the FR efficiency of DAP and OP.

Morphology and Chemical Components in the Charred Residue. Upon combustion, the phosphorus-based FRs liberated volatile phosphorus materials in the gas phase while simultaneously leaving a glass-like solid residue containing phosphorus compounds in the condensed phase.[41] To determine whether this assertion was valid for the FRs employed in this study and to understand how char formation affected the flame retardancy of the RUP materials, solid residues of RUP, RUP/OP, and RUP/DAP mixtures combusted in a furnace at 400 and 500 °C under air were collected and exam-

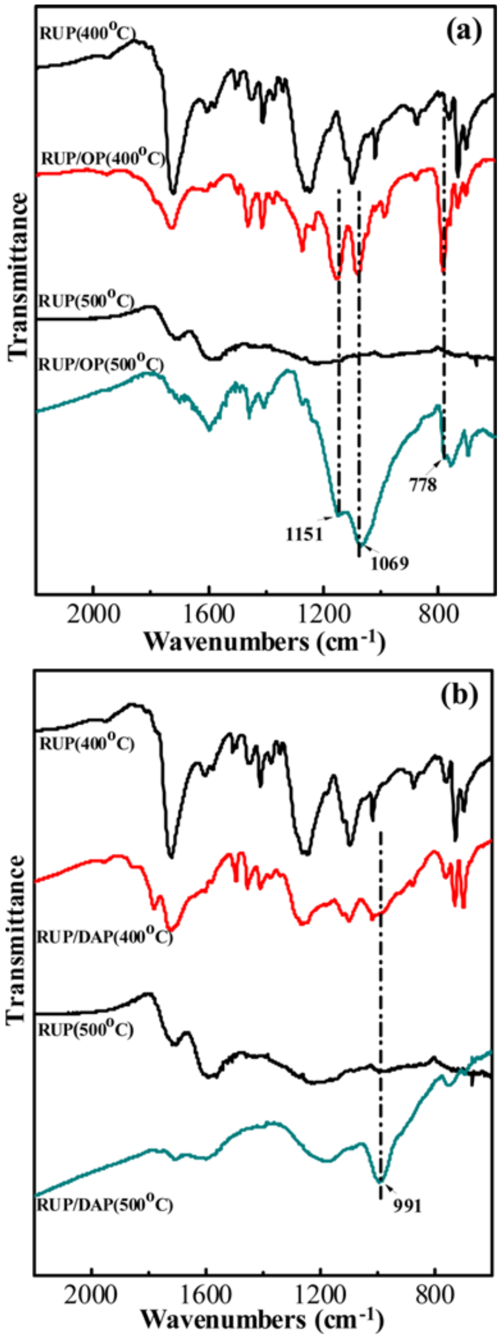


Figure 4. FTIR spectra of solid charred residues for RUP and RUP/OP mixture (a) and RUP/DAP mixture (b) obtained after combusting in the furnace at 400 and 500 °C.

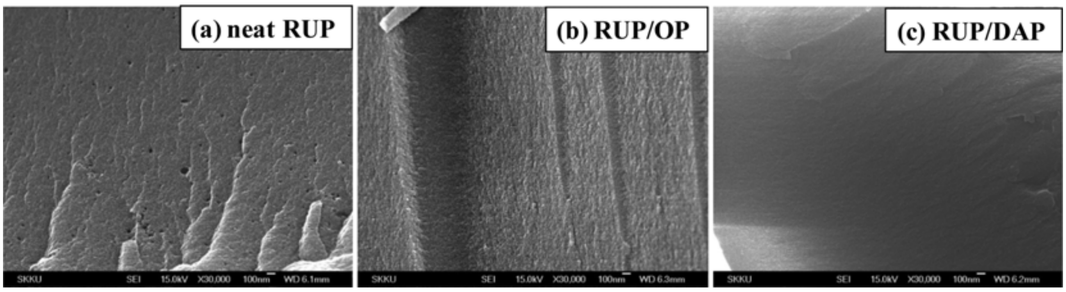


Figure 5. FE-SEM micrographs of residual chars of RUP (a), RUP/OP (b), and RUP/DAP (c) obtained after combusting in the furnace at 500 °C.

ined *via* FTIR, FE-SEM, and XPS. The two temperatures were chosen based on a consideration of the TGA results presented in Figure 1. 400 and 500 °C were relevant to the temperatures prior to and after the main decomposition events were observed.

In Figure 4, the characteristic absorptions of combusted RUP materials at 400 °C were observed at 1721, 1094 cm^{-1} (C=O stretch and C-O-C symmetrical stretch vibrations of ester groups, respectively); 1606, 1501, 1451-1410 cm^{-1} (C-C stretch vibrations of the aromatic ring); 1266-1238 cm^{-1} (-CH_2- bending vibrations); and 725, 697 cm^{-1} (C-C deformation vibrations of the mono-substituted aromatic ring).[26] These bands were found to largely decrease in the residue of RUP, which decomposed at 500 °C, indicating that most of the RUP materials were volatized at this temperature. Charred residues of the RUP/FR mixtures were combusted at 400 °C, revealing additional bands at 1151, 1069, 991 cm^{-1} which were characteristics to P=O, P-O-C, and P-O-P,[42-44] respectively, along with the presence of the carbonaceous char peak at 1598 cm^{-1}. The peak at 778 cm^{-1} was attributed to aluminum phosphate.[45,46] The results implied that phosphorus-containing moieties, *e.g.* phosphoric/polyphosphoric and/or their derivatives, were present in the solid residue. Phosphorus-containing moieties remained in the combusted RUP/FR mixtures at 500 °C. The charred RUP/OP residues obtained at 500 °C exhibited not only phosphorus-containing moieties but also exhibited the typical RUP absorptions. The results of the FTIR investigation clearly revealed that, in the case of the RUP/OP mixture, non-volatile phosphorus compounds such as aluminum polyphosphate, aluminum pyrophosphate, or aluminum orthophosphate, remained in the charred residue and contributed to the formation of a barrier layer.

Surface structures of the charring layer played a crucial role in the performance of the FR. The high quality char acted as an insulating barrier during degradation and the formation of this protective barrier could prevent the transfer of mass and heat between the gas and condensed phases.[47] The FE-SEM micrographs seen in Figure 5 show the morphology of the charred residues obtained after specimen combustion at 500 °C. From the FE-SEM micrograph of neat RUP shown in Figure 5(a), one could observe the presence of cavities that became gas fragment pathways generated from combustion and heat evolution during the burning process. This result was consistent with the TGA results discussed earlier. RUP materials are flammable and exhibit a single-step decomposition. As a result, large quantities of volatile materials are released within a very short period of time during their decomposition. These volatile materials can vigorously agitate the polymer substrate and lead to the formation of a porous, flaky, and brittle char.[28,48] On the contrary, the formation of a compact, continuous, and smooth char layer which could serve as a protective layer and consequently inhibit the transmission and diffusion of heat during contact with fire, was observed for the RUP/FR mixtures.

XPS can reflect chemical interactions at the atomic scale, *i.e.* the bonds between adjacent atoms and can also provide structural characteristics for amorphous surface layers with complex compositions.[27] Thus, the chemical composition of the residual char for RUP/OP and RUP/DAP were investigated *via* XPS. The XPS spectra of C_{1s}, O_{1s}, P_{2p}, and Al_{2p} of the residual char can be seen in Figures 6 and 7. In Figures 6(a) and 7(a), the C_{1s} spectra revealed a peak at 284.5 eV which could be attributed to the contribution of C-C and/or C-H in aliphatic

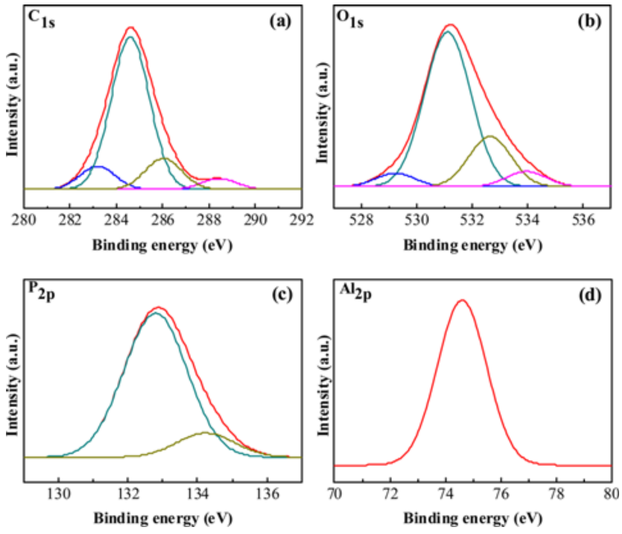


Figure 6. XPS spectra of residual chars of RUP/OP mixture obtained after combusting in the furnace at 500 °C.

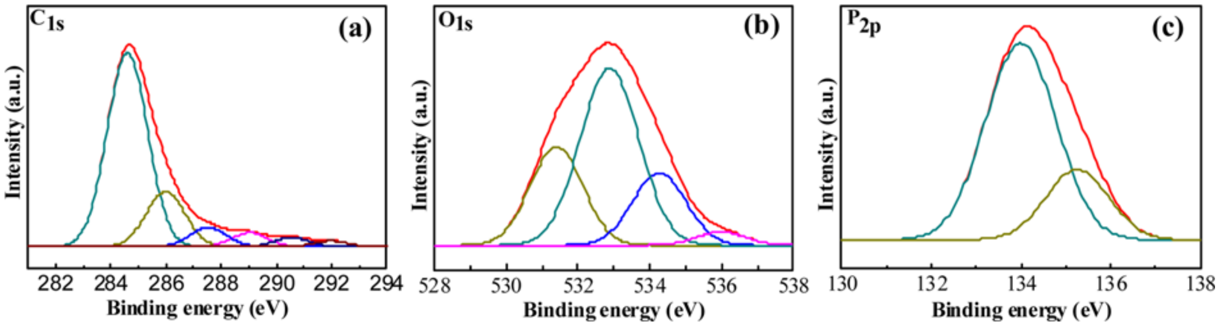


Figure 7. XPS spectra of residual chars of RUP/DAP mixture obtained after combusting in the furnace at 500 ºC.

and aromatic species; the binding energy of 286.0 eV could be attributed to C-O (ether and/or hydroxyl groups) and/or C-O-P in hydrocarbonated phosphate; the binding energy of 287.5 eV was assigned to C=O; and the binding energy around 288.5-290.3 eV could be assigned to the carboxyl group.[49,50] The O_{1s} spectra featured a peak at 531.4 eV which could be attributed to O=C and/or O=P while the peak at 532.9 eV was assigned to the -O- in the C-O-C, C-O-P, and/or C-OH groups.[51,52] The binding energy of 534.1 eV was attributed to -COO- (Figures 6(b) and 7(b)). The peaks between 132.8 and 135.3 eV in the P_{2p} spectra could be attributed to P-O-C and/or PO_3^- groups in pyrophosphate and/or polyphosphate and/or P_2O_5 (Figures 6(c) and 7(c)).[27,53] A single peak at 74.6 eV in the Al_{2p} spectrum corresponded to aluminum phosphate and/or Al_2O_3 (Figure 6(d)). The above XPS results clearly indicated that RUP/FR produced phosphorus-containing moieties during decomposition, which could act as dehydration agents, leading to the formation of a heat-resistant char. Meanwhile, aluminum phosphate and/or Al_2O_3 migrated to the surface of the char and worked together with phosphorus-containing chars to form a protective layer, avoiding fuel/oxygen transmission and heat diffusion and thus significantly enhancing the flame retardancy and thermal degradation of the RUP materials.

Conclusions

In this study, unsaturated polyester resins (RUP) derived from recycled PET were incorporated with four different organophosphorus FRs; triphenyl phosphate (TPP), aluminum hydrogen phosphonate (AHP), diammonium hydrogen phosphate (DAP), and aluminum diethyl phosphinate (OP).

It was found that the incorporation of phosphorus-containing FRs into RUP materials significantly improved the flame retardancy and thermal stability of RUP. A UL-94 V-0 rating was obtained and LOI values of 28% were reached for an FR loading of 8 and 10 wt% for DAP and OP, respectively. On the contrary, no rating was recorded for the mixture containing 30 wt% of TPP or AHP. It was noted that the P content was much higher in the RUP/TPP and RUP/AHP mixtures than in the RUP/DAP and RUP/OP mixtures, indicating that the condensed phase mode of action made a profound contribution with regard to the flame retardant characteristics of RUP, although the primary mode of action was still in the gas phase. This assertion was supported by the TGA and FTIR results. Recently, Wang *et al.* reported that a 25 wt% of OP was needed to achieve a UL-94 V-0 rating for a typical unsaturated polyester consisting of UP chains and styrene monomers.[29] On the other hand, 10 wt% of OP was enough to achieve the same rating in the case of RUP. This again supported our assertion that the condensed phase mode of action played an important role toward the flame retardation characteristics of RUP. From this study, it was concluded that the efficiency of phosphorus-based FRs mainly depended on the quantity of phosphorus elements existing in the FR itself, although the interaction of the FRs with the target polymer should also be accounted for when determining its effectiveness as a flame retardant.

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