Hexa-[4-(glycidyloxycarbonyl) phenoxy]cyclotriphosphazene chain extender for preparing high-performance flame retardant polyamide 6 composites

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Abstract
The effects of phosphazene based epoxy resin hexa-[4-(glycidyloxycarbonyl) phenoxy]cyclotriphosphazene (CTP-EP) as a synergistic agent on fire retardancy, thermal and mechanical properties of polyamide 6/aluminum diethylphosphinate (PA6/AlPi) composites were investigated. AlPi and CTP-EP presented an obviously synergistic flame retardant effect for the PA6 matrix. The PA6/AlPi/CTP-EP composites with a thickness of 1.6 mm successfully passed UL-94 V-0 rating with the limiting oxygen index value of 31.0% when the loading amount of AlPi/CTP-EP (mass fraction of 97/3) was 11 wt%. The incorporated CTP-EP improved the complex viscosity of PA6/AlPi/CTP-EP composites due to the chain extending reaction between the epoxide groups of CTP-EP and the terminal groups of PA6 matrix. The CTP-EP stimulated the formation of more sufficient and compact char layer during combustion. The higher melt viscosity and more compact char layer of PA6 composites further inhibited the volatilization of flammable gases, thus the ignition time of PA6/AlPi/CTP-EP composites was prolonged and the released heat was reduced. The introduction of CTP-EP simultaneously enhanced the flame retardant and mechanical properties of PA6/AlPi/CTP-EP composites compared with that of PA6/AlPi composites.

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1. Introduction

Polyamide 6 (PA6) has been widely used in automotive, telecommunication, electronic and electrical industries as it has high mechanical strength, self-lubrication and electrical insulation in recent years [1–3]. However, its applications were limited attributed to inadequate flame retardancy and severe flammable melt dripping during combustion [4]. Consequently, the enhancement of flame retardancy of PA6 matrix attracts researchers’ interests in the last decades. Halogen-containing flame retardants are effective for PA6, whereas its application has been restricted due to the release of poisonous, corrosive gases and black smoke during combustion [5]. In this case, development of halogen-free flame retardant has become an extensive research topic for PA6 matrix. Up to now, a wide variety of halogen-free flame retardants have been proposed for polyamides including melamine polyphosphate [1], metal hydroxides [2], red phosphorus [6–8], ammonium polyphosphate [9,10], melamine cyanurate [11,12], organoclay nanocomposite [13,14], and multiwall carbon nanotubes (MWCNTs) composites [15–17]. The phosphorus-containing flame retardant is considered to be an effective additive for flame retardant PA6 matrix. The alkylphosphinate salts have been used as novel effective flame retardants for PA6 matrix in the past few years [18,19] because they exhibit excellent flame retardant behaviors and thermal stability. Aluminum salt of diethylphosphinic acid (AlPi) has been proved as an effective flame retardant for PA6 [19,20]. Braun’s group investigated the mechanism of flame retardant of AlPi. They found that AlPi mainly acted as flame inhibition [21]. Moreover, PA6 matrix...
molecular chain contains plenty of amide groups, and during high temperature processing the presence of small amount of impurities and moisture would lead to their hydrolysis [22]. In consequence, the incorporation of AlPi into PA6 matrix could reduce the molecular weight and mechanical performance of the composites, and conceivably limit its application in particular fields [23,24].

The addition of chain extender has been regarded as an alternative method to solve this problem. The molecular weight and melt viscosity of composites are increased by the introduction of the chain extender which could comprise the coupling of many polymer chains and the mechanical performance of composites is ultimately enhanced [25]. Since the amino and carboxyl groups at the end of the PA6 molecular chain could react with caprolactam, oxazoline and epoxide [25–27]. The epoxide group has been revealed to be highly reactive with carboxyl and amino groups of PA6, and a small addition of chain extender to PA6 could increase its tensile strength and melt viscosity [28]. Consequently, the method of flame retardant incorporated with chain extender was supposed to be an acceptable flame retardant system for preparing flame retardant PA6 composites with superior flame retardancy and mechanical performance simultaneously. The reaction of the functional groups during composites processing would implement the extension of molecular chains, meanwhile, the mechanical performance was enhanced. In this case, a flame retardant synergistic effect could be generated. Moreover, the polymeric materials incorporated with cyclotriphosphazenes exhibited excellent flame retardancy and self-extinguish ability caused by the flame retardant synergistic effect between phosphorus and nitrogen [29,30]. However, few reports have been appeared about the effects of a combination of chain extender and flame retardant on the properties of PA6 composites, thus, the mechanism of flame retardant synergistic effect between chain extender and flame retardant needs be further investigated.

In this paper, phosphazenes based epoxy resin hexa-[4-(glycidyloxycarbonyl) phenoxycyclophosphazene (CTP-EP) was used as chain extender and flame retardant PA6 composites was prepared by the combination of CTP-EP and AlPi. The thermal degradation and combustion behavior, flame retardant synergistic mechanism, flame retardancy, rheological and mechanical performance of the produced flame retardant PA6 composites were researched.

2. Experimental section

2.1. Materials

Aluminum diethylphosphinate (AlPi) and Polyamide 6 (PA6) were provided by Qingdao Fusilin Chemicals Co., China and DUPONT Company Ltd., USA, respectively. Hexachlorocyclophosphazene and 4-hydroxybenzaldehyde were purchased from Wuhan Yuancheng Chemical Co., Ltd., China. Epichlorohydrin was purchased from Aladdin reagent (Shanghai) Co. Ltd., China. Tetrahydrofuran, triethylamine, ethyl acetate, sodium hydroxide, potassium permanganate, sodium sulfate, sulfuric acid and ethanol were purchased from Tianjin Kemiu Chemical Reagent Co., Ltd., China. All the materials were used in this paper without any treatment.

2.2. Preparation of PA6 composites

According to our reported work [30], the hexa-[4-(glycidyloxycarbonyl) phenoxycyclophosphazene (CTP-EP) was synthesized from hexachlorocyclophosphazene, 4-hydroxybenzaldehyde and epichlorohydrin, and the chemical structure of CTP-EP was illustrated in Scheme 1. The obtained sticky CTP-EP was firstly diluted with a certain amount of ethanol and then mixed homogeneously with AlPi following different mass fraction, finally ethanol was removed by a rotary evaporator. The PA6, flame retardants including AlPi and AlPi/CTP-EP composite were firstly heated in drying oven under vacuum at 70 °C and then mixed homogeneously with a high-speed mixer. Granules of the flame retardant PA6 composites were obtained by extruding the mixtures of PA6, AlPi and CTP-EP with different mass fractions in a twin-screw extruder at a temperature profile of six heating zones (215, 225, 230, 230 and 220 °C). The granules were molded through the injector at a temperature profile of 215, 225, 230, 230 and 225 °C as testing samples. Tables 1–3 show the flame retardants contents in PA6 composites.

2.3. Characterization

The limiting oxygen index (LOI) values were measured by oxygen index meter at room temperature with a specimen dimension of 130 × 6.5 × 3 mm³ (ISO 4589-2: 2006).

Vertical burning tests (UL-94) were characterized by vertical combustion apparatus with a specimen dimension of 130 × 13 × 3.2 mm³ and 130 × 13 × 1.6 mm³. The best flame retardancy of polymeric materials would pass V-0 rating.

The tensile and flexural performances of all samples were conducted by the tensile testing machine with the speed of 5 and 2 mm min⁻¹, respectively. The Izod impact strength of all samples with the nick depth of 2 mm was tested through Notched Izod
impact instrument (ASTM D256). Five specimens were used for each test at least and the average values were reported.

Rheological properties of melts were measured by using AR2000ex rheometer (TA Instruments, USA) setting a chamber temperature of 230 °C. The extruded pellets with diameter and thickness of 25 and 1 mm were molded into disks.

The thermal gravimetric analysis (TGA) was carried out by a thermal gravimetric analyzer with heating rate of 10 °C/min, and the 4–5 mg samples were heated with a flow rate of 20 mL min⁻¹ under nitrogen (50–800 °C). The combustion was measured by Fire Testing Technology cone calorimeter behavior under ventilated conditions (ISO 5660-1). The samples (100 × 100 × 4 mm³) were exposed to the cone with heat flux of 50 kW m⁻². At least three samples were tested for each sample.

The morphology of the char was examined by SEM (accelerating voltage, 15 kV). A gold layer was sputter-coated on char residues surface for better imaging.

The compositions of char residues were characterized through FTIR, XPS, and XRD, respectively. The transmittance mode of FTIR was used (wavenumber from 4000 to 500 cm⁻¹).

The C, N, P, O, and Al elements were analyzed by XPS, using a monochromated Al Kx source at a base pressure of 1.0 × 10⁻⁷ mbar. XRD spectra were recorded in the 5-60° range using a Bruker AXS D8 diffractometer in configuration 2-theta/theta.

### 3. Results and discussion

#### 3.1. Flame retardancy

The results of UL-94 and LOI tests of PA6 with AlPi are shown in Table 1. The LOI value of neat PA6 was 21.0% and the materials were easily flammable along with continual and severe dripping after ignited. However, the flame retardancy of PA6 composites was obviously enhanced with the introduction of AlPi. The LOI value of PA6 with 10 wt% AlPi composites increased to 27.5% compared with pure PA6 and the value was improved with increasing the AlPi content. The PA6 composites containing 14 wt% AlPi (1.6 mm) successfully passed UL-94 V-0 rating and the LOI value reached 30.6%. AlPi possessed an efficient flame retardant effect for PA6 matrix. This can be attributed to the formation of phosphinate compound obtained from the decomposition of AlPi [20], which was further degraded and released the PO free radicals. The PO free radicals could act as radical scavenger and exert quenching effect on the gaseous phases. On the other hand, the phosphate and pyrophosphate of the decomposition product of AlPi remained in the condensed phase prevent the underlying materials from degradation and combustion [31].

With the development of the electronics towards miniaturization and ultra-thin thickness, the polymeric materials used in electronic and electrical areas require excellent flame retardancy and comprehensive performance. For further improving the flame retardancy of PA6/AlPi composites, the cyclotriosphene-based CTP-EP is used as flame retardant synergist and the results of PA6/AlPi/CTP-EP composites are summarized in Table 2. In AlPi/CTP-EP system, the loading amount of flame retardant is fixed at 11 wt% and the mass ratio of AlPi and CTP-EP can be regulated. As shown in Table 2, the samples failed to pass UL-94 tests and the LOI value was 27.5% when AlPi alone was used in the flame retardant PA6 matrix. However, the flame retardancy of the PA6 composites was enhanced with the introduction of CTP-EP. The PA6/AlPi/CTP-EP composites (1.6 mm) passed UL-94 V-0 rating and when the mass ratio of AlPi/CTP-EP was 97:3, and the LOI value was 31.0%. The epoxy groups in CTP-EP reacted with amino and carboxyl end groups in PA6 matrix and extended the polymer chains, thus enhanced the complex viscosity. The higher viscosity benefits to inhibit the volatilization of decomposition products during combustion, which declines the combustion intensity of PA6 composites. Moreover, the cyclotriosphene-based CTP-EP can stimulate the carbonization of PA6 matrix and benefit the flame retardancy of composites by exerting an isolation effect in the condensed phase [32]. As a result, AlPi and CTP-EP present superior synergistic flame retardant effect for PA6 matrix both in the condensed and the gaseous phases. Moreover, the flame retardancy of PA6 composites decreases with further increasing the CTP-EP content in the composites (Table 2). For example, the LOI value of PA6/AlPi/CTP-EP composites (S11) was 30.2% when the mass ratio of AlPi/CTP-EP was 95:5, it only passed UL-94 V-2 rating. The fact can be attributed to that excessive CTP-EP in the AlPi/CTP-EP system destroyed the optimal flame retardant synergistic effect between gaseous and condensed phase.

When the mass ratio of AlPi/CTP-EP was 97:3, AlPi and CTP-EP exerted an optimal synergistic flame retardant effect for the PA6 composites. The effects of the total loading amount of AlPi/CTP-EP on the flame retardancy of PA6 composites are investigated and the results are summarized in Table 3. The samples with a thickness of 3.2 and 1.6 mm passed UL-94 V-0 rating when the loading amount of AlPi/CTP-EP was 97:3, and the LOI value was 31.0%. The epoxy groups in CTP-EP reacted with amino and carboxyl end groups in PA6 matrix and extended the polymer chains, thus enhanced the complex viscosity. The higher viscosity benefits to inhibit the volatilization of decomposition products during combustion, which declines the combustion intensity of PA6 composites. Moreover, the cyclotriosphene-based CTP-EP can stimulate the carbonization of PA6 matrix and benefit the flame retardancy of composites by exerting an isolation effect in the condensed phase [32]. As a result, AlPi and CTP-EP present superior synergistic flame retardant effect for PA6 matrix both in the condensed and the gaseous phases. Moreover, the flame retardancy of PA6 composites decreases with further increasing the CTP-EP content in the composites (Table 2). For example, the LOI value of PA6/AlPi/CTP-EP composites (S11) was 30.2% when the mass ratio of AlPi/CTP-EP was 95:5, it only passed UL-94 V-2 rating. The fact can be attributed to that excessive CTP-EP in the AlPi/CTP-EP system destroyed the optimal flame retardant synergistic effect between gaseous and condensed phase.

### 3.2. Mechanical properties

The mechanical performance of the neat PA6, PA6/AlPi and PA6/AlPi/CTP-EP (mass fraction of AlPi/CTP-EP fixed at 97:3) composites with different loading levels of flame retardant were evaluated by the tensile, flexural and impact strength tests (Table 4). Compared with the neat PA6 composites, the tensile, flexural and Izod impact strength of the PA6/AlPi and PA6/AlPi/CTP-EP composites...
decreased to some extent due to the incorporation of flame retardants, and the mechanical performance for PA6 composites gradually decreased with the increase of the flame retardant loading, as revealed in Table 4. However, it is worth noting that the tensile, flexural and Izod impact strength for PA6/AlPi/CTP-EP composites was higher than that of PA6/AlPi composites under the same loading amount of flame retardant. For example, when the loading amount of flame retardants was 11 wt%, the tensile, flexural and Izod impact strength was 57.0 MPa, 85.2 MPa and 9.2 kJ m⁻² for the PA6/AlPi composites and 60.3 MPa, 90.1 MPa and 9.9 kJ m⁻² for the PA6/AlPi/CTP-EP composites and presented an enhancement of 5.8, 5.8 and 7.6% compared with that of PA6/AlPi composites, respectively. This fact can be primarily attributed to that the epoxide groups of CTP-EP reacted with the terminal amino or carboxyl groups in the PA6 matrix, and the chain extending reaction improved the molecular weight. The increment of molecular weight benefits the increase of the friction of chain segmental motion [22], thus the mechanical performance of PA6/AlPi/CTP-EP composites was enhanced compared with that of PA6/AlPi composites due to the incorporation of small amount of CTP-EP.

### 3.3. Rheological properties

Rheological measurement is an effective method to evaluate the chain extension on the linear viscoelastic behavior of polymeric materials [22,33]. The rheological behaviors of pure PA6, PA6/AlPi (S2) and PA6/AlPi/CTP-EP (S9) composites were investigated at 230 °C with stress-controlled rheometer. As a function of angular frequency, Fig. 1 shows the storage modulus ($G'$) and loss modulus ($G''$) of the PA6 materials. The $G'$ and $G''$ of the three samples gradually increase over the whole range of angular frequency and present a similar tendency. As revealed in Fig. 1, the $G'$ and $G''$ for PA6/AlPi composites are higher than that of neat PA6 caused by the hydrogen bonding association effect between the P=O bonds in AlPi and hydrogen atom in PA6 matrix. With the incorporation of CTP-EP into PA6/AlPi composites, the $G'$ and $G''$ for PA6/AlPi/CTP-EP composites were further improved compared with that of PA6/AlPi composites, which can be attributed to the coupling reaction between CTP-EP and the terminal groups of PA6 matrix. Consequently, the molecular size of the PA6 composites is increased [22].

Fig. 2 depicts the complex viscosity ($η$) of neat PA6, PA6/AlPi (S2) and PA6/AlPi/CTP-EP (S9) composites over the whole frequency range. Similar to the tendency of $G'$ and $G''$, the $η$ for PA6/AlPi composites is higher than that of neat PA6, as shown in Fig. 2. It can be attributed to that the hydrogen bonding association effect between AlPi and PA6 matrix enhanced the friction effect between molecular chains of PA6. The movement of the PA6 molecular chains is hindered, thus the $η$ for PA6/AlPi composites is improved. As shown in Fig. 2, the $η$ for PA6/AlPi/CTP-EP composites is obviously higher than that of neat PA6 and PA6/AlPi composites due to the introduced small amount of CTP-EP. The relatively higher melt viscosity of PA6/AlPi/CTP-EP composites could result from the special structure of CTP-EP with six epoxy groups in each molecule, which may contribute to form a network and crosslink structure through the interaction between the epoxy groups in CTP-EP and the terminal groups of PA6 matrix during the melting process illustrated in Fig. 3. Consequently, the $η$ for PA6/AlPi/CTP-EP composites is further enhanced. The higher $η$ for PA6 composites in melt state will limit the volatilization of degradation products during combustion, which may contribute to improve the flame retardancy of the PA6 composites [34].

### Table 4

Mechanical properties of PA6 composites with different loading amount of flame retardant.

<table>
<thead>
<tr>
<th>Loading (wt%)</th>
<th>Mechanical properties</th>
<th>Tensile strength (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Izod impact strength (kJ m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67.3 ± 2.1</td>
<td>67.3 ± 2.1</td>
<td>90.2 ± 2.6</td>
<td>12.0 ± 0.4</td>
</tr>
<tr>
<td>11</td>
<td>57.0 ± 1.3</td>
<td>60.4 ± 1.2</td>
<td>85.2 ± 1.7</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td>12</td>
<td>56.5 ± 1.1</td>
<td>60.3 ± 1.0</td>
<td>84.3 ± 1.2</td>
<td>8.9 ± 0.2</td>
</tr>
<tr>
<td>13</td>
<td>56.3 ± 1.0</td>
<td>59.4 ± 1.1</td>
<td>82.6 ± 0.9</td>
<td>8.7 ± 0.1</td>
</tr>
<tr>
<td>14</td>
<td>56.3 ± 1.1</td>
<td>59.1 ± 1.2</td>
<td>82.4 ± 0.8</td>
<td>8.4 ± 0.2</td>
</tr>
<tr>
<td>15</td>
<td>55.9 ± 1.2</td>
<td>58.9 ± 1.0</td>
<td>81.7 ± 1.0</td>
<td>8.2 ± 0.2</td>
</tr>
<tr>
<td>16</td>
<td>55.5 ± 1.0</td>
<td>58.5 ± 1.0</td>
<td>81.3 ± 1.0</td>
<td>8.1 ± 0.2</td>
</tr>
<tr>
<td>17</td>
<td>55.2 ± 1.0</td>
<td>58.3 ± 1.0</td>
<td>81.0 ± 1.0</td>
<td>8.0 ± 0.2</td>
</tr>
<tr>
<td>18</td>
<td>54.9 ± 1.0</td>
<td>57.9 ± 1.0</td>
<td>80.7 ± 1.0</td>
<td>7.9 ± 0.2</td>
</tr>
</tbody>
</table>

**Fig. 1.** Storage modulus (a) and loss modulus (b) as a function of angular frequency for neat and flame retardant PA6.
3.4. Thermal degradation behavior

The thermal stability, charring capability and degradation behavior of neat PA6 (S0), PA6/AlPi (S2) and PA6/AlPi/CTP-EP (S9) composites were evaluated by thermogravimetric analysis (TGA) tests under nitrogen atmosphere. Fig. 4 shows the TGA and DTG curves. Table 5 shows the corresponding characteristic of thermal decomposition parameters with the temperature of 5 wt% weight losses (T_initial), the temperature of maximum weight loss rate (T_peak), the weight loss rate at maximum weight loss rate (R_peak) and the char residue at 800 °C. Pure PA6 began to decompose at 396.1 °C and the material was almost completely decomposed with only 0.6 wt% residues at 800 °C. Meanwhile, the thermal degradation presented one step with a maximum loss weight rate of 26.2% min⁻¹ at 450.8 °C associated with the release of H₂O, CO, CO₂, NH₃, its derivatives and hydrocarbon fragments [35] (Fig. 4(b) and Table 5). The initial decomposition temperature of PA6/AlPi composites decreased from 396.1 °C for pure PA6 to 383.4 °C with the addition of AlPi to PA6, which was caused by catalytic activity of the metal hypophosphite. The metal hypophosphite acted as a weak Lewis acid-base for the aromatization of the PA6 matrix, interacted with the matrix and then reduced the thermal stability of the PA6/AlPi composites [36]. Moreover, the final residue of PA6/AlPi composites reached 4.9 wt% (800 °C). The thermal degradation of the PA6/AlPi composites also presented one degradation step with a maximum loss weight rate of 20.7% min⁻¹ (432.9 °C) shown in Fig. 4(b) and Table 5, and the T_peak appeared earlier and the R_peak was lower than that of neat PA6. The fact was caused by the decomposition products of AlPi that were covered the materials surface and the formed insulation layer produced the isolation effect, thus the loss weight rate was decreased. With the incorporation of CTP-EP into the PA6/AlPi composites, the T_initial for PA6/AlPi/CTP-EP composites slightly decreased from 383.4 °C for the PA6/AlPi composites to 368.3 °C because the decomposition products of phosphazene groups promoted the PA6 matrix degradation and charring during heating process. As shown in Fig. 4(b), the PA6/AlPi/CTP-EP composites presented one step during the thermal degradation process and the T_peak increased from 432.9 °C for the PA6/AlPi composites to 434.2 °C, and the R_peak decreased from 20.7% min⁻¹ for the PA6/AlPi composites to 19.8% min⁻¹. The fact can be attributed to the formed network structure caused by the reaction between CTP-EP and the terminal groups of PA6 matrix. Meanwhile, the decomposition products of phosphazene groups promote the PA6 matrix charring, and the formed organic char layer combines with inorganic layer of the decomposition product of AlPi effectively insulated the material from thermal degradation. Consequently, the char residue for PA6/AlPi/CTP-EP composites at 800 °C increased from 4.9 wt% for the PA6/AlPi composites to 8.4 wt % and increase by 71.4%.

3.5. Flammability behavior

The flammability behavior of PA6 composites was characterized by cone calorimeter tests. The time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR) and average of effective heat of combustion (av-EHC) were used to investigate the effect of AlPi and AlPi/CTP-EP composite on the burning behavior of PA6 matrix in a real fire environment. The detailed information of burning behavior of pure PA6 (S0), PA6/AlPi (S2) and PA6/AlPi/CTP-EP (S9) composites burned by the cone calorimeter at a heat flux of 50 kW m⁻² are shown in Fig. 5 and Table 6.

As revealed in Table 6, the TTI decreased from 65 s (pure PA6) to 44 s (PA6/AlPi composites), corresponding to that the incorporated AlPi was decomposed in advance and then stimulated the PA6 matrix catalytic-degradation ahead of time compared with that of pure PA6. However, PA6/AlPi/CTP-EP composites presented a longer TTI and the value increased from 65 s for neat PA6 and 44 s for PA6/AlPi composites to 89 s for composites and delayed by 24 s compared with that of neat PA6, as indicated in Table 6. The incorporated small amount of CTP-EP possessing a special structure of six epoxy groups effectively enhanced the complex viscosity of PA6 composites and formed the network structure, then retarded the heat enter into the inner PA6 and the release of the combustible
gas [34]. As a result, the accumulation speed of combustible vapors on materials surface became slow and the combustion required more thermal energy, thus the TTI of PA6/AlPi/CTP-EP composite was prolonged. The increase of TTI is very significant for improving the flame retardancy of the PA6 matrix.

Fig. 5(a) presents the HRR of pure PA6, PA6/AlPi and PA6/AlPi/CTP-EP composites. The results indicate that pure PA6 burns fiercely after ignition, which has just one intensive HRR peak during the combustion process with a PHRR of 912.5 kW m$^{-2}$ at 185 s, however PA6/AlPi composites presents two HRR peaks. One peak at 145 s appeared earlier than that of pure PA6 due to that the decomposition of AlPi occurred at the early stage of the heating and the decomposition of AlPi stimulated the PA6 to catalytic-degradation in advance. Meanwhile, the PHRR decreased from 912.5 kW m$^{-2}$ (pure PA6) to 598.1 kW m$^{-2}$ (PA6/AlPi). It can be attributed to that AlPi in the composites decomposed and exerted an important quenching effect in the gaseous phase as free radical scavenger [20]. Moreover, in the condensed phase, the phosphate and pyrophosphate of the decomposition product of AlPi covered the PA6 matrix surface so that the underlying materials were prevented from further combustion. The other HRR peak of PA6/AlPi composites appeared at 201 s with a PHRR of 617.1 kW m$^{-2}$ and was caused by the cracking char or the pyrolysis of the remnant AlPi. After incorporating CTP-EP into the PA6/AlPi composites, two peaks are presented in the HRR curve of PA6/AlPi/CTP-EP composites. One peak was prolonged by 19 s compared with that of the PA6/AlPi (164 s). The PHRR of PA6/AlPi/CTP-EP composites was decreased by 14.9% from 598.1 kW m$^{-2}$ (PA6/AlPi) to 509.2 kW m$^{-2}$. It is mainly attributed to the formed network structure and higher complex viscosity of PA6 composites induced by the reaction between CTP-EP and PA6 matrix. Thus, the formed higher complex viscosity inhibited the heat enter into the inner PA6 matrix and also inhibited the release of combustible gas enter into combustion zone, which delayed the degradation process and reduced the

**Table 5**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{initial}}$ ($^\circ$C)</th>
<th>$R_{\text{peak1}}$/$T_{\text{peak1}}$ ($%$ min$^{-1}$/$^\circ$C)</th>
<th>Char residue (wt %)</th>
<th>$T_{\text{peak1}}$ ($^\circ$C)</th>
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</thead>
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<tr>
<td>Pure PA6</td>
<td>396.1</td>
<td>26.2/450.3</td>
<td>0.6</td>
<td></td>
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<tr>
<td>PA6/AlPi</td>
<td>383.4</td>
<td>20.7/432.9</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>PA6/AlPi/CTP-EP</td>
<td>368.3</td>
<td>19.8/434.2</td>
<td>8.4</td>
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**Table 6**

<table>
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<tr>
<th>Sample</th>
<th>Neat PA6</th>
<th>PA6/AlPi</th>
<th>PA6/AlPi/CTP-EP</th>
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<tr>
<td>TTI (s)</td>
<td>65</td>
<td>44</td>
<td>89</td>
</tr>
<tr>
<td>Peak$_1$-HRR (kW m$^{-2}$)</td>
<td>912.5</td>
<td>598.1</td>
<td>509.2</td>
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<td>$t_{\text{peak1}}$ (s)</td>
<td>185</td>
<td>145</td>
<td>164</td>
</tr>
<tr>
<td>Peak$_2$-HRR (kW m$^{-2}$)</td>
<td>–</td>
<td>617.1</td>
<td>653.2</td>
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<tr>
<td>$t_{\text{peak2}}$ (s)</td>
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<td>240</td>
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<td>THR (MJ m$^{-2}$)</td>
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<td>92</td>
<td>87.7</td>
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<tr>
<td>av-EHC (MJ kg$^{-1}$)</td>
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<td>23.7</td>
<td>21.3</td>
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</tbody>
</table>
The second HRR peak of PA6/AlPi/CTP-EP composite appeared at 240 s and later than that of PA6/AlPi composites. Moreover, the PHRR increased from 617.1 kW m\(^{-2}\) (PA6/AlPi) to 653.2 kW m\(^{-2}\) (PA6/AlPi/CTP-EP composites). The introduction of CTP-EP stimulated the formation of crosslinking structure and enhanced the complex viscosity of composites. Moreover, the decomposition of the phosphazene in CTP-EP promoted the phosphorus-rich char shield [37], the char shield would impede heat exchange and gas release. Meanwhile, the materials underneath accumulated adequate heat from continuous thermal irradiance and evolved combustible gases to promote the breakage of the polymer melt to some degree. Consequently, the combustion intensity at the second HRR peak was relatively higher than that of the PA6/AlPi composites. The incorporated small amount of CTP-EP decreased the THR of composites, and the THR declined from 99.2 MJ m\(^{-2}\) for neat PA6 material and 92.0 MJ m\(^{-2}\) for PA6/AlPi composites to 87.7 MJ m\(^{-2}\) for PA6/AlPi/CTP-EP composites (Fig. 5(b) and Table 6). The combination of CTP-EP with AlPi exerted evidently flame retardant synergistic effect for PA6 matrix.

The av-EHC discloses the burning rate of volatile gases during combustion. Table 6 shows that the av-EHC is decreased from 27.1 MJ kg\(^{-1}\) (neat PA6) to 23.7 MJ kg\(^{-1}\) (PA6/AlPi composites) indicating that the gaseous phase combustion intensity is suppressed due to the introduction of AlPi. It is decomposed to release PO free radicals and then PO free radicals captures the highly reactive H and OH radicals formed during the combustion processes to interrupt the radical action and combustion reaction [20]. With the incorporation of CTP-EP, the av-EHC of PA6/AlPi/CTP-EP composites further declines from 23.7 MJ kg\(^{-1}\) of PA6/AlPi composites to 21.3 MJ kg\(^{-1}\). The phenomenon can be mainly attributed to the enhanced complex viscosity of the PA6/AlPi/CTP-EP composites. It can effectively inhibit the release of flammable gas, thus the released heat in the corresponding gaseous phase decreases during the combustion.

3.6. Morphologies of the char residue

SEM images show the morphologies of the char residues of PA6/AlPi (S2) and PA6/AlPi/CTP-EP (S9) composites after cone calorimeter (Fig. 6). The char layer surface morphology of the PA6/AlPi composite presents an inhomogeneous and relatively loose structure due to the insufficient char formation (Fig. 6(a)). Consequently, the heat and flammable volatiles can transfer between underlying materials and flame zone, which lead to the relatively poor flame retardancy for PA6 matrix. The morphology of the char layer for PA6/AlPi/CTP-EP composites appears more uniform and compact than that of PA6/AlPi composites (Fig. 6(b)), which indicates that the phosphazene groups in CEP-EP stimulate the PA6 matrix degradation and char-forming during the combustion and form more compact char layer on materials surface. Consequently, the formed char layer could effectively produce an isolation effect in the condensed phase. The flame retardancy of PA6/AlPi/CTP-EP composites is enhanced comparing with that of PA6/AlPi composite.

3.7. Chemical compositions of the char residue

The char residues of PA6/AlPi and PA6/AlPi/CTP-EP composites after cone calorimeter are tested by FTIR (Fig. 7). The characteristic absorption peaks of PA6/AlPi composites char residue (1121 and 720 cm\(^{-1}\)) indicate the formation of P-O-C and P-O-P structures [38]. The peak at 3445 cm\(^{-1}\) is due to the stretching vibration of N-H. The peak at 1618 cm\(^{-1}\) corresponds to the aromatic ring caused by the decomposition and charring of neat PA6 matrix. The peak at 1270 cm\(^{-1}\) is assigned to the P-N stretching vibration of the phosphazene groups [37]. The peaks at 2860 and 2937 cm\(^{-1}\) are attributed to the stretching vibration of C-H. The peak at 3081 cm\(^{-1}\)

![Fig. 6. SEM images of the char residue for PA6/AlPi (a) and PA6/AlPi/CTP-EP (b) composites after cone calorimeter tests.](image)

![Fig. 7. FTIR spectra of the char residue for PA6/AlPi (a) and PA6/AlPi/CTP-EP (b) composites after cone calorimeter tests.](image)
is the stretching vibration of O-H induced by the epoxide ring of CTP-EP that reacted with the amino or carboxyl end groups of PA6 matrix, which demonstrate that the chain extension reaction occurs during extrusion processing or combustion. The phosphorus containing oxides and phosphazene structure remained in the char residue enhance the strength of char residue, thus the flame retardancy of PA6/AlPi/CTP-EP composites is improved.

The chemical compositions of the outer residual char surface of PA6/AlPi and PA6/AlPi/CTP-EP composites after cone calorimeter were tested by XPS (Table 7 and Fig. 8). The relative content of phosphorus and nitrogen was obviously increased from 2.21 to 1.08% for the PA6/AlPi composites to 3.89 and 5.99% for the PA6/AlPi/CTP-EP composites, respectively. The incorporated CTP-EP reacted with the molecular chain of PA6 matrix and the phosphazene structure of CTP-EP was remained in char residue. The phosphazene structure possesses excellent thermal stability [29,30] and benefits to improve the thermal oxidation performance for char layer. The relative content of carbon was also increased from 67.41% for PA6/AlPi composites to 69.74% for PA6/AlPi/CTP-EP composites due to the catalytic charring effect of the remained phosphazene. Moreover, the relative content of aluminum was also increased from 2.55% for PA6/AlPi composites to 4.41% for PA6/AlPi/CTP-EP composites, which can be attributed to the more decomposition product of AlPi remained in the condensed phase induced by the higher complex viscosity of PA6/AlPi/CTP-EP composites during the combustion. As a result, more amount flame retardant elements including phosphorus, nitrogen, carbon and aluminum benefited the formation of sufficient char layer with high quality, which effectively prevented the PA6 matrix from further oxidation and decomposition resulting in the improved flame retardancy for PA6 matrix during combustion.

Fig. 8. XPS spectra of char residue of PA6/AlPi and PA6/AlPi/CTP-EP composites after cone calorimeter tests.

Table 7
Element relative content of the char layer for flame retardant PA6 by XPS analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Char layer of PA6/AlPi</th>
<th>Char layer of PA6/AlPi/CTP-EP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak BE (eV)</td>
<td>Atomic percentage (%)</td>
<td>Peak BE (eV)</td>
</tr>
<tr>
<td>C1s</td>
<td>284.55</td>
<td>67.41</td>
</tr>
<tr>
<td>N1s</td>
<td>386.4</td>
<td>1.08</td>
</tr>
<tr>
<td>O1s</td>
<td>531.87</td>
<td>26.82</td>
</tr>
<tr>
<td>P2p</td>
<td>134.61</td>
<td>2.21</td>
</tr>
<tr>
<td>Al2p</td>
<td>75.41</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The X-ray diffractions of the residues of PA6/AlPi and PA6/AlPi/CTP-EP composites after cone calorimeter tests were tested (Fig. 9). The two samples were degraded into amorphous phase, which was characterized by a broad band between 15° and 35°, as shown in Fig. 6. These bands are generally attributed to pregraphitic carbon species [39], which reveals the formation of the char. Compared with the curve of PA6/AlPi, an additional band (9°) corresponding to the crystallized AlPi [40] appears in the curve of PA6/AlPi/CTP-EP. The introduced CTP-EP effectively enhanced the isolation effect of char layer in the condensed phase during combustion, thus AlPi can be maintained in the residue of PA6/AlPi/CTP-EP.

4. Conclusion

The combination of AlPi and CTP-EP presented obviously synergistic flame retardant effect to the PA6 matrix, and the AlPi/CTP-EP system exerted flame retardant effect both in gaseous and condensed phases. The specimen (1.6 mm) passed UL-94 V-0 rating and the LOI value reached 31.0% with the addition of 11 wt% AlPi/CTP-EP. The TTI of PA6/AlPi/CTP-EP composite was delayed from 44 s for PA6/AlPi to 89 s, and the PHRR was also obviously postponed compared with that of PA6/AlPi composites due to the chain extending and tackifying effect of CTP-EP. The chain extending reaction between CTP-EP and the terminal groups of PA6 matrix granted a significant enhancement of the storage modulus, loss modulus and complex viscosity for PA6 composites. The mechanical properties of PA6/AlPi/CTP-EP composites were improved with the introduction of CTP-EP compared with that of PA6/AlPi composites. As a result, the flame retardant and mechanical performance of PA6/AlPi/CTP-EP composites were simultaneously enhanced. With adding proper nanofillers, these composites can be used to produce unique nanocomposites that can provide different properties and performances for various applications such as
electromagnetic interference (EMI) shielding [41,42], structural and functional materials [43–59] and sensing [60–65].

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References


