The effect of phosphorus based flame retardants on the thermal and fire retardant properties of chicken feather/thermoplastic polyurethane biocomposites

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Abstract

In this study, phosphorus-based additives (ammonium polyphosphate (APP), aluminum hypophosphite (AHP), and aluminum diethyl phosphinate (AlPi)) were used to improve the flame retardant properties of chicken feather (CF) reinforced thermoplastic polyurethane (TPU) composites. The additives were used in three concentrations of 5, 10, and 20 wt%. The fire-retardant properties of the composites were investigated by using limiting oxygen index (LOI), vertical burning test (UL 94 V), thermogravimetric analysis (TGA), and mass loss calorimeter test (MLC). According to the test results, the additives exerted flame retardant performance in the descending order of APP, AHP and AlPi. All additives showed flame retardant action both in the condensed and gas phases. However, the better fire retardant performances of APP and AHP with respect AlPi stemed from enhanced char formation.

1. Introduction

Thermoplastic polyurethane (TPU), block copolymer bearing hard and soft segments, is synthesized mainly from polyether and/or polyester based long chain diols and diisocyanates. With altering the kind and amount of hard and soft segments, the final properties of TPU can be adjusted with outstanding characteristics of mechanical strength, flexibility, good abrasion resistance, excellent chemical resistance, and processability diversity. With these special properties, it finds numerous applications in many engineering fields [1, 2]. However, its flammable character with dense smoke and heat genereation limits its use. Intense effort is seen in the literature to enhance the fire retardant performance of TPU [3, 4].

Animal-based fibers such as wool, silk and feathers are the most important second class natural reinforcement elements used in thermoplastic polymer-based composite materials. 15 million tons of chicken feather (CF) are approximately released each year as waste material to the environment. To find novel applications to CF has growing interest with increasing enviromental concisious. CF is used as reinforcing material in biocomposite applications due to its low cost, light weight, and reasonable mechanical characteristics [5–7].

CF mainly composed of protein (90 wt%) reffered to as keratin. Keratin, containing heteroatoms of nitrogen, oxygen, and sulfur, leaves remarkable ash when it burns. Accordingly, feather and/or modified keratin-based materials are considered as promising additives in flame retardant applications [8–10]. In the literature, the mechanical and thermal properties of feather containing composites are investigated with various matrix materials including TPU [11–14]. However, the fire retardant performance of CF containing TPU composites is not studied.

In the current study, commercially avaliable phosphorus-based flame retardant additives are selected for producing environmentally friendly and light weight biocomposites due to their remarkably low toxic nature, low densities, and potential effectiviness. It is well known fact that phosphorus based additives are higly effective in heteroatom containing polymers like CF, and TPU [15, 16]. The flame retardant performances of ammonium polyphosphate (APP) [17, 18], aluminum diethylphosphinate (AlPi) [19–21], and aluminium hypophosphite (AHP) [22–26] in TPU take into consideration for selecting these additives in TPU/CF based composites, as well.

Chen et al. observed that the addition of 10 wt% APP increased limiting oxygen index (LOI) value from 23.5 to 31.3% [17]. Chen et al. found that the inclusion of 20 wt% APP in TPU cause increament from 21.5 to 31.3% in LOI value [18]. Sut et al. used AlPi with different synergistic additives. They observed that the highest vertical UL 94 (UL 94 V) rating of V0 was obtained with flame retardant mixture containing AlPi [19, 20]. Li et al. found that 30 wt% AlPi was required to get V0 rating and the LOI value was about 23%. Chen et al. made two different studies with the use of AHP. In these studies, it was detected that 10 wt% AHP was required to get V1 rating and LOI value increased from 24 to 32.5% with the inclusion of 20 wt% AHP [23, 24]. Xiao found that 30 wt% AHP was needed to get V0 rating and the LOI value of 30.2% [25] Savas et al. observed that the addition of 20 wt% AHP was required to get V0 rating and the LOI value of 29% [26]. In all these studies, enhanced flame retardant performance was observed with reduced peak heat release rate (pHRR), and total heat evolved (THE).

In the current study, the effect APP, AlPi, and AHP amount on the thermal and flame retardant characteristics of CF containing TPU composites are investigated. The properties of the biocomposites are examined using thermal gravimetric analysis (TGA), UL 94 V, LOI, and mass loss calorimeter studies.

2. Experimental

2.1 Materials

TPU (PEARLTHANE™ CLEAR 15N85-CF) was purchased from Brenntag (Istanbul, Turkey). It has hardness and density of 86 (Shore A) and 1.11 g/cm^3, respectively. CF was supplied from local sources located in Bursa, Turkey. APP (Exolit® AP 750), and AlPi (Exolit® OP 930) were kindly supplied from Clariant (Istanbul, Turkey). Exolit® AP 750, the mixture of APP and the aromatic ester of tris (2-hydroxyethyl) isocyanurate, develops its effect through phosphorus/nitrogen synergism [27]. It has density, phosphorus, and nitrogen contents of 1.8 g/cm^3, 20–22 wt% and 11.5–13.5 wt%, respectively. Exolit® OP 930 has density, particle size, and phosphorus content of 1.35 g/cm^3, < 20 μm (D95), and 23.3–24 wt%, respectively. AHP was bought from Wuhan Ruiji Chemical Co. Ltd. (Wuhan, China). It has an AHP content over 96% with an average particle size of 10 μm.

2.2. Production of the composites

Prior to the grinding process, CF was cleaned with soapy water at 60 ^oC to remove the oil and other unwanted substances. After washing process, CF was dried at 80 ^oC for 16 hours. CF was pulverized with quills using blade grinding machine (FRITSCH PULVERISETTE 19, Germany). CF in powder was used in the composite production. CF, and phosphorus compounds were dried in an oven at 80°C for 24h before the extrusion process. The compounding process was carried out in twin screw extruder (GULNAR MAKINA, Istanbul, Turkey) with the temperature profile of 50, 165, 170, 175, 170, 165°C from hopper to die at 100 rpm. The samples for LOI and UL-94 tests were molded by injection-molding machine (DSM Xplore

12 ml Micro-Injection Molder, Netherlands) under the processing conditions of 190 ^{o}C barrel temperature and 30 ^{o}C mold temperature. Mass loss calorimeter samples were manufactured using hydrolytic hot-press (GULNAR MAKINA, Istanbul, Turkey) at 160°C in 3 minutes. The flame retardant efficiencies of phosphorus compounds were examined in constant CF loading of 20 wt%. Phosphorus compounds were used in three different concentrations of 5, 10 and 20 wt%. For sample coding, the abbreviations TPU, CF, APP, AlPi, and AHP were used for thermoplastic polyurethane, chicken feather, ammonium polyphosphate, aluminum diethyl phosphinate, and aluminium hypophosphite, respectively. The abbreviation, TPU/CF/10 APP, shows the sample containing 20 wt% CF and 10 wt% APP.

2.3. Characterization Methods

TGA tests were made for phosphorus based additives, and the composites using Hitachi-High Tech STA-7300 instrument with the heating rate of 10 ºC/min from room temperature up to 800 ºC under the N_2 atmosphere. LOI and UL 94 V tests were performed according to the standards of ASTM D2863, and ASTM D3801, respectively. The dimensions of LOI and UL-94 V samples were 130 × 13 × 3.2 mm^3, and 130 ×6.5 × 3.2 mm^3, respectively. Mass loss calorimeter test was made on specimens with the dimensions of 100 × 100 × 3 mm^3 using Mass Loss Cone with thermopile attachment (Fire testing Technology, U.K) under the heat flux of 35 kW/m^2 according to ISO 13927 standard. The microstructures of the residual chars remained after mass loss calorimeter test were investigated with SEM (FEI Quanta 400F). The sample surfaces were covered with gold with a sputter-coater to achieve the conductivity.

3. Results And Discussion

3.1. Thermal decomposition of the additives

Thermal decomposition characteristics of the additives are analyzed by TGA under nitrogen atmosphere. TGA and DTGA graphs of the additives and the relevant data are given in Fig. 1 and Table 1, respectively. As seen from Fig. 1, CF decomposes in two steps with the loss of physically absorbed water at 68 ^{o}C and the decomposition of keratin at 311 ^{o}C. It leaves 21.7% carbenecous residue formed via crosslinking and cyclization reactions [28, 29]. APP decomposes in three successive steps occurred at 295, 352, and 414 ^{o}C and leaves 63.2 wt% phosphocarbonaceous residue. In the first step, crosslinked polyphosphoric acid is formed via releasing ammonia, and water. In the second step, esterification reaction occurs between between acid groups and carbon source (aromatic ester of tris (2-hydroxyethyl) isocyanurate). In the last step, the decomposition of ester compounds takes place via dehydration [30–32]. AlPi decomposes in a single step with the maximum decomposition temperature of 468°C with the release of intact AlPi molecule and diethylphosphinic acid. It leaves 7 wt% aluminium phosphate based residue [33, 34]. AHP decomposes in three steps with the maximum degradation rates at 320, 404, and 442 ^{o}C and leaves 76 wt% aluminum phosphate based residue. In the first step, aluminum hydrogen phosphate is formed by releasing phosphine gas. In the second and third successive degradation steps, the transformation of aluminum hydrogen phosphate to aluminium pyrophosphate and aluminium phosphate take place via dehydration reactions [35–37].

Table 1
TGA data of the fillers, polymer and composites

SAMPLE	$T_{5\%}$ (^oC)^a	T_{max1} (^oC) ^{b}	T_{max2} (^oC)^b	T_{max3}(^oC)^b	Residue Yield Calc. (%) ^{c}	Residue Yield Exp. (%) ^{d}
APP	288	295	352	414	-	63.2
AlPi	419	468	-	-	-	7.0
AHP	306	320	404	442	-	76.0
CF	88	68	311	-	-	21.7
TPU	317	404	-	-	-	2.3
TPU/CF	279	322	400	-	6.2	6.6
TPU/CF/5 APP	274	279	373	-	9.2	17.9
TPU/CF/10 APP	270	281	354	-	12.3	21.1
TPU/CF/20 APP	267	277	329	-	18.4	31.4
TPU/CF/5 AlPi	266	305	314	-	6.4	8.1
TPU/CF/10AlPi	270	312	323	-	6.7	10.9
TPU/CF/20AlPi	267	315	-	-	7.1	14.3
TPU/CF/5AHP	263	326	380	-	9.9	22.2
TPU/CF/10AHPP	261	311	375	-	13.6	24.2
TPU/CF/20AHP	258	293	367	-	20.9	34.1

a: Temperature at 5% weight loss **b**: The maximum degradation rate temperatures **c**: Char Yield at 800°C (calculated)
d:Char Yield at 800°C (experimental)

3.2. Thermal decomposition of the composites

TGA and DTGA curves of the composites and the relevant data are given in Fig. 2 and Table 1, respectively. Pristine TPU degrades in single step with leaving 2.3 wt% carbonaceous residue. With the addition of CF, the composite decomposes in two steps at 322 ^oC (shown as shoulder) and 400 ^oC. The first step arises from the decomposition of CF. The second step stems mainly from the decomposition of TPU. Owing to the low thermal stability of CF, the addition of CF gives rise to reduction at about 40 ^oC in the initial thermal stability ($T_{5\%}$) of TPU. The residue yield increases to 6.6 wt% owing to the thermally stable decomposition products of CF.

All phosphorus containing composites decompose in two steps except for 20 wt% AlPi containing one due to the large reduction in T_{max2} value. Accordingly, T_{max1} and T_{max2} values are masked eachother and the composite decomposes in single step. All phosphorus containing additives cause similar effects on the thermal decomposition characteristics of the composites with different extent depending upon the type. With the use of phosphorus-based additives, the reductions in thermal stabilities ($T_{5\%}$, T_{max1}, and T_{max2}) are observed due to the formed acidic compounds (polyphosphoric acid (APP), phosphinic acid (AlPi), and phosphoric acid (AHP)), and (water (APP, AHP)) which accelerate the hydrolysis of CF and TPU. Experimental residue yields are higher than the calculated ones. It is well known fact that phosphorus compounds can react with hetero atom containing polymers like TPU and CF and enhance the char formation. Supportive findings are observed in the literature with the use of phosphoric acid with CF [38, 39], APP [17, 18, 40], AlPi [21], and AHP [23–26] in TPU.

3.3. Mass Loss Calorimeter Studies

Mass loss calorimeter (MLC) study investigations can be used to compare and evaluate the fire performance of polymer-based composites. The data such as time to ignition (TTI), peak heat release rate (pHRR), average heat release rate (aHRR), total heat evolved (THE), THE/TML (total heat evolved/total mass loss) ratio, residue yield, etc. are obtained from MLC test. The average MLC test results and HRR curves of composites are given in Table 2 and Fig. 3, respectively. The digital char photographs of APP, AHP and AlPi including composites are depicted in Fig. 4, Fig. 5, and Fig. 6, respectively. SEM images (50X (left side) and 250X (right side)) of the samples containing 20 wt% additive are given in Fig. 7.

As given in Fig. 3, TPU burns fastly giving one sharp HRR peak after ignition and leaves 1.8% carbon-based residue. TTI value shifts to an earlier time with the incorporation of CF due to the lower thermal stability of CF compared to TPU. Thus, the concentration of flammable volatile compounds required for ignition is reached in a short time. With the addition of protein fibers, the decrease in TTI value is observed in literature [31, 39, 41]. With the addition of CF, the little amount of char is increased and accumulated on the sides of aluminum foil as seen in Fig. 4. Moreover, pHRR value does not change significantly because the protective function of the char structure is not good. However, 14% reduction in THE value is observed due to the enhanced char formation. THE/TML value gives the information that the flame retardant additive shows its effect in the gas phase [42]. No meaningful change is observed in THE/TML value with the inclusion of CF. This situation shows that the inclusion of CF has no remarkable gas phase action.

All composites containing APP and AHP give typical HRR curve of thick char forming materials, as seen from Fig. 3. As the concentration increases, pHRR and THE values are reduced steadily in both additives. The highest reduction in pHRR and THE values are observed in 20 wt% addition. pHRR value decreases at about 75% and 70% with 20wt% APP and AHP addition, respectively. THE value reduces at about 46%

and 28% with the addition of 20wt% APP and AHP, respectively. The reductions in pHRR and THE values arise mainly from decrease in fuel source and the barrier effect of compact char structure with remarkably intumescent character (see Fig. 4 and Fig. 5). The reduced TPU content with increasing APP and AHP amount and enhanced char formation provide the reduction of fuel source. With the addition of APP and AHP, THE/TML value is changed slightly due to the gas phase flame retardant action of additives. The gas phase flame retardant action of AHP and APP stems from the decomposition products such as PO, P radicals and water (from AHP) [36, 37], water and ammonia (from APP) [30].

Table 2
MLC data of the composites

SAMPLE	TTI (sec)	pHRR ($Kw.m^{-2}$)	AvHRR ($Kw.m^{-2}$)	THE (MJ/m^2)	THE/TML (MJ/m^2g)	Residue (%)
TPU	63	371 ± 9	244 ± 8	68 ± 2	2.1	1.8
TPU/CF	48	350 ± 8	197 ± 7	54 ± 2	2.0	5.7
TPU/CF/5 APP	35	141 ± 5	59 ± 4	40 ± 1	1.8	35.1
TPU/CF/10 APP	25	101 ± 5	55 ± 3	36 ± 2	1.8	41.6
TPU/CF/20 APP	25	87 ± 6	42 ± 3	29 ± 2	1.6	45.8
TPU/CF/5 AHP	50	125 ± 7	71 ± 7	46 ± 3	1.9	30.1
TPU/CF/10 AHP	41	111 ± 4	58 ± 6	43 ± 4	1.9	33.2
TPU/CF/20 AHP	35	106 ± 4	44 ± 5	39 ± 3	1.8	36.8
TPU/CF/5 AlPi	28	294 ± 9 **TPU/CF/10 AHP** **TPU/CF/20 AHP**	160 ± 5	52 ± 3	1.7	11.1
TPU/CF/10 AlPi	23	296 ± 13	158 ± 7	50 ± 2	1.6	13.2
TPU/CF/20 AlPi	26	250 ± 12	152 ± 10	47 ± 2	1.5	15.9

All composites including AlPi combust rapidly after ignition and give sharp HRR curve resembling as non-char forming material. With the addition of AlPi in all concentrations, pHRR value decreases but it changes insignificantly when the concentration of AlPi increases from 5 wt% to 10 wt%. pHRR value reduces at about 29% with the addition of 20 wt% AlPi. The reduction in pHRR stems from the barrier effect of char structure (see Fig. 6). However, pHRR value of AlPi containing sample is higher than those of APP and AHP containing samples. It is thought that the observed trend stems from low residue yield with respect to APP and AHP containing ones. With low residue yield, the reduction in fuel source is less. Accordingly, the reduction in pHRR and THE is less than those of APP and AHP containing ones. THE value reduces gradually at about 4%, 7% and 13% with respect to TPU/CF as the added amount of AlPi increases. The lowest THE/TML ratio is observed with the use of AlPi due to flame dilution with the release of intact AlPi molecule and diethyl phosphonic acid and the flame inhibition with the release of phosphorus radicals [43–45]. In brief, all additives exert their flame retardant effects in both gas and condensed phases. However, AlPi exerts predominantly its flame retardant effect in the gas phase via flame inhibition. As for the predominant flame retardant effect of APP and AHP is the condensed phase via the improved char formation with intumescent character.

3.4. Flammability Properties

The flammability properties of the composites are examined by using UL-94 V and LOI tests. The related data are showed in Fig. 8. The proposed flame retardant actions are given in Fig. 9. TPU burns to clamp (BC) and has 22.8% LOI value. With the addition of CF, UL-94 V rating stays as BC and LOI value slightly decreases to 21.9%. UL-94 V rating turns to V2 with the addition of 5wt% APP and AHP. When the concentrations of APP and AHP reach to 10 wt%, the highest UL-94 V rating of V0 is obtained. LOI value steadily inceases as the added amount of APP increases. The highest LOI value of 31.5% is achieved with the use of 20wt% APP. However, the highest LOI value of 27.7% is obtained with the use of 10wt% AHP. The further addition causes slight reduction in LOI value. With the addition of 5wt% AlPi, UL-94 V rating turns to V2, whereas the further addition of AlPi causes UL-94 V rating to BC. LOI value increases from 21.9–26.7% with the addition 20 wt% AlPi. According to flammability performances, phosphorus based flame retardants are ranked in ascending order of AlPi, AHP and APP. All fillers exert same flame retardant mechanisms of heat sink action, improved intumescent char formation, and fuel dilution. However remarkable enhanced char formation in the case of APP, and AHP causes better fire retardant performance with respect to AlPi containing ones.

4. Conclusion

This study deals with the effect of three different phosphorus compounds (APP, AHP and AlPi) on the thermal and flame retardant properties of CF containing TPU composites. The effect of filler amount on thermal and fire retardant properties of the composites is investigated by using TGA, MLC, LOI, and UL 94 V tests. According to TGA results, the addition of CF and all additives decreased the thermal stability of TPU. APP and AHP are more effective for favoring the char formation than AlPi. According to the flammability test results, the highest UL-94 V rating was observed with the inclusion of APP and AHP, and the highest LOI was obtained in the presence of APP. According to the MLC test results, APP and AHP including samples showed lower pHRR and THE values than AlPi containing ones due to the condensed phase retardant effect with the formation of more enhanced char structure. AlPi bearing sample showed lowest THE/TML value than those of APP and AHP containing ones due to gas phase flame retardant action via fuel dilution and flame inhibition.

Declarations

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Author contribution

Conceptualization: Mehmet Dogan, Methodology: Aysenur Mutlu, Mehmet Dogan, Formal analysis and investigation Aysenur Mutlu, Writing—original draft preparation: Aysenur Mutlu, Mehmet Dogan,

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Figures

Figure 1

TGA and DTGA curves of the composites

Figure 2

TGA and DTGA curves of the composites

Figure 3

HRR curves of the composites

Figure 4

Photographs of APP containing samples remained after MLC test

Figure 5

Photographs of AHP containing samples remained after MLC test

Figure 6

Photographs of AlPi containing samples remained after MLC test

Figure 7

SEM images of 20 wt% flame retardant additive containing samples

Figure 8

Flammability properties of the composites

Figure 9

Proposed flame retardant actions of the additives