Effect of Ammonium Polyphosphate and Melamine Pyrophosphate on Fire Behavior and Thermal Stability of Unsaturated Polyester Synthesized from Poly(ethylene terephthalate) Waste

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Abstract: The fire behavior and thermal stability of unsaturated polyester prepared from recycled poly(ethylene terephthalate) (RUP) in the present of two phosphorus-nitrogen flame retardants (FRs) including ammonium polyphosphate (APP) and melamine polyphosphate (MPP) have been investigated. The effectiveness of FRs on the fire proofing of material was test by UL-94 vertical classification and limiting oxygen index (LOI). The obtained data showed that the fire retardancy and thermal stability were remarkably enhanced with addition of FRs. The best grade of UL-94V standard, V-0 ranking was attained as loading of 25 wt% of APP or 30 wt% of MPP. LOI significantly were enhanced from 20 to 36%. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Scanning electron microscope (SEM) were applied to determine the structure and morphology of char layers of RUP and RUP/FR mixtures. Thermogravimetric analysis (TGA) method was applied to investigate thermal stability of neat RUP, FRs, and RUP/FR and to evaluate kinetic parameters of the decomposition of RUP/FR. The mechanism of action of FRs, schemes for the possible decomposition mechanism RUP and FRs, and the cooperation of matrix and additives were also discussed.
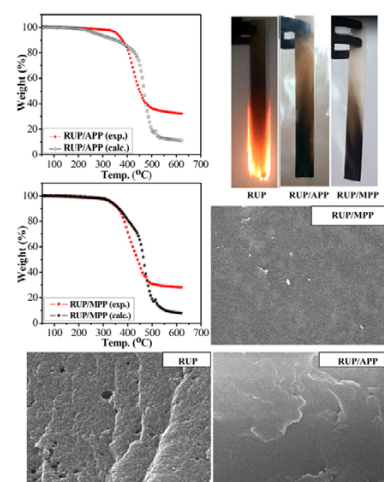
Keywords: ammonium polyphosphate, melamine pyrophosphate, unsaturated polyester, PET waste, thermal stability, fire proofing.

1. Introduction

Polyethylene terephthalate (PET) is a kind of polymeric material applied as an ecological and consumer-friendly material in the wide range of application such as video tapes, X-ray films, food packing, drinking bottles, and jars because of its excellent properties.[1-4] However, the considerable use of PET materials leads to the waste disposal management problems. Among the technologically feasible recycling approach, chemical treatment is the most adequate method because it can lead to the formation of monomers/oligomers. PET can be depolymerized by several chemical reactions such as hydrolysis, alcoholysis, glycolysis, and aminolysis. Among them, products of the glycolysis reaction can be used to prepare high economical values other polymers such as unsaturated polyester (UP) which is one of the significant industrial thermosets.[1-9] UP is used in the field of transportation vehicle, building construction, and composite technology because of their excellent ease of molding, good chemical proof, high flexural moduli, and reasonable cost.[3,6,7,10-17] From glycolyzed PET, UP was obtained and then it was referred to as RUP. However, RUP and UP are high flammability and high smoke densities associated during burning. During the combustion, the pyrolysis of polymer leads to formation of flammable volatiles, toxic gases, radicals, and some other products. Poor resistance to fire of RUP will limit its applications.[17,18]

Addition of a wide range of flame retardants (FRs) is necessary for improvement the fire resistance of RUP. Many reports show high levels of fire resistance of UP can achieve with addition of halogenated compounds.[19,20] However, halogenated chemicals have proven to be persistent, bio-accumulative, and toxic to animals and humans.[21-24] To protect human health and environment, non-halogen FRs have been focused on investigation to replace halogenated additives. Metallic hydroxide compounds are remarkable candidates which were attended because of their effective, environmentally friendly property, and economical properties. However, the use of these compounds requires high loading to achieve high level of fire resistance leading to difficulties in processing and dramatically affecting mechanical properties of polymer.[15,25,26] As non-halogen flame retardants, phosphorus- and phosphorus-nitrogen based FRs have greatly been interested.[12,22,23] They indicate effective in wide range of polymeric

material *e.g.* polypropylene, unsaturated polyester, poly (butylene terephthalate), etc. Zhiman Bai *et al.* reported the effectiveness of phosphorus-containing star-shaped flame retardant (TRIPOD-DOPO) on the flammability of UP.[11] It is reported that phosphorus FRs can act in gaseous and/or condensed phase,[12,24,27] and the phosphorus-nitrogen containing often have good fire-retardant ability and excellent heat behavior. Ammonium polyphosphate (APP) and melamine pyrophosphate (MPP) are the most popular used non-halogen fire retardant for UP.[28] In a research of Yeng-Fong Shih *et al.*, APP was used in combination with expandable graphite leading to improvement on fire resistance for UP.[29] In a similar attempt, a significant synergistic effect was found by combination of APP and triphenyl phosphate (TPP) into UP.[30] V-0 status was achieved and LOI greatly increased from 20.9 to 27.2%. Effect of MPP used in polymeric materials has been investigated, for example, polypropylene,[31] poly(vinyl alcohol),[32] and polyamide.[33,34] Thus, the presence of nitrogen-phosphorus containing FRs promisingly leads to the excellent effectiveness for UP.

However, not many researches have been focused on investigating fire behavior of UP prepared from PET waste (RUP). In a previous work, we had studied the fire behavior of RUP in the presence of phosphorus-based FRs and the results showed that the incorporation of phosphorus-containing FRs into RUP materials significantly improved the flame retardancy and thermal stability of RUP.[35] In this paper, two phosphorus-nitrogen FRs; ammonium polyphosphate (APP) and melamine pyrophosphate (MPP) were used for quenching the flammability of RUP and to evaluate their thermal stabilities as well as the residue composition after combustion.

2. Experimental

2.1. Materials

Ammonium polyphosphate (APP-FR Cros 484) and Melamine pyprophosphate (MPP- Budit 311) were supplied from Budenheim. Maleic Anhydride (MA), ethylene glycol, styrene, and zinc acetate dehydrate were purchased from Xilong Chemical Co., Ltd. Methyl ethyl ketone peroxide was obtained from Keum Jung Akzo Nobel Peroxide Co., Ltd.

The RUP was prepared by the reaction of glycolyzed PET with MA. Styrene as dilute and co-curing solvent and methyl

ethyl ketone peroxide as curing catalyst were also used in the final step to prepare product. The detail process described in the literatures.[3,4,9,36] Structures of FRs were given in Table 1.

2.2. Characterization

FTIR was analyzed by using a Nicolet 380 FT-IR equipment. X-ray photoelectron spectroscopy (XPS) was analyzed on a Kratos AXIS HSi spectrometer. The morphology of the surface of char layer was taken by scanning electron microscope (SEM, JEOL JSM-7401F). Thermogravimetric (TG) was measured using TGA 2050 system. Fire retardancy property was determined by the UL94 standard according to FMVSS 302/ZSO 3975 with a test dimension of $127 \times 12.7 \times 3.0$ mm^3 and was measured on a LOI tester (Qualitest, USA) with a test dimension of $100 \times 10 \times 3$ mm^3 according to ASTMD 2863.

3. Results and discussion

3.1. Thermal behavior

The TG curves of neat RUP, FRs, and RUP/FR and the detailed results are shown in Figure 1 and Table 2. Figure 1(a) reveals
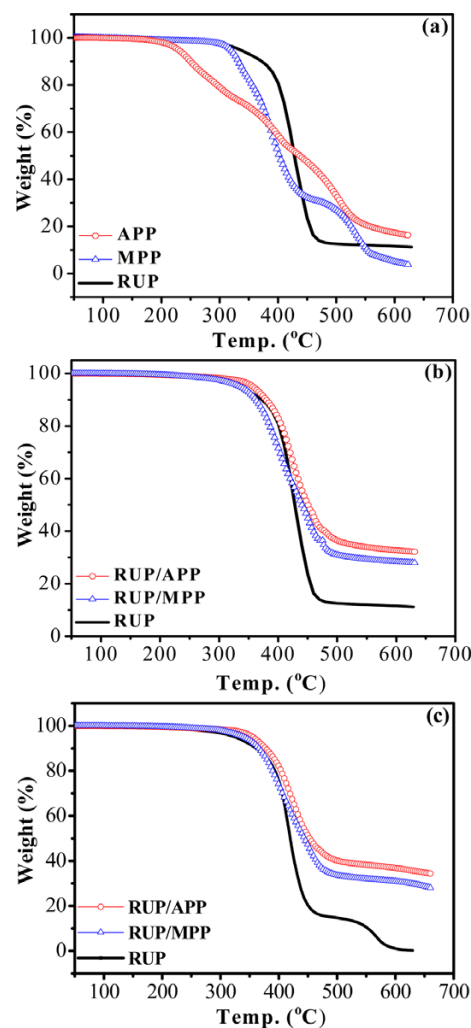
Figure 1. TG curves of RUP and FRs in nitrogen (a) and of RUP/FR in nitrogen (b) and air (c).

Table 1. Structures of FRs Employed

FR	Generic name	Abbreviated name
	Ammonium Polyphosphate	APP
	Melamine Pyrophosphate	MPP

Table 2. Summary of thermal stability parameters from the TG 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
RUP		337	327	373	359	11.6	0.89
RUP/MPP$_{30}$	70/30	334	342	361	366	28.4	30.9
RUP/APP$_{25}$	75/25	356	357	380	379	33.1	37.1

that the early mass loss step of APP and MPP under nitrogen atmosphere began at about 214 and 302 °C, respectively, and the content of residual chars remained at 600 °C was 17.4% for APP and 4.8% for MPP. The thermal decomposition of RUP in the range of 350-480 °C reveals only one step due to the chain scission of polystyrene and polyester segments. The carbonaceous char of 12.1% in N_2 and 14.9% in air were obtained at 550 °C. RUP was decomposed completely at 600 °C in air and leaved a small charred residue (1.1%).

It is reported that the decomposition of APP produced incombustible gases including ammonia and water which can contribute on preventing the combustion by physical effect, and phosphoric acid furthermore dehydrated to form P_4O_{10} (or P_2O_5).[28,37-41] As a result, the further formation of protecting layer can serve as a barrier coating that inhibits the heat, flame, and oxygen trans-portation. In the one hand, the products of volatilization of APP activated the flame inhibition by dilution effect. The incorporation of APP into RUP exhibited the high thermal resistance (Table 2). APP can accelerate the char-forming leading to produce the remarkably higher amount of residues (33.1% under nitrogen and 37.1% under air). An interaction between decomposed products of APP and RUP generated in the first step of decomposition results in a protective layer which protects the matrix from the heat and further decomposition. The possible decomposition scheme presented in Figure 2 could be accepted because at 450-650 °C, RUP/APP created a greater charred residue than that of RUP. The heat stability of RUP/APP was greatly enhanced in comparison to RUP (Table 2).

Similar to APP, decomposition of MPP also produced the products such as ammonia, melamine, and phosphoric acid.[34] Melamine
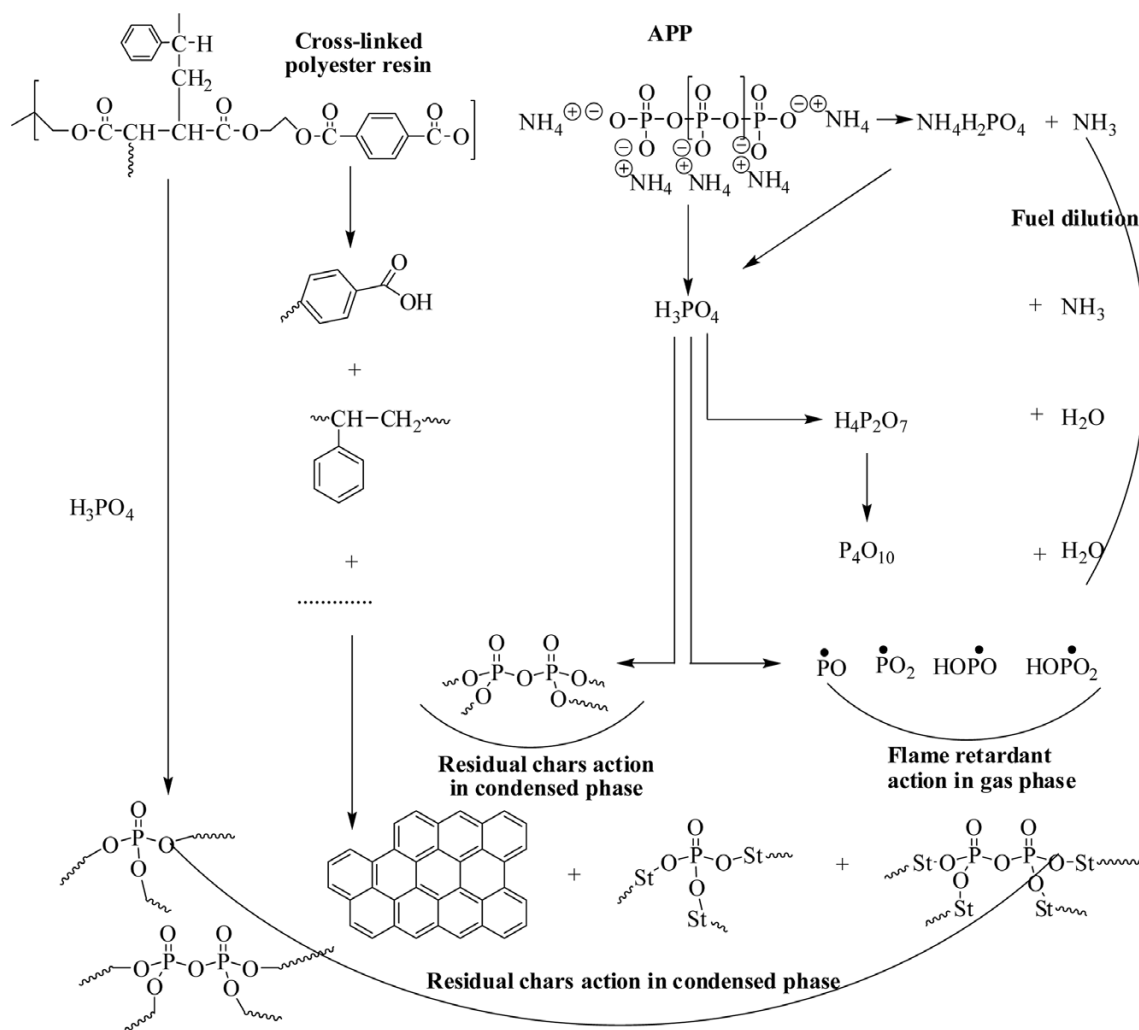
Figure 2. Possible schemes for the main decomposition of RUP and APP and interaction between them.
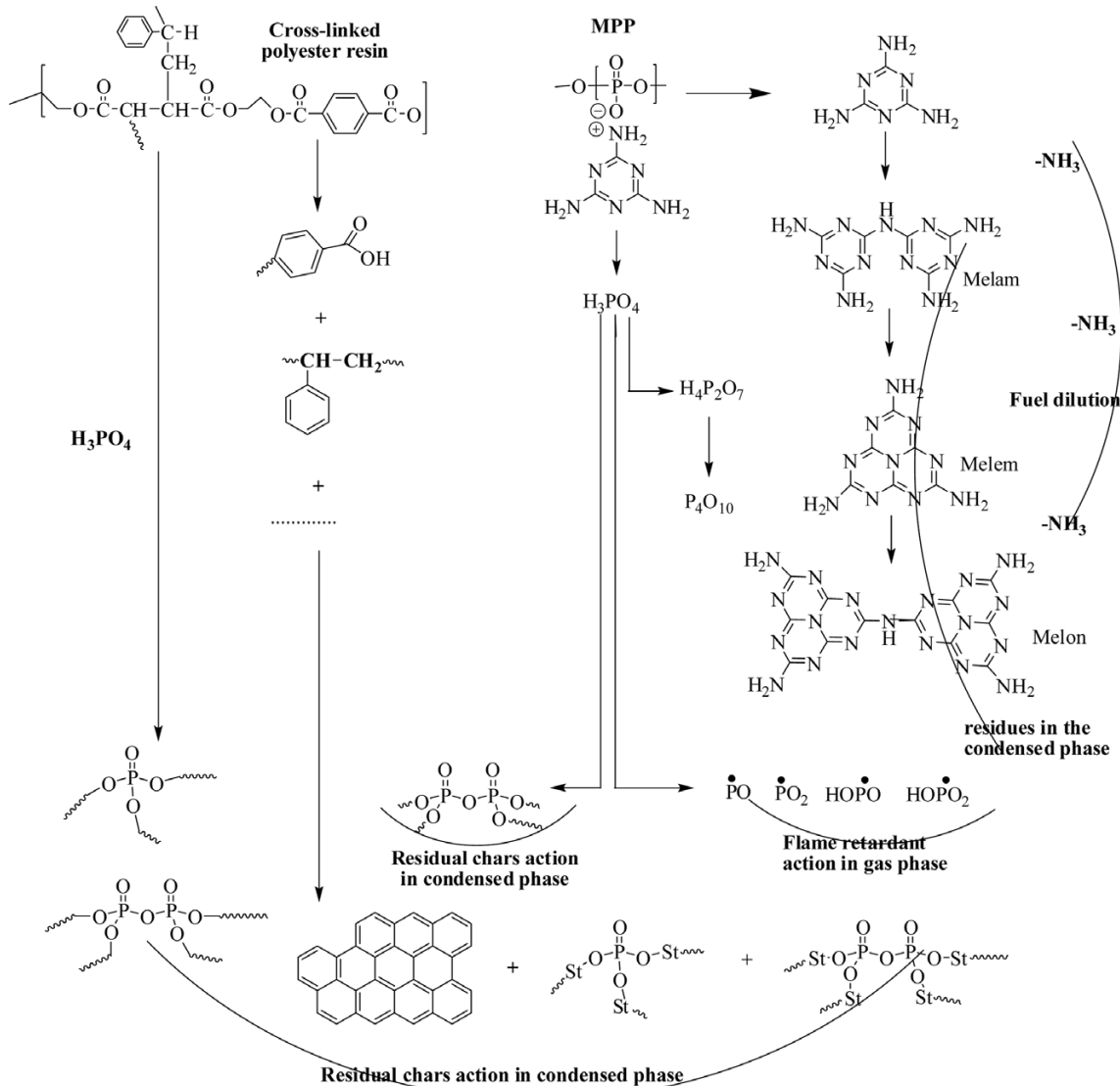
Figure 3. Possible schemes for the main decomposition of RUP and MPP and interaction between them.

decomposed to form ammonia at high temperature range. This released gas diluted O_2 and combustible gases to form thermally stable condensates, such as melam, melem, and melon.[20] Phosphoric acid condensed readily to produce pyrophosphate structures that can promote the carbonaceous char formation.[20,27] The possible decomposition scheme is presented in Figure 3.

To further understand thermal degradation behaviors of RUP/FR mixtures, calculated TG values were compared with experimental TG curves (Figure 4).

In the presence of APP and MPP, at later stages of decomposition, the quantity of experimental char residues (28-37 wt% at 600 °C) was significantly higher than the calculated values (3-12 wt% at 600 °C). This indicated that there was some interaction between decomposed FR products and RUP. The decomposition of FRs produced phosphorus-containing derivatives that can react with the decomposed RUP at the first pyrolysis step and consequently formed a stable layer that resist a further pyrolysis of RUP, and then led to better flame retardance.

To evaluate the thermal property of sample with the presence of FRs, by TG, the activation energies (E) of RUP/APP and
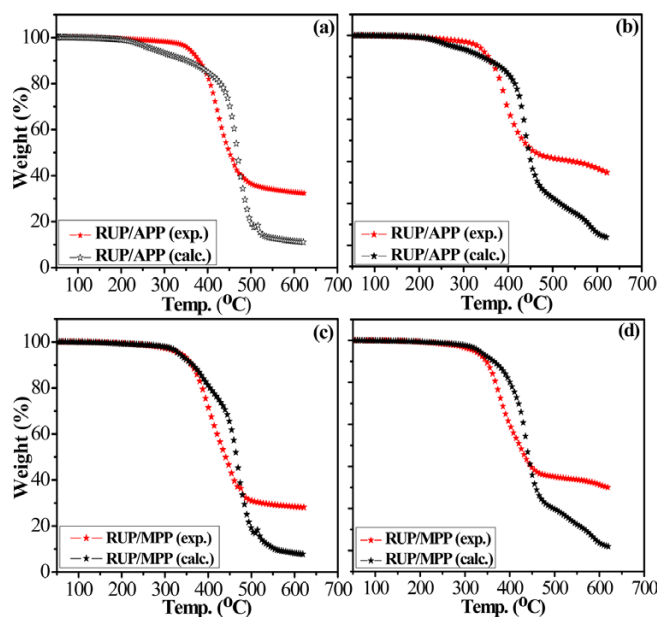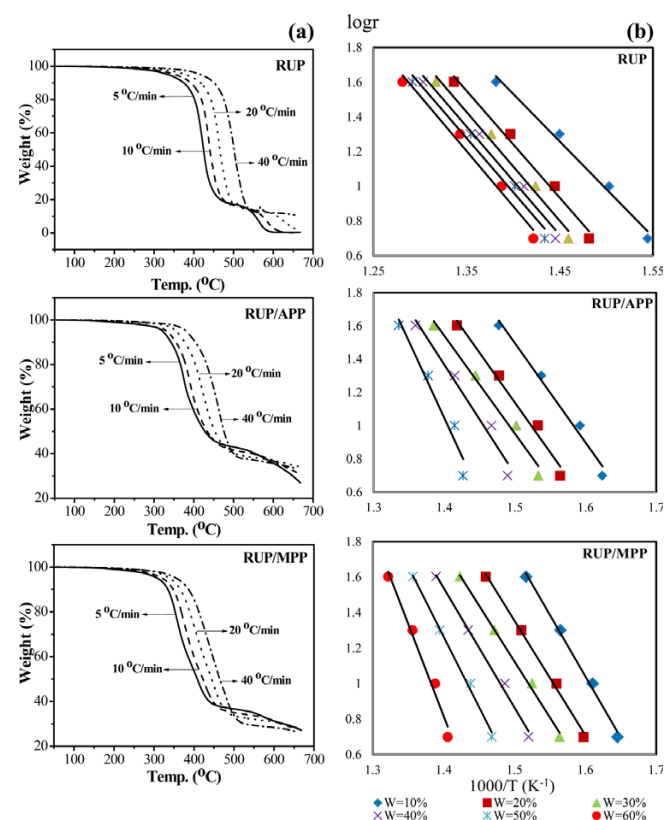

Figure 4. Experimental and calculated TG curves for RUP/FR in nitrogen (a, c) and air (b, d).

Table 3. Calculated activation energy of RUP and RUP/FR

Mass loss	Activation energy (kJ/mol)		
	RUP	RUP/APP	RUP/MPP
0.1	99.9	108.9	126.1
0.2	112.2	109.2	117.7
0.3	113.9	107.2	114.8
0.4	113.7	120.0	122.8
0.5	113.3	168.0	144.4
0.6	115.6	-	189.1

Figure 5. (a) TG curves of RUP and RUP/FR in air at different heating rates and (b) the logarithm of heating rate vs. reciprocal temperature for RUP and RUP/FR at various mass losses (W: mass loss).

RUP/MPP were determined following the modified Ozawa's method.[42,43]

As results shown in Table 3 and Figure 5, at high mass loss, the E values of RUP/FR mixtures were higher than that of RUP. The formation of residual layer protecting material from further decomposition extremly contributed to fuel inhibition and played as an efficient barrier layer for heat and O_2 transport. The thermal behavior of RUP was significantly enhanced by the addition of FR.

3.2. Fire retardance activity

RUP reached UL-94 HB while UP was failed this test. This is because RUP from PET waste contains a large aromatic composition and was thermally more stable. To decrease fire hazards and meet fire protection standard for RUP, the phosphorus-nitrogen additives including APP and MPP were employed with amount of 20-30 wt% loading. UL-94 vertical classification and LOI were used to assess the flammability of products and the results were shown in Table 4.

The tested results showed that no rating in UL-94V was achieved for RUP due to its high flammability and LOI value of 20% was obtained. Addition of 20 wt% loading for APP or 25 wt% loading for MPP was not enough to pass UL-94V test, but it showed the decrease in combustion speed compared to RUP. The best effectiveness achieved when 25 wt% loading of APP or 30 wt% of MPP was used. V-0 status was attained and LOI remarkably increased to 35% for addition of APP and 36% in the case of MPP. These results indicated that APP and MPP exhibit good flame-retardant effect on the RUP. A higher amount of MPP used than that of APP to reach simultaneous result reveals that APP is more enhancing fire retardancy than MPP. The results are matched very well with TG analysis. The above results demonstrated the effectiveness of phosphorus-nitrogen FRs; APP and MPP on enhancing fire resistance of RUP.

3.3. Chemical composition and morphology analysis of the residual char

In order to elucidate the effect mechanism of FRs used in this study on the flammability of RUP, the condensed products of RUP and RUP/FR at 450 and 550 °C were analyzed by FTIR, FE-SEM, and XPS. The detail results were presented in Figures 6-9.

The FTIR spectrum of RUP residue at 450 °C (Figure 6) exhibited the characteristic bands for C=O and C-O-C of ester groups at 1700 cm⁻¹ and 1100 cm⁻¹, respectively. The absorptions of C-C of aromatic, -CH₂- vibrations, and C-C bands of mono-substituted aromatic ring were also observed at around 1450-1600, 1238-1266, and 697, 725 cm⁻¹, respectively.[25] However, the strong decrease of these absorption vibrations for RUP combusted at 550 °C were obtained due to the main decomposition of matrix resin. In the case of RUP/FRs at 450 °C, the addition of vibration bands of P=O, P-O-C, and P-O-P at 1200, 1050, and 990 cm⁻¹ were also found.[28,44] FTIR spectra demonstrated the existance of phosphorus-containing moieties in the residue. Especially, these bands still remained in the char at 550 °C with the typical absorptions of neat RUP. It is cleared that the decomposition of additives APP and MPP produced phosphorus acid and its derivative contributed to formation of solid barrier protecting material
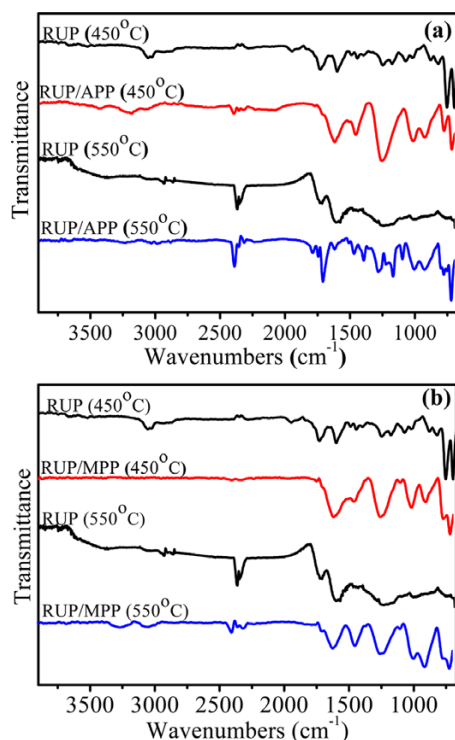
Table 4. UL-94V and LOI Results for RUP and RUP/FR

FR	Samples	RUP/FR (wt/wt)	UL-94V Rating	LOI (%)
	RUP		No rating	20
APP	RUP/APP₂₀	80.0/20.0	No rating (1st/2nd application: 4 s/burn)	-
	RUP/APP₂₅	75.0/25.0	V-0	36
MPP	RUP/MPP₂₅	75.0/25.0	No rating (1st/2nd application: 7 s/burn)	-
	RUP/MPP₃₀	70.0/30.0	V-0	35

Figure 6. FTIR spectra of residual chars of RUP/APP (a) and RUP/MPP (b).
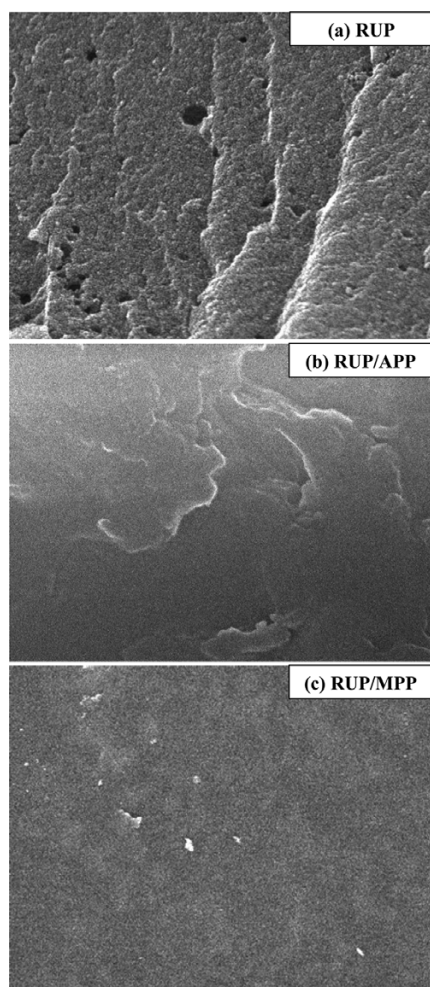

Figure 7. FE-SEM micrographs of residual chars of RUP (a), RUP/APP (b), and RUP/MPP (c) obtained after combusting in the furnace at 550 °C.

from further decomposition.

Morphology of charred residue is an important element to evaluate the quality of protective barrier in the prevention the mass transfer and the attack of oxygen to combustion zone. Figure 7 reveals the morphology of residues attained after combusting at 550 °C. Figure 7(a) shows that a porous, flaky, and brittle char could be observed for RUP while the compact and continuous layer were formed in the case of RUP/FR mixtures. The compact char layers of RUP/APP and RUP/MPP significantly contributed in preventing further decomposition of polymeric matrix. These char layers could serve as a good barrier for the beneath polymeric substrate during the burning and prevent the fuel volatiles.

XPS spectra that determine the chemical interactions and investigate the chemical composition of solid surface are presented in Figures 8 and 9. C_{1s} spectra (Figures 8(a) and 9(a)) show the binding energy of C-C and/or C-H in polymer chains at 284.7 eV. The peaks at 286.2 eV and 287.8 eV were assigned to C-O and/or C-O-P, and C=O, respectively. The peak around 288.7-290.5 eV was characteristic of C=O (carboxyl group). O_{1s} spectra given in Figures 8(b) and 9(b) show the peak at 531.5 eV was characteristic of O=C and/or O=P while the peak at 532.7 eV was correspond to -O- in C-O-C, C-O-P, and/or C-OH groups. The binding energy of 534.3 eV was correspond to -COO-.[10,32] The N_{1s} spectra (Figures 8(c) and 9(c)) could be resolved into three bands attributed to nitrogen in pyridinic (398.8-399.3 eV) and in pyrrolic (400.6 eV) groups, to quaternary nitrogen (401.9 eV).[45] The bands around 132.6-135.1 eV from P_{2p} spectra were assigned to P-O-C, PO_3^-, and/or P_2O_5 (Figures 8(d) and 9(d)).[32] XPS results certainly demontrated that RUP/APP and RUP/MPP are thermally decomposed to produce phosphorus-containing moieties during combustion, which may react with the degraded RUP segments to form a compact char *via* cross-linking. The char layer would avoid the release of flammable gaseous, oxygen transporation,
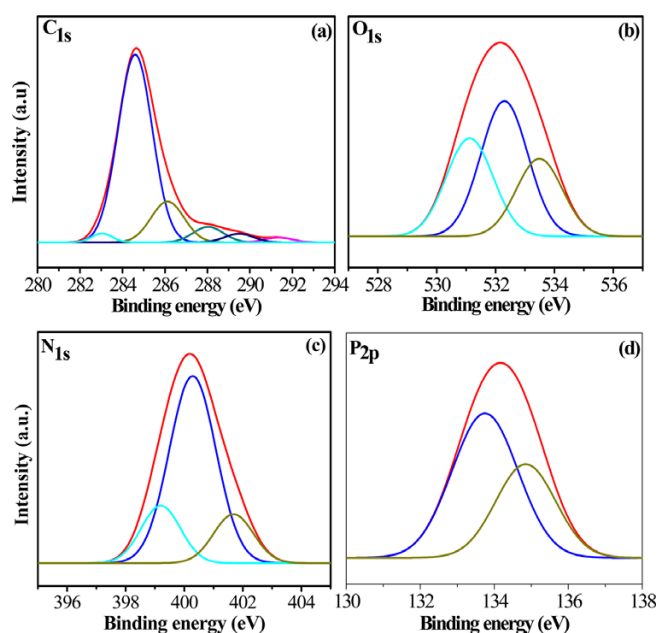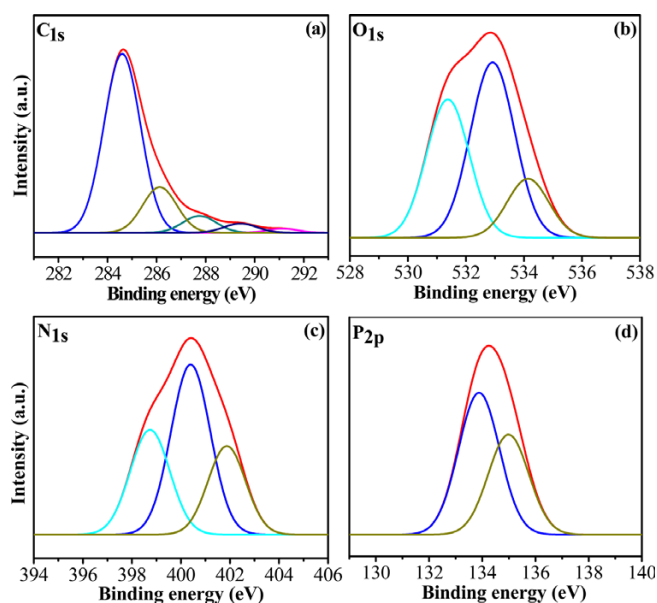

Figure 8. XPS spectra of residual chars of RUP/APP obtained after combusting in the furnace at 550 °C.

Figure 9. XPS spectra of residual chars of RUP/MPP obtained after combusting in the furnace at 550 °C.

and heat spread. This enhanced the fire resistance behaviours and heat stability of RUP very significantly.

4. Conclusions

Two phosphorus-nitrogen flame retardants including APP and MPP were incorporated into unsaturated polyester prepared from recycled PET (RUP). APP and MPP are effective in promoting flame retardancy for RUP. The mixtures of RUP/FR presented the significantly higher fire performance and thermal stability compared to RUP without additives. Addition loading of 25 wt% of APP or 30 wt% of MPP into the matrix showed UL-94 V-0 rating and LOI of 35% for APP and 36% for MPP. TG, FE-SEM, and XPS results showed that the FRs contributed to the improvement of the char yield and thermal more stability for RUP. There was some interaction between decomposed FR and RUP products and the char residues increased drastically (from 3-12 wt% to 28-37 wt%). It is believed that mode of action of FRs used in this work presented mainly in condensed phase with supporting of physical effects which improved very significantly the fire proofing of RUP.

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