High-Performance TPE-S Modified by a Flame-Retardant System Based on Black Phosphorus Nanosheets

Jiaxuan Li, Jun Wu, Xianzhe Wei, Qing Yu, Yuxi Han,* Jinhong Yu,* and Zhongwei Wang*

ABSTRACT: Few-layer black phosphorus nanosheets (BPs) combined with melamine cyanurate and poly(phenylene oxide) were used to prepare a flame-retardant thermoplastic elastomer based on polystyrene (TPE-S) for the first time. Compared with neat TPE-S, BP-modified TPE-S with a phosphorus content of 7.98% (TPE-S/BP-7.98) passed the UL-94 vertical burning V-0 rating, and the limiting oxygen index value increased to 24.0%. The peak heat release rate (PHRR), total heat release, and the average combustion effective heat of TPE-S/BP-7.98 were decreased by 61.8, 26.0, and 35.3%, respectively. The time to PHRR was increased from 90 s (neat TPE-S) to 170 s. Scanning electron microscopy of frozen fracture sections showed favorable compatibility and dispersibility of BPs in TPE-S. In addition, the introduction of BPs showed the most negligible effect on the mechanical properties of TPE-S compared with other flame retardants (aluminum hypophosphite and red phosphorus).

1. INTRODUCTION

Thermoplastic elastomer (TPE) is a polymer material between the rubber and resins.1 It has the elasticity of rubber at room temperature and plasticity at high temperatures.2 Moreover, it can be produced by injection molding, extrusion molding, blow molding, and other processing methods.3,4 Due to their excellent aging resistance, insulativity, and mechanical properties, polystyrene-based thermoplastic elastomers (TPE-S) composed of poly(styrene-ethylene-butylene-styrene) (SEBS), white oil, and polypropylene (PP) are widely used in electric wire and cable, construction, and automobile industries.5−10 However, because of their high flammability, the applications of TPE-S in other industries are greatly limited. Therefore, it is particularly urgent to improve the flame retardancy of the TPE-S.

Since halogen flame retardants have been restricted due to environmental problems,3,11 various halogen-free flame retardants such as metal hydroxides, inorganic phosphorus, organic phosphorus, and silicon have been applied to prepare the flame-retardant TPE-S.12−15 However, these flame retardants showed poor effects when used alone, and they are generally combined with other flame retardants.16−18 Xiao et al.19 investigated the individual and combined flame-retardant effects of magnesium hydroxide (MH) and aluminum hydroxide (ATH) on the TPE-S. The results showed that the flame-retardant efficiency of MH and ATH combined was superior to that of used alone. But the mechanical properties were obviously reduced. Zhu et al.5 modified TPE-S with piperazine pyrophosphate (PPAP) and aluminum diethylphosphinate (AlPi). The TPE-S composites passed the UL-94 V-0 rating, and the limiting oxygen index (LOI) value was 29.5% at 38 wt % PPAP. However, when 25 wt % PPAP/AlPi was used, a UL-94 V-0 rating and an LOI value of 28.5% were achieved. Lu et al.20 used MH and microencapsulated red phosphorus (MRP) as the flame retardants for ethylene-propylene-diene monomer/polypropylene (EPDM/PP). The samples incorporating 82 phr MH and 18 phr MRP exhibited superior flame retardancy than the 140 phr MH samples.

Due to their high charge mobility, controlled band gap thickness, good mechanical properties, and dimension effects as the nanomaterial,23,24 few-layer black phosphorus nanosheets (BPs) exfoliated from bulk black phosphorus (BP) have been widely used in electrochemistry, biomedicine, catalysis, and optoelectronics.23−26 BP, one of the allotropes of phosphorus, has thermostability better than RP and is suitable for some composites as a flame retardant. Qu et al.27 combined a ruthenium sulfonate ligand (RuL3) with BPs to prepare the...
frame-retardant epoxy resin (EP). The results showed that when 3.0 wt % RuL3@BP was added into the EP, the LOI value was increased by 26.72%, and the sample passed the UL-94 V-0 rating. The carbon residue after combustion was also significantly increased. Qiu et al.28 found that polydopamine encapsulated BPs (BP-PDA) effectively improved the flame retardancy and mechanical properties of poly(vinyl alcohol) (PVA) nanocomposite films. In summary, BPs are a valuable flame retardant for various plastics.29−31 However, its application in the TPE-S has rarely been reported.

| samples          | TPE-S (phr) | AHP (phr) | RP (phr) | BP (phr) | MCA (phr) | PPE (phr) | P (%) |
|------------------|-------------|-----------|----------|----------|-----------|-----------|-------|
| neat TPE-S       | 100         |           |          |          |           |           | 0     |
| TPE-S/AHP-6.72   | 59          | 16        |          |          | 20        | 5         | 6.72  |
| TPE-S/AHP-7.14   | 58          | 17        |          |          | 20        | 5         | 7.14  |
| TPE-S/AHP-7.56   | 57          | 18        |          |          | 20        | 5         | 7.56  |
| TPE-S/AHP-7.98   | 56          | 19        |          |          | 20        | 5         | 7.98  |
| TPE-S/AHP-8.40   | 55          | 20        |          |          | 20        | 5         | 8.40  |
| TPE-S/BP-7.56    | 66.11       |           | 8.89     |          | 20        | 5         | 7.56  |
| TPE-S/BP-7.98    | 65.61       |           | 9.39     |          | 20        | 5         | 7.98  |
| TPE-S/BP-8.40    | 65.12       |           | 9.88     |          | 20        | 5         | 8.40  |
| TPE-S/BP-7.56    | 67.44       |           | 7.56     |          | 20        | 5         | 7.56  |
| TPE-S/BP-7.98    | 67.02       |           | 7.98     |          | 20        | 5         | 7.98  |
| TPE-S/BP-8.40    | 66.60       |           | 8.40     |          | 20        | 5         | 8.40  |

Figure 1. SEM images of bulk BP (a) and BPs (b); TEM image and SAED image of BPs (c); HRTEM image of BPs (d); SPM image of BPs (e); size distribution of BPs (f); Raman spectrum of BPs (g); XPS spectrum; (h) and XRD pattern of BPs (i).
The incorporation of large loading of flame retardants generally reduces the mechanical properties of TPE-S. In this study, BPs were combined with melamine cyanurate (MCA) and poly(phenylene oxide) (PPE) to prepare flame-retardant TPE-S composites. The effects of the flame retardant on thermal stability, flame-retardant performance, fire behaviors, and mechanical properties of the flame-retardant TPE-S composites were studied. The results were compared with those of RP and aluminum hypophosphite (AHP)-modified TPE-S. This study may help to prepare the flame-retardant TPE-S with better mechanical properties.

2. EXPERIMENTAL SECTION

2.1. Materials. SEBS (YH503) was produced by Sinopec Baling Petrochemical Co., Ltd. (Beijing, China). PP (homopolymer, T30s, melt flow index: 3.0 g/10 min) was purchased from Sinopec Qingdao Refining & Chemical Co., Ltd. (Qingdao, China). White oil (32#) was supplied by Suzhou Hesen Special Oil Products Co., Ltd. (Suzhou, China). AHP retardant was manufactured by Shouguang Weidong Chemical Co., Ltd. (Qingdao, China). MCA (MC15) was supplied by Qingdao Fuslin Chemical Science & Technology Co., Ltd. (Qingdao, China). PPE (LXR045) was provided by Bluestar Weifang Chemical New Materials Co., Ltd. (Weifang, China). Red phosphorus (RP) was purchased from Jining Yimin Chemical Plant. (Jining, China). The bulk black phosphorus was provided by Sino-Linchem Group. (Guangxi, China). BP nanosheets were prepared in our laboratory. Antioxidants Irganox 1010 and 168 were manufactured by BASF SE (Germany).

2.2. Sample Preparation. BPs were obtained by ultrasonic treatment of bulk BP and N-methyl pyrrolidone mixed solution. The detailed preparation process was described in our previous work. Oil-filled SEBS (O-SEBS) was prepared by soaking SEBS in white oil at the 26:12 ratio and allowed to expand for 24 h. Then, O-SEBS and PP were mixed at a 38:17 proportion, and 0.3 wt % antioxidant was added to prepare the TPE-S. MCA, PPE, PP, etc., were used after drying at 80 °C for 4 h. TPE-S and flame retardants were mixed in an internal mixer and processed for 10 min at 190 °C. Then, the TPE-S sheet was pressed under 10 MPa at 190 °C, and a standard size sample was cut from the sheet for testing. Table 1 shows the composition of different flame-retardant TPE-S. The sample was labeled as TPE-S/M-x, where M represents the used flame retardant (AHP/RP/BPs) and x represents the phosphorus content of the composites.

2.3. Characterization. Universal testing machines (AI 7000 S, Gotech Testing Machines Inc., China) performed the tensile tests. According to ASTM D638-2014, five specimens were used for each mechanical test at room temperature at a speed of 50 mm/min. The LOI test was performed on a BGS207 oxygen index instrument (Bingo Instrument Co., Ltd., Suzhou, China) according to the ASTM D2863-2010 standard with a specimen size of 130 × 6.5 × 3 mm³. The UL-94 test was carried out on the BGS210 instrument (Bingo Instrument Co., Ltd., Suzhou, China) according to the ASTM D3801 standard, and the specimen size was 130 × 13 × 3 mm³. The cone calorimeter (CC) test (CCT, East Grinstead FTT, U.K.) examined the combustion behaviors of pure TPE-S and flame-retardant TPE-S according to ISO-5660, with an external heat flow of 50 kW/m², a sample size of 100 × 100 × 3 mm³, and the distance from the cone was 25 mm. Thermogravimetric analysis (TGA, Hengjiu HTG-1, China) evaluated the thermal stability of TPE-S composites. The sample was ramped up from room temperature to 700 °C at a rate of 10 °C/min in a nitrogen atmosphere with a 50 mL/min gas flow rate. Fourier transform infrared (FTIR) spectroscopy was performed with a spectrometer (Nicolet iS50 FTIR). Thermogravimetric analysis/infrared spectrometry (TG-IR) was carried out on a TG209F3/Tensor 27 thermoanalyzer instrument combined with a Netsch/Brucker spectrometer from 20 to 800 °C at 10 °C/min (N₂ atmosphere, the flow rate is 100 mL/min). The structure of BP was characterized as described in the literature.

3. RESULTS AND DISCUSSION

3.1. Characterization of BPs. Microscopic morphology of the bulk BP and BPs is observed by SEM. A prominent layered structure with a large size is observed for bulk BP (Figure 1a). BPs obtained after exfoliation are about 500 nm, in which the anodic aluminum oxide (AAO) substrate can be observed through it (Figure 1b). The lamellar structure of BPs can also be confirmed by transmission electron microscopy (TEM, Figure 1c). The orthorhombic crystal system and the (040) crystal plane of BPs are detected with selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM), respectively (Figure 1c,d). Scanning probe microscopy (SPM) results show that the average thickness of BPs is 3.35 nm (Figure 1e), corresponding to 6–7 layers (the thickness of single-layer P atoms is considered to be 0.55 nm). According to dynamic light scattering results, most of BPs is 200–450 nm (Figure 1f). Three typical vibrational modes are found in the Raman spectra of BPs.
(Figure 1g), which correspond to the peaks of A_{1} at 355.5 cm\(^{-1}\), B_{2g} at 429.7 cm\(^{-1}\), and A_{2} at 465.1 cm\(^{-1}\). Besides, the complete vibration structure of BPs is confirmed by the strong peaks of Raman spectra.\(^{34}\) The characteristic peaks of P 2p_{3/2} (at 129.9 eV) and P 2p_{1/2} (at 130.7 eV) are detected in the XPS spectrum of BPs (Figure 1h). The weak peak at 134.5 eV represents PO\(_{4}\). The weak peak at 134.5 eV, which indicates the slight oxidation of BPs. This is due to the exposure of BPs to air shortly during the preparation, storage, and testing process.\(^{32,34}\)

3.2. Dispersibility of Fillers in TPE-S. The frozen fracture cross sections of TPE-S composites are observed by SEM (Figure 2). Low-magnified SEM images\(^{36,37}\) show that the cross section of the neat TPE-S is smooth (Figure 2a). However, the introduction of flame retardants makes the fracture surface of TPE-S/AHP-7.14 (Figure 2b) and TPE-S/RP-8.40 (Figure 2d) rough. High-magnified SEM images\(^{38-40}\) present many holes and convex particles (Figure 2f). This is caused by the fillers being pulled out with the fracture of the matrix. As a result, the fracture surface presents the morphology of multiple pits and convex particles. This indicates the poor compatibility and adhesion between flame retardants and the TPE-S matrix in the TPE-S/AHP-7.14 and TPE-S/RP-8.40 samples. In contrast, the surface of TPE-S/BP-7.98 is relatively flat and smooth. At high magnification, the BPs are tightly embedded in the matrix (see the white arrows in Figure 2g). As a nanomaterial, BPs have a high specific surface area and can be well dispersed and adhered to the matrix, and no obvious sheet/matrix gaps\(^{40}\) are observed on the fracture surface. This represents the favorable dispersibility and strong interface adhesion of BPs in the TPE-S matrix.

3.3. Thermal Stability. The thermal properties of different flame retardant TPE-S composites under a nitrogen atmosphere are tested by TGA, and the corresponding TGA and DTG curves (Figure 3) are obtained. Table 2 shows the selected data of the temperature at 1 wt % mass loss (\(T_{1}\)), the temperature at the maximum weight loss rate (\(T_{\text{max}}\)), and the char yield at 700 °C. Neat TPE-S degrades in two steps: the first one at 307 °C is caused by the pyrolysis of white oil and the second one at 433 °C is due to the degradation of the carbon bone chain. Similar degradation process is observed for the samples modified with RP and BPs, but the presence of flame retardants promotes the early degradation of the TPE-S composites. The \(T_{1}\) values of TPE-S/AHP-7.14 and TPE-S/BP-7.98 are slightly lower than that of neat TPE-S (253 °C), while the \(T_{\text{max}}\) of TPE-S/RP-8.40 is reduced to 234 °C, which is 19 °C lower than that of neat TPE-S. The \(T_{\text{max}}\) of TPE-S/RP-8.40 is 304 °C, which is almost the same as that of neat TPE-S (307 °C), but the \(T_{\text{max}}\) of TPE-S/BP-7.98 is increased by 30 °C. This is due to the good thermal stability of BPs, whose two-dimensional lamellar nanostructures act as a physical barrier,\(^{41}\) preventing heat transfer and delaying the matrix degradation. The degradation process of TPE-S/AHP-7.14 is different from others: the first and third steps are similar to neat TPE-S, and the second step is caused by the decomposition of AHP itself. Table 2 shows that the carbon residue content at 700 °C of each sample is increased after the addition of the flame retardant.

3.4. Flame Retardancy. 3.4.1. LOI and UL-94. The flame retardant properties of TPE-S composites are studied by the LOI and UL-94 vertical burning test. Typical digital images of different TPE-S composites in the UL-94 test\(^{42}\) are shown in Figure 4. The neat TPE-S burns rapidly and intensely after ignition, accompanied by a serious dripping phenomenon.\(^{43}\)

The introduction of flame retardants makes the samples extinguished in a short time after the first and second ignition. The carbon layer on the surface can protect the matrix inside and maintain the shape of the sample well. The data in Table 3 shows that the samples of TPE-S/AHP-7.14, TPE-S/BP-7.98, and TPE-S/RP-8.40 reach the UL-94 V-0 rating, and the LOI values are 23.9, 24.0, and 24.5%, respectively. These results indicate that the introduction of flame retardants can improve the flame retardancy and the melt-dropping properties of TPE-S composites.

3.4.2. Fire Behaviors. CC test is performed to investigate the fire behaviors of the TPE-S composites. Figure 5 shows the HRR, THR, and rate of smoke release (RSR) curves of TPE-S composites, and the detailed data are listed in Table 4. The neat TPE-S exhibits high flammability with a spiky HRR curve. When introducing the flame retardant, the HRR trend slows.

![Figure 3](https://doi.org/10.1021/acsomega.1c05854)
Figure 4. Typical digital images of different TPE-S composites in the UL-94 test.

| samples        | LOI (%) | $t_1$ (s)     | $t_2$ (s)     | dripping | igniting cotton | rating |
|----------------|---------|---------------|---------------|----------|-----------------|--------|
| neat TPE-S     | 17.6    | burning out   |               | yes      | yes             | NR     |
| TPE-S/AHP-6.72 | 23.7    | 5.0           | 67.0          | yes      | yes             | NR     |
| TPE-S/AHP-7.14 | 23.9    | 2.0           | 3.3           | no       | no              | V-0    |
| TPE-S/AHP-7.56 | 23.9    | 1.2           | 3.0           | no       | no              | V-0    |
| TPE-S/AHP-7.98 | 24.1    | 1.1           | 2.0           | no       | no              | V-0    |
| TPE-S/AHP-8.40 | 24.4    | 0.6           | 1.7           | no       | no              | V-0    |
| TPE-S/RP-7.56  | 23.8    | 13.0          | 42.0          | yes      | yes             | NR     |
| TPE-S/RP-7.98  | 23.9    | 3.1           | 52.0          | yes      | yes             | NR     |
| TPE-S/RP-8.40  | 24.5    | 1.0           | 2.0           | no       | no              | V-0    |
| TPE-S/BP-7.56  | 23.9    | 3.5           | 63.0          | yes      | yes             | NR     |
| TPE-S/BP-7.98  | 24.0    | 0.8           | 2.2           | no       | no              | V-0    |
| TPE-S/BP-8.40  | 24.1    | 0.4           | 1.2           | no       | no              | V-0    |
down and changes to a plateau shape with a lower peak. This indicates that the flame retardant reduces the intensity of the matrix combustion. The PHRR and THR of neat TPE-S are 889.9 kW/m² and 110.7 MJ/m², respectively. With the addition of flame retardants, PHRR and THR decrease in different ranges: the PHRR of TPE-S/AHP-7.14, TPE-S/RP-8.40, and TPE-S/BP-7.98 decreases by 65.6, 55.5, and 61.8%, respectively. Similarly, the THR of the TPE-S composites decreases to 86.6, 81.9, and 91.1 MJ/m² for TPE-S/AHP-7.14, TPE-S/RP-8.40, and TPE-S/BP-7.98, respectively. Figure 5c shows that the introduction of flame retardants also reduces the peak value of RSR. These results prove that the flame retardancy of TPE-S composites is improved by the introduction of flame retardants. The av-EHC of TPE-S/AHP-7.14, TPE-S/RP-8.40, and TPE-S/BP-7.98 presents the same trend with 31.3, 33.6, and 35.3% reduction, respectively. The results indicate that the flame retardants play a role in quenching free radicals in the gas phase and promoting the incomplete combustion of the matrix. The time to PHRR (tPHRR) of neat TPE-S is 90 s, and the tPHRR of TPE-S/AHP-7.14 and TPE-S/RP-8.40 is 50 and 55 s, respectively. It is worth noting that the tPHRR of TPE-S/BP-7.98 is 170 s. This is related to the two-dimensional nanosheet structure of BPs, which inhibited the transfer of heat inside the material, thereby delaying the degradation of the TPE-S, consistent with the results of TGA. The introduction of flame retardants also promotes the formation of carbon layers and increases the mass of the final residual carbon layer.

3.4.3. Morphology of the Residual Char. To explore the influence of different flame-retardant systems on the carbon layer after TPE-S combustion, the morphology of the residue after the CC test is observed by the digital camera and SEM (Figures 6 and 7). The digital images show that there is almost no residue left after the CC test for neat TPE-S (Figure 6a). It is evident from the low-magnified SEM images that the carbon residues of TPE-S/AHP-7.14 and TPE-S/BP-7.98 are more continuous and denser than those of TPE-S/RP-8.40 (Figure 7a–c). AHP can form phosphoric acid, polyphosphoric acid, and other substances in the combustion process to promote the dehydration of the matrix into carbon, while the aluminum-containing substance residues in the carbon layer play a role in strengthening the carbon layer.6 Similarly, phosphoric acid and polyphosphoric acid can also be formed in the combustion process of BPs,48 which promotes the formation of a continuous and dense carbon layer. However, at high-magnified SEM images,49,50 there are many large holes on the surface of TPE-S/AHP-7.14 and TPE-S/RP-8.40 carbon residues (Figure 7d,f). The size distribution of the holes ranges from 50 to 200 μm. A small number of 20–30 μm holes are found on the surface of the TPE-S/BP-7.98 carbon residue (Figure 7e). The dense carbon layer can better block the transfer of combustible gas, oxygen, and heat during the combustion of the matrix,6,51 thereby improving the flame-retardant performance. There are large holes on the inner surface of each sample, which can store gases (H₂O, CO, CO₂, N₂, NH₃, etc.) during the pyrolysis process.52,53 The gases can be released in large quantities after reaching the limited,

### Table 4. Combustion Data of TPE-S Composites

| sample                  | tPHRR (s) | PHRR (kW/m²) | THR (MJ/m²) | TML (wt%) | av-EHC (MJ/kg) |
|-------------------------|-----------|--------------|-------------|-----------|----------------|
| neat TPE-S              | 90        | 889.9        | 110.7       | 97.9      | 41.1           |
| TPE-S/AHP-7.14          | 50        | 306.5        | 86.6        | 83.5      | 28.2           |
| TPE-S/RP-8.40           | 55        | 395.9        | 91.1        | 93.5      | 27.3           |
| TPE-S/BP-7.98           | 170       | 339.6        | 81.9        | 87.5      | 26.6           |

*aAbbreviations: tPHRR, time-to-peak heat release rate; PHRR, peak heat release rate; THR, total heat release; av-EHC, the average effective heats of combustion; TML, total mass loss.*
conducive to blowing out the flame and reducing the concentration of oxygen and flammable gases.56

3.4.4. FTIR of the Residual Char. The residuals after the CC test are analyzed by FTIR, and the relevant results are shown in Figure 8. The FTIR spectra show bands 724 (P−C−P), 1018 (P−O), and 1247 cm⁻¹ (PO) for the residual carbon of TPE-S/AHP-7.14, indicating phosphorus compounds in the residue. The strong peak at 1130 cm⁻¹ is due to the tensile vibration of C−O on Ar−O−Ar. Similarly, bands 883 (O−P−O), 1001 (P−O), and 1141 cm⁻¹ (P=O) are also observed in the TPE-S/BP-7.98 samples. Due to the skeleton vibration of the aromatic ring, there is also a peak at 1589 (C=C) and 2331 cm⁻¹ (P−H). The bands 877 (O−P−O) and 1071 cm⁻¹ (P−O−P) in the TPE-S/RP-8.40 sample and the strong peak at 1430 cm⁻¹ are caused by the asymmetric phase shift of the aliphatic C−H bond. A peak representing (C=C) skeletal vibrations is detected near 500 cm⁻¹ for all three samples. Thus, the residues contain unsaturated polyaromatic, phosphoric, and polyphosphoric compounds and some unsaturated TPE-S matrixes.

3.4.5. TG-IR Analysis. TG-IR is used to investigate the pyrolysis gaseous products of neat TPE-S and TPE-S/BP-7.98. The FTIR spectra of gaseous products at representative temperatures are shown in Figure 9. For neat TPE-S, the absorption peak is detected at 2930, 1461, 1379 cm⁻¹ (−CH₃, −CH₂−), and 1650 cm⁻¹ (Ph−H) for its mainly gaseous products (Figure 9a). These alkanes and aromatic hydrocarbon products are produced by the degradation of PP and SEBS. In particular, for TPE-S/BP-7.98 (Figure 9b), different gas products are detected: aromatic amines (3082 cm⁻¹), hydrocarbons (2930 and 1449 cm⁻¹), CO₂/CO (2362 and 2284 cm⁻¹), carbonyl compounds (1790 cm⁻¹), carbonyl compounds (1790 cm⁻¹), and NH₃ (967 cm⁻¹). The results show that the flame-retardant system based on BPs can capture free radicals and release nonflammable gases in the gas phase.

3.4.6. Flame Retardant Mechanism. Based on the above results, a possible flame-retardant mechanism is proposed. In the gas phase, BPs can form P· and PO·, which can capture the H· and HO· produced by the matrix degradation, thereby interrupting the free radical chain reaction, reducing the release of combustible gas and inhibiting the combustion of materials. Also, in the condensed phase, BPs can generate phosphoric acid and polyphosphate, promoting dehydration and carbonization of the matrix. It is conducive to forming a continuous and dense carbon layer, which blocks the transfer of heat, oxygen, and flammable gases, thus slowing down the degradation of the matrix. Some holes in the carbon layer can store the gases (H₂O, CO, CO₂, N₂, NH₃, etc.) produced during the matrix degradation. Due to its unique two-dimensional layered nanostructure, BPs can act as a physical barrier to inhibit heat and oxygen transfer at lower temperatures.

3.5. Mechanical Properties. Figure 10 shows the influence of different flame retardants on the tensile strength and elongation at the break of TPE-S. The tensile strength of neat TPE-S is 13.7 MPa, and the elongation at break is 531%. Compared with neat TPE-S, the mechanical properties are reduced by different degrees due to the introduction of flame retardants, whereas the tensile strength and elongation at break...
of TPE-S/BP-7.98 are only decreased by 26 and 32%, respectively. This indicates that the addition of BPs exhibits the least effect on the mechanical properties of TPE-S materials, which is due to the favorable dispersibility between BPs and the TPE-S matrix.

4. CONCLUSIONS
The incorporation of large loading of flame retardants generally reduces the mechanical properties of TPE-S. In this work, the flame-retardant TPE-S composites were prepared by composite BPs with MCA and PPE. The thermal, flame-retardant, and mechanical properties of the TPE-S and the BPs structure were evaluated. Results showed that BPs can readily disperse in TPE-S and enhance the flame retardancy by acting in the gas and condensed phases. Compared with other flame-retardant systems, such as AHP and RP, the introduction of BPs showed apparent better thermal and mechanical properties of TPE-S composites. This study may help to prepare the flame-retardant TPE-S with better mechanical properties.

AUTHOR INFORMATION
Corresponding Authors
Yuxi Han − College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China; Email: hanyuxichem@163.com

Jinhong Yu − Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences, Ningbo 315201, China; orcid.org/0000-0001-9134-7568; Email: yujinhong@nimte.ac.cn
Zhongwei Wang − College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China; orcid.org/0000-0003-0427-4116; Email: wangzhongwei@fusilinchem.com

Jiaxuan Li − College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

Jun Wu − R&D Department, Qingdao Fusilin Chemical Science & Technology Co. Ltd., Qingdao 266000, China

Xianzhe Wei − Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences, Ningbo 315201, China

Qing Yu − College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China; orcid.org/0000-0002-2810-486X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c05854

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the Natural Science Foundation of Shandong Province (ZR2020LFG002 and ZR2020QB023), the Foundation of 2019 Science and Technology Projects of Qingdao West Coast New District [Grant Number: 2019-18], and the Research Foundation of Qingdao Fusilin Chemical Science & Technology Co., Ltd. (FSL-RF 2019).

REFERENCES
(1) Tarawneh, M. A.; Yu, L. J.; Tarawni, M. A.; Ahmad, S. H.; Al-Banawi, O.; Batiha, M. A. High performance thermoplastic elastomer (TPE) nanocomposite based on graphene nanoplatelets (GNPs). World J. Eng. 2015, 12, 437−442.
(2) Lu, H.; Yang, W.; Zhou, S.; Xing, W.; Song, L.; Hu, Y. Preparation and flammability of EPDM/PP/Mg(OH)2 dynamic vulcanizates. Polym. Adv. Technol. 2010, 21, 113−117.

(3) Li, J.; Li, X.; Wei, Q.; Yang, J.; Qiu, B.; Xu, J.; Wang, X. Synergistic effect of organophosphate functionalized montmorillonite on properties and water resistance of intumescent flame retarded SEBS. Fire Mater. 2019, 43, 74−83.

(4) Yu, Y.; Shim, E. Process-structure-property relationship of meltblown poly (styrene-ethylene/butylene-styrene) nonwovens. J. Appl. Polym. Sci. 2021, 138, No. 50230.

(5) Zhu, P.; Xu, M.; Li, S.; Zhang, Z.; Li, B. Preparation and investigation of efficient flame retardant TPE composites with pipierazine pyrophosphate/aluinium diethylphosphinate system. J. Appl. Polym. Sci. 2020, 137, No. 47711.

(6) Cheng, X.; Wu, J.; Li, Y.; Yao, C.; Yang, G. SEBS-based thermoplastic elastomers containing aluminum hyphosphite and melamine cyanurate: Thermal degradation, flame retardancy, and mechanical properties. J. Fire Sci. 2019, 37, 137−154.

(7) Wu, H.; Krifa, M.; Koo, J. H. Rubber (SEBS-g-MA) Toughened Flame-Retardant Polyamide 6: Microstructure, Combustion, Extension, and Izod Impact Behavior. Polym.—Plast. Technol. Eng. 2018, 57, 727−739.

(8) Yang, Y.; Li, B.; Xu, M. Flame retardancy and water resistance of novel intumescent flame-retardant oil-filled styrene-ethylene-butadiene-styrene block copolymer/polypropylene composites. J. Appl. Polym. Sci. 2014, 131, No. 39575.

(9) Paes, L. H. G.; Stellen, T. T.; Becker, D. Comparative performance of carbon nanotube and nanoclay on thermal properties and flammability behavior of amorphous polyamide/SEBS blend. Polym. Eng. Sci. 2020, 60, 1333−1342.

(10) Zeng, J.; Ma, W.; Wang, Q.; Yu, S.; Innocent, M. T.; Xiang, H.; Zhu, M. Strong, high stretchable and ultrasensitive SEBS/CNTs hybrid fiber for high-performance strain sensor. Compos. Constr. 2021, 25, No. 100735.

(11) Lee, W.; Liu, L.; Chen, C.; Lin, J. Syntheses and flame retarding properties of DOPO polymers, melamine polymers, and DOPO-melamine copolymers. Polym. Adv. Technol. 2014, 25, 36−40.

(12) Wille, A.; Langfeld, K.; Ulmer, B.; Andreivici, V.; Horold, A.; Limbach, P.; Bastian, M.; Schartel, B. Halogen-Free Multicomponent Flame Retardant Thermoplastic Styrene—Ethylene—Butylene—Styrene Elastomers Based on Ammonium Polyphosphate—Expandable Graphite Synergy. Ind. Eng. Chem. Res. 2017, 56, 8251−8263.

(13) Wang, L.; Pan, G.; Lu, Y. Study on the char-forming and synergistic flame retardant performance of SEBS/HIPS/PPO composites applied for cable. Plast. Rubber, Compos. 2020, 49, 222−229.

(14) Sut, A.; Greiser, S.; Jäger, C.; Schartel, B. Aluminum diethylphosinphate versus ammonium polyphosphate: A comprehensive comparison of the chemical interactions during pyrolysis in flame-retarded polyolefine/poly(phenylene oxide). Thermochim. Acta 2016, 640, 74−84.

(15) Sut, A.; Greiser, S.; Jäger, C.; Schartel, B. Interactions in multicomponent flame retardant polymers: Solid-state NMR identifying the chemistry behind it. Polym. Degrad. Stab. 2015, 121, 116−125.

(16) Li, X.; Tang, S.; Zhou, X.; Gu, S.; Huang, K.; Xu, J.; Wang, X.; Li, Y. Synergistic effect of amino silane functional montmorillonite on intumescent flame-retardated SEBS and its mechanism. J. Appl. Polym. Sci. 2017, 134, No. 449553.

(17) Long, S.; Qiu, D.; Long, R.; Li, X.; Chen, H.; Huang, Y.; Li, X. Design of aluminum trihydroxide and P-N core-shell structures and their synergistic effects on halogen-free flame retardant polyethylene composites. Polym. Adv. Technol. 2020, 31, 2020−2030.

(18) Lu, H.; Shao, J.; Ding, M.; Zhao, D.; Tian, C. Study on Flame Retardant LLDPFE/EPDM Thermoplastic Elastomers with Magnesium Hydroxide Sulfate Hydrate Whiskers. Polym.—Plast. Technol. Eng. 2012, 51, 578−582.

(19) Xiao, W.; Kibble, A. Comparison of Aluminum Hydroxide and Magnesium Hydroxide as Flame Retardants in Sebs-Based Compotes. Polym. Polym. Compos. 2008, 16, 415−422.
(36) Wan, Y.; Tang, L.; Gong, L.; Yan, D.; Li, Y.; Wu, L.; Jiang, J.; Lai, G. Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties. *Carbon* 2014, 69, 467−480.

(37) Wan, Y.; Gong, L.; Tang, L.; Wu, L.; Jiang, J. Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. *Composites, Part A* 2014, 64, 79−89.

(38) Gong, L.; Pei, Y.; Han, Q.; Zhao, L.; Wu, L.; Jiang, J.; Tang, L. Polymer grafted reduced graphene oxide sheets for improving stress transfer in polymer composites. *Compos. Sci. Technol.* 2016, 134, 144−152.

(39) Tang, L.; Wan, Y.; Yan, D.; Pei, Y.; Zhao, L.; Li, Y.; Wu, L.; Jiang, J.; Lai, G. The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* 2013, 60, 16−27.

(40) Wan, Y.; Tang, L.; Yan, D.; Zhao, L.; Li, Y.; Wu, L.; Jiang, J.; Lai, G. Improved dispersion and interface in the graphene/epoxy composites via a facile surfactant-assisted process. *Compos. Sci. Technol.* 2013, 82, 60−68.

(41) Liu, L.; Zhu, M.; Ma, Z.; Xu, X.; Seraji, S.; Yu, B.; Sun, Z.; Wang, H.; Song, P. A reactive copper-organophosphate-MXene heterostructure enabled antibacterial, self-extinguishing and mechanically robust polymer nanocomposites. *Chem. Eng. J.* 2022, 430, No. 132712.

(42) Cao, C.; Wang, P.; Zhang, J.; Guo, K.; Li, Y.; Xia, Q.; Zhang, G.; Zhao, L.; Chen, H.; Wang, L.; Gao, J.; Song, P.; Tang, L. One-step and green synthesis of lightweight, mechanically flexible and flame-retardant polydimethylsiloxane foam nanocomposites via surface-assembling ultralow content of graphene derivative. *Chem. Eng. J.* 2020, 393, No. 124724.

(43) Zhang, Y.; Jing, J.; Liu, L.; Xi, L.; Sai, T.; Ran, S.; Fang, Z.; Huo, S.; Song, P. A molecularly engineered bioderived polyporphosphate for enhanced flame retardant, UV-blocking and mechanical properties of poly(lactic acid). *Chem. Eng. J.* 2021, 411, No. 128493.

(44) Markwart, J.; Battig, A.; Zimmermann, L.; Wagner, M.; Fischer, J.; Schartel, B.; Wurm, F. Systematically Controlled Decomposition Mechanism in Phosphorus Flame Retardants by Precise Molecular Architecture: P−O vs P−N. *ACS Appl. Polym. Mater.* 2019, 1, 1118−1128.

(45) Liu, L.; Zhu, M.; Shi, Y.; Xu, X.; Ma, Z.; Yu, B.; Fu, S.; Huang, G.; Wang, H.; Song, P. Functionalizing MXene towards highly stretchable, ultrathin, fatigue- and fire-resistant polymer nanocomposites. *Chem. Eng. J.* 2021, 424, No. 130338.

(46) Mao, M.; Yu, K.; Cao, C.; Gong, L.; Zhang, G.; Zhao, L.; Song, P.; Gao, J.; Tang, L. Facile and green fabrication of flame-retardant Ti3C2Tx MXene networks for ultrafast, reusable and weather-resistant fire warning. *Chem. Eng. J.* 2022, 427, No. 131615.

(47) Yu, Z.; Mao, M.; Li, S.; Xia, Q.; Cao, C.; Zhao, L.; Zhang, G.; Zheng, Z.; Gao, J.; Tang, L. Facile and green synthesis of mechanically flexible and flame-retardant clay/graphene oxide nanoribbon interconnected networks for fire safety and prevention. *Chem. Eng. J.* 2021, 405, No. 126620.

(48) Qu, Z.; Wu, K.; Jiao, E.; Chen, W.; Hu, Z.; Xu, C.; Shi, J.; Wang, S.; Tan, Z. Surface functionalization of few-layer black phosphorene and its flame retardancy in epoxy resin. *Chem. Eng. J.* 2020, 382, No. 123991.

(49) Guo, K.; Wu, Q.; Mao, M.; Chen, H.; Zhang, G.; Zhao, L.; Gao, J.; Song, P.; Tang, L. Water-based hybrid coatings toward mechanically flexible, super-hydrophobic and flame-retardant polyurethane foam nanocomposites with high-efficiency and reliable fire alarm response. *Composites, Part B* 2020, 193, No. 108017.

(50) Zhang, Z.; Zhang, J.; Cao, C.; Guo, K.; Zhao, L.; Zhang, G.; Gao, J.; Tang, L. Temperature-responsive resistance sensitivity controlled by L-ascorbic acid and silane co-functionalization in flame-retardant GO network for efficient fire early-warning response. *Chem. Eng. J.* 2020, 386, No. 123894.

(51) Jin, Y.; Huang, G.; Han, D.; Song, P.; Tang, W.; Bao, J.; Li, R.; Liu, Y. Functionalizing graphene decorated with phosphorus-nitrogen containing dendrimer for high-performance polymer nanocomposites. *Composites, Part A* 2016, 86, 9−18.

(52) Huang, N.; Xia, Q.; Zhang, Z.; Zhao, L.; Zhang, G.; Gao, J.; Tang, L. Simultaneous improvements in fire resistance and alarm response of GO paper via one-step 3-mercaptopyrroltrimethoxysilane functionalization for efficient fire safety and alarm prevention. *Composites, Part A* 2020, 131, No. 105797.

(53) Jin, X.; Cui, S.; Sun, S.; Gu, X.; Li, H.; Sun, J.; Zhang, S.; Bourbigot, S. The Preparation of an Intumescent Flame Retardant by Ion Exchange and Its Application in Polyacrylic Acid. *ACS Appl. Polym. Mater.* 2019, 1, 755−764.

(54) Huang, N.; Cao, C.; Li, Y.; Zhao, L.; Zhang, G.; Gao, J.; Guan, L.; Jiang, J.; Tang, L. Silane grafted graphene oxide papers for improved flame resistance and fast fire alarm response. *Composites, Part B* 2019, 168, 413−420.

(55) Wu, Q.; Gong, L.; Li, Y.; Cao, C.; Tang, L.; Wu, L.; Zhao, L.; Zhang, G.; Li, S.; Gao, J.; Li, Y.; Mai, Y. Efficient Flame Detection and Early Warning Sensors on Combustible Materials Using Hierarchical Graphene Oxide/Silicone Coatings. *ACS Nano* 2018, 12, 416−424.

(56) Duan, H.; Xu, X.; Leng, K.; Zhang, S.; Han, Y.; Gao, J.; Yu, Q.; Wang, Z. A (4-fluorophenyl)(phenyl)phosphine oxide-modified epoxy resin with improved flame-retardancy, hydrophobicity, and dielectric properties. *J. Appl. Polym. Sci.* 2021, 138, No. 50792.

(57) Ma, Z.; Liu, X.; Xu, X.; Liu, L.; Yu, B.; Maluk, C.; Huang, G.; Wang, H.; Song, P. Bioinspired, Highly Adhesive, Nanostructured Polymeric Coatings for Superhydrophobic Fire-Extinguishing Thermal Insulation Foam. *ACS Nano* 2021, 15, 11667−11680.

(58) Yu, J.; Yin, H.; Cai, X. Effects of common synergistic agents on intumescent flame retardant polypropylene with a novel charring agent. *J. Therm. Anal. Calorim.* 2013, 111, 725−734.

(59) Wang, J.; Qiu, S.; Cheng, L.; Chen, W.; Zhou, Y.; Zou, B.; Han, L.; Xu, Z.; Yang, W.; Hu, Y.; Song, L. Synergistic effects of aryl diazonium modified Few-Layer black Phosphorus/Ultrafine rare earth yttrium oxide with enhancing flame retardancy and catalytic smoke toxicity suppression of epoxy resin. *Appl. Surf. Sci.* 2022, 571, No. 151356.

(60) Wang, X.; Hu, Y.; Song, L.; Xing, W.; Lu, H.; Lv, P.; Jie, G. Flame retardancy and thermal degradation mechanism of epoxy resin composites based on a DOPO substituted organophosphorus oligomer. *Polymer 2010, 51*, 2435.

(61) Ren, X.; Mei, Y.; Lian, P.; Xie, D.; Yang, Y.; Wang, Y.; Wang, Z. A Novel Application of Phosphorene as a Flame Retardant. *Polymers 2018, 10*, No. 227.