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Flame retardant effect of aluminum hypophosphite in heteroatom-containing polymers

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Abstract

In the present study, the effect of the aluminum hypophosphite (AlHP) concentration on the flame retardant properties of the four different polymers [polyamide 6 (PA6), poly(lactic acid) PLA, thermoplastic polyurethane (TPU) and poly(methyl methacrylate) (PMMA)] was investigated through mass loss calorimeter tests (MLC), thermogravimetric analysis, limiting oxygen index (LOI) and vertical burning test (UL-94). Test results from UL-94 test revealed that 20 wt% AlHP was needed to reach V0 rating in the PA6, TPU and PMMA and 10 wt% was required for PLA. LOI values and the char yields of all composites were increased with increasing AlHP amount. However, peak heat release (pHRR) and total heat evolved values decreased as the added amount of AlHP increased. The highest LOI value (31) and the lowest pHRR value (134 kW/m^2) were obtained in TPU/30 AlHP composites. In brief, the comprehensive test results showed that the incorporation of the AlHP improved the flame retardant properties of the PA6, PLA, TPU and PMMA via the formation of the char in the condensed phase and radical trapping and dilution effect in the gas phase.

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Introduction

Thermoplastic polymers (TPs) are widely used in many products in human being's daily lives. It is possible to see wide range of TPs use, ranging from household appliances to toy construction, coatings, decorative materials, automobile tires, packaging, electronics, and so on. It is very important to reduce the flammability properties of TPs in their application areas. Thus, various flame retardant additives including halogen- or non-halogen-containing ones have been used in order to increase the combustion resistance of TPs for many years [1–3]. The use of halogen-containing flame retardants (HFRs) is restricted since they produce toxic and corrosive gases that are life-threatening and harmful to the human body [4–12]. The phosphorus-based flame retardants seem to be the best alternative of HFRs in terms of performance and cost [4, 6, 12–15]. Accordingly, recent studies focused on the use of new type of phosphorus-containing flame retardants. Metal hypophosphite compounds are considered as the emerging type of phosphorus flame retardants [9, 12, 16].

Aluminum hypophosphite (AlHP) has been reported as new potential filler to improve the flame retardant properties of the polymers. It is considered as environmental friendly and cost-effective flame retardant [4–6]. In the literature available, the flame retardant effect of AlHP was studied in poly(lactic acid) (PLA), thermoplastic polyurethane (TPU), polyethylene (PE), polystyrene (PS), poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET) and polyamide 6 (PA6) [4–16]. Tang et al. examined the effect of the various concentrations of AlHP (10, 20 and 30 wt%) on the flammability and mechanical properties of the PLA. The results showed that the addition of AlHP into PLA could improve the flame retardancy of PLA. When 20 wt% of AlHP was added into PLA, the LOI value was increased from 19.5 to 28.5%, and the composite achieved V0 rating [8]. Xiao et al. investigated the flammability properties of TPU-containing AlHP with the loading ratios ranging from 25 to 35 wt%. It was concluded that the flame retardant TPU was obtained with V0 rating with the addition of 30 wt% of AlHP [14]. Li et al. studied the flame retardant and thermal degradation behavior of the PA6-containing magnesium hypophosphite (MgHP) and AlHP with the concentrations ranging from 18 to 28 wt%. They observed noticeable difference between MgHP and AlHP in terms of their flame retardant efficiency. Although PA6-containing 18 wt% AlHP obtained the highest UL-94 rating of V0, MgHP-containing composites did not attain V0 rating even in the highest loading level of 28 wt% [9]. Jian et al. studied the use of AlHP as flame retardant additive in acrylonitrile–butadiene–styrene (ABS). The LOI value increased from 18.5 to 24.1, and UL-94 rating increased from N.R. (no rating) to V0 with the addition of 25 wt% AlHP [7].

The aim of the current research is to evaluate the flame retardant effect of the AlHP in PA6, PLA, TPU and PMMA in three different concentrations of 10, 20 and 30 wt%. The literature regarding the flame retardant effect of the AlHP in TPU, PLA and PA6 has been quite scarce. Also to date, there has been no relevant work focusing on the flame retardant properties of AlHP in PMMA composites.

Table 1 Materials and their suppliers

Materials	Product code	Supplier
Aluminum hypophosphite	–	Beijing Purkinje General Instrument Co. Ltd., China
Polyamide 6	NB40	Eurotech, Turkey
Poly(lactic acid)	6202D	NatureWorks LLC
Thermoplastic polyurethane	1045D	Desmopan, Germany
Poly(methyl methacrylate)	LG2	Sumipex, Europe

Table 2 Production parameters in the extrusion process

Composites	Die (°C)	4. Zone (°C)	3. Zone (°C)	2. Zone (°C)	1. Zone (°C)	Hopper (°C)	Screw speed (rpm)
PA6/AlHP	220	215	210	205	200	50	100
PLA/AlHP	180	200	200	190	180	50	100
TPU/AlHP	190	195	200	200	195	50	100
PMMA/ AlHP	200	215	215	200	200	50	100

Experimental

Materials

The materials with their suppliers are given in Table 1. The density of the PA6 is 1.13 g/cm^3. PLA has the density and melt flow index (MFI) of 1.24 g/cm^3 and 15–30 g/10 min (2.16 kg, 210 °C). PMMA has the density and MFI of 1.19 g/cm^3 and 15 g/10 min (3.8 kg, 230 °C). The density of TPU is 1.22 g/cm^3. All given properties are provided by suppliers.

Sample preparation

PA6, PLA, TPU, PMMA and AlHP were dried at 80 °C for approximately 16 h before use to remove the physically absorbed water. They were mixed with different weight ratios of AlHP (10, 20 and 30 wt%) using twin-screw extruder (GULNAR MAKINA, Istanbul, Turkey). The barrel temperatures of six zones and the screw speeds of the extruder for each composite system are given in Table 2. Extrudates were cut into pellets, and the pellets were molded by a laboratory-scale injection-molding machine (DSM Xplore 12 ml Micro-Injection Molder, Netherlands) to obtain standard specimen. The barrel temperatures of the injection-molding machine for PLA, TPU, PMMA and PA6 were 205 °C, 200 °C, 220 °C and 240 °C,

respectively. The mold temperature and the injection pressure were fixed at 25 °C and 8 bar during the injection-molding process. The MLC test samples were produced by using laboratory-scale hot press (GULNAR MAKINA, Istanbul, Turkey) for 3 min, at 220 °C, 185 °C, 200 °C and 210 °C for PA6, PLA, TPU and PMMA, respectively.

Characterization

The combustion behaviors of all samples were measured by the LOI, UL-94 and mass loss calorimeter (MLC). The LOI values were measured according to ASTM D2863 by Fire Testing Technology Limiting Oxygen Index Analyzer instrument. The dimensions of the specimens used for the LOI test were $130 \times 6.5 \times 3.2$ mm^3. The UL-94 tests were performed according to ASTM D3801. The specimens used for the test had the three-dimensional size of $130 \times 13 \times 3.2$ mm^3. TGA tests were carried out from 50 to 800 °C using Hitachi-High Tech STA-7300 instrument with the heating rate of 10 °C/min under N_2 atmosphere [9, 13]. The MLC (Fire Testing Technology, UK) was performed according to the ISO 13927. Flat horizontal samples ($100 \times 100 \times 3$ mm^3) were irritated at a heat flux of 35 kW/m^2 to stimulate mild fire scenario. The microstructures of the char residues remained after MLC tests were characterized with SEM (LEO 440, 20 kV). The surface of samples was sputter-coated with a thin layer of gold before examination.

Results and discussion

Thermal decomposition

TGA technique has been widely used to estimate the thermal properties of the materials. TGA analyses are performed on AlHP, neat polymers and their composites under nitrogen atmosphere. TGA and DTGA curves of the AlHP are given
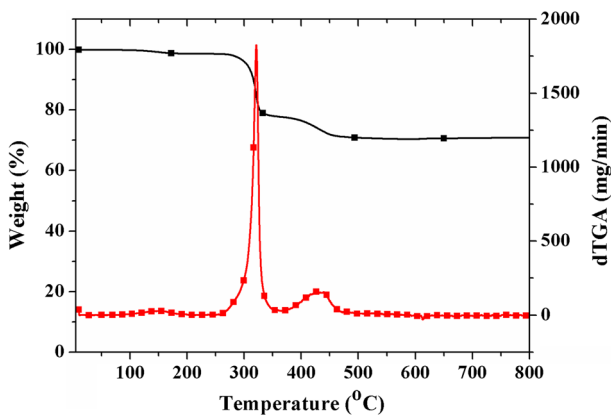

Fig. 1 TGA and DTGA curves of AlHP

in Fig. 1. As can be seen from Fig. 1, the thermal decomposition of AlHP occurs through two steps with maximum rates at 322 °C and 430 °C. In the first step, AlHP decomposes to produce phosphine (PH_3) and aluminum hydrogen phosphate [$Al_2(HPO_4)_3$]. In the second step, $Al_2(HPO_4)_3$ degrades into aluminum pyrophosphate [$Al_4(P_2O_7)_3$] and releases water [17–20]. It leaves 70.8% inorganic residue at 800 °C.

The TGA and DTGA curves of the pristine polymers and the composites are shown in Fig. 2. The relevant data including $T_{5\%}$ (the temperature at 5 wt% of mass loss occurs), T_{max} (the temperature at maximum decomposition rate) and the calculated and experimental char residues at 800 °C are listed in Table 3. Thermal decomposition of the PA6 is occurred by single degradation step at 481 °C with leaving 0.7 wt% char residue at 800 °C. The degradation step of the PA6 is related to the evolution of caprolactam and other volatile gases such as CO_2 and NH_3 [9, 10, 12]. AlHP-containing PA composites also degrade in one step, whereas a shoulder (shown with black arrow in figure) which arises from the degradation of the AlHP is seen in the DTGA curve of the composites. This is also observed in other studied polymers in the current study. $T_{5\%}$ and T_{max} values reduce with the addition of the AlHP. The reductions in $T_{5\%}$ and T_{max} values stem from the low thermal stability of the AlHP. It is concluded that PA6/AlHP composites have poorer thermal stabilities than pure PA6. The char formation increases with the increasing AlHP contents. The same trend is also observed with other studied polymers in the current study.

PLA decomposes in single step at 367 °C with leaving 0.3% char residue. PLA mainly degrades via the intramolecular transesterification, cis-elimination and fragmentation with the formation of lactide, cyclic oligomers, acrylic-based oligomers, acetaldehyde and CO_2 [21]. The AlHP-containing PLA composites also decompose in a single step with a shoulder at around 320 °C. The $T_{5\%}$ of PLA/AlHP composites is lower than pure PLA. This may attribute to the lower thermal stability of AlHP than that of pure PLA, as in the case of PA-6. The addition of AlHP has little influence on the T_{max} of pure PLA.

The degradation of TPU is identified as two steps at 322 °C and 403 °C with leaving 7.1% char residue. The first degradation step stems from the decomposition of urethane bond. The second degradation step is attributed to the decomposition of the polyol segments [15]. The addition of AlHP does not cause decrease in the initial thermal stability ($T_{5\%}$) unlike the other studied polymers. It is thought that the observed trend arises from the similar first decomposition temperatures of AlHP and TPU. The addition of the AlHP causes the reduction in both T_{max1} and T_{max2} values.

Thermal decomposition of the PMMA occurs through single step at 380 °C with leaving 1.0% char residue. The degradation of the PMMA is mainly related to the evolution of methyl methacrylate monomer via depolymerization under the nitrogen atmosphere [22, 23]. In the presence of the AlHP, the $T_{5\%}$ and T_{max} values increase slightly. Different factors cause thermal stability increase in PMMA. One of the factors that increase the thermal stability of PMMA is the radical trapping effect [24–26]. It is thought that PO_2 and PO radicals which are the decomposition products of AlHP make the radical trapping effect and increase the thermal stability of PMMA. Similar thermal stability increase is observed in PMMA in the presence of different phosphorus-based flame retardants via radical scavenging effect [27–29].
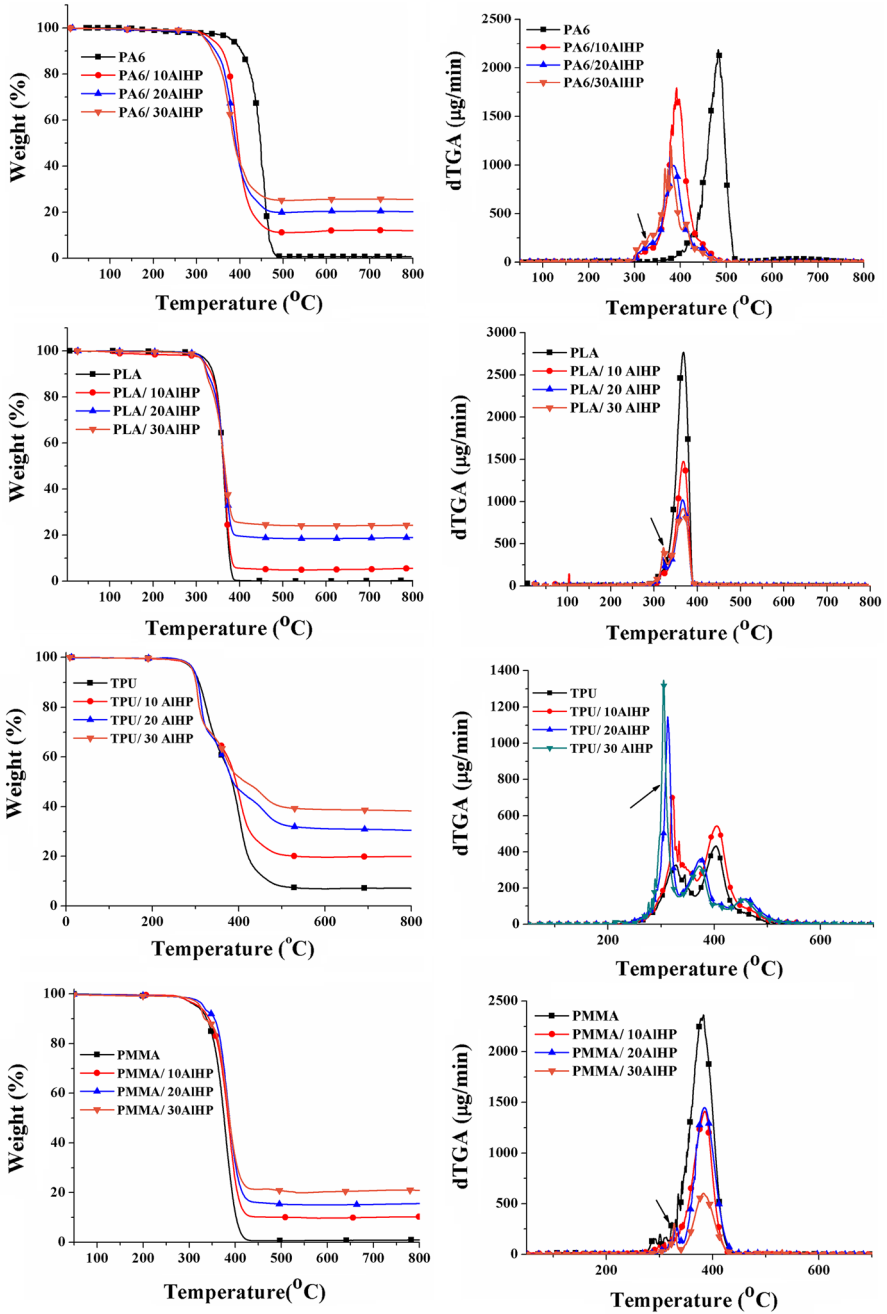
Fig. 2 TGA and DTGA curves of pure polymers and composites

Table 3 TGA data of the composites

Sample	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield (%)	
				Calculated	Experimental
AlHP	304	322	430	–	70.8
PA	375	481	–	–	0.7
PA/10 AlHP	332	390	–	7.6	12.0
PA/20 AlHP	321	376	–	14.7	20.2
PA/30 AlHP	317	378	–	21.7	25.5
PLA	326	367	–	–	0.3
PLA/10 AlHP	318	366	–	7.4	5.6
PLA/20 AlHP	317	364	–	14.4	19.0
PLA/30 AlHP	315	364	–	21.5	24.3
TPU	291	322	403	–	7.1
TPU/10 AlHP	294	321	400	13.9	19.8
TPU/20 AlHP	293	313	378	20.2	30.5
TPU/30 AlHP	290	305	370	26.6	38.3
PMMA	315	380	–	–	1.0
PMMA/10 AlHP	328	386	–	8.0	10.3
PMMA/20 AlHP	329	385	–	15.0	15.6
PMMA/30 AlHP	321	383	–	22.0	21.0

For all composites except for PLA/10 AlHP and PMMA/30 AlHP, the experimental char yields are higher than the calculated ones. The calculated char yields are found from the TGA data of the each component. It reveals that there is interaction between AlHP and polymers leading to char residue improvement. Phosphorus flame retardants can react with polymers containing heteroatoms (nitrogen and oxygen) in the condensed phase [30, 31]. Thus, more residue is obtained. The increase in char amount shows that some part of the polymer chain remains in the condensed phase rather than acting as fuel source.

Mass loss calorimeter

Mass loss calorimeter (MLC) is used to determine the fire performance of the polymer composites. The heat release rate (HRR), which is the measure of the heat release per unit surface area of the burning material, is considered to be the most important data obtained from the test [32]. Several other valuable data such as time to ignition (TTI), total heat evolved (THE), peak mass loss rate (pMLR), fire growth rate (FIGRA) and fire performance index (FPI) can also be obtained from MLC, during the combustion of the samples. Figure 3 shows HRR curves of all samples, and their corresponding data are given in Table 4. The digital photographs of the char residues are shown in Fig. 4. The SEM images of the char residues of 30 wt%
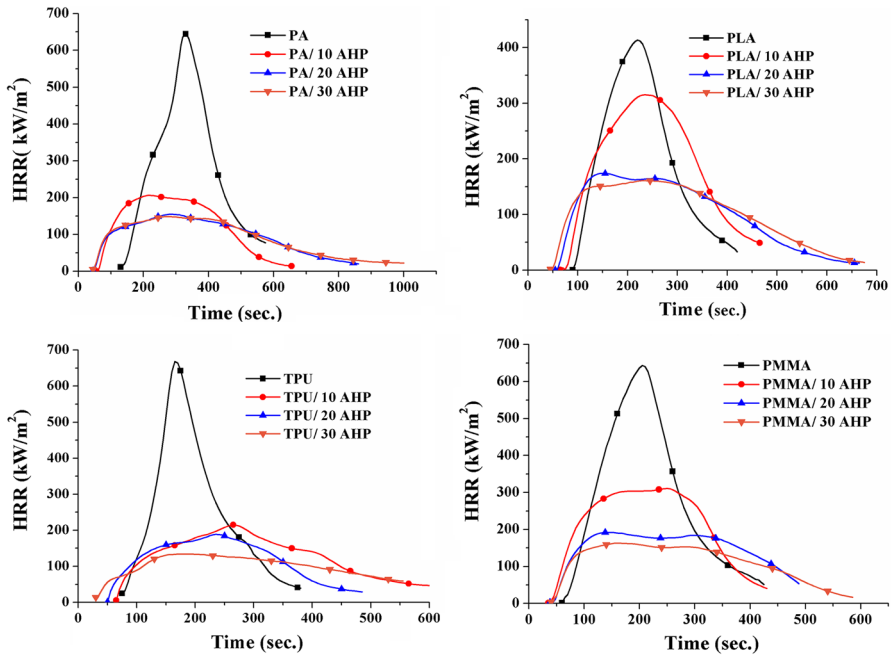
Fig. 3 HRR curves of the composites

AlHP-containing composites with low (left side) and high (right side) magnifications are shown in Fig. 5.

One of the most prominent effects of the AlHP addition is observed on TTI values. All AlHP-containing composites have lower TTI values than those of respective pure polymers. The decrease in TTI values arises from the flammable pyrolysis product of the AlHP, namely phosphine [8, 33, 34].

According to Fig. 3, the pure polymers burn rapidly after ignition and have sharp HRR curves. The addition of AlHP causes reduction in peak heat release rate (pHRR), average heat release rate (avHRR), pMLR and THE values as the added amount increases. The reductions in these values primarily show that the fire performance of the pristine polymers increases with the addition of AlHP. The decrease in fuel source and the formation of foamed char structure (see Fig. 4) are the main reasons for the reduction of these values. The decrease in fuel source also arises from the interaction between AlHP and polymers. Some part of the matrix material reacts with the decomposition products of the AlHP and stays in the condensed phase as a part of the char residue rather than acting as fuel source. The AlHP shows different performances in the studied polymers. For instance, pHRR value reduces at about 77, 61, 80 and 75% in PA6, PLA, TPU and PMMA. THE reduces at about 39, 31, 43 and 44% in PA6, PLA, TPU and PMMA with the addition of 30 wt% AlHP. It is thought that the performance difference arises from the char characteristics. The amount, height and morphology of the foamed char are different in the studied polymers. As seen

Table 4 Mass loss calorimeter data of the pristine polymers and composites

| Sample	TTI (s)	pHRR (kW/m^2)	THE (MJ/m^2)	pMLR (g/s)	avHRR (kW/m^2)	THE/TML (MJ/m^2/g^1)	FIGRA	FPI	Residue (%)
PA	133	644	118	0.93	350	3.3	1.9	0.21	4.8
PA/10 AHP	58	206	82	0.14	158	2.8	0.9	0.28	13.5
PA/20 AHP	42	154	78	0.11	109	2.9	0.5	0.27	23.7
PA/30 AHP	47	148	72	0.09	104	2.9	0.5	0.31	30.5
PLA	91	413	65	0.23	230	2.0	1.8	0.22	3.2
PLA/10 AHP	77	315	57	0.17	223	1.8	1.3	0.24	10.3
PLA/20 AHP	58	164	47	0.11	101	1.8	1.0	0.35	23.4
PLA/30 AHP	44	160	45	0.10	106	1.6	0.6	0.27	28.8
TPU	76	668	90	0.42	242	3.0	4.0	0.11	7.2
TPU/10 AHP	63	214	65	0.16	140	2.1	0.8	0.29	19
TPU/20 AHP	48	188	57	0.13	115	2.1	0.8	0.25	25
TPU/30 AHP	31	134	51	0.07	103	2.5	0.7	0.23	31.2
PMMA	60	643	93	0.29	352	2.6	3.1	0.09	2.8
PMMA/10 AHP	37	310	74	0.15	254	2.3	1.2	0.11	5.7
PMMA/20 AHP	38	184	59	0.14	144	2.1	1.3	0.20	17.8
PMMA/30 AHP	42	163	52	0.10	104	2.2	1.0	0.25	32.1
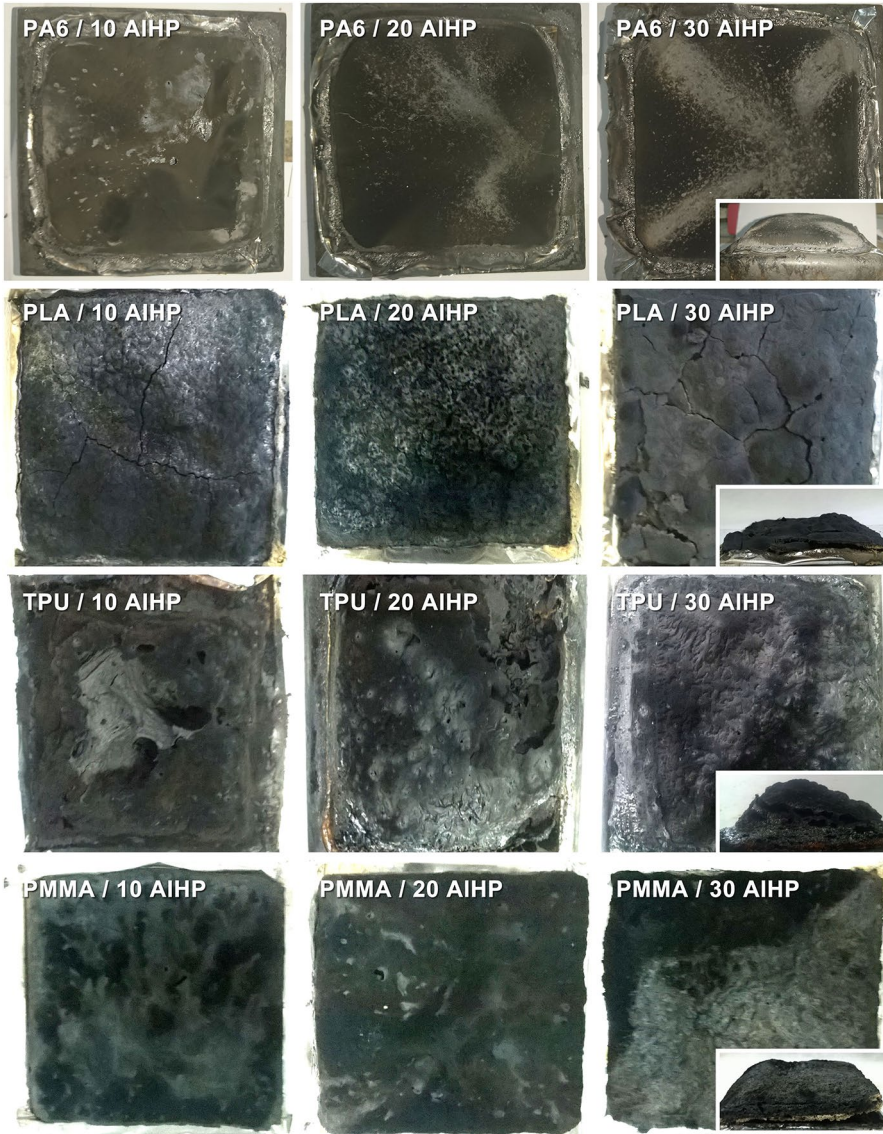
Fig. 4 Digital photographs of selected char residues obtained during mass loss calorimeter tests

from Fig. 4, all char residues have smooth and compact structure with some small holes and cracks. However, they have different morphologies as seen in higher-magnification SEM images. The char residue of the PLA-containing composite has highly porous structure with lowest intumescent height. Thus, the lowest fire performance is seen in the PLA. The char of the TPU-containing composite has smooth and compact structure with the highest intumescent height. Accordingly, the highest performance is observed in TPU.
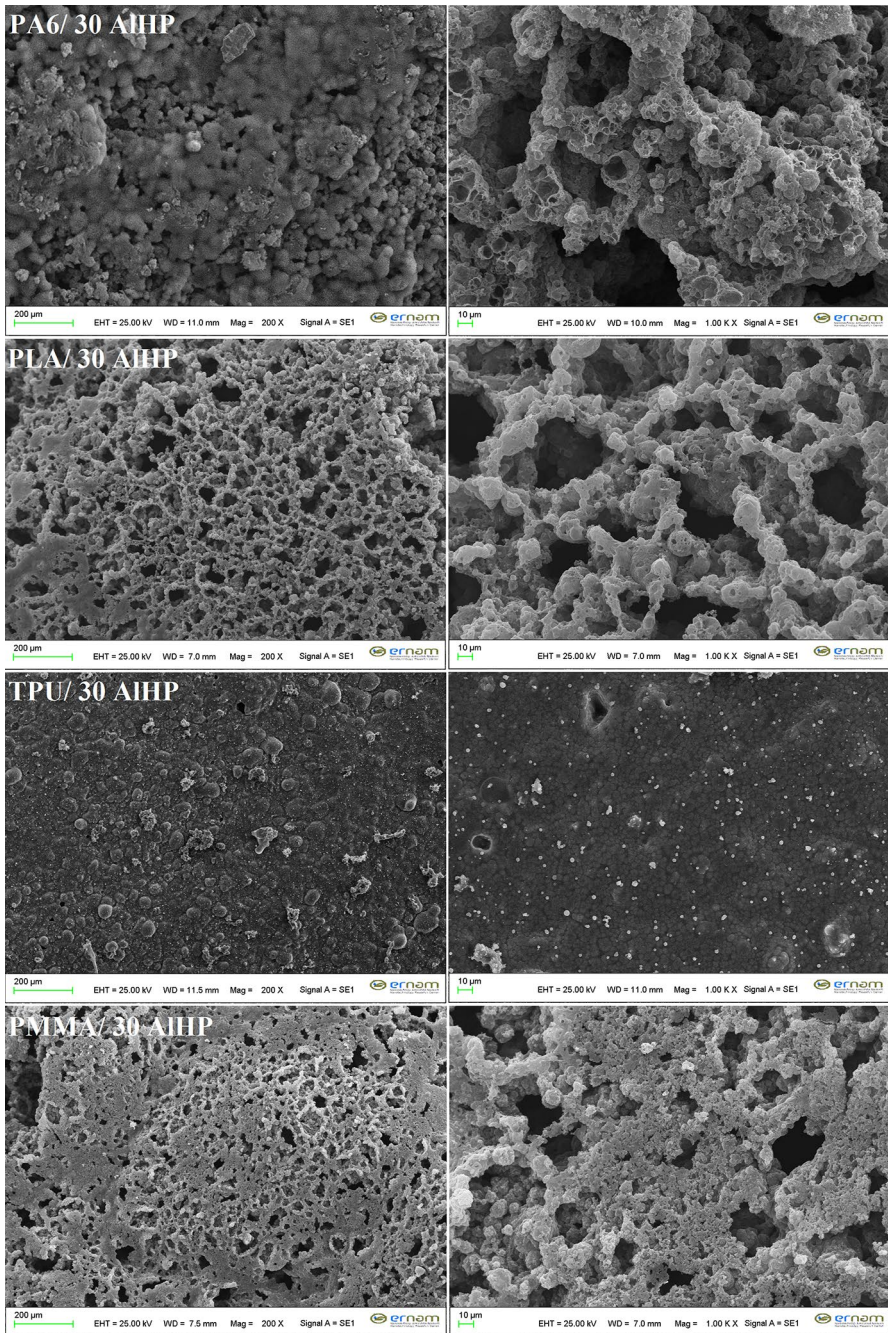
Fig. 5 SEM micrographs with low (left side) and high (right side) magnifications of char residues obtained during mass loss calorimeter tests

Another obvious change takes place in the total heat evolved/total mass loss ratio (THE/TML) which is the measure of the effective heat of combustion. The reduction of this value shows effective flame inhibition or dilution in the gas phase. With the addition of the AlHP, the THE/TML value of the composites decreased with respect to pristine polymers. AlHP shows gas phase actions in two ways. Water makes dilution effect, and PO_2 and PO radicals make scavenger effect in the gas phase [9, 35]. It is concluded that AlHP shows its flame retardant effect in both the condensed and gas phase in the studied polymers.

FIGRA is calculated as ratio of pHRR to time of pHRR. FPI is calculated as the ratio of time to ignition (TTI) to pHRR. The lower FIGRA means the slower flame growth rate. Higher the FPI, higher is the product safety rank [36, 37]. FIGRA value reduces and FPI value increases with the addition of AlHP. This result indicates that AlHP improves the fire performance and reduces the fire risk of the composites.

LOI and UL-94 tests

LOI and UL-94 tests are effective methods to understand the flammability characters of the composites. The results are shown in Fig. 6. The LOI value of pure PA6 is 20.8%. LOI value increases to 23.4, 24.5 and 26.2 with the addition of the 10, 20 and 30 wt% of AlHP, respectively. In addition, the highest UL-94 rating of V0 is observed with the addition of 20 and 30 wt% AlHP in PA6. Pure PLA is easily flammable polymeric material, and its LOI value is only 22.0%. However, it fails to pass during the UL-94 testing. LOI values increase to 25.7, 28.4 and 28.7% with the loading of 10, 20 and 30 wt% of AlHP, respectively. All the PLA/AlHP composites reach V0 rating. Pure TPU has the LOI value of 20.1% and cannot pass the UL-94 test. The LOI values increase to 21.2, 29.0 and 31.0% with the loading of 10, 20 and 30 wt% of AlHP. In addition, the highest UL-94 rating of V0 is observed with the addition of 20 and 30 wt% AlHP. Pure PMMA is a flammable material with the low LOI value of 17.3%, and it shows no rating in UL-94 test. The LOI values of the PMMA/AlHP composites increase to 21.5, 22.7 and 25.5 with the incorporation of 10, 20 and 30 wt% of AlHP, respectively. The highest UL-94 rating of V0 is observed with the addition of 20 and 30 wt% of AlHP. AlHP exerts mainly its flame retardant effect both in the condensed phase via the formation of intumescent char and via dilution and radical trapping effect in the gas phase.

Conclusion

In this work, the flame retardant behavior of the AlHP in PA6, PLA, TPU and PMMA is investigated. TGA results show that the thermal stabilities of the composites decrease with the addition of the AlHP except for PMMA/AlHP composites. At the same time, the char residue of the composites increases with increasing AlHP content. The MLC test results show that the presence of the AlHP causes the earlier ignition of the composites. However, the fire performances of the composites increase as the added amount of the AlHP increases. According to the flammability

Fig. 6 LOI and UL-94 ratings of the composites
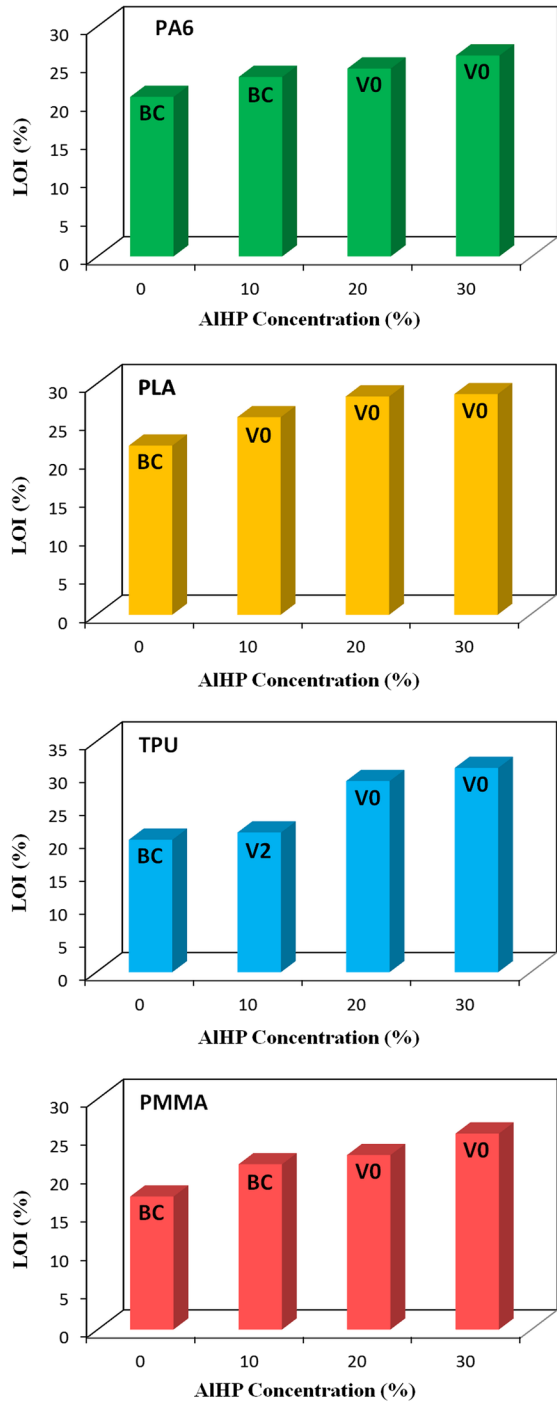
test results, LOI value increases steadily as the added amount of the AlHP increases. 20 wt% AlHP is needed to reach V0 rating in the PA6, TPU and PMMA and 10 wt% was needed for PLA. In brief, it follows from all test results that AlHP shows its flame retardant effect through the formation of compact char structure in the condensed phase and reactive and diluting effect in the gas phase.

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