

Research Article

Intrinsically Noncombustible Thermosets from Sulfur-Containing Epoxy Resin and Benzoxazines: Evaluation of Thermal and Mechanical Properties

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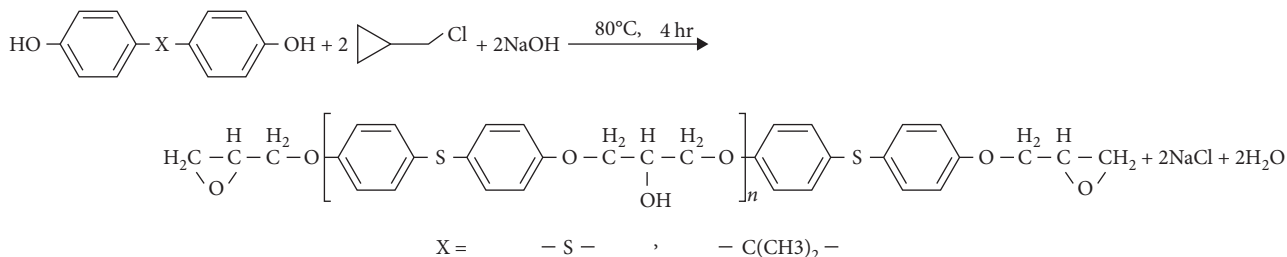
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Benzoxazine (BZ)-epoxy copolymers exhibit favorable mechanical properties, but their thermal and flame-retardant characteristics are impaired at high epoxy fractions. Here, we report a new type of sulfur-containing epoxy resin (EPS), which we synthesized using 4,4'-thiobisphenol (TBP) instead of bisphenol A (BA) and then blended with three sulfur-containing BZs (TBP-a, TBP-fa, and TBP-tma). The polymerization behavior of the resins was analyzed using Fourier transform infrared spectroscopy and differential scanning calorimetry for determining the optimal curing procedure. This analysis revealed that the oxazine and epoxy rings undergo ring-opening and cross-linking reactions at the same time and that double-substituted structures originating from the furan and thiophene rings appeared during the curing process. Thermogravimetric analysis showed that the addition of EPS increased the initial decomposition temperature by hindering the formation of double-substituted structures. The char yield at 800°C decreased owing to the unstable C–O–C–O groups derived from the ring-opening of EPS. To prepare the self-extinguishing copolymers with a char yield of 24%, a smaller quantity of BZ was needed for the EPS-based blends than for the BA-based ones. The heat release capacities—measured using micro-combustion calorimetry—of all copolymers except TBP-a/EPS were less than 300 J/g·K, demonstrating that the presence of thioether bonds and double-substituted structures resulted in excellent flame retardancy. The TBP-fa/EPS copolymer also exhibited excellent flame retardancy in cone calorimeter measurement. Finally, the glass transition temperature of the TBP-fa/EPS copolymer at a ratio of 5:5 (w/w) reached as high as 289°C. A TBP-fa/EPS copolymer with an epoxy content of 70% had nearly the same storage modulus (2,206 MPa) at 50°C as poly(BA-a) and thus similar mechanical properties. In summary, BZ-epoxy copolymers prepared from sulfur-containing epoxy combine the advantages of the constituent components and extend their areas of application.

1. Introduction

Polybenzoxazines are a special class of phenolic resin that have attracted attention because of their useful properties, such as near-zero shrinkage during polymerization, good resistance to chemicals, a high glass transition temperature (T_g), and excellent thermal stability and mechanical properties. They find applications in a wide range of areas, including the aerospace and automotive industries, oil and gas exploitation, and electronic manufacturing. Despite these advantages, polybenzoxazines have serious drawbacks, such as high polymerization temperature, poor processability at room temperature, and brittleness, which limit their use in many high-performance fields [1–5].

To address these problems, researchers have modified benzoxazine (BZ) resins using different methods, such as designing molecular structures by choosing particular phenols and amines [6–9], preparing composites with functional solid materials [10–13], and blending modification. The most common method is blending modification, which is usually achieved by adding rubber [14–17], polyurethane [18, 19], phenolic resin [20], maleimide [21, 22], and epoxy resin (EPS) [23]. The copolymerization products of this process usually exhibit superior properties to their parent substances. Polybenzoxazines' low crosslink network structures in comparison with ordinary thermosetting resins with similar properties may be tightened by copolymerization with an epoxy to achieve a



SCHEME 1: Synthesis of sulfur-containing and bisphenol A-based epoxy resins.

higher crosslink density. This is because phenolic groups, which are produced by the ring-opening polymerization of BZ, react with EPSs at elevated temperatures [24, 25]. Ishida and Allen [26] found that the addition of epoxy to the polybenzoxazine network increased the crosslink density and influenced its mechanical properties. Specifically, they noted an increase in glass-transition temperature, flexural stress, and flexural strain at break and a slight decrease in stiffness. Zhang et al. [27] found that the temperature at 5% weight loss ($T_{5\%}$) increased with increasing epoxy fraction, which improved the thermal stability, albeit with a reduction in char yield. He et al. [28] demonstrated that the addition of siloxane-containing EPS eliminated the high brittleness of polybenzoxazines and their poor adhesion properties. Liquid epoxy can be used as an active diluent of BZ in its typical solid powder form, which is beneficial for resin processing [29]. However, the addition of epoxy slows the polymerization reaction and, in general, slightly increases the exothermic peak temperature [23, 27, 30]. Nowadays, epoxy monomers have developed in the direction of bio-based with superior heat resistance [31, 32], the same as BZs [4], so homopolymer thermosets from them combine the advantages of the constituent components and extend their areas of application.

Because of the great flexibility in the design of the molecular structure of the BZ monomer, flame-retardant elements (such as phosphorus or sulfur) can be incorporated into the molecular structure of the polybenzoxazines to further improve their thermal stability and flame-retardant performance [33–35]. In our previous work [36, 37], we found that polybenzoxazines based on 4,4'-thiobisphenol (TBP) had superior thermal performance to that of common bisphenol A (BA)-based BZs, which we attributed to the higher structural stability imparted by the thioether bonds. We inferred that the derived thioether bond could enhance the thermal stability and flame retardancy of EPSs. In this study, we used TBP to synthesize an EPS, which we then blended with three sulfur-containing BZs to obtain copolymers. The polymerization behavior, thermal stability, flame retardancy, and mechanical properties of BZ/EPS blends with different epoxy contents were studied. We expect that the results will guide the future manufacturing of high-performance thermosets.

2. Experimental Details

2.1. Materials. TBP (98%), BA (98%), paraformaldehyde (96%), aniline (99%), furfurylamine (99%), 2-thiophenemethylamine (99%), and epichlorohydrin (99%) from Shanghai Macklin

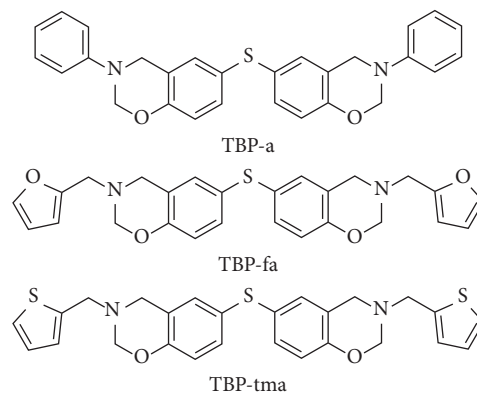


FIGURE 1: Structures of three sulfur-containing benzoxazine monomers.

Biochemical Co., Ltd. were used without further purification. Toluene, acetone, anhydrous ethanol, sodium hydroxide, and hydrochloric acid were obtained from Titan Chemicals.

2.2. Synthesis of Sulfur-Containing Epoxy Resins (EPSs). TBP (0.020 mol, 4.36 g) and epichlorohydrin (0.200 mol, 18.50 g) were added to a 50 mL round-bottom flask. The mixture was heated to 75°C with constant stirring until the TBP had completely dissolved. After that, the temperature was lowered to 70°C. Then, NaOH solution (1 M) was slowly added and stirred for 4 hr at 80°C. The crude product was dissolved in 20 mL of toluene and washed with warm water five times. The final product—liquid EPS—was obtained by drying the organic layer with air overnight and then placing it in a vacuum oven for 24 hr. BA-based epoxy resin (EPBA) was synthesized from BA and epichlorohydrin (Scheme 1).

2.3. Preparation of BZ/EPS Copolymers. BZ/EPS copolymers were prepared by mixing sulfur-containing BZ monomers with sulfur-containing EPS in various weight ratios. The BZ/EPS copolymers were cured at 180°C, 200°C, 220°C, 240°C, and 250°C for 1 hr each. The molecular structures of the three sulfur-containing BZ monomers synthesized are shown in Figure 1. These were synthesized according to the procedures in our previous work.

2.4. Measurements. The epoxy values of EPS and EPBA were determined according to GB/T 1677-2008, 'Determinating the epoxy value of plasticizers (the hydrochloric acid-acetone method)'. Fourier transform infrared (FTIR) spectra were

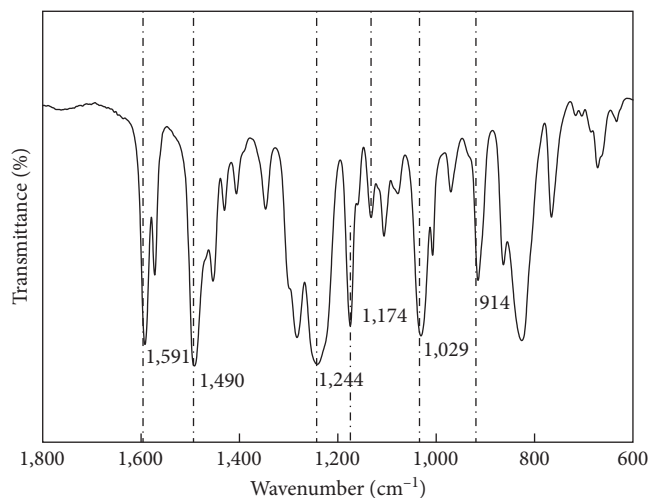


FIGURE 2: Fourier transform infrared (FTIR) spectra of sulfur-containing epoxy resins (EPS).

obtained using a Nicolet6700 FTIR spectrometer, with a wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. For differential scanning calorimetry (DSC; model 2920 DSC, TA Instruments), all samples were loaded on a hermetic aluminum pan and heated from $50\text{ to }300^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a flow rate of $60\text{ mL}/\text{min}$. For thermogravimetric analysis (TGA; TGA Q500, TA Instruments), samples were heated from 50°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a flow rate of $60\text{ mL}/\text{min}$. The heat release rate (HRR) and total heat release (THR) were measured using a microscale combustion calorimeter (MCC; GOVMARK MCC-2) with a heating rate of $1^\circ\text{C}/\text{s}$ to 800°C in a nitrogen flow of $80\text{ mL}/\text{min}$; the pyrolysis products were then delivered into a 900°C combustion furnace under an oxygen atmosphere at a flow rate of $80\text{ mL}/\text{min}$. According to the standard ISO 5660, conical calorimetric analysis was completed on a Vouch 6810 cone calorimeter with a sample dimension of $100 \times 100 \times 3\text{ mm}^3$. The heat flux used was $50\text{ kW}/\text{m}^2$. Dynamic mechanical analysis (DMA; TA model DMA 2980) was performed with sample dimensions of $60\text{ mm} \times 12\text{ mm} \times 3\text{ mm}$. The storage moduli E_0 and $\tan \delta$ of the samples were determined by sweeping the temperature from 50°C to 325°C at a rate of $5^\circ\text{C}/\text{min}$ and a frequency of 1 Hz . The test was performed in bending mode with an amplitude of 5 mm .

3. Results and Discussion

3.1. Analysis of the Copolymerization Process of EPS and BZ. The FTIR spectrum of EPS (Figure 2) features a strong absorption peak at 914 cm^{-1} , which we assign to the epoxy group, and peaks at $1,029$ and $1,244\text{ cm}^{-1}$, which we assign to C–O–C. The absorption peak for C–S is observed at $1,174\text{ cm}^{-1}$ [38–40]. These results indicate that the synthesized product was a sulfur-containing EPS. The epoxy value of the copolymer was 0.476 , which was close to that of the EPBA (0.468).

Figure 3 shows the FTIR spectra of copolymers with a ratio of BZ:EPS = 1 : 1 (w/w) after curing for 1 hr at different

temperatures. For all copolymers, the absorption peak (914 cm^{-1}) of the epoxy group gradually decreased with increasing temperature and disappeared at 240°C . The oxazine rings of TBP-a/EPS and TBP-tma/EPS appeared at 930 cm^{-1} and that of TBP-fa/EPS appeared at 940 cm^{-1} . With increasing temperature, the intensity of this peak decreased, indicating the opening of the oxazine rings; this peak disappeared when the temperature reached 240°C . The disappearance of the epoxy ring and oxazine ring proves that they open simultaneously during curing and that cross-linking occurs (Scheme 2). The peak at $1,461\text{ cm}^{-1}$, which represents tetra-substituted benzene, increased with temperature, whereas the peak at $1,479\text{ cm}^{-1}$, which represents tri-substituted benzene, weakened. This indicates that the tri-substituted phenol rings participate in the cross-linking reaction during the ring-opening of BZ, resulting in tetra-substituted phenol rings. Although the curing process of the copolymers involves ring-opening and cross-linking of the oxazine and epoxy rings, the final temperature of ring-opening was found to be lower for the oxazine ring than for the epoxy ring. In Figures 3(b) and 3(c), the peak at $1,630\text{ cm}^{-1}$, which we attribute to the furan ring and thiophene ring, broadened during the heating process, which demonstrates the formation of the double-substituted five-membered ring. In summary, the copolymerization of TBP-fa/EPS and TBP-tma/EPS involves ring-opening of the oxazine and epoxy rings, as well as cross-linking of the furan and thiophene rings in cross-linking reactions, to form double-substituted structures.

The DSC curves of the copolymers are shown in Figure 4. For TBP-a/EPS and TBP-fa/EPS, the melting point decreased with increasing epoxy content. When the EPS content was 70% , the resins were close to their liquid state, which is why the melting points were not determined. The TBP-tma/EPS blends were solid, and melting points can be observed in DSC curves even when the TBP-tma content was 70% . For all BZ/EPS blends, the initial polymerization temperatures decreased with increasing EPS content. Thus, the decrease in the initial polymerization temperature is due to the addition of epoxy groups. The active phenol groups in BZ promote the ring-opening of epoxy groups. This promotes the ring-opening of oxazine, which decreases the onset temperature. For most BZ/EPS blends, the end polymerization temperature increased. The increase in the final polymerization temperatures is due to the tight cross-linked structure of the copolymers.

With the exception of TBP-fa/EPS, there is only one polymerization peak in each DSC curve. This proves that the ring-opening of the epoxy group and oxazine occurs at the same time [41]. However, at a weight ratio of TBP-fa:EPS = $5 : 5$, the polymerization peak of the copolymer split. This implies that furan participates in the cross-linking reaction. The oxazine ring opens first to crosslink with the epoxy, and later, the reactive furan ring participates in the cross-linking reaction [42].

Table 1 lists the DSC data for all resin blends. The maximum polymerization temperatures of the three BZ/EPS

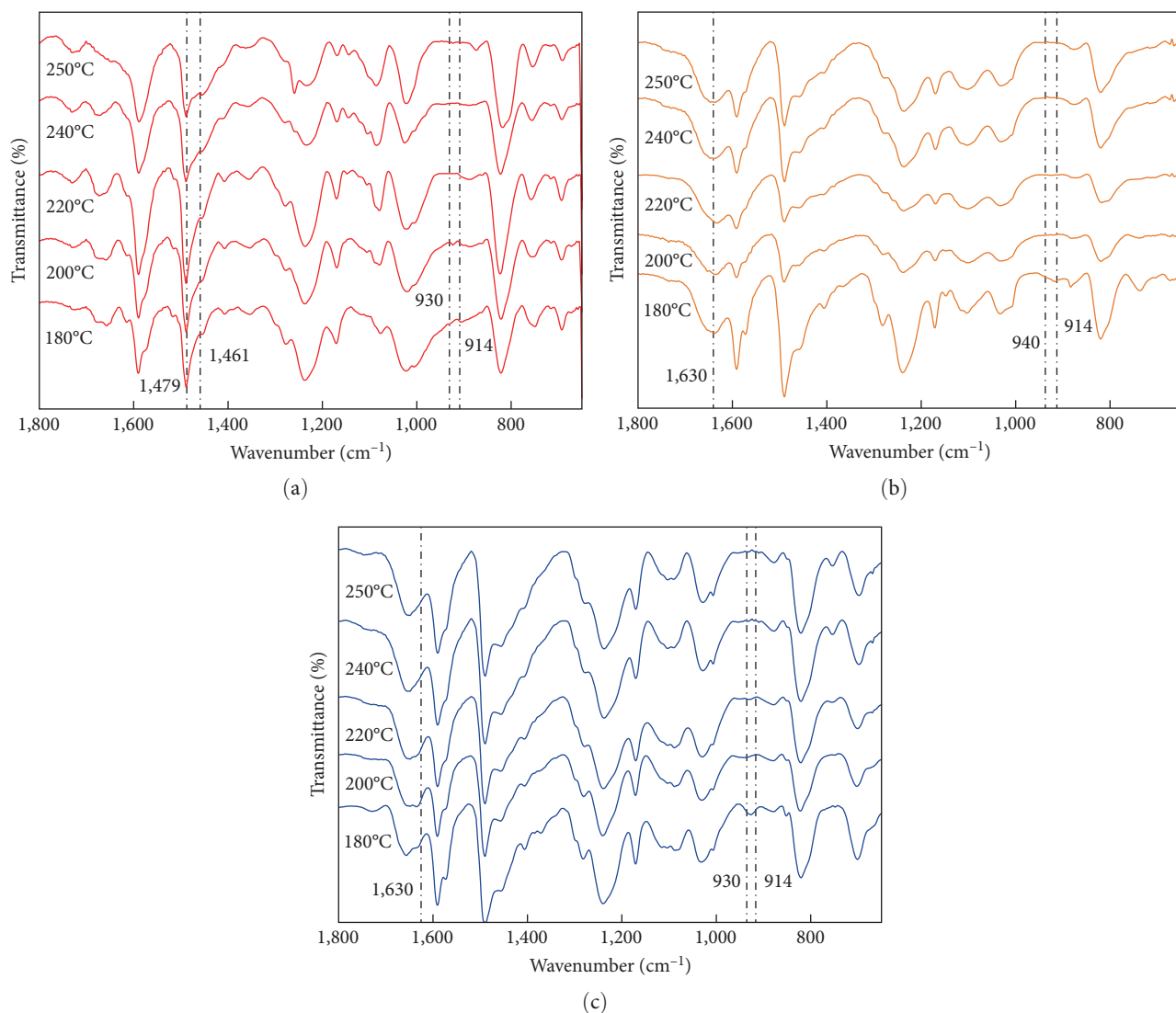
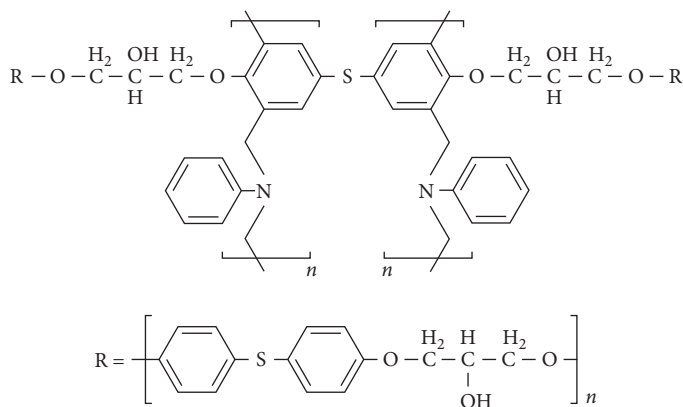


FIGURE 3: FTIR spectra of blend resins (a) TBP-a/EPS, (b) TBP-fa/EPS, and (c) TBP-tma/EPS.



SCHEME 2: The network structure of copolymers.

blends with three different BZ:EPS ratios were slightly lower than those of the corresponding pure BZs. However, all blends had the same maximum polymerization temperature, with only a 1°C difference among them. The polymerization

enthalpies of the blends were also considerably greater than those of the neat BZs. These results indicate that small amounts of EPS can catalyze the ring-opening of oxazine and the cross-linking curing process.

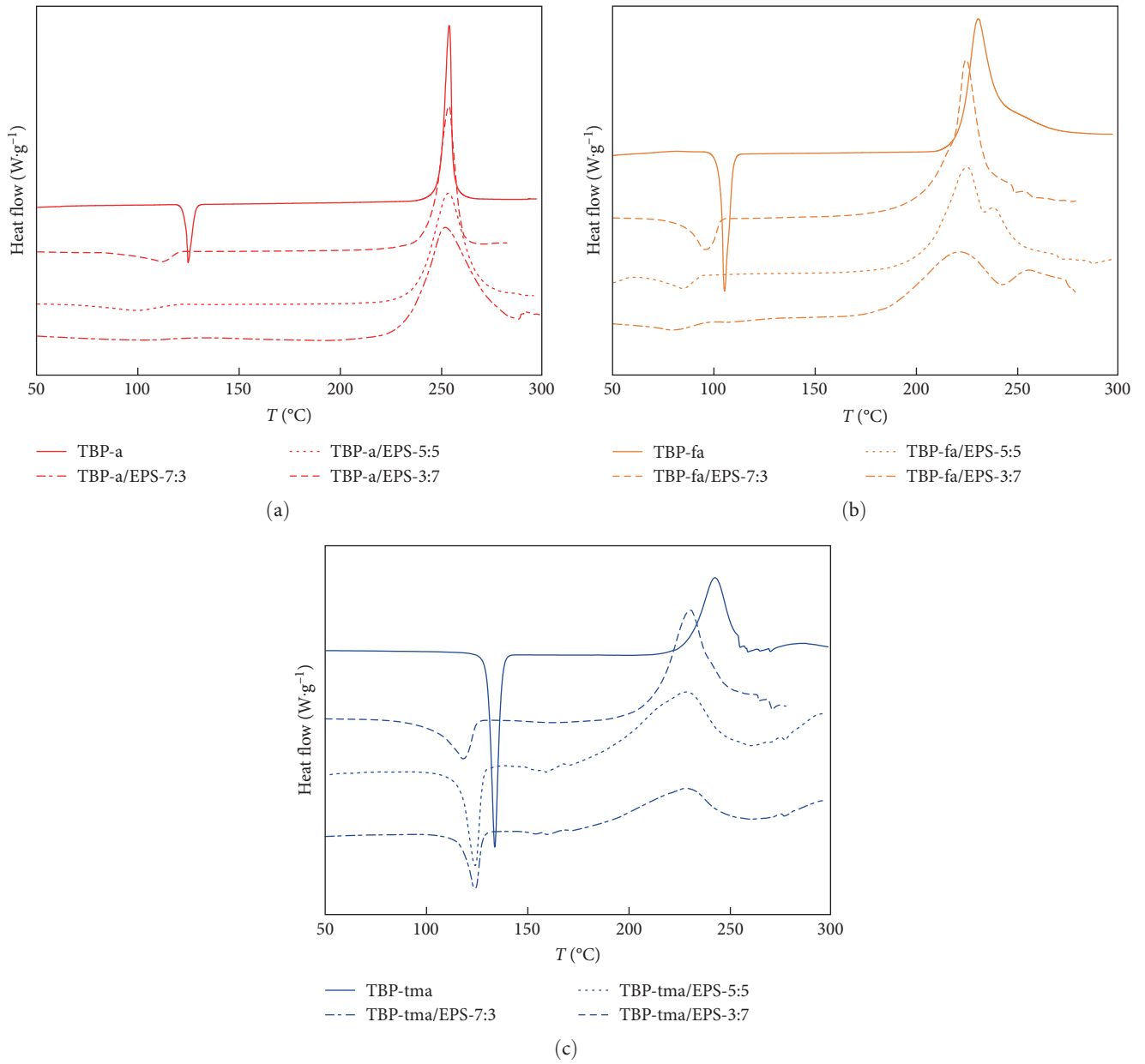


FIGURE 4: Differential scanning calorimetry curves of blend resins (a) TBP-a/EPs, (b) TBP-fa/EPs, and (c) TBP-tma/EPs.

TABLE 1: Differential scanning calorimetry data of blend resins.

	w (BZ): w (EPs)	T_{onset} (°C)	T_{max} (°C)	T_{offset} (°C)	ΔH (J·g ⁻¹)
TBP-a/EPs	10:0	237	254	261	291
	7:3	220	250	265	361
	5:5	218	251	280	325
	3:7	210	251	285	309
TBP-fa/EPs	10:0	216	230	244	309
	7:3	175	223	251	398
	5:5	174	224	260	353
	3:7	163	224	275	338
TBP-tma/EPs	10:0	218	240	253	104
	7:3	185	230	259	211
	5:5	170	229	260	189
	3:7	168	230	263	178

DSC, differential scanning calorimetry; TBP, 4,4'-thiobisphenol; EPs, epoxy resin; BZ, benzoxazine.

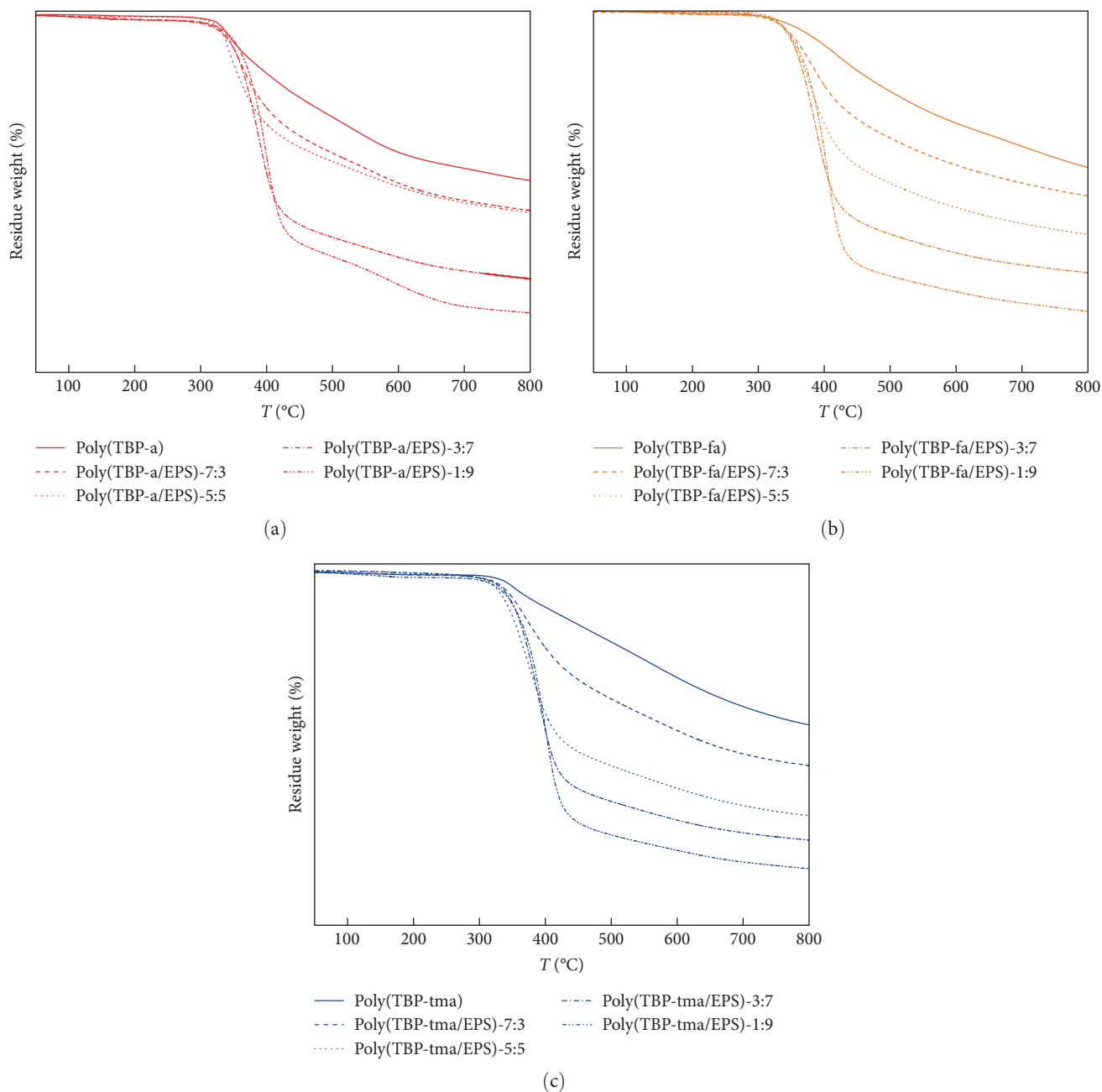


FIGURE 5: Thermogravimetric analysis (TGA) curves of blend resins (a) TBP-a/EPS, (b) TBP-fa/EPS, and (c) TBP-tma/EPS.

3.2. Thermal Stability and Flame-Retardant Properties of the Sulfur-Containing Copolymers. The TGA curves of the BZ/EPS copolymers are shown in Figure 5. The three pure polybenzoxazines demonstrated the best thermal stability. With the addition of EPS, the char yields gradually decrease.

The initial temperatures of decomposition (T_{int}) are shown in Table 2. The addition of EPS increased the T_{int} of the TBP-a/EPS copolymers. However, the T_{int} of the TBP-fa/EPS and TBP-tma/EPS copolymers initially decreased and then rose with increasing EPS content. This demonstrates that the introduction of epoxy groups blocked some of the originally formed double-substituted structures. By adding

EPS, the 10% weight-loss temperature ($T_{10\%}$) and char yields decreased. For BZ:EPS = 1:9 (w/w), the $T_{10\%}$ of the copolymers based on TBP-a, TBP-fa, and TBP-tma decreased by 8°C, 78°C, and 54°C, respectively, compared with pure polybenzoxazines; the char yields decreased by 28%, 31%, and 31%, respectively. The flexible $-C-O-C-C-O-$ groups formed by epoxy groups extended the main chain of the copolymer resins. This, in turn, decreased the effective crosslink density, making it easier to decompose and leading to a decrease in the char yield [35, 41, 43].

The limiting oxygen index (LOI) is a commonly used value to quantify the flame retardancy of polymers. It can

TABLE 2: Thermogravimetric analysis data of blend resins.

	w (BZ): w (EPS)	T_{int} ($^{\circ}\text{C}$)	$T_{10\%}$ ($^{\circ}\text{C}$)	Char yield, %	LOI
Poly(TBP-a/EPS)	10:0	305	373	63	43
	7:3	306	361	58	41
	5:5	308	365	58	41
	3:7	310	363	43	35
	1:9	312	365	35	32
Poly(TBP-fa/EPS)	10:0	325	446	68	45
	7:3	315	375	63	43
	5:5	315	363	58	41
	3:7	318	366	45	36
	1:9	319	368	37	32
Poly(TBP-tma/EPS)	10:0	314	425	66	44
	7:3	306	375	60	41
	5:5	308	364	50	38
	3:7	310	369	45	36
	1:9	311	371	35	32

TBP, 4,4'-thiobisphenol; EPS, epoxy resin; BZ, benzoxazine; LOI, limiting oxygen index.

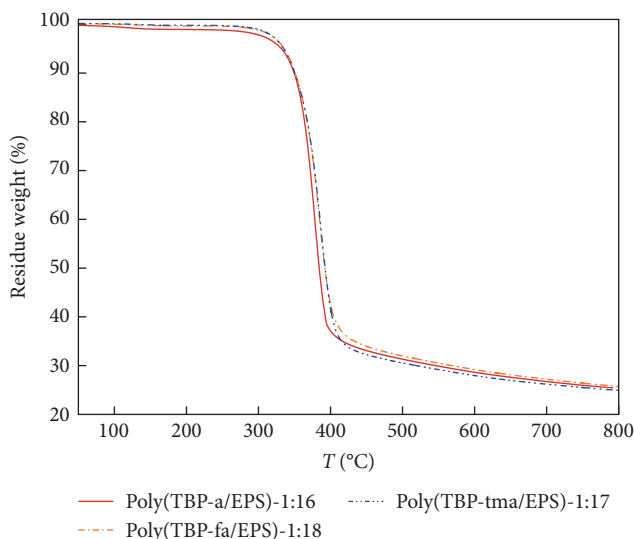


FIGURE 6: TGA curves of blend resins (CR = 24%, LOI = 27).

be calculated by the van Krevelen equation [44]:

$$\text{LOI} (\%) = 0.4\text{CR} + 17.5, \quad (1)$$

where CR is the char yield (%) at 800°C in a nitrogen atmosphere.

All BZ/EPS copolymers had LOIs greater than 27, which is the critical LOI for self-extinguishing behavior. Thus, although the addition of EPS reduces the char yields, the BZ/EPS copolymers are self-extinguishing and can be used as flame-retardant materials. When the ratios of copolymers were TBP-a:EPS = 1:16 (w/w), TBP-fa:EPS = 1:18 (w/w), and TBP-tma:EPS = 1:17 (w/w), the char yields were all 24% (Figure 6), which corresponds to the critical LOI. We also mixed EPBA with TBP-fa, whose the thermal stability is the best among the three polybenzoxazines, for comparison

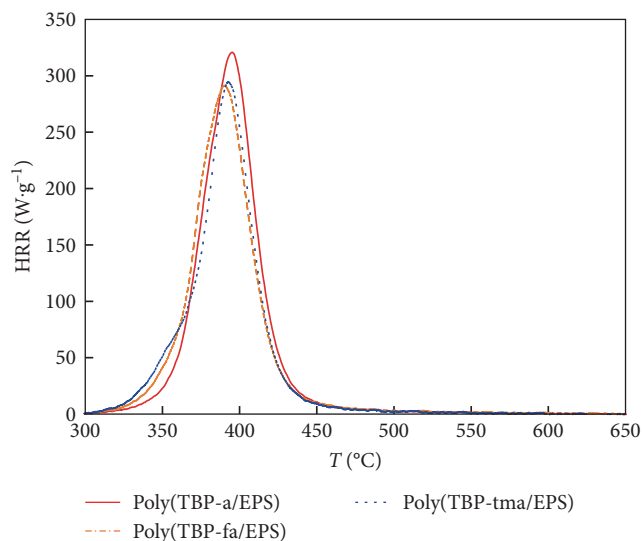


FIGURE 7: Microscale combustion calorimeter curves of copolymers (LOI = 27).

with the BZ/EPS copolymers. The TBP-fa/EPBA copolymer with a ratio of TBP-fa:EPBA = 1:15 (w/w) also had a char yield of 24% (Figure S1), while EPBA was verified with the FTIR spectrum (Figure S2).

The combustibility of the BZ/EP copolymers was evaluated by the MCC. The MCC results are shown in Figure 7 and summarized in Table 3. Only one exothermic peak in the curves was observed for the three sulfur-containing copolymers. The exothermic temperature ranges were mostly within 350°C–450°C, and the three T_{PHRR} values (peak temperature of HRR) were similar. There are two exothermic peaks (390°C and 430°C) in the MCC curve of the TBP-fa/EPBA copolymer (Figure S3). We attribute the first peak, which approaches the T_{PHRR} of the copolymers, to the breaking of phenolic groups during degradation. We attribute the peak at 430°C to the burning of a large number of

TABLE 3: Microscale combustion calorimeter data of copolymers (LOI = 27).

	HRC ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)	PHRR ($\text{w}\cdot\text{g}^{-1}$)	THR ($\text{kJ}\cdot\text{g}^{-1}$)	T_{PHRR} ($^{\circ}\text{C}$)
Poly(TBP-a/EPs)	320.6	319.2	14.1	395
Poly(TBP-fa/EPs)	292.5	291.3	13.6	390
Poly(TBP-tma/EPs)	293.4	294.2	13.1	392

TBP, 4,4'-thiobisphenol; EPs, epoxy resin; THR, total heat release; LOI, limiting oxygen index; HRC, heat release capacity.

BA main chains in the cross-linked network formed by the BA epoxy.

Materials with an heat release capacity (HRC) less than $300 \text{ J/g}\cdot\text{K}$ are considered to be self-extinguishing and to have excellent flame retardancy [33, 45]. The HRC values of three copolymers were less than $300 \text{ J/g}\cdot\text{K}$. Although the LOI values of four copolymers were 27, the TBP-a/EPs copolymer had a higher HRC value ($320.6 \text{ J/g}\cdot\text{K}$) and the TBP-fa/EPBA had a lower HRC value of $271 \text{ J/g}\cdot\text{K}$ (Table S1). Thus, the calculated LOIs based on the char yield lead to an inaccurate conclusion about the flame-retardant behavior of polymers. We attribute the higher HRC of TBP-a/EPs to the aniline group in TBP-a, which is less stable than the thiophene and furan groups and degrades at 350°C – 450°C . The lower HRC of TBP-fa/EPBA is due to the high ratio of BZ in the blends and the cross-linking system formed by furan rings.

The THR values of the copolymers of the sulfur-containing EPs were lower than that of the BA epoxy copolymer, which results from the higher temperature for the cleavage of the thioether bonds. Moreover, the S–C bonds generated by the cleavage further hinder combustion and reduce the amount of heat released. This also explains the narrow exothermic ranges of the sulfur-containing epoxy copolymers.

Furthermore, to explore the combustion characteristics of double substitution structures in the combustion process, conical calorimetric analysis was performed on the three sulfur-containing epoxy copolymers. Figure 8 presents the curves of HRR, THR, and total smoke production (TSP) versus time. In addition to these parameters, the longest time to ignition (TTI), the maximum average heat release rate (MARHE) of materials, and the smoke release rate (TSR) were recorded in Table 4. The poly(TBP-fa/EPs) showed the longest TTI (33 s) and gradually decreased along the sort of poly(TBP-fa/EPs) > poly(TBP-tma/EPs) > poly(TBP-a/EPs). The smaller PHRR reflects the better flame retardant property [46, 47], while there was a decreasing trend of poly(TBP-fa/EPs) < poly(TBP-tma/EPs) < poly(TBP-a/EPs). Besides, the THR, MARHE, TSR, and TSP also followed the same order. These results showed that double substitution structures based on two aromatic five-membered rings can efficiently restrain the heat release of copolymers. However, poly(TBP-tma/EPs) showed lower PHRR with higher THR, TSR, and TSP than poly(TBP-a/EPs), which proved that the thiophene ring burns violently during the final combustion process. Among all the copolymers, poly(TBP-fa/EPs) showed the best flame retardancy and smoke suppression performance simultaneously, which can effectively reduce fire hazards due to the introduction of furan ring.

In summary, these results demonstrate that the sulfur-containing EPs have excellent flame-retardant performance

owing to the formation of cross-linking structures based on the main chain of diphenyl sulfide during polymerization and the formation of S–C bonds based on the cleavage of C–S–C. The double substitution structures also contributed to the flame retardancy of the copolymers prepared in this work.

3.3. Thermomechanical Properties of the Sulfur-Containing Copolymers. We expected that the BZ/EPs copolymers would have good mechanical properties because of the high cross-linking density of epoxy and BZ. We selected the TBP-fa/EPs copolymer, which had the best thermal performance, for mechanical testing.

The DMA curves of the copolymers at different ratios of TBP-fa and EPs are shown in Figure 9, where E' is the storage modulus, E'' is the loss modulus, and $\tan \delta$ is the loss factor. The E' of poly(TBP-fa) at 50°C was measured to be 2521 MPa . With an increasing ratio of sulfur-containing EPs, the E' of the copolymers decreased, reaching 2206 MPa at 70% epoxy. In polybenzoxazines, oxygen atoms in phenolic hydroxyl groups and nitrogen atoms participate in intermolecular and intramolecular hydrogen bonding, which results in their high E' [48]. In BZ/EP copolymers, the epoxy groups react with the phenolic hydroxyl group to reduce the extent of hydrogen bonding. Moreover, the rigidity in the glass state is related to the resistance of the movement of the molecular segments [27]. The cross-linking segments of the EPs cannot effectively store the modulus, resulting in a lower E' . Nevertheless, the copolymer with TBP-fa:EPs = 3 : 7 (w/w) had an E' of 2206 MPa . This was the smallest value among the three copolymers, but it was equivalent to that of poly(BA-a) (2200 MPa) [26] and greater than that of poly(TBP-fa/EPBA) (1949 MPa), as shown in Table S2. These results demonstrate that copolymers based on sulfur-containing EPs have good mechanical properties.

The T_g was determined according to the peak of the $\tan \delta$ curve. For TBP-fa:EPs = 5 : 5 (w/w), the T_g was 289°C . At a ratio of TBP-fa:EPs = 3 : 7 (w/w), the T_g decreased to 273°C but was still superior to that of poly(TBP-fa) (265°C). The phenolic hydroxyl groups generated by the ring-opening of oxazine functioned as catalysts and were also consumed as reactants. There was an insufficient number of hydroxyl groups to react with the epoxy because of the high epoxy content. The remaining EPs acted as a plasticizer, lowering the T_g and impairing the mechanical properties of the copolymers. The T_g of the TBP-fa/EPBA copolymers followed the same trend with increasing EPBA content. At a weight ratio of 3 : 7, the T_g of TBP-fa/EPBA was 239°C , which was lower than that of neat polybenzoxazine; this is in contrast with the aforementioned results for TBP-fa/EPs. These results

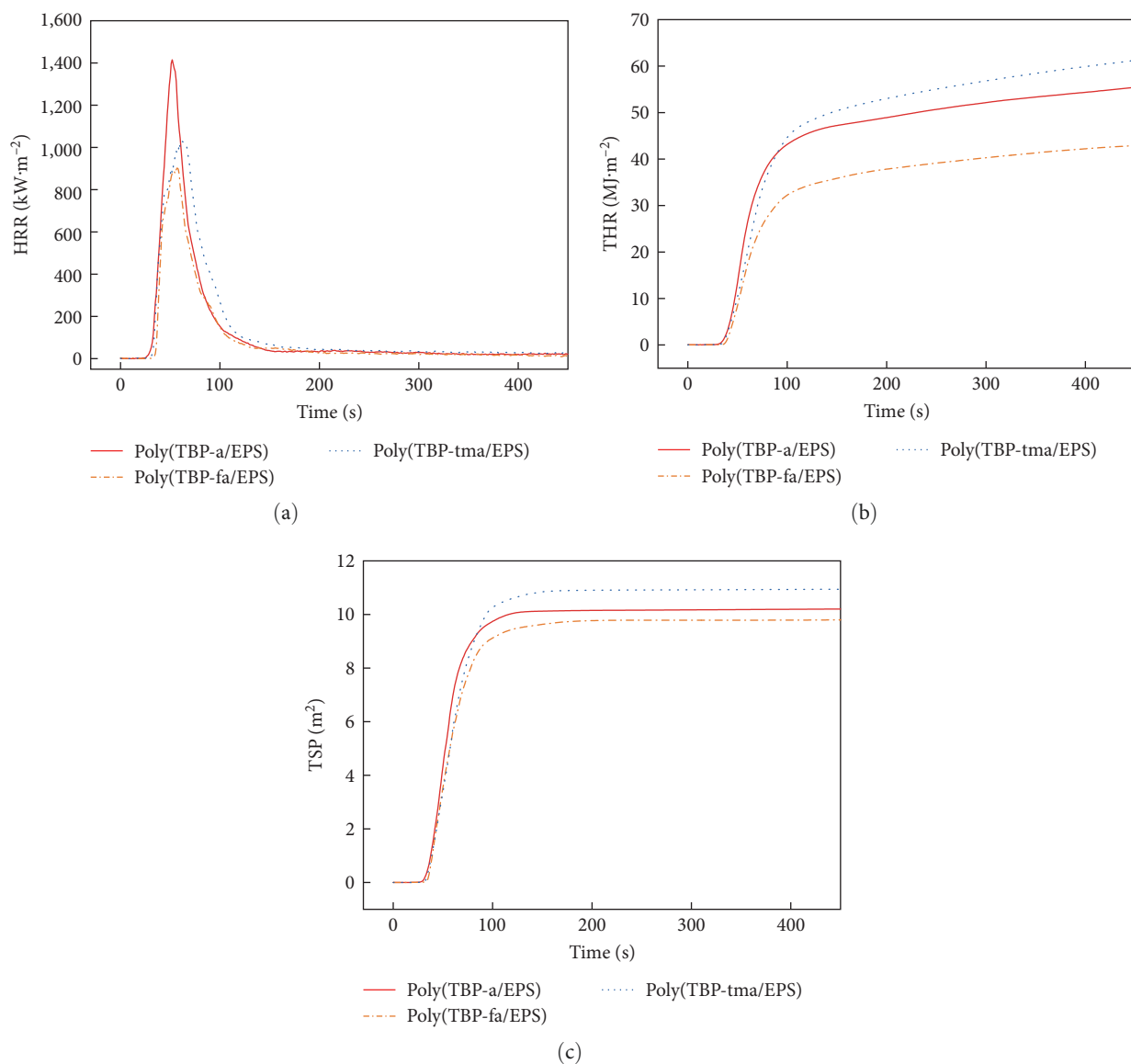


FIGURE 8: Curves of (a) heat release rate (HRR), (b) THR, and (c) TSP curves for copolymers (LOI = 27).

demonstrate the steric hindrance of the isopropyl groups in EPBA and the benefit of $-\text{S}-$ segments in sulfur-containing EPS.

The $\tan \delta$ values of TBP-fa/EPs decreased with increasing EPS content, indicating an increase in the degree of cross-linking. The half-peak widths of the $\tan \delta$ curves of the EPS-containing copolymers broadened because the EPS contains different graft groups and segments in very different sizes, which move at different temperatures. The peaks of the $\tan \delta$ curves of the EPS copolymers showed no obvious phase separation, indicating that TBP-fa and EPS have good compatibility after polymerization. However, the $\tan \delta$ peaks of poly(TBP-fa/EPBA) at a weight ratio of 3:7 tended to split (Figure S4), indicating the compatibility for EPBA copolymer is poor for this ratio.

Furthermore, the crosslink density of thermosetting resin was calculated by the relationship of its elastic modulus,

which can be well explained by the statistical theory of rubber elasticity. The following equation is used to obtain the crosslink density of TBP-fa/EPs copolymer [49, 50]:

$$n = E'/3RT, \quad (2)$$

where n is crosslink density, E' is the equilibrium store modulus at $T_g + 50^\circ\text{C}$ (Pa), R is the gas constant ($8.314 \text{ L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and T is the absolute temperature (K). The calculated crosslink density results are displayed in Table 5. It can be seen that the addition of sulfur-containing EPS significantly increases the crosslinking density of the TBP-fa/EPs copolymers. When the ratio is 3:7, the crosslinking density of TBP-fa/EPs reaches the highest (28.1 mol/L). With the increase in the content of EPS, the cross-linking density decreased, demonstrating that the

TABLE 4: Data of cone calorimeter for copolymers (LOI = 27).

	TTI/s	PHRR ($\text{kW}\cdot\text{m}^{-2}$)	THR ($\text{MJ}\cdot\text{m}^{-2}$)	MARHE ($\text{kW}\cdot\text{m}^{-2}$)	TSR ($\text{m}^2\cdot\text{m}^{-2}$)	TSP (m^2)
Poly(TBP-a/EPs)	25	1415	61.7	482	1,145	10.2
Poly(TBP-fa/EPs)	33	902	43.9	390	1,101	9.8
Poly(TBP-tma/EPs)	31	1,029	66.2	458	1,227	11.0

TBP, 4,4'-thiobisphenol; EPs, epoxy resin; TTI, time to ignition; LOI, limiting oxygen index; THR, total heat release; MARHE, maximum average heat release rate; TSP, total smoke production; TSR, the smoke release rate.

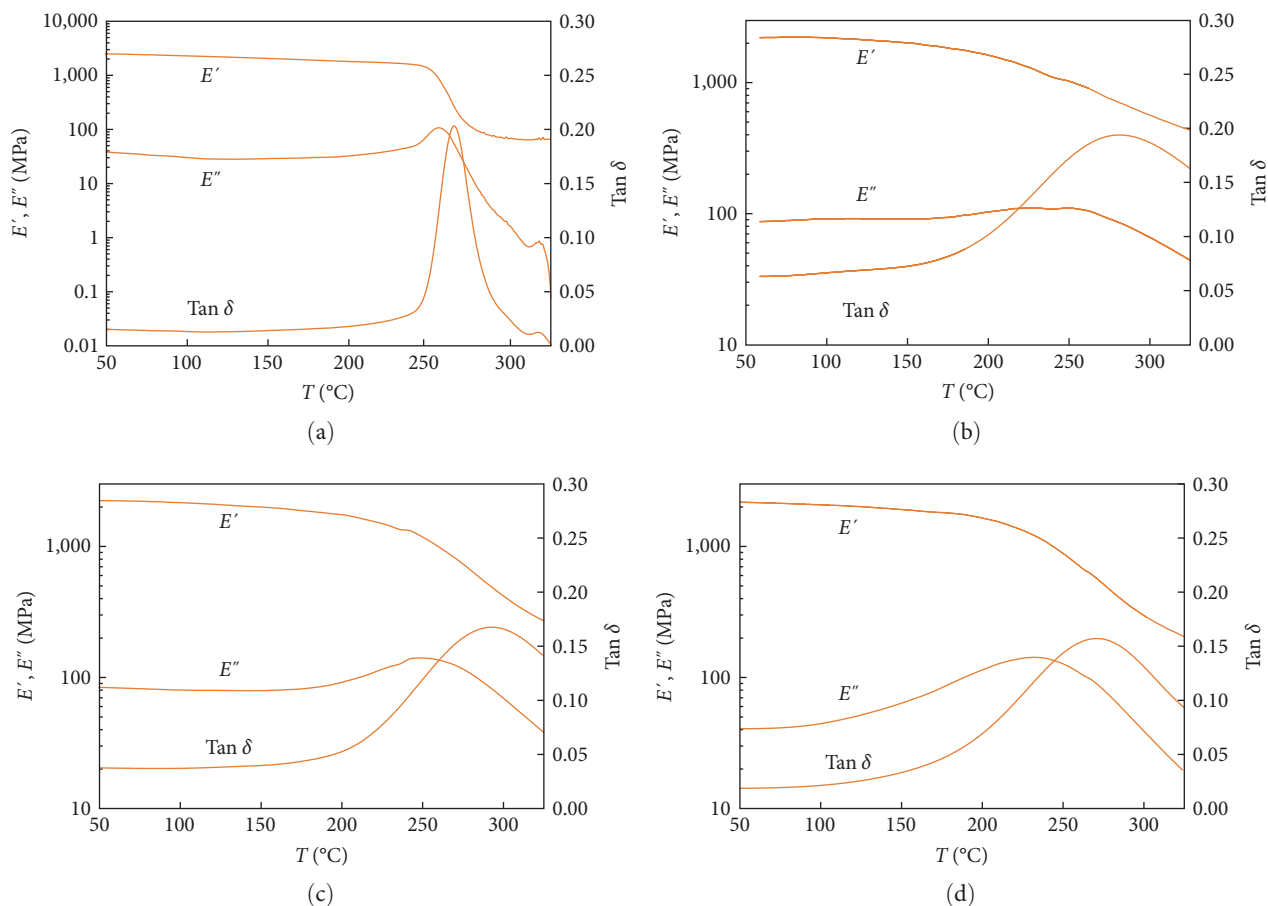


FIGURE 9: Dynamic mechanical analysis curves of blend resins (a) pure poly(TBP-fa); (b) w (TBP-fa): w (EPs) = 7 : 3; (c) w (TBP-fa): w (EPs) = 5 : 5; (d) w (TBP-fa): w (EPs) = 3 : 7.

TABLE 5: Dynamic mechanical analysis data of blend resins.

w (BZ): w (EPs)	E' (MPa (50°C))	T_g (°C)	$\text{Tan } \delta$	n (mol/L)
10:0	2,521	265	0.211	4.43
7:3	2,415	278	0.190	28.1
5:5	2,250	289	0.173	14.9
3:7	2,206	273	0.165	14.1

EPs, epoxy resin; BZ, benzoxazine.

cross-linking enhancement effect of the epoxy group and hydroxyl group began to be weaker than the plasticizing effect of a large number of epoxy groups. However, it is still higher than that of pure BZ and BZ/EPBA (Table S2), which also proves that TBP-fa /EPs has a higher crosslink density.

4. Conclusions

In this work, we synthesized an EPs using a sulfur-containing phenol source (TBP), the epoxy value of which was close to that of a BA-based one. We found that the curing process of the copolymers of sulfur-containing BZs and sulfur-containing EPs involved simultaneous ring-opening and cross-linking processes of the oxazine and epoxy rings. For TBP-fa/EPs and TBP-tma/EPs, the furan rings and thiophene were rings also cross-linked to form a double-substituted structure, which helped increase the thermal stability. However, the participation of EPs in copolymerization hindered the formation of the double-substituted structure, resulting in an increase in weight loss in the early stages of decomposition. The C–O–C–O groups produced by the epoxy ring-opening

reaction tended to break, decreasing the final char yield at 800°C. We prepared self-extinguishing copolymers (char yield = 24%) with EPS contents increasing in the order: TBP-fa/EPBA < TBP-a/EPS < TBP-tma/EPS < TBP-fa/EPS. The HRC for these materials (except TBP-a/EPS) was less than 300 J/g·K, which is indicative of strong flame-retardant properties. We attribute the excellent flame-retardant properties to the breaking of the thioester bonds at high temperatures. In cone calorimeter measurement, the TBP-fa/EPS copolymer showed the longest time of ignition (33 s), the lowest THR (43.9 MJ/m²), and the total smoke production (9.8 m²), which represented the best flame retardancy due to the formation of double-substituted structures. The T_g of the TBP-fa/EPS copolymer with a BZ:EPS ratio of 5:5 (w/w) reached 289°C. In addition, the storage modulus of this copolymer reached 2206 MPa for an EPS content of 70%, which is equivalent to that of neat poly(BA-a). Compared with BZ/EPBA copolymers, sulfur-containing epoxy systems have a higher storage modulus, a more advantageous T_g and crosslink density, and better compatibility with BZ resins.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

The manuscript was written with the contributions of all authors: Ya Lyu, Haibo Fan, and Liliang Qiu. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Supplementary Materials

Figure S1: TGA curve of poly(TBP-fa/EPBA); Figure S2: FTIR spectrum of BA-type epoxy resins (EPBA); Figure S3: MCC curve of poly(TBP-fa/EPBA); Table S1: MCC data of poly(TBP-fa/EPBA) (LOI = 27); Figure S4: DMA curves of copolymers based on EPBA; Table S2: DMA data of copolymers based on EPBA. (*Supplementary Materials*)

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