Preparation and oxidation resistance of polyphenylene sulfide modified by high-temperature antioxidants

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Abstract

Two types of high-temperature antioxidants (Revonox 608 and GA-80) were used to improve the oxidation resistance of polyphenylene sulfide (PPS) through melt blending, and the resistance against oxidation and other properties were characterized. The results showed that GA-80 exhibited better dispersibility and compatibility with the PPS matrix than did Revonox 608. Revonox 608 could act as a heterogeneous nucleation agent that can promote crystallization and improve the crystallinity of PPS, whereas GA-80 could delay the movement of chain segments and limit crystallization. The thermal-oxidative stability of PPS can be improved by adding antioxidants due to prior oxidative decomposition. The dynamic oxidation induction temperature of PPS increased by more than 10 °C because of the capture of free radicals and the decomposition of hydroperoxides by antioxidants. The XPS results showed that both GA-80 and Revonox 608 could retard the oxidative cleavage of the C-S-C bond in the PPS macromolecular chains and protect the S atoms from oxidizing to sulfone groups.

1. Introduction

Polyphenylene sulfide (PPS) has been garnering increasing attention owing to its good mechanical properties, friction resistance, electrical insulation, chemical resistance, excellent flame retardancy and outstanding thermal stability [1–5]. PPS fibers prepared through melt spinning with PPS fiber-grade resin have been widely used in high-temperature filtration and chemical corrosion industries [6–8]. The macromolecular chain of PPS was constructed with alternating phenyl rings and sulfur atoms. However, the energy of C–S bond is relatively weak, and can be susceptible to attack by oxidizing gas and heat in a high-temperature environment, leading to bond breakage and the crosslinking of macromolecular chains [2, 4, 7, 8]. This can degrade the mechanical properties of PPS fibers, and darken the color, limiting the application and shortening the service life of the PPS fibers. In recent decades, extensive research has been conducted on the enhancement of the mechanical properties, abrasive resistance, thermal conductivity and electrical conductivity [9–13]. However, only a few studies on improving the oxidative stability of PPS have been reported.

Currently, the antioxidative modification of PPS resin and fibers can be divided into two types: (1) the surface coating method and (2) the direct addition of nanoparticles. The surface coating method is commonly used to improve the oxidation resistance of PPS fibers and fiber products [14, 15]. The surface of the PPS fibers or fiber products is covered with a protective coating composed of antioxidants. However, the nonuniformity and easy peeling of protective coating limit the potential application of surface coating method.

The direct addition of nanoparticles is often used to improve the oxidation resistance of PPS resin through melt blending. The PPS resin is blended with various nanoparticles, such as black carbon, titanium dioxide (TiO₂) [16–18], silicon dioxide (SiO₂) [16, 19, 20], montmorillonite (MMT) [21, 22], and graphene [23–25], through melt blending. Our previous work [22, 24] proved that both MMT and graphene could enhance the oxidation resistance of PPS resin and fibers. However, the extent of the improvement in the oxidation resistance caused by the nanoparticles is limited, because most nanoparticles cannot capture and destroy the free radicals.
generated by the oxidation of the PPS macromolecule. Most nanoparticles can limit and delay the diffusion of heat, oxidizing substances, and free radicals to enhance oxidative stability [21, 24, 25].

For most polymers, adding organic antioxidants is the main method to resist oxidation [26–28]. Organic antioxidants can effectively capture and destroy free radicals and prevent chain extension, crosslinking and branching of polymer macromolecules. Based on their mechanism of action, organic antioxidants can be divided into chain termination antioxidants, hydroperoxidation decomposition antioxidants, and metal ion passivators. As a type of chain termination antioxidant, hindered phenol antioxidants have been widely used in polymer materials because they are non-toxic, highly efficient, and environmentally friendly. They can capture the oxygen free radicals generated during the aging of polymer materials to interrupt the growth of the active chains. However, the synergistic stability between hindered phenol antioxidants and auxiliary antioxidants and the staining stability of resistance to NOx are poor, thereby restricting their application [29, 30]. Phosphite antioxidants are auxiliary antioxidants, that can decompose high activity hydroperoxides into low-activity molecules to inhibit the thermal oxidation degradation of polymer materials. However, the poor hydrolysis resistance of phosphite antioxidants has become a bottleneck in the application [31, 32]. Moreover, primary antioxidants are usually used together with auxiliary antioxidants to obtain excellent results on improving the oxidation resistance of polymers.

Organic antioxidants are usually micromolecular; however, the processing temperature of PPS resin is above 300 °C, whereas the degradation temperature of most organic antioxidants is below 250 °C. Most organic antioxidants decompose and gasify during melt blending; therefore, they cannot achieve the efficacy of antioxidants and influence the structure of PPS. Currently, there are few studies on the modification of PPS using organic antioxidants via melt blending. Therefore, selecting high-temperature antioxidants is the key to modifying PPS through melt blending.

GA-80 is a semi-hindered phenol antioxidant having much better synergistic stability and staining stability of resistance to NOx, in addition to the advantages of hindered phenol antioxidants [30]. It is suitable for polymer materials, which can be easily thermally oxidized and degraded and require high heat stability and color stability. Moreover, Revonox 608 is a phosphite antioxidant with excellent hydrolysis resistance and processing stability. Most importantly, both GA-80 and Revonox 608 have excellent thermal stability, making them usable in melt blending above 300 °C. They will not be decomposed and volatilized during the melting process of the PPS resin. However, research on the oxidation resistance of PPS modified by GA-80 or Revonox 608 has not been reported. Therefore, in this study, two types of high-temperature resistance antioxidants (GA-80 and Revonox 608) were screened to modify the PPS resin through melt blending. The structure and crystallization behavior of the PPS/antioxidant composites were investigated. The oxidation resistance of PPS was characterized by measuring the change in the thermal-oxidative stability, dynamic oxidation induction temperature, and valence state of the element.

2. Experimental

a. Materials
PPS resin ($d = 1.35 \text{g cm}^{-3}$, $T_g \approx 89 ^\circ\text{C}$, $T_m \approx 280 ^\circ\text{C}$) was purchased from Deyang Keji High-tech Materials Co., Ltd (Sichuan, China). Two kinds of powdered antioxidants, bis(2,4-dicumylphenyl) pentaerythritol diphosphite (Revonox 608), and 3,9-bis[1,1-dimethyl-2-[(3-tert-butyl-4-hydroxy-5-methylphenyl) propionyloxy] ethyl] –2,4,8,10-tetraoxaspiro[5.5]undecane (GA-80), were obtained from Shanghai Pu Zhan Industry Co., Ltd (Shanghai, China). The chemical formula of organic antioxidants is shown in figure 1.

b. Preparation of PPS/antioxidants composites
The PPS/antioxidant composites with different contents of antioxidants (0.5 and 1 wt.%) were manufactured by using an SISZ-10A corotate twin-screw extruder (Ruiming Co., Ltd, Wuhan, China) via melt blending. The melt blending process was continued for 3 min with a screw speed of 25 rpm at 290 °C. The samples are listed in...
necessary to characterize the thermal stability of antioxidants. The thermogravimetric analysis (TGA)

The preparation of PPS-based composites requires a high temperature of approximately 300 °C. Therefore, it is necessary to characterize the thermal stability of antioxidants. The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of Revonox 608 and GA-80 are shown in figure 2. It can be observed that both Revonox 608 and GA-80 exhibit high thermal stabilities. The initial decomposition temperature (T_d) of Revonox 608 is 283.8 °C, whereas that of GA-80 is 337.2 °C, which is higher. The DTG curves show only one main mass step at 349.1 °C for Revonox 608. For GA-80, two main mass loss steps at 416.9 °C and 606.8 °C can be observed. Therefore, GA-80 exhibits better thermal stability than Revonox 608. Moreover, it should be noted that both Revonox 608 and GA-80 exhibit excellent thermal stability compared with common antioxidants, and thus can be suitable for melt blending with PPS.

table 1. Hereafter, the samples of the PPS/Revonox 608, PPS/GA-80, and PPS/Revonox 608/GA-80 composites are named PPSR_x, PPSG_x, and PPSR_xG_x, respectively. x represents the content of organic antioxidants.

c. Characterization

The structure of PPS/antioxidant composites was observed by using an S-4800 scanning electron microscope (Hitachi Co. Ltd, Japan). Scanning electron microscopy (SEM) images of the cryo-surface of the PPS-based composites were obtained. The tensile properties of PPS/antioxidant composites were characterized by using an EX-SX tensile tester (Tester Sangyo Co., Ltd, Osaka, Japan) with a 50 kN load cell at 25 °C. The clamping distance was 15 mm at a strain speed of 5 mm min⁻¹. Each sample was tested at least five times, and the data were reported corresponding to the average value.

The crystallization behavior of PPS/antioxidant composites was measured by using a TA-Q200 differential scanning calorimeter (TA Instruments Co., Ltd, New Castle, DE, USA). Samples of 6–8 mg were heated from 35 °C to 320 °C at a heating rate of 10 °C min⁻¹. The samples were kept at 320 °C for 3 min to eliminate the thermal history. The samples were then cooled to 30 °C at a cooling rate of 20 °C min⁻¹ and heated to 320 °C again at a heating rate of 20 °C min⁻¹. All tests were performed under a nitrogen atmosphere at a gas flow rate of 50 ml min⁻¹. The crystallinity of PPS/antioxidant composites was calculated using equation (1).

\[
X_c = \frac{\Delta H_m}{\Delta H_f (1 - W_f)} \times 100\%
\]

where \(X_c\) is the crystallinity of the PPS/antioxidant composites, \(\Delta H_m\) is the melting enthalpy of the PPS/antioxidant composites, \(\Delta H_f\) is the melting enthalpy of 100% crystalline PPS, 77.5 J g⁻¹ [20], and \(W_f\) is the content of antioxidants in the PPS-based composites.

The thermo-oxidative stability of organic antioxidants and PPS/antioxidant composites was characterized by using a Q500 thermogravimetric analyzer (TA Instruments Co., Ltd, New Castle, DE, USA) from 30 °C to 800 °C at a heating rate of 10 °C min⁻¹ in an air atmosphere. The airflow rate was 50 ml min⁻¹. The dynamic oxidation induction temperature (dynamic OIT) was also measured by using a TA-Q200 differential scanning calorimeter according to the ISO11357-6:2008. Samples of 8–10 mg were heated from 30 °C to 500 °C at a heating rate of 10 °C min⁻¹ under an oxygen atmosphere. The gas flow rate was 50 ml min⁻¹.

The oxidation resistance test was performed as follows. The pure PPS and PPS-based composites were heated at 220 °C for 120 h. The oxidation resistance of the samples was then characterized by using an AXIS-ULTRA DLD X-ray photoelectron spectrometer (Shimadzu Co., Ltd, Kyoto, Japan). The change in the elemental content and valence state of the element can be used to reflect the oxidation resistance of PPS.

3. Results and Discussion

a. Thermal stability of organic antioxidants

The preparation of PPS-based composites requires a high temperature of approximately 300 °C. Therefore, it is necessary to characterize the thermal stability of antioxidants. The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of Revonox 608 and GA-80 are shown in figure 2. It can be observed that both Revonox 608 and GA-80 exhibit high thermal stabilities. The initial decomposition temperature (T_d) of Revonox 608 is 283.8 °C, whereas that of GA-80 is 337.2 °C, which is higher. The DTG curves show only one main mass step at 349.1 °C for Revonox 608. For GA-80, two main mass loss steps at 416.9 °C and 606.8 °C can be observed. Therefore, GA-80 exhibits better thermal stability than Revonox 608. Moreover, it should be noted that both Revonox 608 and GA-80 exhibit excellent thermal stability compared with common antioxidants, and thus can be suitable for melt blending with PPS.

| Samples | Compositions (wt. %) |
|---------|---------------------|
|         | PPS  | Revonox 608 | GA-80 |
| PPS     | 100.0|           |       |
| PPSR_0.5| 99.5 | 0.5        |       |
| PPSR_1  | 99.0 | 1.0        |       |
| PPSG_0.5| 99.5 |           | 0.5   |
| PPSG_1  | 99.0 |           | 1.0   |
| PPSR_0.5G_0.5| 99.0 | 0.5        | 0.5   |

Table 1. Composition of various composites based on PPS and antioxidants.
b. Structure of PPS/antioxidants composites

The SEM images of the dispersion of antioxidants in the PPS matrix are shown in figure 3. All test specimens are presented at 20,000 × magnification.

The cryo-fracture surface of pure PPS is relatively smooth and flat, and the addition of organic antioxidants has little influence on the surface morphology. Figures 3(b) and (c) show that Revonox 608 is uniformly dispersed in the PPS matrix without obvious agglomeration. However, the particle size of Revonox 608 in the PPS matrix is inhomogeneous, particularly when the content of Revonox 608 is high. The particle size of some Revonox 608 is small, whereas some is large. This phenomenon can be attributed to the fact that part of the molten Revonox 608 causes the agglomeration during the melt blending process. For PPSG0.5 and PPSG1, it can be found that GA-80 shows excellent dispersibility in the PPS matrix, and the particle size of GA-80 in the PPS matrix is considerably uniform, as depicted in figures. 3(d) and (e). Therefore, the dispersibility and compatibility of GA-80 in the PPS matrix are better than those of Revonox 608. For PPSR0.5G0.5, it can be observed that Revonox 608 and GA-80 have no effect on their respective dispersibility without obvious agglomeration.

c. Crystallization behavior of PPS/antioxidants composites

The crystalline behavior of the PPS/antioxidant composites is shown in figure 4, and the thermal properties of the differential scanning calorimetry (DSC) curves are summarized in table 2. From the figure 4(a) and Table 2 show that there is only one melting peak in the heating curves of pure PPS and PPS/antioxidant composites,
demonstrating that the organic antioxidants have good compatibility with PPS \[33\]. Moreover, the addition of Revonox 608 can slightly increase the melting peak temperature (\(T_m\)) of PPS. Figure 4(b) and table 2 show that the addition of Revonox 608 can lead to an increase in the crystallization temperature (\(T_c\)) and degree of crystallinity (\(X_c\)), and the degree of supercooling (\(\Delta T\)) of PPS shows a declining trend. This phenomenon indicates that the Revonox 608 can act as a heterogeneous nucleation agent to promote the crystallization and improve the crystallinity of PPS \[22, 24, 34\].

In contrast, the addition of GA-80 can decrease the \(T_c\) and \(X_c\) of PPS and increase the \(\Delta T\). This result shows that the GA-80 cannot act as a heterogeneous nucleation agent to promote the crystallization. This can be attributed to the fact that the addition of GA-80 can inhibit the rotation of macromolecules and delay the movement of chain segments, causing a decrease in \(T_c\). Moreover, the good dispersion of GA-80 in the PPS matrix can also destroy the structural regularity and inhibit the accumulation of PPS molecular chains to crystallize, thereby limiting the crystallization and decreasing the \(X_c\). For the PPSR0.5G0.5 composites, it can be found that the mixture of antioxidants also leads to a decrease in the \(T_c\) and \(X_c\), and an increase in the \(\Delta T\). Therefore, it can be concluded that the GA-80 plays a leading role in influencing the crystallization performance of PPS.

d. Oxidation resistance of PPS/antioxidants composites
At present, the methods for measuring the oxidation resistance of PPS are varied. In this work, the thermo-oxidative stability, dynamic oxidation induction temperature, and type and content of functional groups were used to characterize the oxidation resistance of PPS.

i. Thermo-oxidative stability
Figure 5 shows the TGA curves of the PPS and PPS/antioxidant composites under an air atmosphere. Moreover, the degradation temperature at different decomposition phases (\(T_{10\%}, T_{30\%}, T_{50\%}\), and \(T_{max}\)) and the temperature at the maximum decomposition rate (\(T_{max}\)) are listed in table 3. Figure 5 shows that pure PPS exhibits a one-step thermal oxidative degradation process over the entire test temperature range, and PPS/antioxidant composites also show this characteristic. Table 3 shows that the initial degradation temperature (\(T_i\)) of pure PPS is 476.3 °C, and the addition of antioxidants leads to a decrease in the \(T_i\). In particular, the \(T_i\) drops by more than 100 °C for PPSGx. This can be attributed to the fact that the antioxidants begin to oxidize and decompose at a lower temperature than the PPS resin, as shown in Fig. 2. Owing to the prior oxidative decomposition of antioxidants,
the oxidation of the PPS resin can be prevented or limited. However, the $T_i$ of PPSG$_x$ is approximately 100 °C lower than that of PPSRx, whereas the $T_i$ of GA-80 is significantly higher than that of Revonox 608. This phenomenon can be explained by the fact that GA-80 has almost no mass loss during melt blending with PPS. In contrast, part of Revonox 608 begins to decompose during melt blending owing to its low thermal stability. Therefore, the $T_i$ of PPSG$_x$ depends on the decomposition of GA-80 because of its high content, whereas the $T_i$ of PPSRx is mainly related to the self-decomposition of PPS. In terms of thermal stability, GA-80 is more suitable than Revonox 608 for melt blending with PPS.

Figure 5(a) depicts that there is no mass loss for pure PPS and PPS/antioxidant composites before 200 °C. It should be noted that pure PPS resin has a slight increase of approximately 0.5% in mass during the heating process from 200 °C to 450 °C. This phenomenon can be attributed that the combination of sulfur and carbon with oxygen during the heating process [18, 20]. It also can be found that PPSSG$_{0.5}$, PPSPG$_1$, and PPSSG$_{0.3}$R$_{0.5}$ show a slight increase in mass before 350 °C, but the degree of increase is lower than that of pure PPS. This indicates that the addition of antioxidants can limit their combination with oxygen during the heating process. However, there is a slight decrease in mass that can be observed for PPSRx composites after 350 °C; this can be attributed to the decomposition of Revonox 608, which is greater than that of the combination with oxygen. Moreover, PPSSG$_{0.5}$, PPSPG$_1$ and PPSSR$_{0.5}$G$_{0.5}$ show clear degradations between 350 °C and 400 °C, which can be attributed to the degradation of GA-80.

Figure 5 also shows that the decomposition rates of PPSR$_x$ and PPSSR$_{0.5}$G$_{0.5}$ are lower than that of pure PPS after 550 °C. This is because the decomposition of Revonox 608 can form pyrophosphoric carbon to delay or isolate the diffusion of heat and gas decomposition products [35–37]. The decomposition of GA-80 cannot form the protective carbon layer to delay the degradation of PPS, whereas the decomposition products of GA-80 can promote the degradation of PPS. Therefore, the $T_{max}$ of PPSR$_x$ increases, whereas that of PPSSG$_x$ decreases. Moreover, it can be observed that the mass retention ratio of pure PPS is 53.8% at 800 °C; the mass retention ratio of PPSR$_x$ and PPSSR$_{0.5}$G$_{0.5}$ is slightly higher than that of pure PPS, as shown in figure 5(a). However, the mass retention ratio of PPSSG$_x$ is approximately 1% lower than that of pure PPS. Figure 2 shows that GA-80 can be completely decomposed at 800 °C, whereas Revonox 608 still has 10% decomposition residual. Therefore, the mass retention ratio of PPSR$_x$ is higher than that of pure PPS and PPSSG$_x$.

The heat-resistance index ($T_{HRI}$) is often used to exhibit the thermal stability of polymers, and can represent the restrictive temperature of long time serves [5, 13, 38, 39]. The $T_{HRI}$ can be calculated by the following equation:

![Figure 5. TGA curves of pure PPS and PPS/antioxidants composites; (a) TG curves, (b) DTG curves.](image.png)

Table 3. TGA parameters of pure PPS and PPS/antioxidants composites.

| Samples   | $T_i$ (°C) | $T_{50}$ (°C) | $T_{15}$ (°C) | $T_{30}$ (°C) | $T_{HRI}$ (°C) | $T_{max}$ (°C) |
|-----------|------------|---------------|---------------|---------------|----------------|----------------|
| PPS       | 476.3      | 509.1         | 530.6         | 552.8         | 262.3          | 546.1          |
| PPSR$_{0.5}$ | 472.7      | 505.8         | 507.5         | 556.7         | 263.4          | 555.9          |
| PPSR$_1$  | 475.8      | 502.9         | 530.2         | 555.3         | 261.3          | 554.8          |
| PPSSG$_{0.5}$ | 374.5      | 500.8         | 526.2         | 546.8         | 260.1          | 544.8          |
| PPSPG$_1$ | 376.6      | 502.3         | 528.1         | 551.1         | 261.6          | 541.5          |
| PPSPR$_{0.5}$G$_{0.5}$ | 452.9      | 506.1         | 531.5         | 553.4         | 263.0          | 543.4          |
where $T_{5\%}$ and $T_{30\%}$ are the corresponding degradation temperature of 5% and 30% weight loss, respectively. Since the organic antioxidants can be almost degradation before 500 °C, the interference of antioxidants on $T_{5\%}$ and $T_{30\%}$ should be eliminated. From Table 3, it can be observed that the single addition of Revonox 608 and the mixed addition of Revonox 608 and GA-80 can increase the $T_{HRI}$ of composites, while the single addition of GA-80 decreases the $T_{HRI}$ of composites. It needs to pointed out that the rangeability of $T_{HRI}$ is small. This because the decomposition of organic antioxidants, the induced decomposition of PPS and the reaction between decomposition products and PPS all can influence the $T_{5\%}$ and $T_{30\%}$. Therefore, the influence factors are more complex than by adding inorganic nanoparticles [5, 13].

### ii. Dynamic oxidation induction temperature

Dynamic OIT is commonly used to estimate the stability of polymeric materials under oxidation conditions. In general, a higher dynamic OIT means that antioxidants are more efficient for PPS [40, 41]. The dynamic OIT of pure PPS and PPS / antioxidant composites with different contents is shown in Figure 6. It can be observed that pure PPS exhibits a relatively low dynamic OIT at 458.6 °C. Clearly, the addition of Revonox 608 and GA-80 improves the dynamic OIT of PPS. The dynamic OIT of PPSR$_{0.5}$ and PPSR$_{1}$, which is 471.2 °C and 468.4 °C, increase by 12.6 °C and 9.8 °C, respectively. The dynamic OIT of PPSG$_{0.5}$ and PPSG$_{1}$ composites also has an increase of 14.2 °C and 16.2 °C, respectively. The dynamic OIT of PPSR$_{0.5}G_{0.5}$ is 471.8 °C, which is 13.2 °C higher than that of pure PPS. This phenomenon indicates that the starting oxidation temperature of the PPS / antioxidant composites increases by more than 10 °C. This is because GA-80 is a semi-hindered phenol antioxidant, possessing a large number of groups (phenolic hydroxyl groups) with the ability to capture free radicals. When PPSG$_{x}$ is exposed to a high-temperature aerobic environment, the H atoms in the phenolic hydroxyl groups exhibit high activity and can quickly capture the oxygen free radicals around the composites. Moreover, the R free radicals formed by the C–S bond breakage in the PPS macromolecule caused by the oxygen attack can be captured to form a stable RH compound. Revonox 608 is a phosphite antioxidant that can decompose hydroperoxides and capture peroxy radicals formed during the oxidation of PPS. Therefore, the addition of Revonox 608 and GA-80 can limit the corrosion of PPS by oxygen and high temperature, and restrict the oxidative cleavage and oxidative cross-linking of PPS macromolecules to improve the dynamic OIT. It should be noted that PPSG$_{x}$ exhibits a higher dynamic OIT than PPSR$_{x}$.

### iii. Surface element analysis

Pure PPS and PPS / antioxidant composites were oxidized at 220 °C for 120 h under an air atmosphere. X-ray photoelectron spectroscopy (XPS) was used to determine the change in the elemental content and valence state in the PPS macromolecular chains. Figure 7 shows the XPS spectra of pure PPS, PPSR$_{1}$, PPSG$_{1}$, and PPSR$_{0.5}G_{0.5}$ after normalized processing. The presence of oxygen (O), sulfur (S), and carbon (C) is evident from the XPS spectra of pure PPS and PPS-based composites. Because the content of antioxidants is very small, the effect on the element content can be ignored. Before the oxidation treatment, the relative intensity ratio between O and C of pure PPS is 0.46, and that of PPSR$_{1}$, PPSG$_{1}$, and PPSR$_{0.5}G_{0.5}$ is 0.37, 0.40, and 0.41, respectively. After the oxidation treatment, the relative intensity ratio between O and C of pure PPS increases to 0.58, whereas that of...
PPSR1, PPSG1, and PPSR0.5G0.5 reaches 0.43, 0.48, and 0.47 respectively. This phenomenon indicates that S in the PPS macromolecular chains can react with a large number of oxygen atoms during the oxidation treatment of pure PPS, and that the ratio shows an obvious increase. However, the chemical reaction between S and O can be limited by the addition of GA-80 or Revonox 608 to improve the oxidation resistance during the oxidation treatment. Moreover, the addition of antioxidants can restrict the oxidation of PPS during melt blending.

To clarify the effect of antioxidants on the valence state change of S, the contents of different sulfur forms were characterized by a high-resolution scan of S2p. The fitting curves and relative contents of the different sulfur forms are shown in figure 8 and table 4. As shown in figure 8, S in the PPS macromolecular chains mainly exhibits three forms of C–S–C bond, sulfoxide group (–SO–), and sulfone group (–SO2–) [42–44]. According to the results of curves fitting, the C–S–C bond is the main form of S in pure PPS fibers before the treatment, and a part of S is present in the form of sulfoxide and sulfone. This means that the part of S can be oxidized during melt blending. Furthermore, the content of the C–S–C bond decreases from 85.6% to 66.3% after oxidation treatment, whereas the content of sulfone increases and the sulfoxide disappears, as shown in figure 8b and table 4. This phenomenon indicates that the majority of PPS macromolecular chains are first fractured, and the S atoms are then oxidized into sulfone groups during the oxidation treatment. The original sulfoxide groups in the PPS macromolecular chains are also oxidized to sulfone.

For PPS-based composites, S is mainly in the form of C–S–C bonds and sulfone groups (–SO2–), as shown in figure 8 and table 4. The contents of the C–S–C bond for PPSR1, PPSG1, and PPSR0.5G0.5 before treatment are 91.5%, 88.8%, and 95.2%, respectively, which are higher than that of pure PPS. This result shows that adding antioxidants can limit the oxidation of S in the PPS macromolecular chains during melt blending. After the oxidation treatment, the content of the C–S–C bond for PPSG1 decreases from 88.8% to 77.5%, and the sulfone group increases from 11.2% to 22.3%. This phenomenon also indicates that the oxidation reaction of the PPS macromolecular chains in PPSG1 is similar to that of pure PPS. However, the content loss of the C–S–C bond and the content growth of the sulfone group in PPSG1 are much lower than that of pure PPS after oxidation treatment, indicating that GA-80 can retard the oxidation cleavage of the PPS macromolecule and prevent the S atoms from oxidizing to sulfone during the oxidation treatment. When PPSBGx is oxidized under high temperature and oxygen conditions, the C–S bonds in the macromolecular chains are vulnerable to oxiradicals.
and break first to generate \( R^\cdot \) free radicals due to the low bond energy. The activity of \( R^\cdot \) free radicals is very high, and they easily oxidize to form sulfone groups, causing the molecular chains to cross-link \([30–32]\). The phenolic hydroxyl groups present in GA-80 molecules can provide H atoms to combine with oxyradicals and \( R^\cdot \) free radicals to form stable compounds. Therefore, the addition of GA-80 can terminate the chain reaction of oxidation to protect the C–S bond and restrict the cross-linking of molecular chains.

Figure 8. XPS fitting curves of the S_{2p} for pure PPS and PPSR_{1}, PPSG_{1} and PPSR_{0.5}G_{0.5} composites before and after oxidation treatment. (a) pure PPS, (c) PPSR_{1}, (e) PPSG_{1} and (g) PPSR_{0.5}G_{0.5} before treatment; (b) pure PPS, (d) PPSR_{1}, (f) PPSG_{1} and (h) PPSR_{0.5}G_{0.5} after treatment.
For PPSR1 and PPSR0.5G0.5 composites, it was found that the C–S–C bond and the sulfone group contents showed the same varying tendency as PPSG1. However, the variation range of the functional group content was much smaller than that of PPSG1 composites. This result shows that PPS macromolecules in PPSR1 and PPSR0.5G0.5 can be better protected from oxidation compared to PPSG1. The \( \cdot \)\(^{30} \)\(^{32} \) free radicals generated during the oxidation of PPS can be further oxidized to form hydroperoxides, which can generate more active free radicals \([30–32]\). Revonox 608 decomposes hydroperoxides into inactive stable substances and inhibits free radical chain reactions. Moreover, it can also react with oxygen and generate active free radicals at high temperatures to protect the C–S bond and terminate the chain reaction \([30–32]\). Table 4 also shows that the content of C–S–C in PPSR0.5G0.5 is higher than that in PPSR1 and PPSG1 before the oxidation treatment, indicating that the mixed use of GA-80 and Revonox 608 can provide yield performance than their individual use during the melt blending. After the oxidation treatment, the content loss of the C–S–C bond and the content growth of sulfone group in PPSR0.5G0.5 composites are substantially lower than those in PPSG1, but slightly higher than those in PPSR1. This phenomenon indicates that the mixed use of GA-80 and Revonox 608 can enhance the oxidation resistance better than the addition of only GA-80, and the synergistic effect is not so obvious compared with the addition of only Revonox 608. Overall, the addition of antioxidants can effectively prevent C–S–C bond breakage and sulfone formation, and enhance the oxidative stability of PPS.

### 4. Conclusions

Both GA–80 and Revonox 608 exhibit good thermal stability, which is suitable for the melt manufacture of PPS. GA-80 shows excellent dispersibility and compatibility with the PPS matrix, and a slight agglomeration of Revonox 608 in the PPS matrix can be observed. Moreover, Revonox 608 can act as a heterogeneous nucleation agent to promote crystallization, and the addition of GA-80 decreases the crystallization temperature and

| Samples (before treatment) | Number | Position (eV) | Relative content (%) | Assignments |
|----------------------------|--------|--------------|----------------------|-------------|
| pure PPS before treatment  | 1–1    | 163.2        | 85.6                 | C–S         |
|                            | 1–2    | 164.4        |                      |             |
|                            | 2–1    | 165.6        | 2.3                  | –SO–        |
|                            | 3–1    | 168.2        | 12.1                 | –SO\(_2\)–  |
|                            | 3–2    | 169.7        |                      |             |
| pure PPS after treatment   | 1–1    | 163.2        | 66.3                 | C–S         |
|                            | 1–2    | 164.5        |                      |             |
|                            | 3–1    | 168.5        | 33.7                 | –SO\(_2\)–  |
|                            | 3–2    | 169.9        |                      |             |
| PPSR\(_1\) before treatment| 1–1    | 163.2        | 91.5                 | C–S         |
|                            | 1–2    | 164.4        |                      |             |
|                            | 3–1    | 167.6        | 8.5                  | –SO\(_2\)–  |
|                            | 3–2    | 168.9        |                      |             |
| PPSR\(_1\) after treatment | 1–1    | 163.2        | 90.2                 | C–S         |
|                            | 1–2    | 164.5        |                      |             |
|                            | 3–1    | 168.4        | 9.8                  | –SO\(_2\)–  |
|                            | 3–2    | 169.6        |                      |             |
| PPSG\(_1\) before treatment| 1–1    | 163.3        | 88.8                 | C–S         |
|                            | 1–2    | 164.4        |                      |             |
|                            | 3–1    | 167.9        | 11.2                 | –SO\(_2\)–  |
|                            | 3–2    | 169.1        |                      |             |
| PPSG\(_1\) after treatment | 1–1    | 163.3        | 77.5                 | C–S         |
|                            | 1–2    | 164.5        |                      |             |
|                            | 3–1    | 168.6        | 22.5                 | –SO\(_2\)–  |
|                            | 3–2    | 169.9        |                      |             |
| PPSR\(_0.5\),G\(_0.5\) before treatment | 1–1    | 163.2        | 95.2                 | C–S         |
|                            | 1–2    | 164.4        |                      |             |
|                            | 3–1    | 168.8        | 4.8                  | –SO\(_2\)–  |
|                            | 3–2    | 170.5        |                      |             |
| PPSR\(_0.5\),G\(_0.5\) after treatment | 1–1    | 163.2        | 92.6                 | C–S         |
|                            | 1–2    | 164.4        |                      |             |
|                            | 3–1    | 168.2        | 7.4                  | –SO\(_2\)–  |
|                            | 3–2    | 170.0        |                      |             |
crystallinity and increases the degree of supercooling of PPS. Moreover, the thermal-oxidative stability of PPS can be improved by adding GA-80 and Revonox 608. The dynamic OIT of PPS can increase by more than 10 °C due to the addition of antioxidants, this can be attributed to the limiting of oxidative corrosion by oxygen and high temperature. During the thermal oxygen treatment, both GA-80 and Revonox 608 can protect the C–S–C bond in the PPS macromolecule from being broken and hinder the formation of sulfone groups.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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