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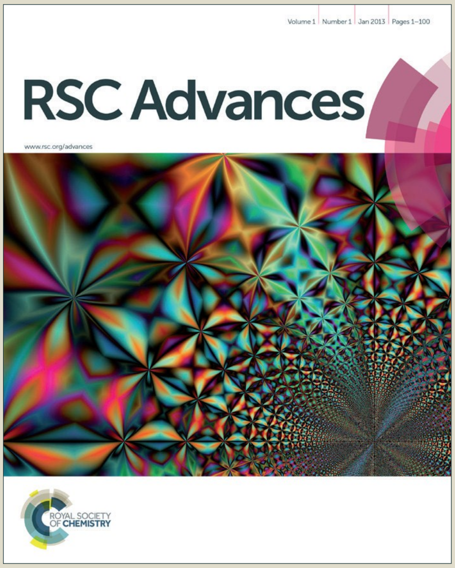

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Synergistic Effects between [Emim]PF_6 and Aluminum Hypophosphite on Flame Retardant Thermoplastic Polyurethane

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ABSTRACT

This article mainly studies the synergistic flame retardant effects and smoke suppression properties of ionic liquid ([Emim]PF_6) and aluminum hypophosphite (AHP) on thermoplastic polyurethane (TPU), AHP was used as main flame retardants and [Emim]PF_6 was used as catalytic/synergistic agents. Then, the flame retardant effects of all TPU composites were tested using limiting oxygen index (LOI), UL 94 test, cone calorimeter test (CCT), smoke density test (SDT), thermogravimetric analysis (TG) and thermogravimetric/fourier transform infrared spectroscopy (TG-IR). Remarkably,with 0.0625 wt% content of [Emim]$PF_6$and 19.9375wt% content of AHP, sample reached UL 94 V-0 rating, and the LOI value increased by 35.75%, theheat releaseand smoke production reached the minimum value among all samples. TG and TG-IR data reveal that AHP and [Emim]PF_6 improve the thermal stability of samples at high temperature and reduce the production of some toxic gases.

Keywords Thermoplastic polyurethane; Aluminum hypophosphitec;[Emim]PF_6;Synergisticflame retardant

1. Introduction

Thermoplastic polyurethane (TPU) is well known for its excellent mechanical properties (high tensility, excellent wear abrasion resistance, good hydrolytic stability, good flexibility over a wide range of temperatures, et. al.) and widely applied in the plastic field [1-3]. However, the same as many other thermoplastics, due to its flammability and melt-dropping during combustion, its applications in many fields are greatly limited. Therefore, the applications of effective and environmentally friendly flame retardants in TPU is quite important and urgent [4-7].

Halogenated flame retardants used to be widely applied in polymers to improve the flame

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retardancy efficiently, but some of them have been prohibited in many fields because of releasing much toxic and corrosive gases during combustion [8, 9]. Recently, halogen-free flame retardants have attracted much more attention. Compounds based on phosphorus, nitrogen, silicon, and other elements gradually replaced the use of halogenated flame retardants [8]. Metal hydroxide is widely used as a kind of cost-effective and environmentally friendly flame retardant. The most widely used metal hydroxide flame retardants include magnesium dihydroxide (MH) and aluminum trihydroxide (ATH). Pinto et. al. [4]found that TPU composites with 70 phr of ATH had good flame retardancy, and reached V-0 rating in UL 94 test. However very high addition levels of this category of flame retardants (generally beyond 50 wt%) are usually required, which is prone to cause deterioration of mechanical properties [10]. Phosphorus-based compounds are another kind of effective and environmentally friendly flame retardants [8]. Phosphorus-based flame retardants can volatilize into gaseous phase and form phosphoric radicals (PO_2•, PO•, etc.), which can capture the radicals for combustion, and hence decrease or even stop the combustion reactions [11]. Moreover, phosphorus-based flame retardants can catalyze the char formation of polymers [10]. The char on the composite surface prevents heat and oxygen from transferring into the underlying polymer, and also prevents pyrolysis of the polymer from transferring to the flame zone, causing improvements in flame retardancy. Intumescent flame retardants (IFRs), which are composed of an acid source, carbonizing agent, and blowing agent, have received great attentions for its low smoke generation, low toxicity, non-dropping, low corrosion, high efficiency, etc, during their fire situation [12]. In the process of polymer flame retardant, IFR preferably showed advantages of high efficiency, more carbon residue, little smoke, little molten drops and low toxicity for the flame retardancy of TPU composites [6, 13-15].

Metal salts of hypophosphorous acid have attracted a lot of interest recently because of their efficient and environmentally friendly flame retardancy[16]. Hu et. al. prepared flame retardant glass-fiber reinforced poly (1, 4-butylene terephthalate) (GRPBT) using aluminum hypophosphite (AHP), polycarbonate and melamine, the composites reached UL 94 V-0 rating [17]. Li et. al. reported that AHP effectively promoted the char formation of PA6[18].Tang et. al.[19]incorporated AHP into PLA to prepare FR-PLA composites, finding that the FR-PLA composites showed excellent flame retardancy and reached UL 94 V-0 rating with 20 wt% AHP incorporation, and the pHRR value decreased by 48.2 % when the content of AHP increased to 30 wt%. Xiao et. al.[20] found that TPU with the 30 wt% loading of AHP reached UL 94 V-0 rating, and the LOI value reached 30.2, the pHRR value decreased by 38.7 % and AHP improved the formation of char residual. Though AHP endowed good flame retardancy for TPU, however, the 30 wt% loading is still very high. Adopting a highly efficient synergistic agent combined with AHP applied in TPU, and efficiently decreasing the content of AHP is an important research topic.

Designing novel flame retardants or introducing catalysts/synergists into the TPU/AHP systems may have good results to increase the flame retardant efficiency of AHP.Among all methods, adopting catalysts/synergists is more convenient and most of them are inorganic materials[21-25]. Though these catalyst/synergists have good effects on flame retardancy, they are difficult to be dispersed uniformly into the resin because of their low content and poor compatibility.Ionic liquid is a kind of organic molten salt, which is consist of a relatively large volume structure asymmetric organic cation and a relatively small size of inorganic anion [26]. Because of its excellent chemical stability and thermal stability, no ignition and flammable, low vapor pressure and high ionic conductivity characteristics, ionic liquid has attracted more and more attention in organic synthesis, catalysis and extraction processes as “green solvents”[27, 28].Despite the ionic liquid has many excellent properties, the application inflame retardancy is quite few.Chenet. al[29-31]found that polyoxometalate based ionic liquid (PIL) can behave as efficient catalyst in many reactions, also in flame retardant fields,they studied the synergistic effect of IFR and PIL in PPsystem,and found that the anion of PIL affected the flame retardant properties of PP greatly.Li et. al.[32]studied the effect of the ionic liquid [Bmim]OTM on flame retardancy, thermal degradation and char yield of PC, and found that when incorporating 0.1 wt% [Bmim]OTM into PC, sample reached to UL 94 V-0 rating, the LOI of PC reached up to 32%, and it could decrease the initial decomposition temperature of PC and promote the degradation of PC.Li et. al. [33, 34]studied the flame retardant effect of imidazole ionic liquids on RPUF by researching the influence of varieties and amount of the ionic liquids on LOI and thermal decomposition properties, they found that imidazole ionic liquids have good flame retardancy on RPUF and the [Bmim]PF_6 showed better flame retardancy and thermostability than [Bmim]BF_4. Therefore, it is a feasible method to adopt an ionic liquid as catalysts/synergists for flame retardant TPU composites.

In this paper, a kind of imidazole ionic liquids ([Emim]PF_6)was adopted as the catalytic/ synergistic agent and combined with AHP as the main flame retardants in TPU composites. Then the flame retardant performance and thermal stability of TPU/AHP/[Emim]PF_6 were characterized by LOI, UL 94 test, CCT, SDT, TG and TG-IR, respectively.

2. Experimental section

2.1. Materials

Thermoplastic polyurethane (TPU, Desmopan 9380A) with a density of 1.110 g/cm^3 and 82 Shore A hardness, was supplied by Bayer Material Science (German). Aluminum hypophosphite (AHP, ≥99%) with particle size of 2000 meshwas provided by Chengdu Weili Flame Retardant Chemicals Industrial Co., Ltd. (China).1-ethyl-3-methylimidazolium hexafluorophosphate ionic liquid ([Emim]PF_6) was obtained from Henan Lihua PharmaceuticalCo., Ltd. (China) with a purity more than 99.5 wt % and molecular weight of 256.13 g/mol.

2.2. Sample preparation

TPU/AHP/[Emim]PF_6composites were prepared by melt-blending method. Before processing experiment, both AHP and TPU were dried in a drying oven at 80 °C for 12 h, [Emim]PF_6 was kept under a vacuum at 80 °C for at least 3 days to reduce the moisture content and volatile compounds to negligible values. A certain amount of TPU was melted in the mixer at 180±5 ^oC. Then a certain amount of AHP and [Emim]PF_6 were added into the mixer, respectively. The blends were mixed for 10 min and hot pressed into sheets in the dimensions of 100×100×3 mm^3 using the plate vulcanizing machine and then cut into suitable sample bars for LOI and UL 94 test. The formulations of flame retardant TPU composites are presentedin Table 1.

(insert Table 1)

2.3. Measurements

Limiting oxygen index (LOI)

LOI was carried out on an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to the standard oxygen index test ASTM D2863. The samples used were of dimensions 100×6.5×3 mm^3. And, five samples were carried out in the LOI test.

UL 94 test

The vertical burn test was measured by a CFZ-2-type instrument (Jiangning Analysis

Instrument Company, China) according to the American National UL 94 test ASTM D3801 on sheets 100×13×3 mm^3. And, three samples were carried out in the UL 94 test.

Cone calorimeter test (CCT)

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions 100×100×3 mm^3 was wrapped in aluminium foil and exposed horizontally to an external heat flux of 35 kW/m^2 with the use of the “frame and grid”. And, three samples were carried out in CCT.

Smoke density test (SDT)

A smoke density test machine (JQMY-2, Jianqiao Co, China) was used to measure the smoke characteristics according to ISO 5659-2 (2012). Each specimen with dimensions of 75×75×3mm^3 was wrapped in aluminum foil and exposed horizontally to an external heat flux of 25 kW/m^2 with or without the application of a pilot flame. Two tests were carried out for each one sample.

Thermogravimetric analysis (TG)

Thermogravimetric analysis of the sample was performed using a DT-50 (Setaram, France) instrument. About 10.0 mg of sample was put in an alumina crucible and heated from ambient temperature to 700 ^oC. The heating rate was set as 20 $^oC/min$ (nitrogen atmosphere, flow rate of 20 ml/min).

Thermogravimetric/Fourier transform infrared spectroscopy (TG-IR)

The TPU/AHP/[Emim]PF_6 composites was also tested by a Thermogravimetric/Fourier transform infrared spectroscopy hyphenated technique. About 10.00 mg of composite was put in to an alumina crucible and heated from 260 ^oC to 700 ^oC at the rate of 20 $^oC/min$. The spectra of volatilized products at various time during the thermal degradation of samples was presented on the computer screen of Fourier infrared spectrum.

3. Results and discussion

3.1 Limiting oxygen index (LOI) and UL 94 test

LOI is defined as the minimum percentage of oxygen in an oxygen-nitrogen mixture that is just sufficient to sustain combustion of the sample after ignition. LOI and UL 94 test are widely used to evaluate the flame retardant properties of materials,especially for screening flame retardant formulations of polymers. Thus, Table 1presents the related LOI and UL 94 data obtained from different content of AHP and[Emim]PF$_6$. It is obvious that the LOI of TPU is only 23.75, and sample cannot pass UL 94 flammability rating test.When incorporating 20 wt% AHP into TPU, sample AHP1 reached UL 94 V-1 rating, and LOI value is as high as 32.50, much higher than that of TPU. Moreover, when [Emim]PF$_6$ was added into TPU/AHP system, the LOI value of samples further increased. For example, the LOI value of AHP2, AHP3 and AHP4 reached 34.25, 35.75, 33.25, respectively. Among all samples, AHP3 with 0.0625 wt% [Emim]PF$_6$ has the highest LOI value. All TPU/AHP/[Emim]PF$_6$samples passed UL 94 flammability rating test, AHP2 and AHP3 reached V-0 rating, and AHP4 reached V-1 rating. The LOI and UL 94 test illustrate that when a moderate content of [Emim]PF$_6$ incorporated into the TPU/AHP system, a remarkable improvement of flame retardancywas observed.

3.2 Cone calorimeter test (CCT)

Although the LOI is a useful small-scale test for high-lighting and ranking flame retardant polymers, the cone calorimeter test (CCT) provides a wealth of information on the combustion behavior under ventilated conditions [35]. The CCT is based on oxygen consumption principle, it truly simulates the combustion of the polymers in a real fire situation, showing great important significance in the research and development of new flame-retardant materials [36-38].

Heat Release Rate (HRR)

The HRR measured by cone calorimeter is a very important parameter as it expresses the intensity of a fire. HRR curves of all samples are presented inFig. 1. It is clear that TPU burns rapidly without any retardant, and has a single sharp peak with a peak heat release (pHRR) value of 1272.6 kW/m^2,which means that the fire intensity increases rapidly. With the incorporation of flame retardants AHP, the HRR values decreased significantly.For TPU/AHP sample, the pHRR value is 105.7 kW/m^2 appeared at about 60 s, and decreased by 91.65 % than that of neat TPU. Then after the first peak, the HRR reduced to below 10 kW/m^2 rapidly, and later the second peak appeared, with the value of 104.4 kW/m^2. The first peak is due to the decomposition ofAHP to release some phosphoric acid and poly phosphoric acid [19], which promoted the formation of intumescent carbon layer as a physical barrier and increasing the difficulty of mass and heat transfer. The latter peaks are due to the fact that the heat broken through the intumescent carbon layer when polymers are continuous exposed to strong thermal radiation of the cone.When a proper content of [Emim]$PF_6$was incorporated into TPU/APP system, the HRR value further decreased. From Fig. 1,it can be seen that the first pHRR values of TPU/AHP/[Emim]PF_6 are a little higher than that of TPU/AHP, it may be due to the ionic liquid[Emim]PF_6 catalysisthat promoted AHP and TPU matrix decomposition to releases some combustible gases at the initial of the combustion process[28, 30].However, later the HRR values of AHP-2 and AHP-3 are apparent lower than that of TPU/AHP composites, especially at the time 100 s to 200 s, there is hardly heat release for the two samples. It suggests that the carbon layer is so dense and compact during the time that prevents the flammable gases released into the flame zone and the outside oxygen into the inside of polymer. As for AHP-4 with 0.125wt% [Emim]PF_6, the HRR curve is similar to that of AHP-1, and the HRR value is even higher, which illustrates that excessive amount of[Emim]PF_6goes against catalytic effect for TPU/AHPcomposites.

The synergistic effect of [Emim]PF_6on TPU/AHP system may be explained as follows: (1) The ionic liquid [Emim]PF_6 can be well dispersed in TPU matrix as the organic phase, the phosphorus and fluorine element in ionic liquid [Emim]PF_6 themselves have good flame retardancy; (2) Both[Emim]PF_6 and AHP can accelerate the cross-linking and charforming reaction of TPU by generating polyphosphoric acid and phosphorus oxide, and enhanced the structure and intensity of carbon layer as a good physical barrier.

(insert Fig. 1)

Total Heat Release (THR)

THR values represent the fire load of combustion under the test conditions [37], and the slope of the THR curves can be assumed to be representative of fire spread [39].Fig.2presents THR curves of all samples at a flux of 35 kW/m^2. It is clear that the THR values and the slope of the THR curves significantly decrease with the addition of AHP and [Emim]PF_6, TPU＞AHP-4＞AHP-1＞AHP-2＞AHP-3. Among all samples, AHP-3 containing 0.0625wt% [Emim]PF_6 shows the lowest THR value and slope (decreased by 67.8 % compared with that of neat TPU). It is suggested that there is an obvious improvement of flame retardancy between AHP and [Emim]PF_6 in TPU composites. However, when the content of [Emim]PF_6increases to 0.125 wt%, the THR value is higher than that of AHP-1, but still much lower than that of neat TPU.It may be due to the fact that, when the content of [Emim]PF_6 increased to 0.125 wt%, the catalytic role strengthen and promote the decomposition of polymer matrix, thus releasing more heat.

(insert Fig. 2)

MASS

An intumescent carbon layer may form on the surface of the materials during combustion, creating a physical protective barrier to restrain heat and mass transfers. The carbon layer would limit the oxygen diffusion into the underlying part of the material or isolate from heat and combustible gases, and further retard the pyrolysis of material [6]. Fig. 3 presents the MASS curves for all TPU composites. It is very clear that the MASS of neat TPU decreases rapidly without any retardant, and only 7.04 % mass residue.Whereas, with the incorporation of flame retardants AHP and IG, the mass residue of samples significantly increases, and the mass loss curves become more slowly and shows a low mass loss rate, which is in line with the behaviors of HRR curves, the mass residues are 46.81 %, 58.33 %, 59.62 %, 40.32 %, respectively. It can be ascribed to the formation of intumescent carbon layers on the surface of the materials during combustion, creating a physical protective barrier to restrain heat and mass transfer [40], and AHP-3 containing 0.125 wt% [Emim]PF_6 shows the smallest mass loss rate and most mass residue.This can be concluded that [Emim]PF_6 can improvethe char residue weight in the combustion process. Thisresult also means that there is catalyzing carbonizationeffect by [Emim]PF_6 in the TPU/AHP system.

(insert Fig. 3)

Smoke Production Rate (SPR)

Smoke performance of flame-retardant composites is a significant parameter in fire safety fields. The SPR curves of all samples are presented in Fig. 4. The peak SPR value (pSPR) of TPU is 0.069 m^2/s.It is clearly seen that a significant decrease of the peak SPR value taken on with the additionof flame retardants. The peak SPR value of AHP-1 containing only AHP is greatly decreased, compared with that of neat TPU. However the time to reach peak SPR of flame-retardant TPU, is ahead of schedule than that of neat TPU, which may be attributed to the decompositionof AHP at low temperature to form some smoke particulates. Moreover, afteradding0.0625 wt% [Emim]PF_6, the SPR value further decreases thanthat of TPU/AHP composites, especially at the time 100 s to 200 s, the SPR value is less than 0.005 m^2/s and the curve is very gentle.Such phenomenon can be described as follows, during combustion process, with the addition of AHP, an intumescent carbon layer was formed as a physical barrier, which can restrain the release of pyrolysis gases and smoke particle efficiently. Furthermore, a proper content of ionic liquids play a role of catalytic effect, which helps to promote charring and change the carbon layer structure, and thereby enhances the physical barrier effect. And the carbon layer still keeps good structure whencontinuesexposed to strong thermal radiation.

(insert Fig. 4)

Total Smoke Release (TSR)

Fig. 5presentsTSR curves of all samples at a heat flux of 35 kW/m^2. It is clear that the TSR curves of flame-retardant TPU composites are much lower than that of TPU. For neat TPU, the TSR value is 754.05 m^2/m^2, and from AHP-1to AHP-4, the TSR values are 451.48, 378.77, 348.75 and 569.15 m^2/m^2, respectively. Among all samples, AHP-3 containing 0.0625 wt% [Emim]PF$_6$ shows the lowest TSR value, decreased by 53.75 % compared with that of neat TPU.

(insert Fig. 5)

Smoke Factor (SF)

SF value is the product of PHRR and TSP [41]. The SF curves of all TPU composites under CCT are presented in Fig. 6. The SF value of neat TPU is up to 959.3 MW/m^2, and the value of AHP-1 containing onlyAHP is just 48.2 MW/m^2.It is very clear that the addition of flame retardant significantlyreduces the SF values of TPU composites. Furthermore, TPU/AHP system with 0.0625 wt% [Emim]PF$_6$ presents the lowest SF value, 44.83 MW/m^2.This indicates the same conclusion as drawn from the above results of HRR and TSR.

(insert Fig. 6)

Digital photos of carbon residue

The digital photos of char residues after CCT for all samples are shown in Fig. 7. The formation of an efficientcarbon layer can prevent the heat an mass transfer between flame zone andburning substrate, and thus protect the underlying materials fromfurther burning and pyrolysis of polymer composites[5]. It is clearthat the char residue of TPU is the lightest and loosest respondingto the highest HRR and the least mass residue among all samples.This means that the viscosity of molten carbon layer cannot effectively bind the volatile substances during combustion process, resulting large amount of heat and smoke release. AHP-1containing only AHP has relatively high and compact char residue. Moreover, with a low addition ofionic liquid [Emim]PF_6 (0.03125 wt% and0.0625 wt%), the char layer become further more dense and higher. However, when the content of[Emim]PF_6 is up to 0.125 wt%, the residue char layer is not so good, and there are some collapses in the carbon layer.

(insert Fig. 7)

3.3 Smoke Density Test (SDT)

The smoke density test gives detailed information about thesmoke production.Fig. 8 (A, B)presents the luminous flux curves of all TPU composites with flame and without flame, respectively.It is clear from the figure that luminous flux decreases with the addition of AHP and [Emim]PF_6 at the beginning of the test process (about 0-100 s for with flame and about 75-250 s for without flame).It means thatthe smoke density of AHP-1, AHP-2, AHP-3, and AHP-4 arehigher than that of TPUduring that time, whichindicates that an early decomposition of the flame retardants occurs. The early decompositionof the flame retardants is necessary to increasethe fire-proofing properties of the material. The samples with both AHP and [Emim]PF_6decompose earlier than AHP-1,which may be due to the fact that the ionic liquid [Emim]PF_6catalyzes to promote TPU/AHP system decompose at low temperature to form phosphorus oxide. However, after 100 s for with flame condition and after 250 s for without flame condition, the luminous flux curvesof flame-retardant samples become much lower than that of neat TPU, which means less smoke density is observed for AHP-1 to AHP-4. And, at the end of the test (1200 s), AHP-3 containing 0.0625 wt%[Emim]PF_6has the highest luminous flux.

(insert Fig. 8)

3.4 Thermogravimetric analysis (TG)

TG is one of the most widely techniques used for evaluating thermal stability of different materials [6, 42, 43].TG and Derivative TG (DTG) curves of various flame retardant TPU composites under nitrogen atmosphere are shown in Fig.9 (A, B). As is known that, thermal degradation of TPU has two steps: the first step is responsible for the rupture of the TPU main chains, and the second step is attributed to the further destruction of the C-C and C-O bonds on the main chain[40]. For TPU, the temperature at 5 % mass loss ($T_{-5\%}$, taken as the onset of the degradation) is 330.1°C, the maximum weight loss temperature (T_{-max}) of TPU is 428.5°C, and only 12.91 % char residue remains at 700 °C. In the case of flame-retardant TPU composites, the $T_{-5\%}$ is about 285-301°C, and the T_{-max} is about 380.6°C, which is lower than that of TPU. Moreover, it is apparent that thethermal degradation of flame-retardant TPU compositescomprises three steps corresponding to the temperatures of about 313, 378, and 469 °C.As usual, the three thermaldegradation steps are identified as the decomposition of AHP[19],catalysis of the charring process, and further decomposition of the C-C and C-O bonds on the main chain of TPU.It can be seen that the additionof flame retardants reduces the temperature of the formation for carbon layer, so that it protects the TPUcomposites from further thermal degradation and combustion[44].As for the samples containing $[Emim]PF_6$, thedegradation of TPU composites is promoted at an earlier at an earlier periodbut is delayed at a later period than that ofAHP-1. It can be explained by the fact that$[Emim]PF_6$as a kind of catalystwould promote thedecomposition of AHP and the formation of protective carbonlayerwhich results in lower decomposition temperature ofthe samples, and also induces the cross-linking reaction in PP composites at highertemperatures, improving the thermal stability of TPU composites.Compared with AHP-1, the mass residue at 700 °C of the samples with a moderate content of$[Emim]PF_6$is more, and AHP-3 has the most mass residue (41.71 %), which is consistent with MASS values under CCT.

(insert Fig. 9)

3.5 Thermogravimetric analysis/infrared spectrometry (TG-IR)

In order to further study the volatilized products of samples during thermal decomposition process, the thermogravimetric/fourier infrared spectrum analysis (TG-IR) technique was obtained under the nitrogen atmosphere[46]. The TG-IR spectra of volatilized products of TPU, AHP-1 and AHP-3 during the thermal-decomposition process from 240 to 700 °C are presented in Fig. 10, respectively. It is clear from Fig. 10 that, peaks in the regions of around 3750-3600 cm^{-1}, around 3150-2750 cm^{-1}, around 2400-2250 cm^{-1}, around 1800-1700 cm^{-1}, around 1500-1000 cm^{-1}, and around 750-500 cm^{-1} are prominent. Some of the volatilized products of TPU and flame-retardant TPU composites are confirmable identified by strong characteristic FTIR signals. The main share of the bands of the decomposition products can be attributed to the functional groups with characteristic, unambiguous band positions, such as H_2O at 4000-3500 cm^{-1}, N-H at 3370 cm^{-1}, $-CH_3$ and $-CH_2-$ at about 3000-2800 cm^{-1}, CO_2 at 2400-2300 cm^{-1}, C=O at 1750 cm^{-1} [45].

It is obvious that there are significant differences among the peak position and intensity of TPU, AHP-1 and AHP-3during the thermal degradation process.Compared with that of neat TPU, the samples AHP-1 and AHP-3 have little and small peaks in the regions of around 3370 cm^{-1},3000-2800 cm^{-1}, 2350 cm^{-1}, 1750 cm^{-1}, 1500-750 cm^{-1}, which means there are little decomposition compounds releasing for the flame-retardant samples. However, as for non-flammable gases H_2O and CO_2,they are released at lower temperature than those of neat TPU. For example, characteristic peak of CO_2 (2350 cm^{-1}) for neat TPU appears at 340^{o}C and significantly decreases at about600 ^{o}C; the peaks for AHP-1 andAHP-3 appear at 320 ^{o}Cand 300^{o}C and decreases at520^{o}C, respectively. This may be due to the fact that AHPaccelerates samples to release $CO_2$and H_2O as non-flammable gas at lower temperature, and when [Emim]PF_6 is incorporated the temperature future reduced. Meanwhile the intensity of CO_2 peaks for AHP-1 and AHP-3 decrease significantly at high temperature, which means the incorporation of AHP and [Emim]PF_6 improves the thermal stability of samples at high temperature. Moreover, the following characteristic peaks corresponding to the gas volatile products: unsaturated C-H structure (3018 cm^{-1}), saturated C-H structure (2950 cm^{-1}), C=O (1750 cm^{-1}), the frame vibration of aromatic ring (1608-1450 cm^{-1}), C-H bending vibration of aromatic ring (1264-927 cm^{-1}) remarkably decrease for AHP-1 and AHP-3 compared with that of neat TPU. So the incorporation of AHP and [Emim]PF_6 can not only improve the thermal stability of samples at the high temperature but also reduce the release of hazardous gases such as aromatic compounds.

(insert Fig. 10)

Conclusion

LOI results indicate that the addition of AHP and [Emim]PF_6 increases the flame-retardant level of TPU composites obviously. Data from CCT show that AHP can significantly reduce the heat release and smoke production ofTPU composites during combustion process. And,amoderatecontent of [Emim]PF_6 can further reduce the heat and smoke parameters. The SDT results indicate that the ionic liquid [Emim]PF_6 can catalyze to promote TPU/AHP system decompose at low temperature to form phosphorus oxide, and thus reduces the smoke densityat high temperature. TG results show that the [Emim]PF_6 can furtherenhance the thermal stability of TPU/AHP system by making AHP catalytic decomposition to form protective carbonlayer. And TG-IR techniques show that the addition of AHP and [Emim]PF_6 can reduce hazardous and toxic gases releasing, and promote to release CO_2 and H_2O as nonflammable gases at low temperature during thermal degradation. In summary, synergistic effect between ionic liquid [Emim]PF_6 and AHP on flame-retardant TPU is significant effective, and when[Emim]PF_6 content is 0.0625 wt%, there is the best flame-retardant result.

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Legends of Figures

Fig. 1 Heat release rate of TPU composites at a flux of 35 kW/m^2

Fig. 2 Total heat release of TPU composites at a flux of 35 kW/m^2

Fig. 3 Mass loss curves of TPU composites at a flux of 35 kW/m^2

Fig. 4 Smoke production rate of TPU composites at a flux of 35 kW/m^2

Fig. 5 Total smoke release of TPU composites at a flux of 35 kW/m^2

Fig. 6 Smoke factor of TPU composites at a flux of 35 kW/m^2

Fig. 7 Digital photographs of char residues after CCT for all samples

Fig. 8 Luminous flux curves of TPU composites with flame (A) and without flame (B)

Fig. 9 TG (A) and DTG (B) curves of TPU composites at a constant heating rate of 20 K/min

Fig. 10 FTIR spectra of volatilized products at various times during the thermal degradation of TPU composites

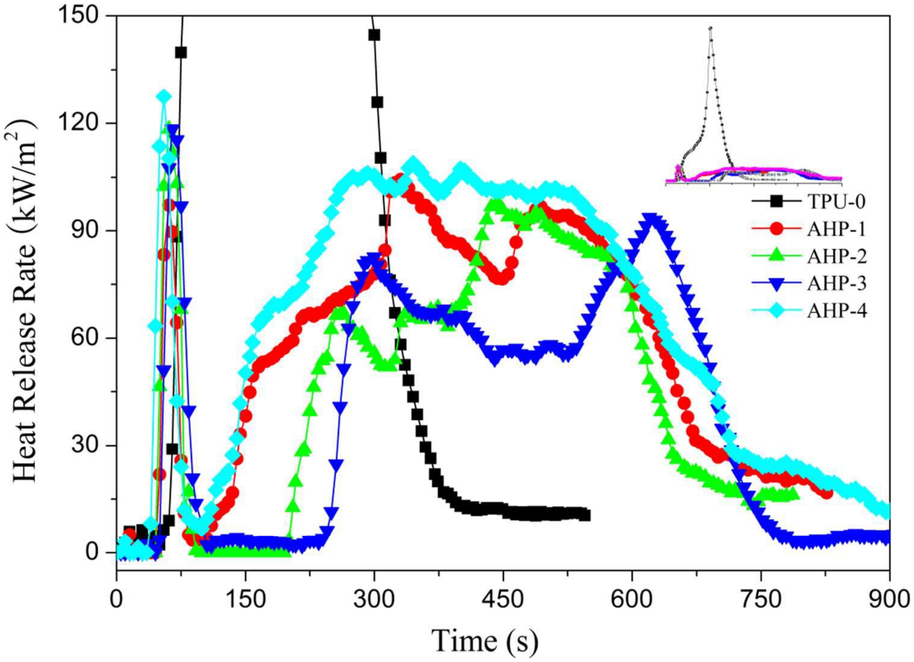

Heat Release Rate (kW/m^2)
Time (s)
0
30
60
90
120
150
0
150
300
450
600
750
900
TPU-0
AHP-1
AHP-2
AHP-3
AHP-4

Fig. 1

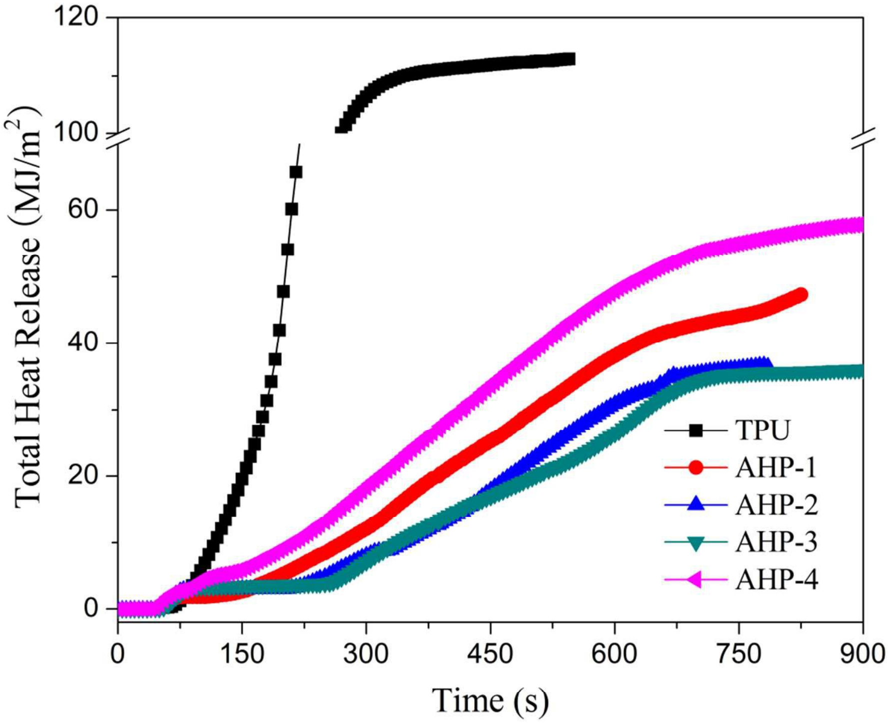

Total Heat Release (MJ/m^2)
120
100
60
40
20
0
0
150
300
450
600
750
900
Time (s)
TPU
AHP-1
AHP-2
AHP-3
AHP-4

Fig. 2

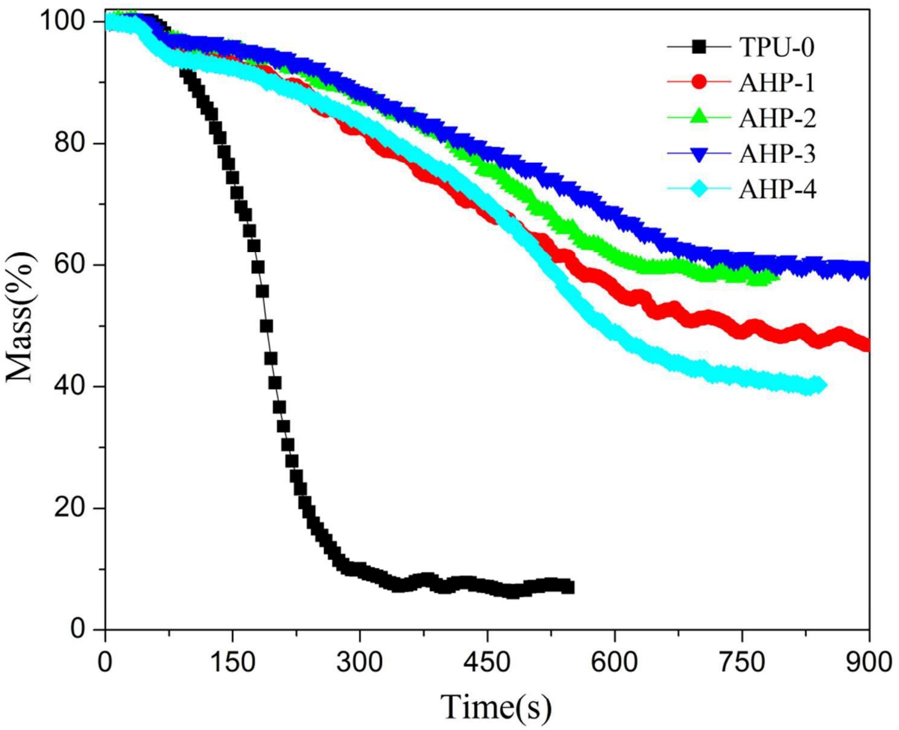

100
80
60
40
20
0
Mass(%)
0
150
300
450
600
750
900
Time(s)
TPU-0
AHP-1
AHP-2
AHP-3
AHP-4

Fig. 3

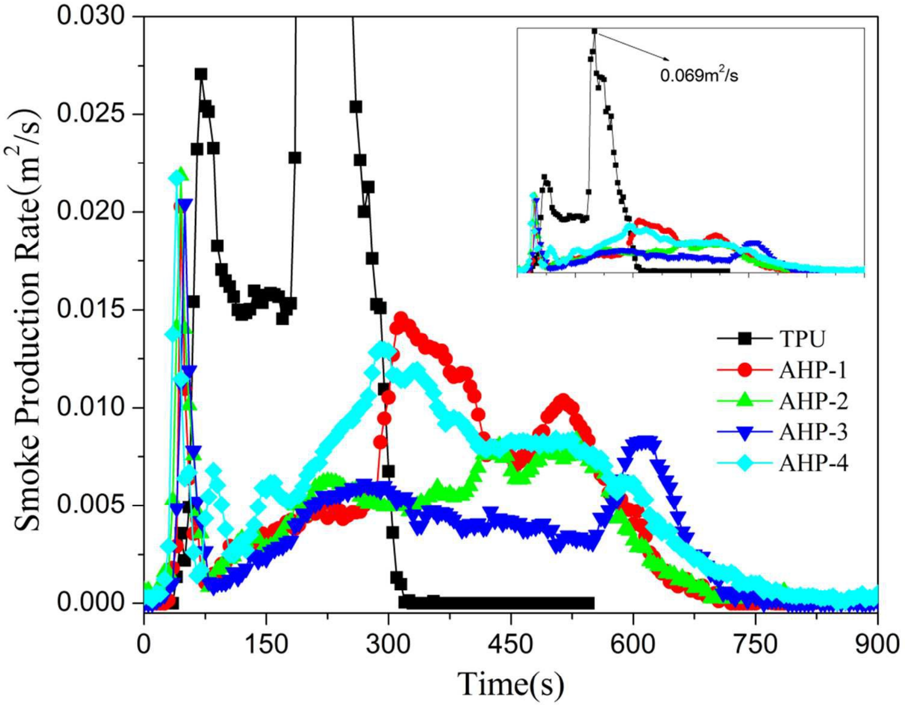

0.069m^2/s
TPU
AHP-1
AHP-2
AHP-3
AHP-4
Smoke Production Rate(m^2/s)
0.000
0.005
0.010
0.015
0.020
0.025
0.030
Time(s)
0
150
300
450
600
750
900

Fig. 4

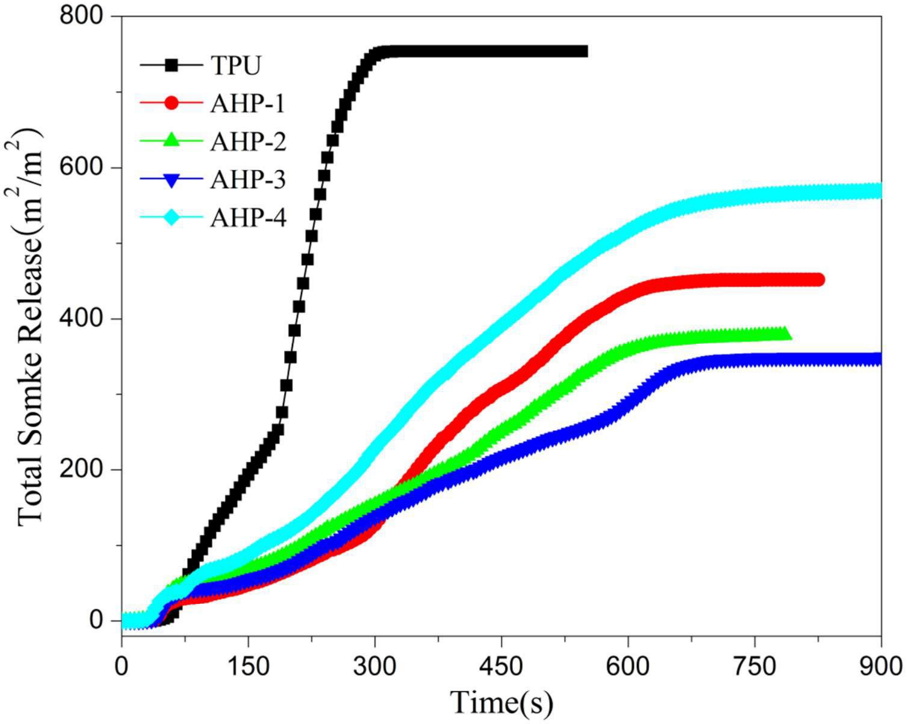

800
600
400
200
0
Total Somke Release(m^2/m^2)
0
150
300
450
600
750
900
Time(s)
TPU
AHP-1
AHP-2
AHP-3
AHP-4

Fig. 5

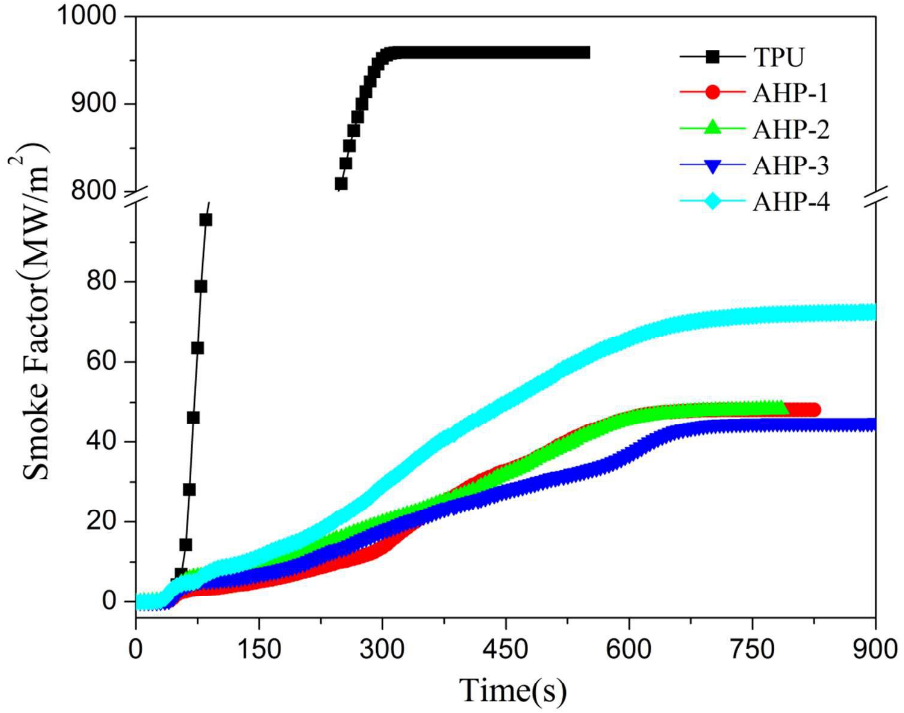

Smoke Factor(MW/m^2)
Time(s)
0
20
40
60
80
800
900
1000
0
150
300
450
600
750
900
TPU
AHP-1
AHP-2
AHP-3
AHP-4

Fig. 6

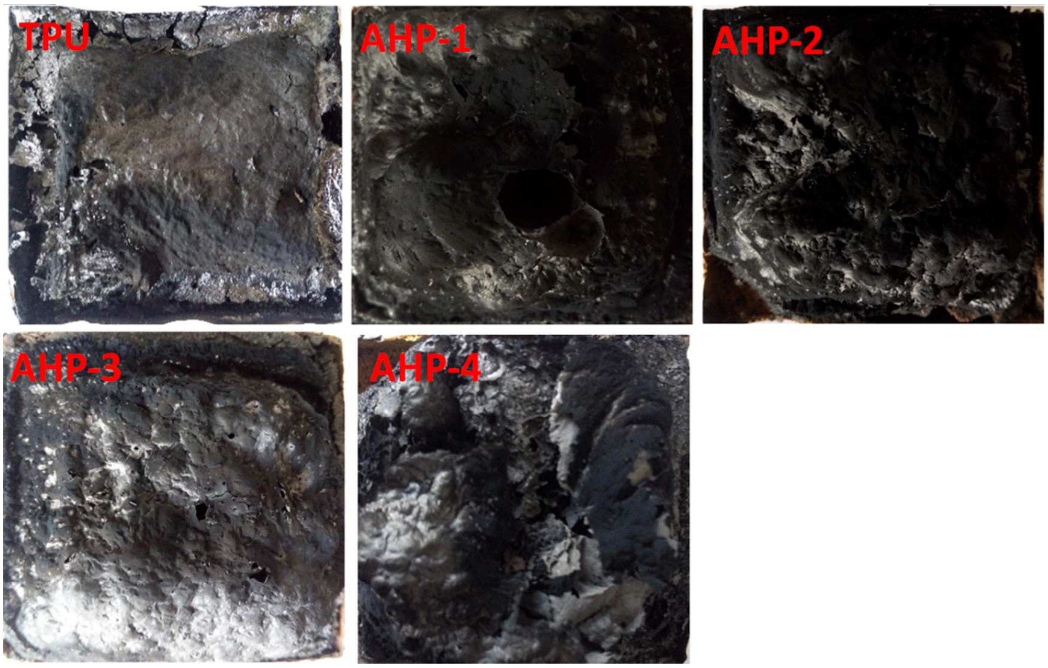
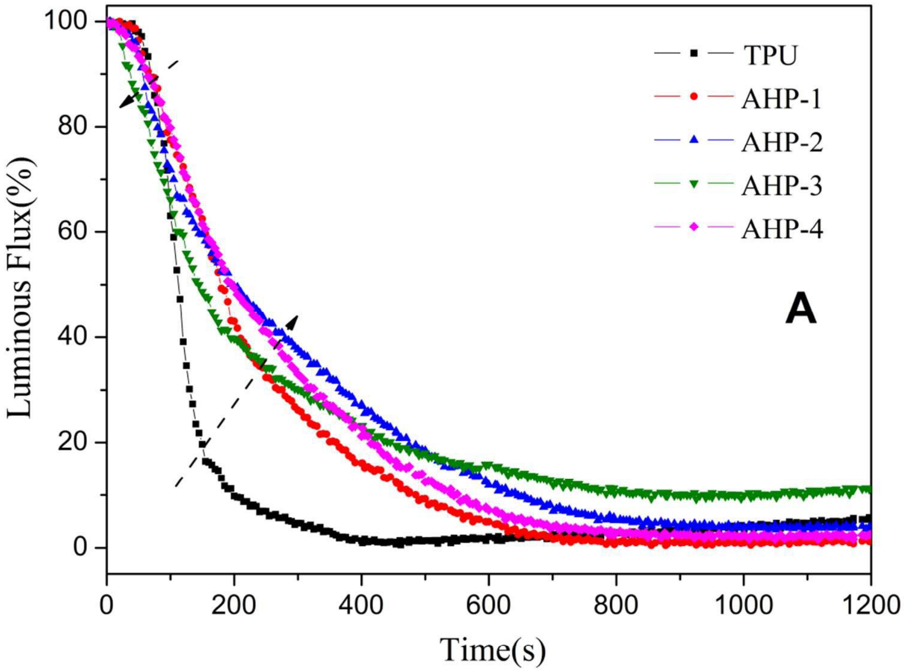


Fig. 7


Luminous Flux(%)
Time(s)
0
20
40
60
80
100
0
200
400
600
800
1000
1200
TPU
AHP-1
AHP-2
AHP-3
AHP-4
A

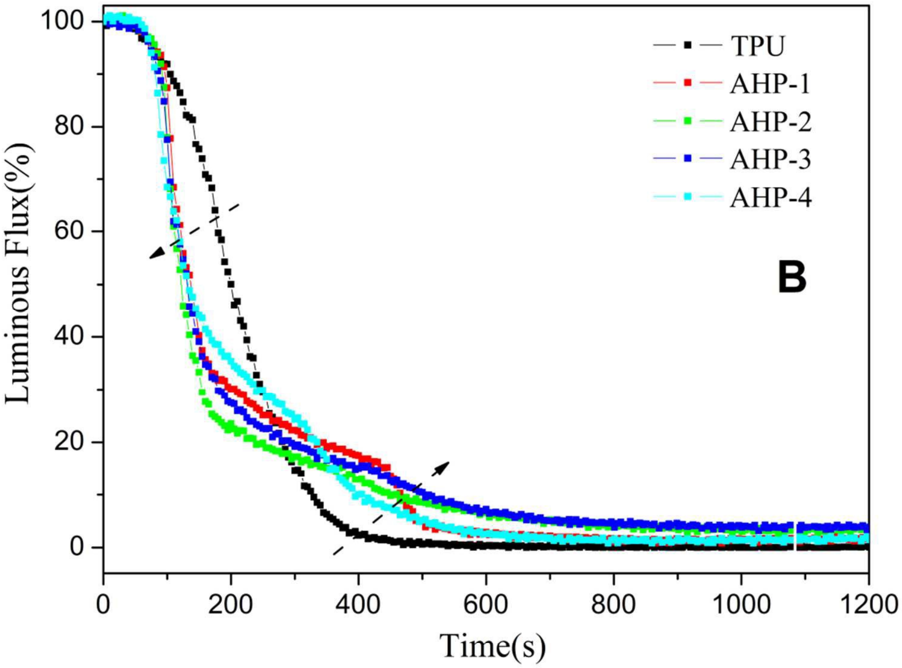
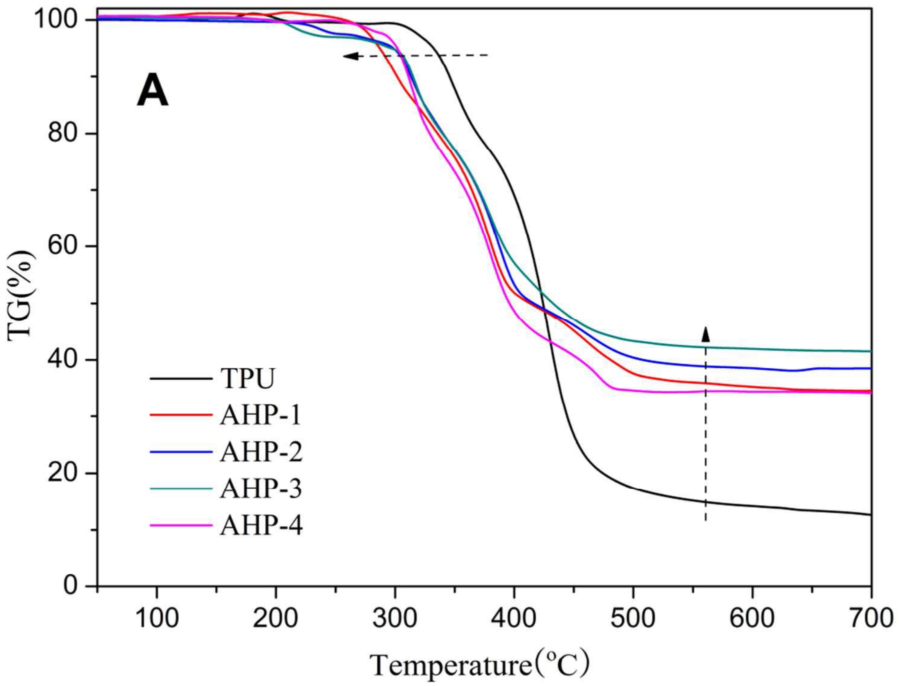

Luminous Flux(%)
Time(s)
100
80
60
40
20
0
0
200
400
600
800
1000
1200
TPU
AHP-1
AHP-2
AHP-3
AHP-4
B

Fig.8


A
TG(%)
Temperature(°C)
TPU
AHP-1
AHP-2
AHP-3
AHP-4
0
20
40
60
80
100
100
200
300
400
500
600
700

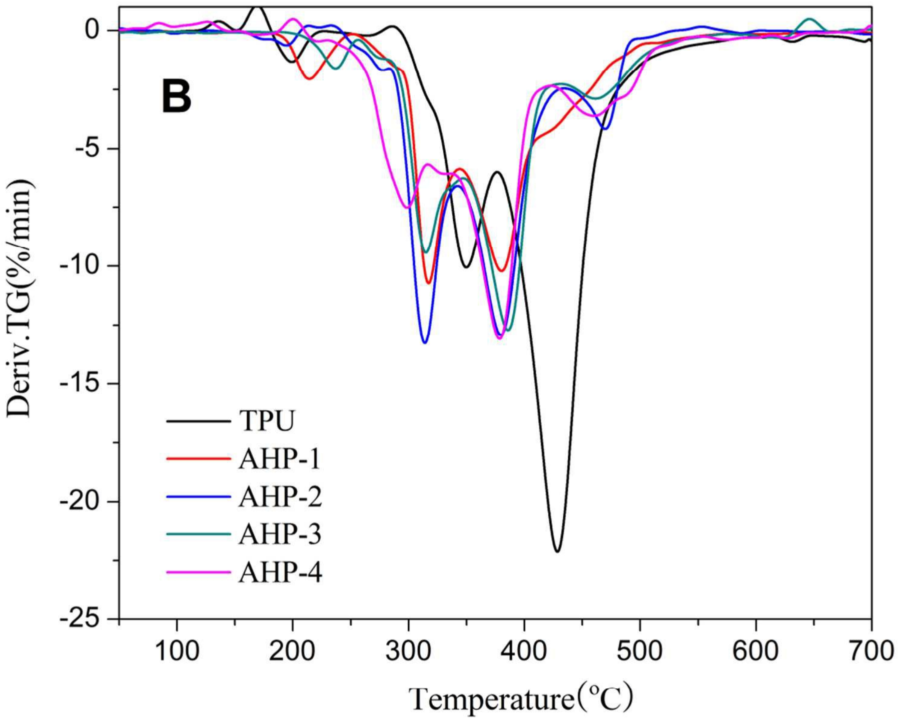
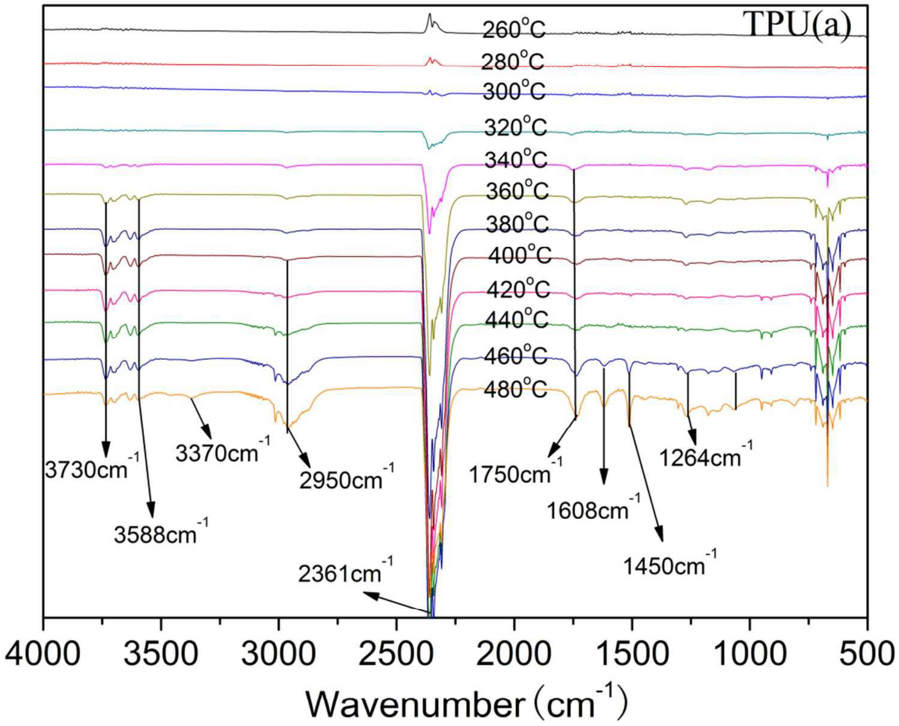
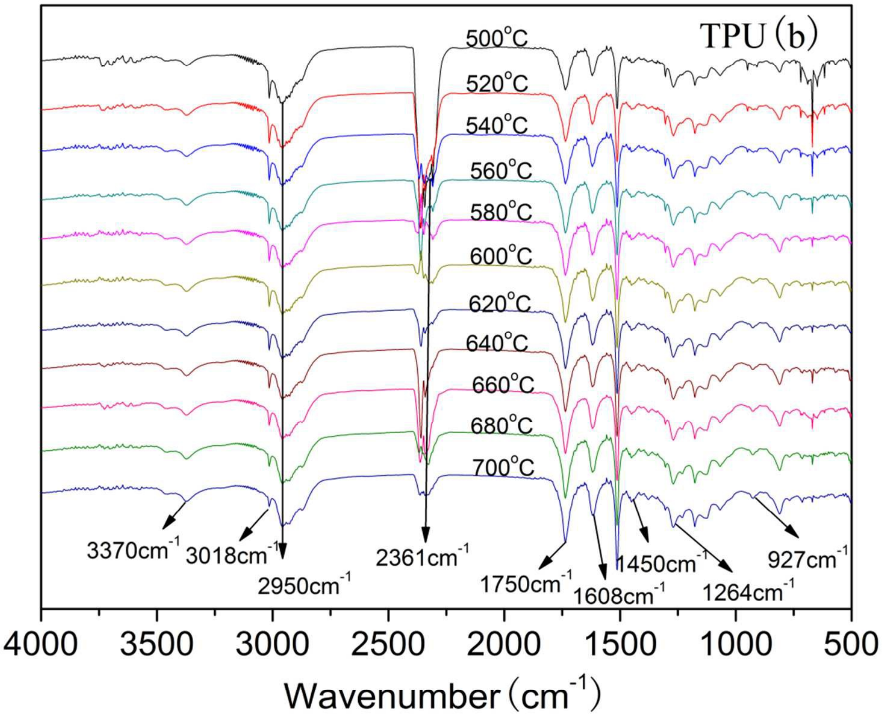
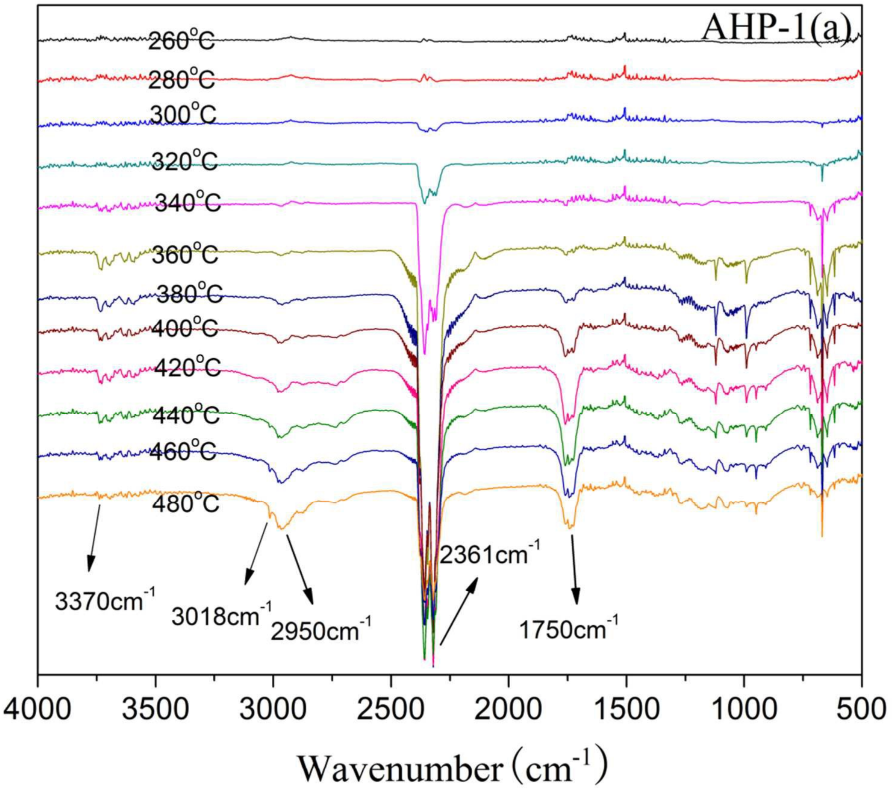
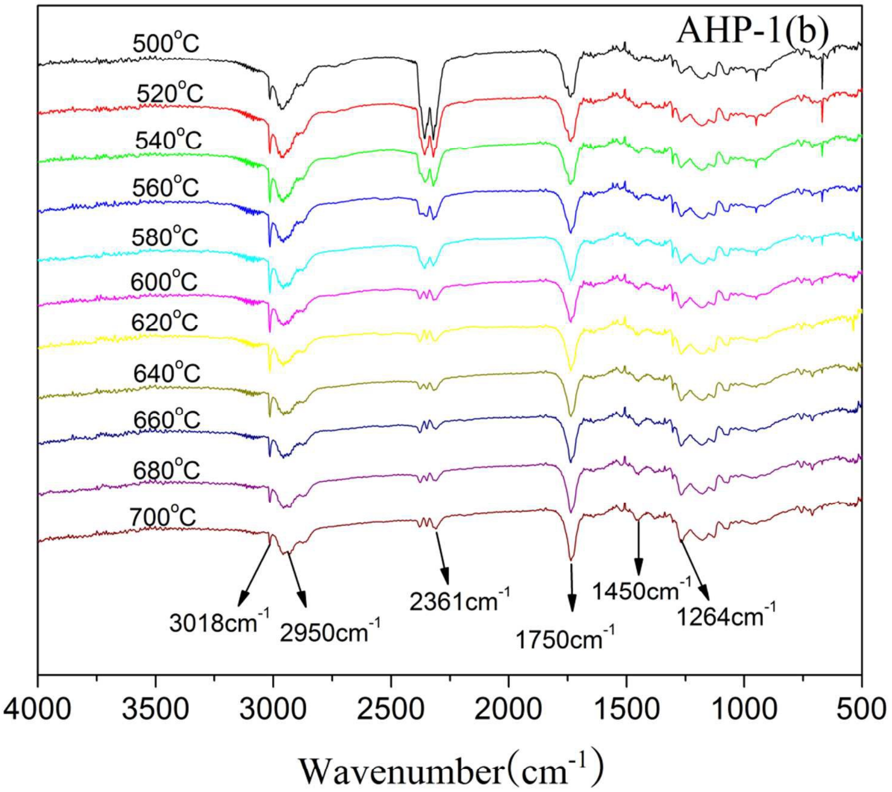

B
Deriv.TG(%/min)
0
-5
-10
-15
-20
-25
100
200
300
400
500
600
700
Temperature(°C)
TPU
AHP-1
AHP-2
AHP-3
AHP-4

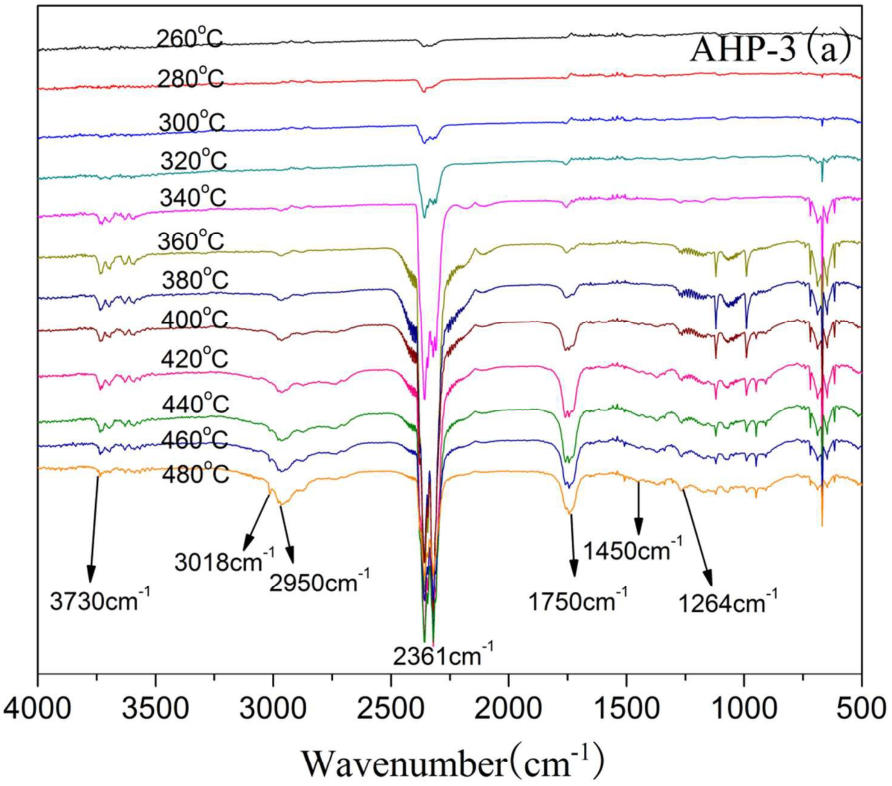
Fig. 9


TPU(a)
260°C
280°C
300°C
320°C
340°C
360°C
380°C
400°C
420°C
440°C
460°C
480°C
3730cm-1
3588cm-1
3370cm-1
2950cm-1
2361cm-1
1750cm-1
1608cm-1
1450cm-1
1264cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


TPU (b)
500°C
520°C
540°C
560°C
580°C
600°C
620°C
640°C
660°C
680°C
700°C
3370cm-1
3018cm-1
2950cm-1
2361cm-1
1750cm-1
1608cm-1
1450cm-1
1264cm-1
927cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


AHP-1(a)
260°C
280°C
300°C
320°C
340°C
360°C
380°C
400°C
420°C
440°C
460°C
480°C
3370cm-1
3018cm-1
2950cm-1
2361cm-1
1750cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


AHP-1(b)
500°C
520°C
540°C
560°C
580°C
600°C
620°C
640°C
660°C
680°C
700°C
3018cm-1
2950cm-1
2361cm-1
1750cm-1
1450cm-1
1264cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


AHP-3 (a)
260°C
280°C
300°C
320°C
340°C
360°C
380°C
400°C
420°C
440°C
460°C
480°C
3730cm^{-1}
3018cm^{-1}
2950cm^{-1}
2361cm^{-1}
1750cm^{-1}
1450cm^{-1}
1264cm^{-1}
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm^{-1})

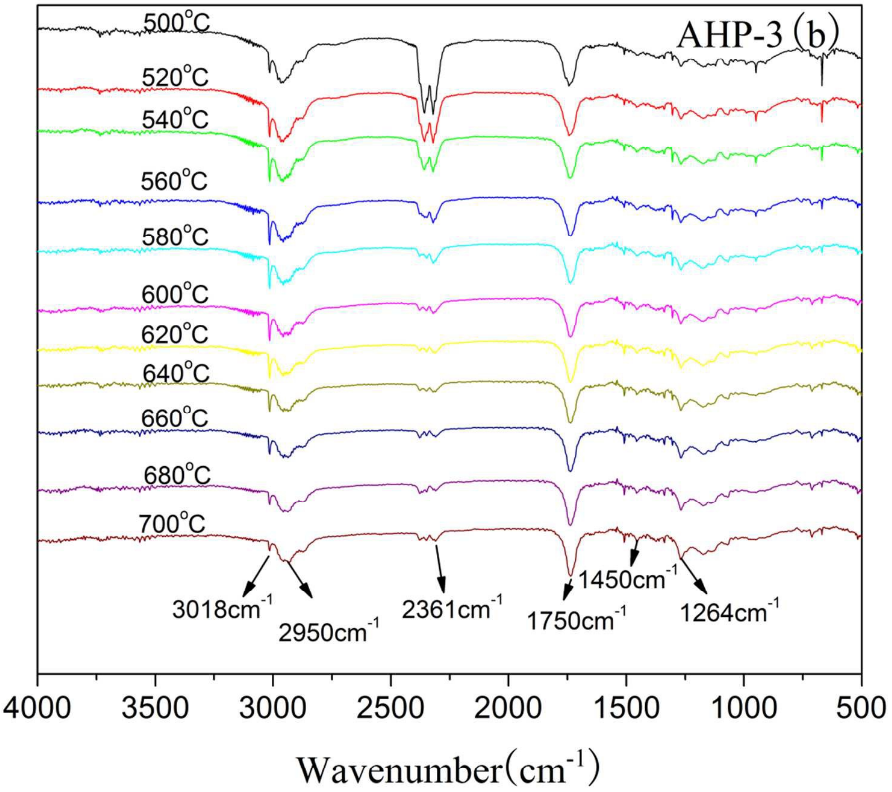

AHP-3 (b)
500°C
520°C
540°C
560°C
580°C
600°C
620°C
640°C
660°C
680°C
700°C
3018cm-1
2950cm-1
2361cm-1
1750cm-1
1450cm-1
1264cm-1
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

Fig. 10

Legends of Tables

Table 1 Formulations and LOI value and UL 94 rating of all samples

Sample	TPU/wt%	[Emim]PF_6/wt%	AHP/wt%	LOI	UL 94
TPU	100	--	--	23.75	No rating
AHP-1	80	--	20	32.50	V-1
AHP-2	80	0.03125	19.96875	34.25	V-0
AHP-3	80	0.0625	19.9375	35.75	V-0
AHP-4	80	0.125	19.875	33.25	V-1