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1 **An Efficient Method to Improve Simultaneously the Water Resistance, Flame**
2 **Retardancy and Mechanical Properties of POE Intumescent Flame-Retardant**
3 **Systems**

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10

11 **ABSTRACT**

12 To improve simultaneously the water resistance, flame retardancy and mechanical
13 properties of polyethylene-octene elastomer (POE) composite containing ammonium
14 polyphosphate (APP), an effective method was developed, in which the APP was first
15 coated by silicon compound with a vinyl group, and then introduced into POE matrix
16 through chemical cross-linking. X-ray photoelectron spectroscopy (XPS) etc.
17 measurements confirmed that the coated APP (CAPP) was prepared successfully.
18 Then, together with charring agent (CA), CAPP was used to flame retard POE. The
19 combustible performance of POE composites was investigated by limiting oxygen
20 index (LOI), vertical burning (UL-94), and cone calorimeter (CC) tests. The results
21 showed that POE composite containing 22.5 wt% CAPP had better flame retardancy
22 than POE containing equal amount of APP, especially CAPP system had much lower
23 heat release rate (HRR), total heat release (THR), smoke production rate (SPR), and

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1 mass loss rate (MLR) than APP system with the same amount of flame retardant.
2 Furthermore, CAPP system passed the UL-94 V-0 rating after water treatment at 70
3 °C for 7 days; while APP system did not. Thermal gravimetric analysis (TGA), XPS,
4 etc. measurements demonstrated that the formation of rich residue containing Si-C,
5 Si-O-C, etc. structures in the residue of CAPP system should be the most important
6 reason for its better flame retardancy than that of APP system. Mechanical tests
7 illustrated that CAPP system had higher tensile strength and elongation at break than
8 APP system at the same condition, which should be due to the good interfacial
9 adhesion resulting from the existence of silicon compound at the surfaces of APP and
10 its cross-linking with POE matrix. All these results illustrate that it should be an
11 efficient method to simultaneously improve the water resistance, flame retardancy and
12 mechanical properties of POE composite containing APP through functionalizing the
13 APP and then chemically incorporating it into the polymer matrix.

14

15 **1. Introduction**

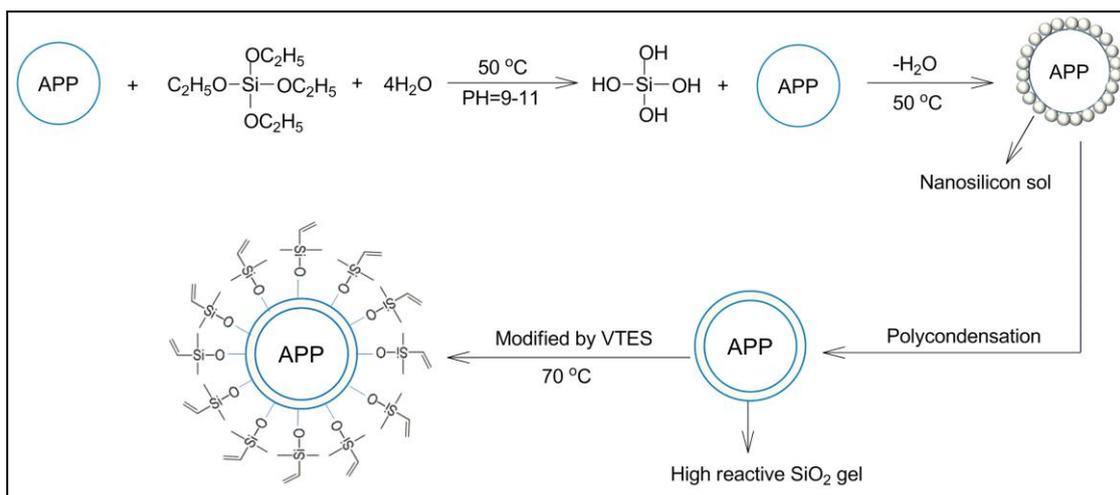
16 Due to the inherent bad flame retardancy of POE, some flame-retarded POE
17 composites were developed to expand its application.¹⁻⁵ At present, the halogen-free
18 flame-retardants are dominant in flame retarding POE. Guo et al.² used ammonium
19 polyphosphate-pentaerythritol (APP-PER) to flame retard POE with the aid of
20 organo-montmorillonite, and found that significant improvements on thermal stability,
21 flame retardancy and mechanical properties for POE composites were achieved
22 compared with those of neat POE. Hong and its co-workers³ applied magnesium

1 hydroxide to flame retard POE blends, and the results showed that the magnesium
2 hydroxide coated with polymeric material was very efficient to achieve simultaneous
3 improvement of both flame retardation and elongation at break for POE blends.

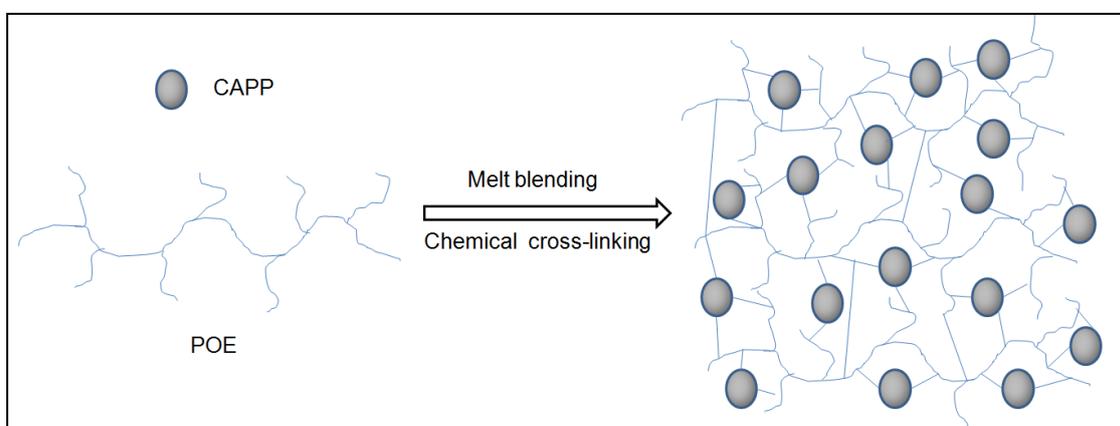
4 According to the past researches, it can be found that intumescent flame retardants
5 (IFRs) is the most efficient to flame retard POE. For POE/IFR composite, the typical
6 IFR is usually composed of three main components: acid source, carbon source, and
7 gas source.^{6,7} APP as an acid source and a gas source in IFR has been extensively
8 investigated. However, the APP is moisture-sensitive, and has bad compatibility with
9 many polymer matrices, resulting in the decrease of flame-retardant efficiency and the
10 damage to mechanical properties of polymer composites, Much work has been carried
11 out to improve the water resistance, flame retardancy and mechanical properties of
12 polymer composite containing APP.^{8,9} At present, the coating through silane coupling
13 agent^{10,11} or different compatibilizer^{12,13} at the surface of APP is regarded as the most
14 efficient method to solve the problems mentioned above. The APP prepared through
15 coating has a so-called core-shell structure, which allows the isolation of encapsulated
16 substance from surrounding, and thus protects APP from any degrading factors. Wang
17 et al.^{14,15} applied two methods to prepare coated APP, in which the first one is that
18 APP was coated by UV-curable epoxy acrylate resin; the second one is that APP was
19 coated by polysiloxane through in situ polymerization. The results showed that both
20 categories of APP products prepared could significantly improve the water resistance
21 and flame retardancy of polypropylene composites.

1 Although the coating is an very efficient method to improve the water resistance
2 and flame retardancy of polymer composites containing APP, its damage to
3 mechanical properties of polymer is still a big challenge. In order to weaken the
4 damage of APP to polymer matrix, some work has been performed. Hu et al.^{16,17}
5 reported that the cross-linking through electron beam irradiation could incorporate the
6 coated APP into polymer matrix through the bonding of coating, and the results
7 indicated that excellent mechanical properties were achieved in EVA composites.

8 Thus, the ideal way to achieve the improvements of water resistance, flame
9 retardancy, and mechanical properties of POE composites containing APP should be
10 that the APP is first functionalized through a material with functional groups, and then
11 the functionalized silica shell are introduced into POE matrix through chemical
12 cross-linking. In this study, a coated APP (CAPP) was prepared by sol-gel process,
13 and then modified with triethoxyvinylsilane, as shown in scheme 1. The CAPP
14 functionalized was used to prepare flame-retardant POE composites, together with a
15 char-forming agent (CA) and a cross-linker. During the preparation process, CAPP
16 was introduced into POE three-dimensioned network through the radical
17 polymerization proposed by Yin et al.,¹⁸ as shown in scheme 2. The effects of CAPP
18 on the flame retardation, mechanical properties, water resistance, and thermal
19 property of POE were investigated with the aid of different measurements. Finally,
20 the flame retardant mechanism was also discussed in detail.



Scheme 1. Schematic diagram for the preparation of CAPP



Scheme 2. Schematic diagram for the preparation of the cross-linked POE composites

5

6 2. Experimental section

7 2.1. Materials

8 The ethylene-octene elastomer (POE, Engage 8150, 25% octene) was supplied by
 9 DOW Co. (USA); ammonium polyphosphate (APP, form II, $n > 1000$) was
 10 purchased from Changfeng Chemical Co. (Shifang, China); dicumyl peroxide (bis
 11 (1-methyl-1-phenylethyl)) (DCP), tetraethoxysilane (TEOS), alkylphenol
 12 polyoxyethylene (10) ether (OP-10) surfactant, ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$),
 13 triethoxyvinylsilane (VTES), and ethanol, were provided by Kelong Chemical

1 Reagent Co. (Chengdu, China); the nitrogen-containing carbonization agent (Poly
2 1,3,5-triazin-2-aminoethanol) was bought from Weili Flame Retardant Chemicals Co.
3 (Chengdu, China).

4 **2.2. Preparation of cross-linked CAPP**

5 The mixture consisting of 50 g APP, 1 g OP-10, 150 mL ethanol, and 50 mL
6 deionized water was fed into 500 mL three-neck flask equipped with a stirrer, and its
7 pH value was adjusted to 9-11 by $\text{NH}_3 \cdot \text{H}_2\text{O}$, then it was stirred for 10 min at 50 °C,
8 followed by the incorporation of 10 g TEOS. The resulting mixture was kept at 50 °C
9 for 4h, and then cooled to room temperature. Next, the mixture was filtered, washed
10 with ethanol, and dried at 80 °C in a vacuum oven. Both the dried product and 10 g
11 VTES were put into high-speed mixing machine at 70 °C for 1h, then then cooled to
12 room temperature, finally dried in a vacuum oven at 80 °C to a constant weight. The
13 resulting powder was CAPP.

14 **2.3. Preparation of the flame retardant cross-linked POE composites**

15 POE composites containing flame retardant and DCP were prepared through a
16 rheometer (XSS-300, Shanghai Kechuang Plastic Machinery Co., Ltd., China) at a
17 temperature of 170 °C for 10 min. After mixing, the sheet samples for different
18 measurements were obtained through hot pressing at 170 °C under 10MPa.

19 **2.4. Measurement**

20 Fourier transform infrared (FTIR) spectra were recorded by a Nicolet FTIR 170 SX
21 spectrometer (Nicolet, America) using the KBr disk, and the wavenumber range is
22 from 4000 to 400 cm^{-1} .

1 The XPS measurement was carried out on a XSAM80 (Kratos Co., UK) using Al
2 K α excitation radiation ($h\nu=1486.6$ eV).

3 Scanning electron microscopy (SEM) was performed on a JEOL JSM 5900LV
4 scanning electron microscope (JEOL, Japan), and the accelerated voltage was 5 KV.
5 The specimens of POE composites were cryogenically fractured in liquid nitrogen,
6 and then sputter-coated with a conductive layer before being examined.

7 The water contact angle (WCA) of the samples was measured on a JC2000D
8 contact angle measurement instrument (Shanghai Zhongchen Digital Technic
9 Apparatus, China). Before being detected, all samples were pressed into disks. In a
10 measurement, 3mL deionized water was used, and the observation time was 30 s.

11 The particle size distributions of APP and CAPP were characterized by a laser
12 diffraction particle analyzer (Master Sizer 2000, Malvern Instruments Ltd., UK).
13 Before the measurement, the samples were dispersed in distilled water and sonicated
14 for 30 min.

15 To measure the solubility in water. 10 g APP or CAPP was put into 100 mL of
16 distilled water at different temperatures, and stirred for 1h. Next, the suspension was
17 filtered, and 50 mL filtrate was taken out, then dried to a constant weight at 100 °C.
18 Finally, the solubility of samples in water could be obtained.

19 The LOI value of all samples with the dimension of 130 mm \times 6.5 mm \times 3.2 mm was
20 measured using an HC-2C oxygen index instrument (Jiangning, China) according to
21 ASTM D2863-97.

22 The UL-94 vertical burning level was tested on a CZF-2 instrument (Jiangning,

1 China) according to ASTM D3801. The dimension of all samples is 130 mm×13
2 mm×3.2 mm.

3 To determine the combustible performance of POE composite after water resistance
4 measurement. The specimens were put in 500 mL of distilled water at 70 °C, and kept
5 at this temperature for 168 h. Then, these specimens were taken out, and dried in a
6 vacuum oven for burning tests.

7 The TGA was performed on a thermogravimetric analyzer instrument (209 F1,
8 NETZSCH, Germany) at a heating rate of 10 °C/min under N₂ atmosphere at a flow
9 rate of 50 mL/min in the temperature range from 40 to 700 °C.

10 The flammability of POE composites was measured by a CC device (Fire Testing
11 Technology, UK). The samples with dimension of 100mm × 100mm × 3mm were
12 exposed to a radiant cone at a heat flux of 50 kW/m².

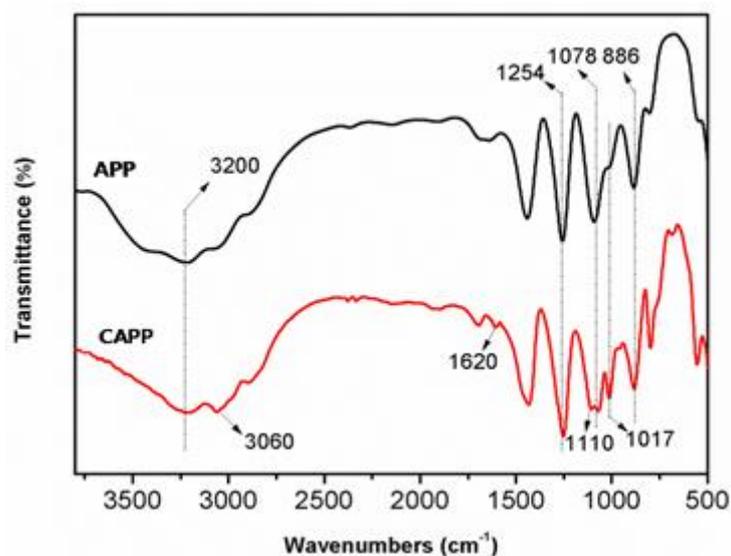
13 The TG-FTIR analysis was performed on a TG 209 F1 apparatus (NETZSCH,
14 Germany) coupled with a 170 SX FTIR spectrometer (Nicolet, America). The sample
15 (about 6 mg) was heated at a rate of 10 °C/min in the temperature range from 40 to
16 700 °C under nitrogen atmosphere.

17 **3. Results and discussion**

18 **3.1. Characterization of CAPP**

19 The FTIR spectra of APP and CAPP are shown in Fig. 1. The typical absorption
20 peaks of APP include 3200 cm⁻¹ (N-H), 1254 cm⁻¹ (P-O), 1078 cm⁻¹ (P-O symmetric
21 stretching vibration), 1017 cm⁻¹ (symmetric vibration of PO₂ and PO₃), 886 cm⁻¹ (P-O
22 asymmetric stretching vibration), and 802 cm⁻¹ (P-O-P) ¹⁹. The spectra of CAPP

1 show new absorption bands at 3060 cm^{-1} , 1620 cm^{-1} , and 1110 cm^{-1} , which
2 correspond to the stretching vibration of unsaturated C-H, C=C and asymmetric
3 Si-O-Si stretching¹⁶, respectively, indicating the existence of silicon compound in
4 CAPP.²⁰

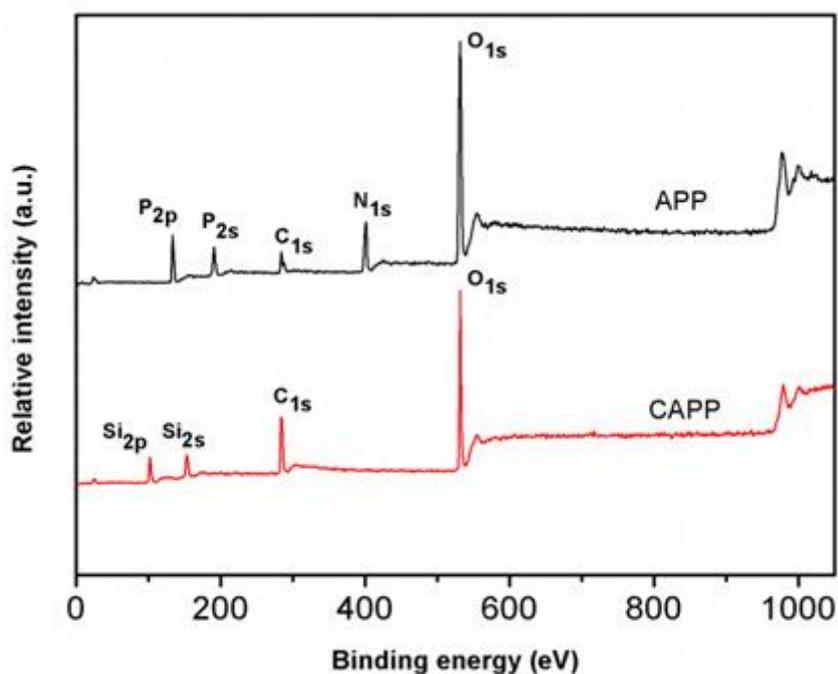


5

6 **Fig. 1** FTIR spectra of APP and CAPP.

7 The XPS spectra of APP and CAPP are shown in Fig. 2. and the related elemental
8 compositions of APP and CAPP are presented in Table 1. For CAPP, the P, N, and O
9 contents are 0.77 wt%, 0.32 wt%, and 33.58 wt%, respectively, which are much lower
10 than the corresponding values of APP. However, the C content of CAPP is 33.45 wt%,
11 much higher than that of APP. Generally, the detected depth for XPS measurement is
12 less than 10 nm, so there might be no the peaks corresponding to P and N in the XPS
13 spectrum of CAPP due to the lack of P and N at the surface of CAPP. Two new peaks
14 locating at 103.7 eV and 153.7 eV can be observed, which are attributed to Si_{2p} and
15 Si_{2s} of silicon compound, respectively. Both the change of elemental contents and the
16 appearance of new peaks demonstrated that APP was well coated by the cross-linking

1 silicon compound.



2
3 **Fig. 2** XPS spectra of APP and CAPP.

4
5 Table 1. Surface elemental compositions of APP and CAPP

6

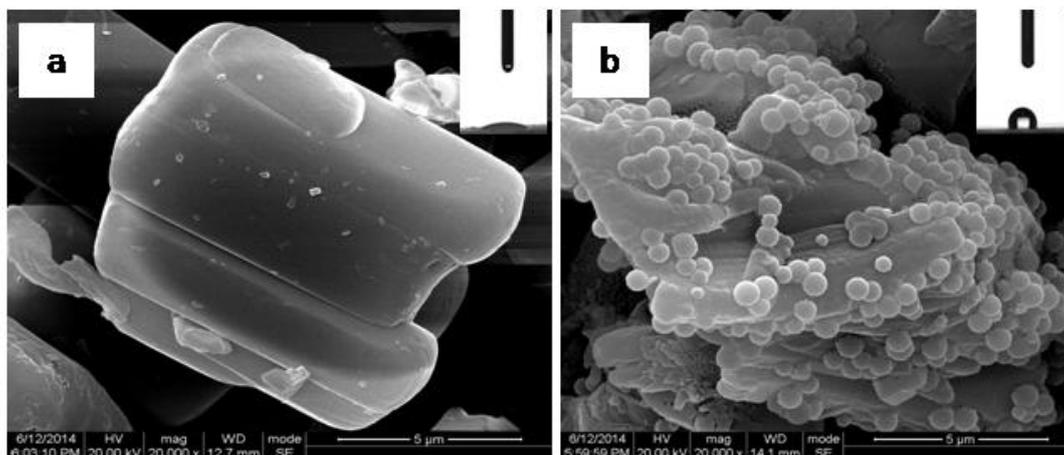
Sample	C (wt%)	O (wt%)	N (wt%)	P (wt%)	Si (wt%)
APP	10.53	45.46	15.33	28.68	0
CAPP	33.45	33.58	0.32	0.77	37.85

7 The surface morphologies of APP and CAPP particles are shown in Fig. 3. It is
8 clear that the surfaces of APP particles are very smooth. After being coated, CAPP
9 particles present quite rough surfaces. It seems that a lot of little particles were stuck
10 on the surfaces of APP, which should be the silicon compound. .

11 3.2. Granularity, morphology, and water solubility for APP and CAPP

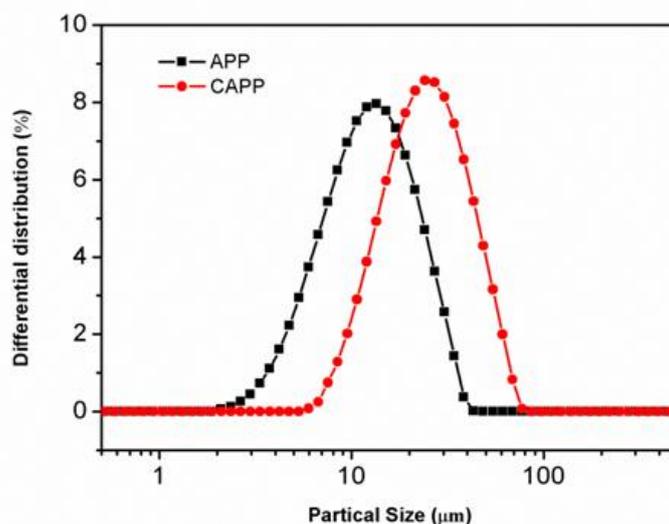
12• The hydrophilicity of CAPP has been evaluated by WCA, as shown in Fig. 3. The
13 WCA of neat APP is 12.5°. However, after being modified by VTES, the WCA
14 increases to about 110.5°, indicating that the incorporation of hydrophobic organic
15 group on the surface of APP resulted in its transformation from hydrophilicity to

1 hydrophobicity. The results presented above also demonstrate that APP was coated by
2 the hydrophobic silicon compound.



3
4 **Fig. 3** SEM photographs of (a) APP and (b) CAPP particles. The inset at top right
5 corner is the corresponding WCA result.

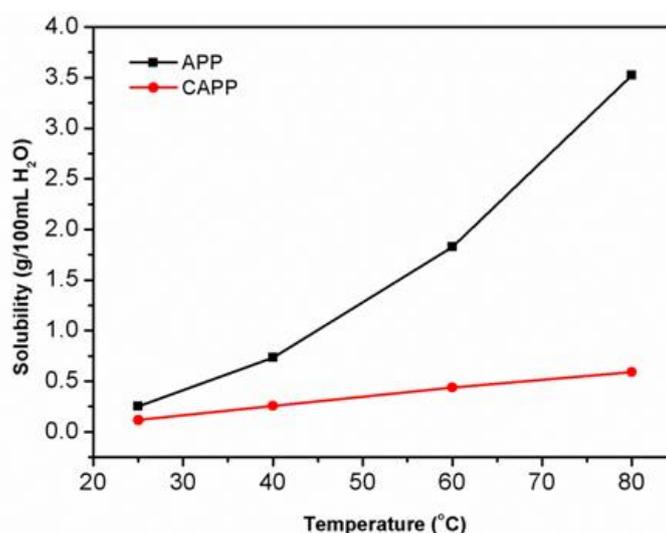
6 Fig. 4. shows the particle size distributions of APP and CAPP. The mean size of
7 CAPP is about 25.5 μm , much larger than 10.34 μm of APP. Obviously, after being
8 coated, CAPP has a larger particle size due to the existence of silicon compound shell.
9 Meanwhile, the larger mean size of CAPP also illustrates that APP was coated by
10 silicon compound successfully.



11

1 **Fig. 4** Particle size distributions of APP and CAPP.

2 The water solubility of APP and CAPP are shown in Fig. 5. Obviously, the
3 solubility of APP increases with increasing the water temperature, and the solubilities
4 of APP are 0.253 g/100 mL H₂O and 3.521 g/100 mL H₂O, respectively, at
5 corresponding 25 °C and 80 °C, indicating that APP was easily attacked by water,
6 especially at high temperature. After the coating, the solubility of CAPP decreases
7 sharply compared that of APP, especially at high temperature. The solubility of CAPP
8 is lower than 0.500 g/100 mL H₂O even though the water temperature reaches 80 °C,
9 which is much lower than that of APP under the same condition, proving that the
10 silica compound on the surface of CAPP effectively protected APP from water, and
11 enhanced its hydrophobicity via the functionalized organic group.



12 **Fig. 5** Solubilities of APP and CAPP at different temperatures.
13

14

15 3.3. Flame Retardancy.

16 The flame retardancy of neat POE and its composites were evaluated by LOI and
17 UL-94 test, and the results are shown in Table 2.

1 The vertical burning test showed that the UL-94 rating of POE/CAPP/CA was V-0
 2 at 30 wt% CAPP/CA with the weight ratio of 4/1, 3/1 or 2/1. When the weight ratio of
 3 CAPP/CA is 3/1, the POE composites have the maximum LOI value, reaching 33.5%.
 4 Although the UL-94 rating of POE/APP/CA system was V-0 rating at 30 wt%
 5 APP/CA with the weight ratio of 2/1 or 3/1, it decreased to V-2 rating at the weight
 6 ratio of 4/1. In addition, each POE/CAPP/CA system has higher LOI value compared
 7 with that of POE/APP/CA system with equal amount of flame retardant. Obviously,
 8 POE/CAPP/CA system has better flame retardancy than that of POE/APP/CA at the
 9 same loading of flame retardant.

10 **Table 2.** LOI and UL-94 results of POE and POE composites

Samples	POE(%)	APP(%)	CAPP(%)	CA(%)	UL-94	LOI(%)
POE1	100	0	0	0	NR	17.2
POE2	70	20.0	0	10.0	V-0	28.5
POE3	70	22.5	0	7.5	V-0	29.5
POE4	70	24.0	0	6.0	V-2	27.5
POE5	70	0	20.0	10.0	V-0	31.0
POE6	70	0	22.5	7.5	V-0	33.5
POE7	70	0	24.0	6.0	V-0	30.0

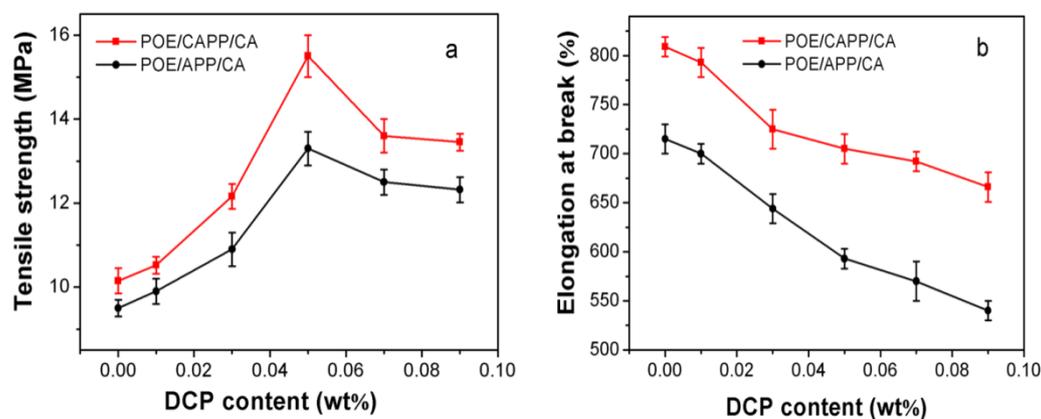
11 3.4. Effect of DCP concentration on mechanical properties.

12 Based on the results of flame retardancy of POE composites, the POE system with
 13 the weight ratio of 3/1 (APP/CA or CAPP/CA) was chosen to study on the effect of
 14 DCP concentration on the mechanical properties of POE composites.

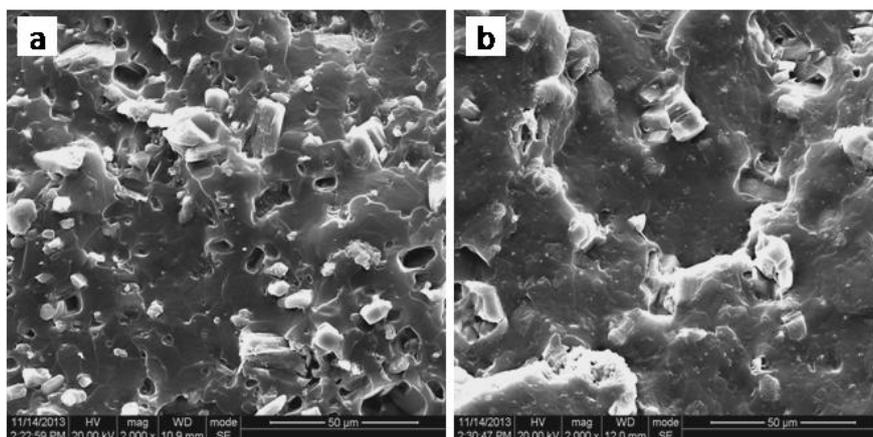
15 Both tensile strength and elongation at break for flame-retarded POE composites
 16 with different DCP concentrations are shown in Fig. 6. The tensile strength of
 17 flame-retarded POE composites drastically increases in the DCP range from 0 to 0.05
 18 wt%. With further increasing DCP concentration, the tensile property of POE

1 composites decreases. Here, the increase of tensile strength may be attributed to both
2 the change of interfacial adhesion between POE and flame retardant, and the
3 formation of a three-dimensional network shown in Scheme 2. In order to investigate
4 the interfacial adhesion between POE and flame retardant, the SEM measurement of
5 fracture sections for POE/APP/CA/DCP and POE/CAPP/CA/DCP composites were
6 performed. As shown in Fig. 7. For POE/APP/CA system, some cavities can be seen
7 on its surface, and there is clear interfaces between flame retardant particles and
8 polymeric matrix, indicating that the compatibility between POE and flame retardant
9 is not good, which should be due to the different polarity between flame retardant and
10 POE, causing a weak interfacial adhesion. After being coated, almost no obvious
11 interface can be observed between fillers and the matrix, as shown in Fig. 7(b),
12 Obviously, the interfacial adhesion between POE and flame retardant was improved
13 compared that between POE and APP, and the reason for the improvement should be
14 from the similar polarity between POE and silicon compound existing on the surface
15 of APP, and the formation of a three-dimensional network. For the contribution of the
16 similar polarity to the tensile strength of POE composite, it can be confirmed by the
17 difference of tensile strengths of POE composites at 0 wt% DCP. As for the formation
18 of a three-dimensional network after cross-linking, as proposed by Yin et al.,¹⁸ the
19 silicon compound shell including the functionalized organic group double bond (C=C)
20 allowed the CAPP to be incorporated into POE three-dimensional network, which
21 could greatly enhance the interfacial adhesion between APP and polymer matrix,
22 consequently led to the improvement of tensile strength. At higher than 0.05 wt%

1 DCP, the tensile strength decreases dramatically with increasing the content of DCP,
 2 which might be ascribed to the excess degree of cross-linking.²¹ The results presented
 3 above proves that the suitable content of DCP to achieve the excellent tensile strength
 4 of POE composites should be about 0.05 wt%. In the range of 0-0.09 wt%, the
 5 elongation at break for POE composites always decreases with increasing the flame
 6 retardant. However, the CAPP system always has higher elongation at break than that
 7 of APP system containing equal amount of flame retardant.



8
 9 **Fig. 6** Effect of DCP on the tensile strength (a) and elongation at break (b) of POE
 10 composites.

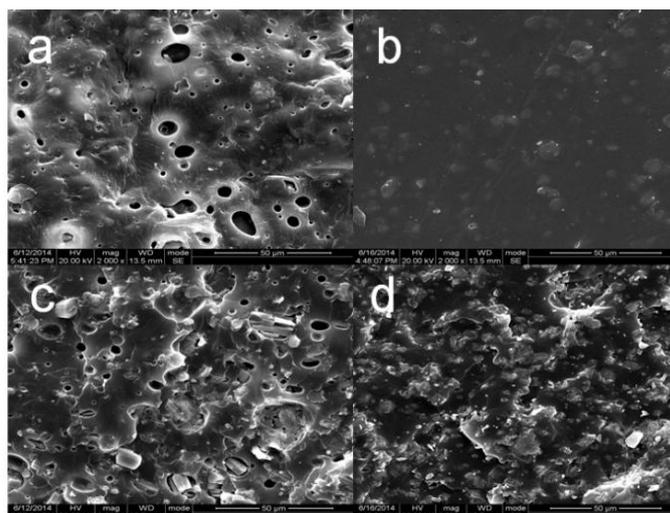


11
 12 **Fig. 7** SEM micrographs of fracture surfaces of (a) POE/APP/CA and (b)
 13 POE/CAPP/CA.

1 From the above results, it can be found that, in the range of 0-0.09 wt% DCP,
2 POE/MCAPP/CA has the best tensile strength and high elongation at break at about
3 0.05 wt% DCP, therefore, in the following work, the investigations on water
4 resistance, combustion performance, and thermal stability are based on the POE
5 system containing 0.05 wt% DCP.

6 **3.5. Water resistance and flame retardancy of cross-linked POE composites** 7 **after water treatment.**

8 Fig. 8. shows the SEM micrographs of POE composites after being treated by water
9 at 70 °C for 7 days. As shown in Fig. 8(a), some pores are exposed on the surface of
10 APP system after being treated by water for 168 h at 70 °C, which should be due to
11 the corrosion of APP particles by water. Fig. 8(b), shows that the surface of CAPP
12 system is smooth, and has almost no hole after the treatment, which might be due to
13 the protection of the silicon compound shell. To further study the effect of CAPP on
14 the water resistance of POE composite, the SEM test of fracture surfaces for
15 flame-retarded POE composites was performed. Fig. 8(c), shows that there are many
16 little holes on the fracture surface of APP system, which is attributed to the
17 hydrolyzed APP particles; while Fig. 8(d), presents that many CAPP particles still
18 exist on the fracture surface of CAPP system after the water treatment, which is
19 ascribed to the hydrophobicity of silicon compound. SEM results directly prove that
20 the water resistance of POE/APP/CA was greatly improved by the incorporation of
21 silicon compound shell on the surfaces of APP.



1

2 **Fig. 8** SEM micrographs of the surfaces of POE composites treated by water for 7
3 days at 70 °C: (a) POE/APP/CA, (b) POE/CAPP/CA, and their corresponding fracture
4 surfaces: (c) POE/APP/CA, (d) POE/CAPP/CA.

5 Table 3 shows the LOI and UL-94 tests results of POE composites after water
6 treatment. After being treated by water at 70 °C for 168 h, POE/APP/CA composite
7 burnt rapidly in UL-94 test, showing no rating, and its LOI value decreased compared
8 with POE/APP/CA untreated. For POE/CAPP/CA treated, the sample still passed the
9 UL-94 V-0 rating. Although its LOI value also reduced, it is still higher than that of
10 APP system treated. These results demonstrate that the POE/CAPP/CA system had
11 better flame retardancy than POE/APP/CA system after water treatment. Here, it
12 should be noted that the burning time of POE/CAPP/CA treated is longer than that of
13 POE/CAPP/CA untreated in UL-94 test, although its burning rating passed the V-0
14 rating. Obviously, both UL-94 and LOI results were affected by the water treatment
15 for POE/CAPP/CA. According to the water solubility test results shown in Fig. 5 and
16 Fig. 8, it can be found that only a little CAPP was attacked by water during the
17 treatment for POE/CAPP/CA system. Generally, a little loss of CAPP is not enough to

1 greatly deteriorate the flame retardant performance of POE/CAPP/CA composite, but
 2 a little damage to the flame retardation of the POE composite might be caused in this
 3 case. So the POE/CAPP/CA treated by water passed the UL-94 V-0 rating, but had
 4 longer burning time than POE/CAPP/CA untreated, and its LOI also decreased to 29.0%
 5 from 33.5% of the CAPP system untreated.

6 **Table 3.** The UL-94 and LOI results of POE composites before and after water
 7 treatment at 70 °C for 7 days

Sample	untreated		After water treatment	
	LOI (%)	UL-94	LOI (%)	UL-94
POE/APP/CA	29.5	V-0	25.0	No Rating
POE/CAPP/CA	33.5	V-0	29.0	V-0

8 3.6. Combustion Performance

9 The CC is an effective method to study the flammability of materials.^{22,23} The HRR,
 10 THR, SPR, and MLR curves of neat POE and POE composites are shown in Fig. 9.
 11 and the corresponding data are presented in Table 4.

12 Generally, when the heat release rate (HRR) is lower than a relatively low value (40
 13 kW/m² in our experiment) in cone calorimeter test, it is thought that the burning ends.
 14 In the CC test, there are three systems with different components. Neat POE burnt out
 15 completely rapidly due to its terrible flame retardancy, and its HRR fell down to
 16 40kW/m² quickly. POE/CAPP/CA could extinguish within short time, owing to its
 17 good flame retardancy resulting from the formation of a compact intumescent char
 18 layer during the combustion process, thus the burning time for POE/CAPP/CA was
 19 very short. However, for POE/APP/CA the intumescent char layer formed during the
 20 combustible process was not compact, and had bad protection for the material

1 underneath, leading the continuous burning of the substrate, so the burning time for
2 POE/APP/CA is longer than that for POE/CAPP/CA or neat POE.

3 Table 4 shows that the TTI of POE/CAPP/CA is far lower than that of
4 POE/APP/CA. Meanwhile, the residue of the former is far more than that of the latter.
5 In CC test, POE/APP/CA system could decompose in advance compared with
6 POE/CAPP/CA system due to the better thermal stability of CAPP, and release the
7 NH₃ etc. gases, which might dilute the concentration of the combustible gases,
8 leading to the delay of TTI for POE/APP/CA system.

9 The HRR curve of flame-retardant POE composites exhibits two peaks. The first
10 peak is assigned to the ignition and the formation of an expanded protective shield;
11 the second peak is ascribed to the destruction of the intumescent shield and the
12 formation of a carbonaceous residue.²⁴ From Fig. 9(a), it can be found that neat POE
13 burnt out within 450 s. A very sharp HRR peak appeared at about 178 s, and the
14 corresponding value for the peak of HRR (pHRR) is about 718 kW/m². However, the
15 flame-retardant POE composites show a dramatic decline in pHRR. The pHRR value
16 for POE/APP/CA is 229 kW/m², much lower than that of neat POE. Moreover, the
17 pHRR for POE/CAPP/CA further decreases to 94 kW/m².

18 **Table 4.** CC data of POE and flame-retarded POE composites

Sample	TTI (s)	PHRR (KW/m ²)	THR (MJ/m ²)	FPI	Peak SPR (m ² /s)	TSP (m ² /m ²)	Char residue mass (wt%)
POE	38	718	111	0.05	0.074	10.90	5.24
POE/APP/CA	28	229	96	0.12	0.044	9.80	22.96
POE/CAPP/CA	18	94	24	0.20	0.008	1.66	77.97

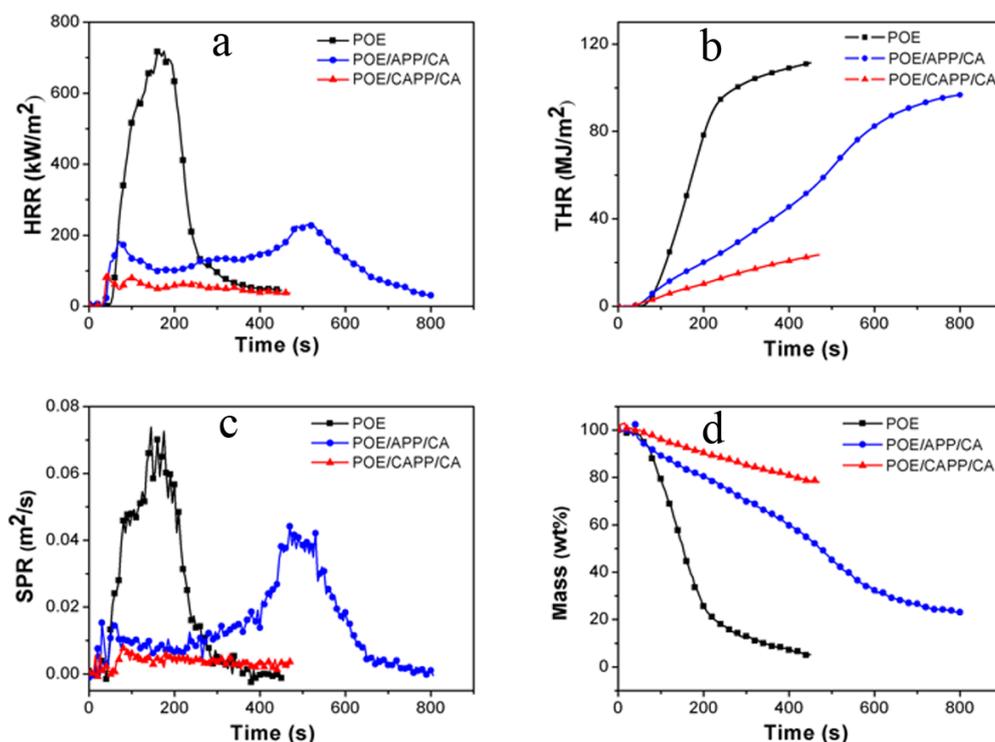
19 In order to judge the fire hazard more clearly, the fire performance index (FPI) was

1 calculated. The FPI is defined as the proportion of TTI and the pHRR.^{25,26} Generally,
2 when the value of FPI reduces, the time to flashover will be advanced. Namely, if the
3 value of FPI of a material is lower, its fire risk is higher. Table 4 shows that the FPI of
4 POE/CAPP/CA composite is 0.20, lower than that of POE/APP/CA system, indicating
5 that the silicon compound locating on the surfaces of APP can reduce the risk of
6 POE/APP/CA in a fire hazard.

7 The THR is also an important parameter to evaluate the fire safety of a material. An
8 obvious decrease for THR can be observed for POE composites compared with neat
9 POE. At the end of the test, neat POE released a total heat of 111 MJ/m²; while
10 POE/APP/CA and POE/CAPP/CA released total heat of 94 and 24 MJ/m²,
11 respectively, indicating that the silicon compound coated on the surfaces of APP could
12 greatly reduce the THR of cross-linked POE/APP/CA composite.

13 The SPR and MLR rate curves of neat POE and POE composites are presented in
14 Fig. 9(c) and (d), respectively. The SPR peak values of both POE/APP/CA and
15 POE/CAPP/CA composites were significantly reduced compared with that of neat
16 POE. The SPR peak of neat POE is 0.074 m²/s. Compared with neat POE, the SPR
17 peak of POE/APP/CA composite was decreased to 0.044 m²/s, and the value of
18 POE/CAPP/CA composite was further reduced to 0.008 m²/s. These results indicate
19 that the smoke suppression effect of POE/CAPP/CA composite is better than that of
20 POE/APP/CA composite. For POE/APP/CA composite, the average MLR was
21 decreased to 0.028 g/s from 0.05 g/s of neat POE, and it was further reduced to 0.014
22 g/s for PP/CAPP/CA composite. Obviously, POE/CAPP/CA system has a much lower

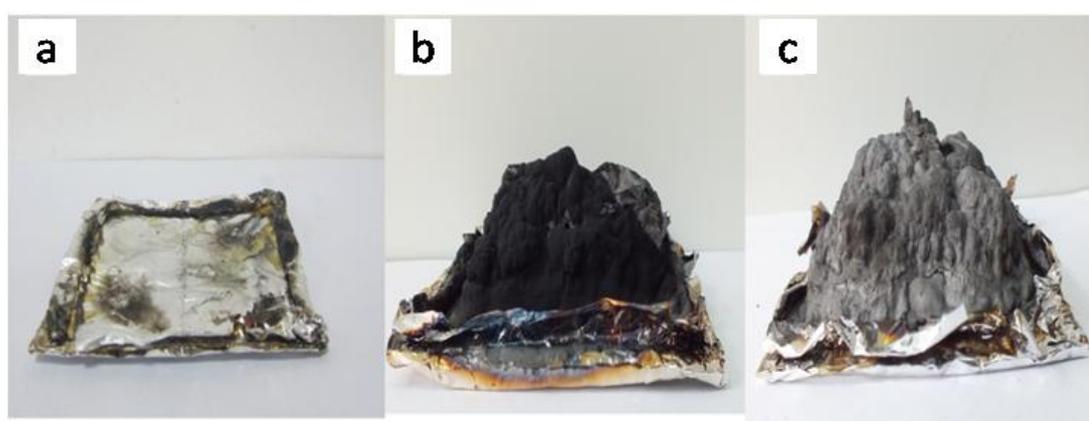
1 MLR, which might be due to the formation of a dense protective carbon layer on the
 2 surface of POE/CAPP/CA during the combustion process, thus prevented the further
 3 degradation and combustion of the underlying material.



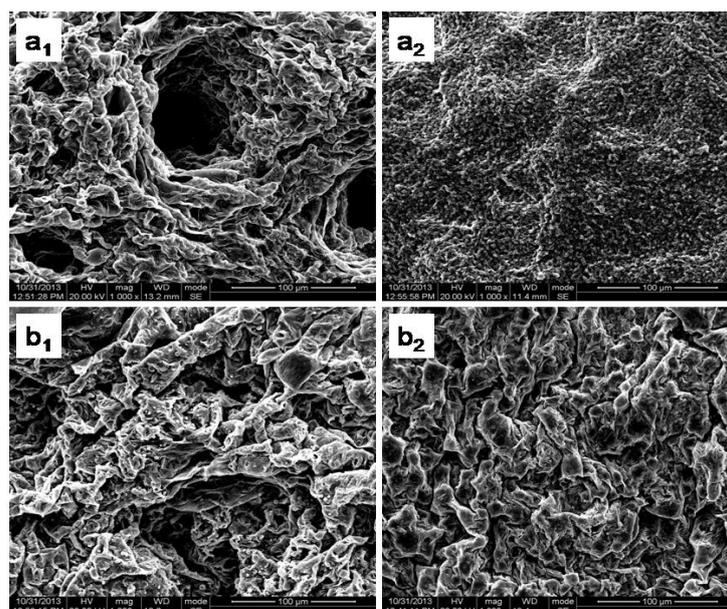
4
 5 **Fig. 9** HRR (a), THR (b), SPR (c), and ML (d) curves of neat POE and POE
 6 composites as a function of time in CC test.

7 The digital photographs of the residual chars after CC test are shown in Fig. 10. At
 8 the end of CC test, there was no residue left for neat POE, while an intumescent char
 9 layer was formed for POE/APP/CA or PP/CAPP/CA. In order to obtain more detailed
 10 information on the residue chars, SEM measurement was performed after CC tests.
 11 Fig. 11(a₁) and (a₂) show that the residue of POE/APP/CA are quite loose, and there
 12 are some big holes at the outer and inner surfaces of the residue. Therefore, it could
 13 not provide good flame shield for the underlying material during burning. However,
 14 as can be seen from Fig. 11 (b₁) and (b₂), compact structures at the outer and inner

1 surfaces were formed for POE/CAPP/CA, and no big hole can be observed.
2 Furthermore, there are some folds on the surface, which could act as a skeleton to
3 strengthen the surface layer.^{27,28} The digital photos and SEM micrographs illustrate
4 that the formation of a compact and intumescent char layer for the cross-linked
5 POE/CAPP/CA system should be an important reason for its better flame retardancy
6 than that of POE/APP/CA in CC test.



7
8 **Fig. 10** Digital photographs of the residues after CC test: (a), neat POE; (b),
9 POE/APP/CA; (c), POE/CAPP/CA.



10
11 **Fig. 11** SEM micrographs of POE/APP/CA (a₁, outer; a₂, inner) and POE/CAPP/CA

1 (b₁, outer; b₂, inner)

2 **3.7. Thermal stability**

3 TGA and DTG curves of POE and flame-retardant POE composites under N₂
4 atmosphere are shown in Fig. 12. and the related TGA data are listed in Table 5. It can
5 be found that the thermal degradation of neat POE is composed of one step. The
6 maximum weight loss occurred at 401 °C, which is defined as T_{max}. Compared with
7 neat POE, the initial degradation temperature (T_{onset}) of flame-retardant POE
8 composites decreases, owing to the thermal degradation of intumescent flame
9 retardant. Here, T_{onset} is defined as the temperature at 5 wt% of weight loss. Obviously,
10 the T_{onset} of POE/CAPP/CA is higher than that of POE/APP/CA, which should be due
11 to the existence of silicon compound on the surface of CAPP. Generally, the silicon
12 compound can play a role in delaying the decomposition of APP due to its good
13 thermal stability. The flame-retardant POE composite exhibited more stable thermal
14 behavior at the temperature range from 465 to 700 °C, and both POE/CAPP/CA and
15 POE/APP/CA had more residue than neat POE. For POE/CAPP/CA system, more
16 residue and better thermal stability than those of POE/APP/CA were achieved at high
17 temperature, indicating that silicon compound facilitated the formation of more
18 residue with good thermal stability than that of POE/APP/CA system at high
19 temperature, which could protect POE from further decomposing during a fire.
20 Therefore, the good flame retardancy of POE/CAPP/CA system should be related to
21 its charring during burning.

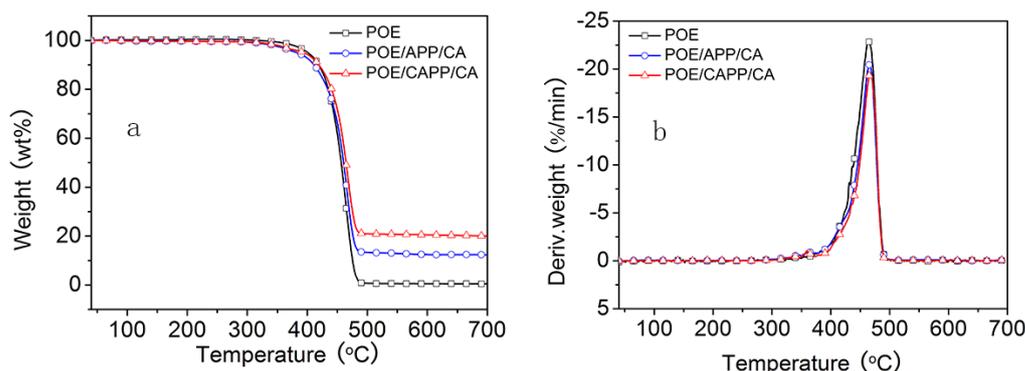


Fig. 12 TGA (a) and DTG (b) curves of neat POE and its composites under nitrogen atmosphere.

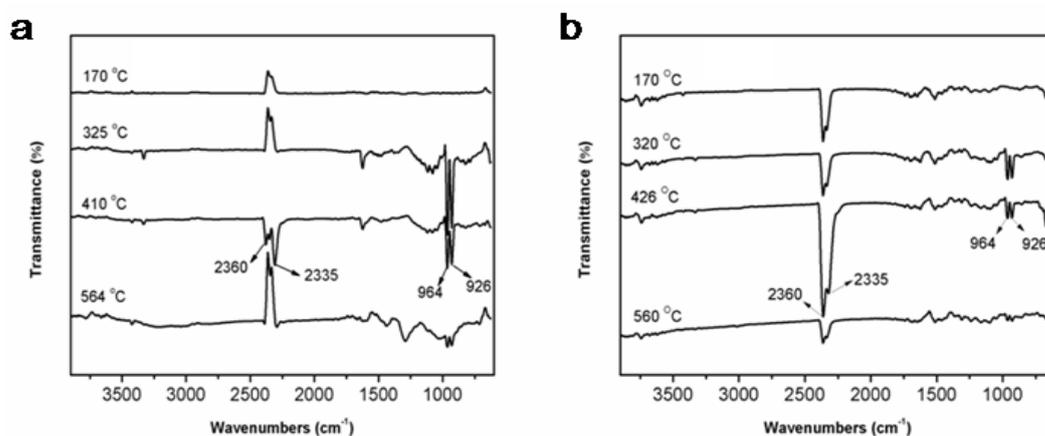
Table 5. TGA data of neat POE and its composites under nitrogen atmosphere

Sample	T _{5%} (°C)	T _{max} (°C)	Residues at 700 °C
POE	401.1	465.0	0.5
POE/APP/CA	382.5	465.8	12.39
POE/CAPP/CA	393.7	466.8	20.07

3.8. Flame-retardant mechanism of CAPP/CA system.

To illustrate the effect of silicon compound on the flame-retardant efficiency of APP, the FTIR test of gas phases and condensed phases for CAPP/CA system at different temperatures were performed. Fig. 13. shows the FTIR-TG spectra of the gaseous phases for CAPP/CA and APP/CA during the thermal degradation. The main evolved gases from the decomposition of two systems include carbon dioxide (CO₂, 2335 and 2360 cm⁻¹), ammonia (NH₃, 926, 964, 1520~1670 cm⁻¹), and water vapor (H₂O, 3920~3520 cm⁻¹).^{29,30} Further, the release of NH₃ should be from NH₄⁺ of APP, while the CO₂ and H₂O might be produced during the carbonization process of IFR system. Interestingly, the intensity of the NH₃ absorbing peak increases sharply at 320 °C for the two systems, and then decreases with increasing the temperature, suggesting that the two systems have similar thermal stability. According to the

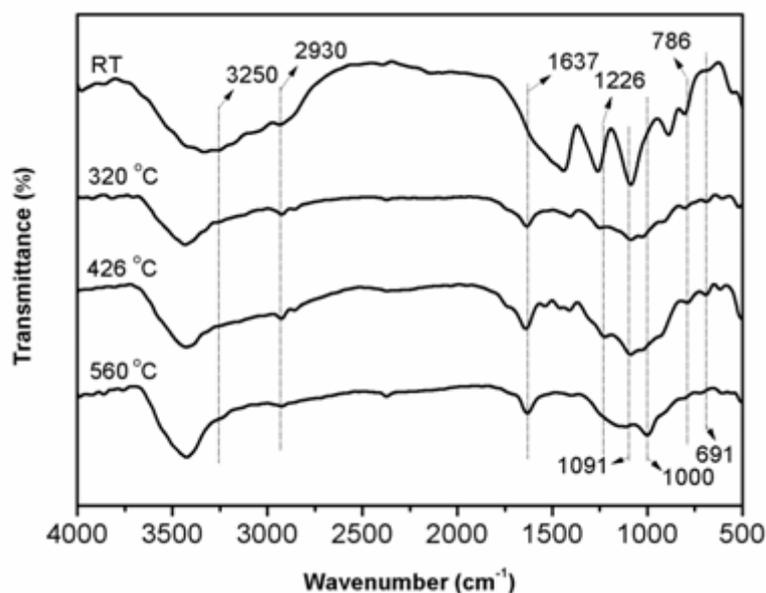
1 results shown above, it can be found that the contribution of the gaseous phase for
 2 APP has not been changed obviously after being coated through silicon compound.



3
 4 **Fig. 13** FTIR spectra of the gaseous products of APP/CA (a) and CAPP/CA (b)
 5 during the thermal degradation.

6 In order to further demonstrate the flame-retardant mechanism of CAPP/CA system,
 7 the condensed phases of CAPP/CA were investigated by FTIR test. Fig. 14. shows the
 8 FTIR spectra of the condensed phases at different temperatures. The strong and broad
 9 absorbing peak at 3250 cm^{-1} is assigned to the stretching vibration of N–H bond of
 10 NH_4^+ ; while the peak gradually decreases at high temperature, suggesting the release
 11 of ammonia from the APP component and the formation of ultra-, pyro- or
 12 poly-phosphoric acid with free acidic hydroxyl groups during thermal dehydration^{31,32}.
 13 The peak at about 1637 cm^{-1} appeared at $320\text{ }^\circ\text{C}$, indicating the existence of species
 14 containing C–H and C=C bond. At $560\text{ }^\circ\text{C}$, the peak at 1000 cm^{-1} is ascribed to the
 15 stretching vibration of P–O–C group.³³ It should be noted that the absorption bands at
 16 1091 cm^{-1} and 1226 cm^{-1} suggest that the cross-linked structure consisting of Si–O
 17 and P=O aromatic structure was formed, which was probably bridged by P–O–P
 18 group, resulting in the formation of the residue with complex structure, which could

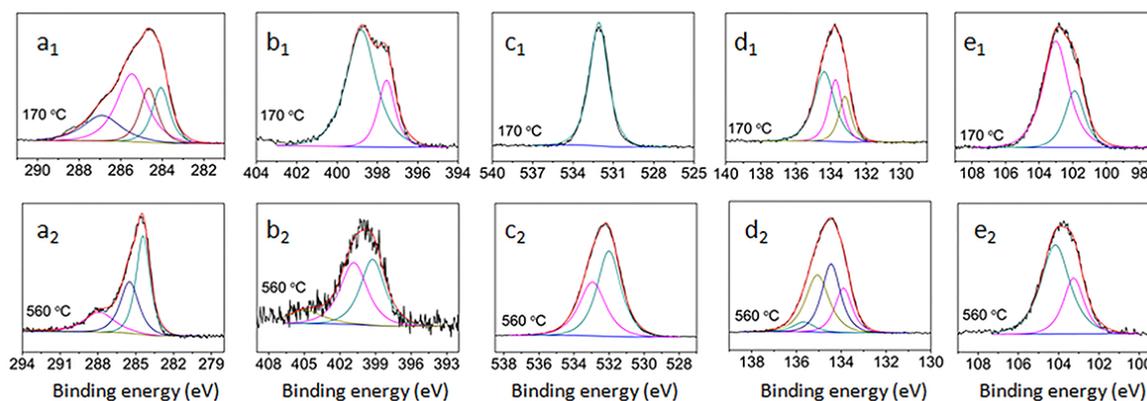
1 efficiently prohibit the evolution of combustible gases and the decomposition of the
2 underlying materials, as well as prevent the heat and oxygen from transferring to the
3 matrix interior, and thus improve the flame-retardant efficiency of APP.



4
5 **Fig. 14** FTIR spectra of the condensed products of CAPP/CA at different
6 temperatures.

7 XPS data for the condensed products of CAPP/CA at different temperatures can be
8 used to further demonstrate the silicon compound on the flame-retardant efficiency of
9 APP. Fig. 15. shows the C_{1s}, N_{1s}, O_{1s}, P_{2p} and Si_{2p} XPS spectra of CAPP/CA at 170 °C
10 and 560 °C. The C_{1s} spectra of CAPP/CA are shown in Fig. 15 (a₁, a₂), The bands at
11 around 284.4 eV could be assigned to C–H and C–C in aliphatic and aromatic species.
12 The peak at 286.0 eV can be ascribed to C–O or C–N in cyclized compounds. At 560
13 °C there is a new peak at 287.8 eV which could be C=O, C=C, and C=N groups,³⁴
14 indicating that more steady cross-links were further formed by aromatization at high
15 temperature. Fig. 15 (b₁, b₂), shows the N_{1s} spectra of CAPP/CA, one peak around
16 399.5 eV is from C=N; the other peak around 401.4 eV is assigned to the N–H bond

1 of NH_4^+ .³⁵ The O_{1s} spectra are shown in Fig. 15 (c₁, c₂), At 170 °C and 560 °C, the
 2 binding energy in the vicinity of 532.3 eV can be ascribed to the C–O or P–O
 3 groups.³⁶ A new peak at 533.5 eV can be attributed to the P–O–P and/or P–O–C
 4 groups at 560 °C. The P_{2p} spectra of CAPP/CA are shown in Fig. 15 (d₁, d₂), The
 5 peaks between 134.0 eV and 135.0 eV can be assigned to P–O–C and /or PO_3^- groups
 6 in the phosphorus-rich crosslinks.³⁷ The Si_{2p} spectra of CAPP/CA are shown in Fig.
 7 15 (e₁, e₂), The Si_{2p} peak locates at 101.9 eV at 170 °C, but the peak moved to 104 eV
 8 at 560 °C. The shift of Si_{2p} might be due to the fact that the Si–C or Si–O–C bonds at
 9 low temperatures were converted into Si–O–Si bonds at high temperatures.



10

11 **Fig. 15** C_{1s} (a₁, a₂), N_{1s} (b₁, b₂), O_{1s} (c₁, c₂), P_{2p} (d₁, d₂), Si_{2p} (e₁, e₂) X-ray
 12 photoelectron spectroscopy spectra of the condensed products of CAPP/CA. The "1"
 13 and "2" represent the results at 170 °C and 560 °C, respectively.

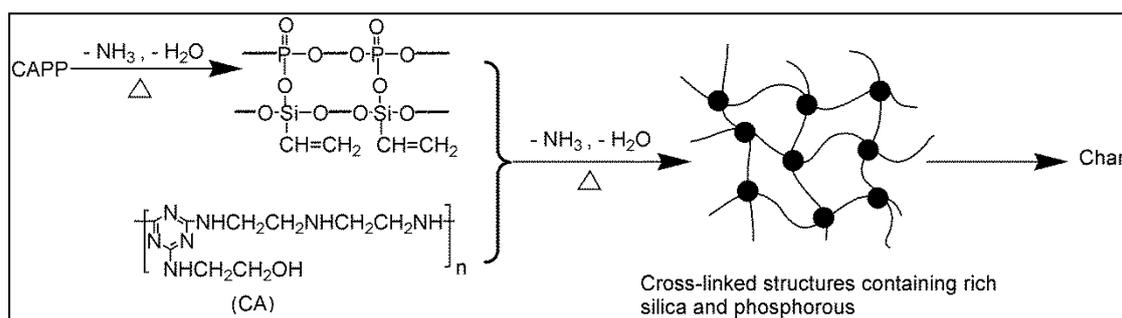
14 The elemental contents obtained in XPS test are shown in Table 6, including C, N,
 15 O, P, and Si. In detail, the content of C decreased from 46.26 wt% to 18.03 wt%
 16 because of the oxidization of unsteady C and the formation of steady C, such as C=C
 17 structure in aromatic moieties; the content of Si also decreased from 16.98 wt% to
 18 8.62 wt%, which should be due to the formation of P–O–Si and C–O–Si. Obviously,

1 the content of N was reduced due to the volatilization of $\text{NH}_4^+/\text{NH}_3$ during heating.
 2 By contrast, the content of O and P increased due to the formation of the P–O–P and
 3 P–O–C structure. The change tendencies of elemental contents are consistent with the
 4 FTIR results at different temperatures, demonstrating that the charring process in
 5 which rich P and Si were deposited should be the most important reason for the better
 6 flame-retardant efficiency of CAPP than that of APP.

7 **Table 6** XPS data of the condensed products of CAPP/CA during the thermal
 8 decomposition

Temperature	C (wt%)	N (wt%)	O (wt%)	P (wt%)	Si (wt%)
170 °C	46.26	11.60	24.24	0.91	16.98
560 °C	18.03	2.44	47.67	23.24	8.62

9 XPS results demonstrate that the silicon compound was engaged in charring process
 10 during the decomposing process, leading to the formation of a stable and compact
 11 char layer, which resulted in the better flame-retardant efficiency of CAPP/CA than
 12 that of APP/CA. On the basis of the above experimental data, we can propose a
 13 potential char-forming mechanism of CAPP/CA was shown in Scheme 3.



15 **Scheme 3.** Possible flame-retardant mechanism of CAPP/CA system

16

17 4. Conclusion

1 In this paper, APP coated by silicon compound containing triethoxyvinylsilane with
2 a vinyl group at its surface was prepared successfully, and the CAPP was used to
3 flame-retarded POE together with CA in the case of DCP. The results demonstrated
4 that CAPP system had better water resistance, flame retardation, and mechanical
5 properties than APP system with equal amount of flame retardant. TG, FTIR, and
6 XPS demonstrated that the improvement of flame retardancy for POE composite
7 containing APP after being coated by silicon compound should be due to the
8 formation of rich residue containing Si-C, Si-O-C etc. structures; The SEM
9 observation confirmed that the increases of tensile strength and elongation at break for
10 CAPP system should be due to the improvement of interfacial adhesion between POE
11 and flame retardant. Obviously, it should be an efficient method to simultaneously
12 improve the water resistance, flame retardancy and mechanical properties of POE
13 composite containing APP through functionalizing the APP and then chemically
14 incorporating it into the polymer matrix.

15

16 **Acknowledgment**

17 Financial support by the National Natural Science Foundation of China (Grant No,
18 51121001) and the Program for Changjiang Scholars and Innovative Research Team
19 in University (IRT1026) would be sincerely acknowledged.

20

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