



# Synthesis of a Novel Spiro Phosphorus–Nitrogen Concerted Reactive Flame-Retardant Curing Agent and Its Application in Epoxy Resin

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Spiro-phosphorus (P)-based reactive flame retardant (SPDPT), a novel reactive flame-retardant epoxy resin (EP) curing agent, was prepared through the one-pot synthesis of triacetonediamine, pentaerythritol, and P oxychloride. The successful preparation of SPDPT was confirmed through Fourier-transform infrared (FTIR) spectroscopy, <sup>1</sup>H NMR spectroscopy, <sup>31</sup>P NMR spectroscopy, and elemental analysis. The flame-retardant epoxy thermoset [e.g., EP/4'4'-diaminodiphenyl sulfone (DDS)/SPDPT] was prepared by using DDS as the co-curing agent. Differential scanning calorimetry (DSC) results show that SPDPT can cure EP. Thermogravimetric analysis (TGA) results show that improve the carbon residue yield of the epoxy thermoset after burning. When the P content was 1.0 wt%, the limiting oxygen index value of the EP/DDS/SPDPT-4 sample was 26.4%, and UL94 reached the V-0 rating. The tensile property of the epoxy thermoset reached 37.20 MPa, the flexural property reached 63.82 MPa, and the impact property reached 21.57 KJ·m<sup>-2</sup>.

**Keywords:** epoxy resin, carbon residue yield, Fourier-transform infrared, curing agent, flame retardant

## INTRODUCTION

Epoxy resin (EP) boasts merits, such as excellent adhesion, strong mechanical strength, low shrinkage, good electrical insulation, and outstanding corrosion resistance (Huo et al., 2019; Luo et al., 2019), and has been widely applied in various industries, such as coating, adhesive, aerospace material, and substrate material (Perret et al., 2011a,b; Qiu et al., 2016; Mestry and Mhaske, 2019; Zhang et al., 2019). However, flammability has been one of the major limiting factors of EP applications (Huo et al., 2016; Lin et al., 2016). Therefore, the flame retardancy of EP composites has been investigated widely (Shi et al., 2017; Xu et al., 2019; Chu et al., 2020; Ding et al., 2020). In the past few years, researchers have strove to improve the flame retardancy of EP by introducing DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-based flame retardants (Luo et al., 2015; Zhang et al., 2017; Deng et al., 2018; Zhao et al., 2018), phenolic resin (Wang P. et al., 2018), PN-containing compound flame retardants (Chen et al., 2005; Jian et al., 2017), and other flame retardants that contain phosphorus (P) and silicon. However, these flame retardants cannot ensure

the flame retardancy of EP and might even release a significant amount of toxic fumes because they cannot easily form char, thereby endangering people's health. Therefore, we need to develop new flame retardants with excellent char-forming ability.

Among the P-based flame retardants, halogen-free spiro P-based flame retardants boast merits, such as high P content, excellent char-forming ability, low toxicity, migration resistance, and durability, which have contributed to their wide applications. Spiro P-based flame retardants consist of three elements, namely, P, oxygen (O), and carbon (C), which give them a stable heterocyclic structure and high thermal stability. With the char-forming property of pentaerythritol, such retardants can inhibit the further combustion of polymer materials and provide flame retardancy in the gas and condensed phases (Zhan et al., 2009; Li et al., 2016; Ma et al., 2019). The molecular structure of their intermediate, spiro P oxychloride, contains a chlorine atom that can be substituted to synthesize multifunctional flame retardants applicable to different flame-retardant systems and can also react with amine group-containing compounds to prepare P–nitrogen (N) concerted self-intumescent flame retardant combining acid, C, and gas sources to allow O isolation, heat insulation, and smoke suppression. Therefore, these retardants boast outstanding char-forming and flame-retardant properties by comparing with additive flame retardant (Huo et al., 2017; Yuan et al., 2017, 2018; Wang C. et al., 2018; Huang et al., 2019; Shang et al., 2019; Ma et al., 2020; Tang et al., 2020a,b).

To date, numerous studies on amino group-containing compounds have been conducted. For example, Huo et al. (2019) prepared a piperidine group-containing flame retardant that can be effectively combined with EP to improve its flame retardancy (Wang X. et al., 2018). Xie et al. (2016) prepared a triazine-based N-alkoxy compound that can effectively improve the flame retardancy of polypropylene film. Existing studies also show that amino group-containing compounds can provide flame retardancy in the gas phase by quenching free radicals (Aubert et al., 2011; Xu et al., 2015; Zhao et al., 2018). Therefore, we can obtain an EP reactive flame retardant with high P content, good char formation, low toxicity, and high curing activity through the reaction between the chlorine atom in the molecular structure of spiro phosphoryl chloride and the N-H in the amino group-containing compounds.

In this study, a novel spiro-P-based reactive flame retardant (SPDPT) was synthesized through the one-pot reaction of P oxychloride, pentaerythritol, and triacetone diamine. SPDPT was used as a co-curing agent for 4,4'-diaminodiphenyl sulfone (DDS) to cure EP and produce the desired flame-retardant epoxy thermoset. A series of tests was conducted to examine the curing properties of SPDPT and the mechanical properties, flammability, and thermal stability of the flame-retardant epoxy thermoset.

## EXPERIMENTAL TESTS

### Subsection

Epoxy resin (DGEBA CYD-128) was purchased from the Baling Petrochemical Branch of Sinopec Group Asset Management

Co., Ltd., with an epoxy equivalent of approximately 196 g/eq. Triacetone diamine and DDS were purchased from Aladdin Industrial Corporation. Acetonitrile, P oxychloride, methylene chloride, and pentaerythritol were purchased from Sinopharm Chemical Reagent Co., Ltd.

### Synthesis of SPDPT

Spiro-P-based reactive flame retardant was synthesized by using the simple one-pot method, and its synthetic route is shown in **Figure 1**.

In a 500-ml three-necked flask equipped with a magnetic stirrer, a thermometer, and a condenser, 13.6 g (0.1 mol) of pentaerythritol and 168.3 g (1.1 mol) of P oxychloride were added and then heated to 130°C (reflux temperature) until no hydrogen chloride gas is produced, in which case the reaction was stopped and the product was cooled to room temperature. The product was filtered, washed twice with distilled water, washed thrice with dichloromethane, and finally dried in a vacuum oven at 50°C for 24 h.

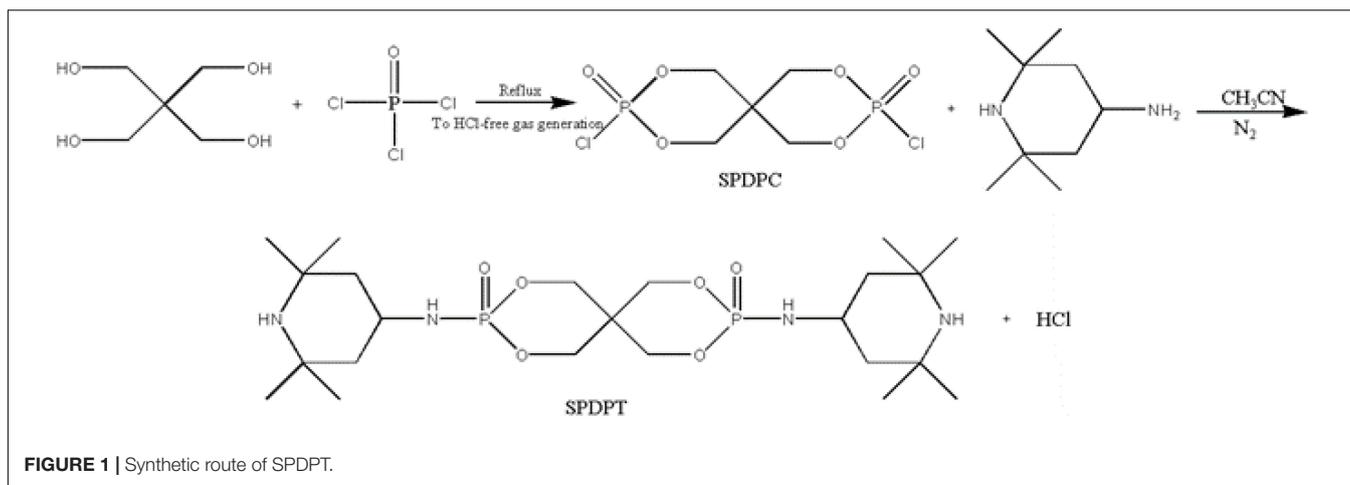
While introducing N<sub>2</sub> gas, 15.65 g (0.11 mol) of triacetone diamine, 300 ml of acetonitrile, and 14.85 g (0.05 mol) of SPDPC were added into a 500-ml three-necked flask equipped with a magnetic stirrer, an oil seal, and a condenser. After the SPDPC was evenly mixed, the solution was first heated to 30°C for a 3-h reaction and then heated to 50°C for another 3-h reaction, after which the product was washed three times with dichloromethane and finally dried in a vacuum oven at 50°C for 24 h.

### Preparation of the Epoxy Thermoset

The SPDPT flame-retardant epoxy thermosets (EP/DDS/SPDPT) with different P contents were obtained through the polymerization among EP, DDM, and SPDPT, where SPDPT is the co-curing agent for DDS, and the sum of the active hydrogen equivalents of DDS and SPDPT is consistent with the epoxy equivalent of EP (see **Table 1**). SPDPT and DDS were added to the EP at a temperature of 110°C, stirred to mix evenly, and vacuum-defoamed. After the solution became transparent, the solution was poured into a mold preheated to 100°C. The mold was subsequently placed in an electric blast drying oven and cured at 130°C, 150°C, 170°C, and 190°C for 2 h. After curing, the mold was naturally cooled to room temperature to obtain the SPDPT flame-retardant epoxy thermoset. The preparation process of the pure epoxy thermoset (EP/DDS) was similar to that of the EP/DDS/SPDPT thermoset with no SPDPT added.

### Preparation of DSC Epoxy Compound for Test Use

A certain amount of EP and SPDPT (epoxy equivalent in EP is equal to the active hydrogen equivalent in SPDPT) was added and stirred to an appropriate amount of acetone, thereby and, uniformly dispersing the EP and the SPDPT in the acetone. The mixture was then dried at 40°C to obtain the EP/SPDPT compound. The preparation of the EP/DDS and EP/DDS/SPDPT compounds (see **Table 1**) was the same as that of the EP/SPDPT compound.



## Testing and Characterization

Fourier-transform infrared (FTIR) spectroscopy was performed using a United States-made Nicolet 6700 FTIR spectrometer. The samples and KBr were ground, mixed, and pressed into thin sheets (measurement range: 400–4000  $\text{m}^{-1}$ ).

$^1\text{H}$  NMR spectroscopy and  $^{31}\text{P}$  NMR spectroscopy were performed using an Agilent 400AR NMR spectrometer and deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ).

Elemental analysis was performed using the Germany-made Vario EL cube element analyzer to determine the C, hydrogen, and N contents of the sample.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 4000 differential scanning calorimeter under N atmosphere at a ramp rate of  $10^\circ\text{C}/\text{min}$  and a temperature range of 25–250°C.

Thermogravimetric analysis (TGA) was performed using a Germany-made NETZSCH STA409PC thermogravimetric analyzer under N atmosphere at a ramp rate of  $10^\circ\text{C}/\text{min}$  (heating from room temperature to 700°C).

The limiting O index (LOI) was tested pursuant to the ASTM D2863 standard using a JF3 O index meter manufactured by Nanjing Jiangning Analytical Instrument Co., Ltd. The standard size of the sample was 100 mm  $\times$  6.5 mm  $\times$  3 mm.

The flammability rating (UL 94) was measured pursuant to the GBT2408 2008 standard (the latest Chinese standard) using a NK8017A UL94 vertical burning test machine manufactured by Dongguan Nayu Testing Equipment Co., Ltd. The standard size of the sample was 130 mm  $\times$  13 mm  $\times$  3 mm.

Tensile property was tested on a GP-TS2000S universal testing machine (at the testing temperature of 25°C, a tensile rate of 5 mm/min), the testing method with reference to GB/T2567-2008.

Flexural property was tested on a GP-TS2000S universal testing machine (at the testing temperature of 25°C, a flexural rate of 2 mm/min), the testing method with reference to GB/T2567-2008.

Impact property was tested on a XJJD-50 impact testing machine (at the testing temperature of 25°C), the testing method with reference to GB/T2570-1995, the specimen size with reference to GB1043-93.

## TEST RESULTS

### Infrared Analysis of SPDPC and SPDPT

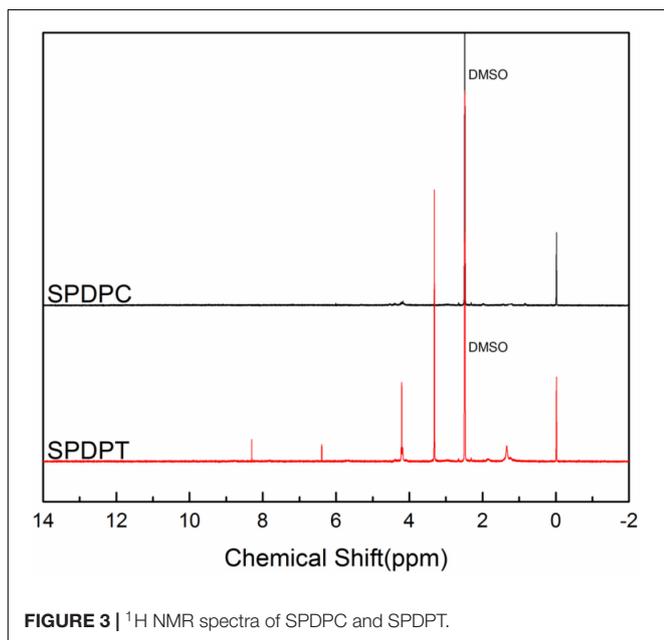
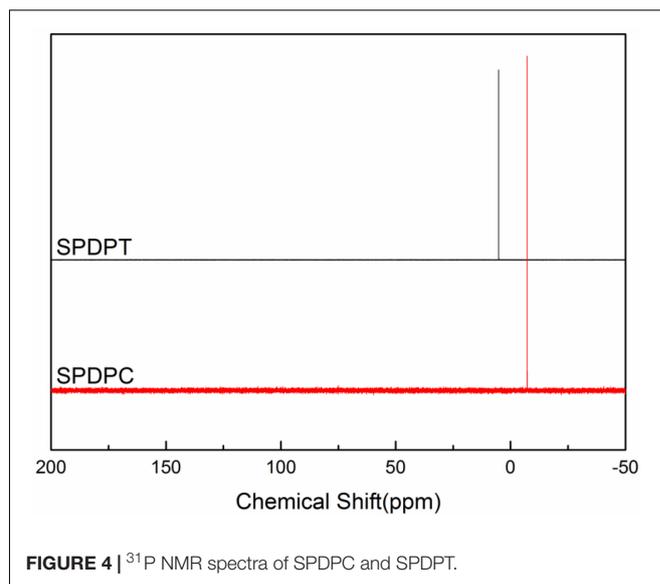
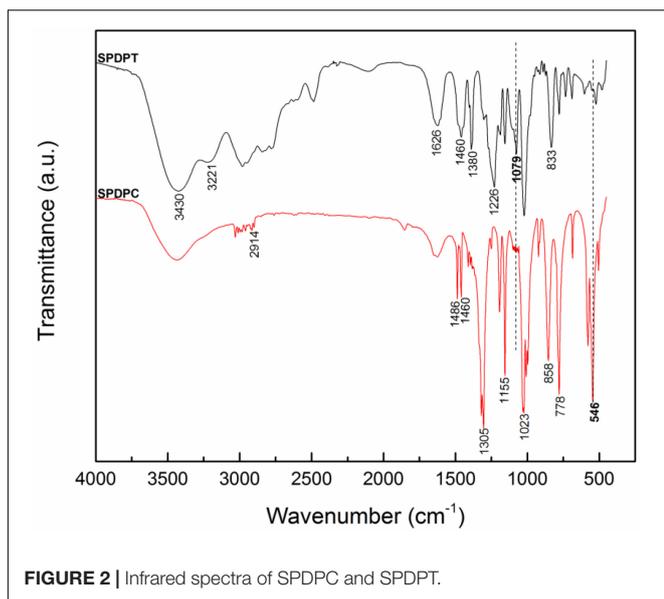
Figure 2 shows the infrared spectra of the intermediate product (e.g., SPDPC) and the final product (e.g., SPDPT). The absorption curve of SPDPC shows that the characteristic absorption peaks of P = O, P-O-C, P-O, and P-Cl appear at 1305, 1023, 858, and 546  $\text{cm}^{-1}$ , respectively. On the absorption curve of SPDPT, the characteristic absorption peaks of  $-\text{NH}_2$  appear at 3430, 3221, and 1626  $\text{cm}^{-1}$ ; that of P = O appears at 1226  $\text{cm}^{-1}$ ; that of P-O-C appears at 1023  $\text{cm}^{-1}$ ; that of P-O appears at 833  $\text{cm}^{-1}$ ; and that of P-N appears at 1079  $\text{cm}^{-1}$ . An obvious characteristic absorption peak of P-Cl (546  $\text{cm}^{-1}$ ) can be observed on the absorption curve of SPDPC, but this peak does not appear on the absorption curve of SPDPT. Instead, the characteristic absorption peak of P-N (1079  $\text{cm}^{-1}$ ) appears on the absorption curve of SPDPT, indicating that SPDPC reacts with triacetone diamine to form SPDPT.

### NMR Spectroscopy of SPDPC and SPDPT

Figure 3 shows the  $^1\text{H}$  NMR spectra of the intermediate product (e.g., SPDPC) and the final product (e.g., SPDPT). According to the  $^1\text{H}$  NMR spectrum of SPDPT, the chemical shifts of imino hydrogen on the piperidine and connecting piperidine rings

**TABLE 1** | The detailed formulations of EP samples.

Sample	EP (g)	SPDPT (g)	DDS (g)	P content (wt%)
EP/DDS	75.97		24.03	0
EP/DDS/SPDPT-1	75.09	2.16	22.75	0.25
EP/DDS/SPDPT-2	74.21	4.31	21.48	0.5
EP/DDS/SPDPT-3	73.33	6.47	20.20	0.75
EP/DDS/SPDPT-4	72.45	8.62	18.93	1

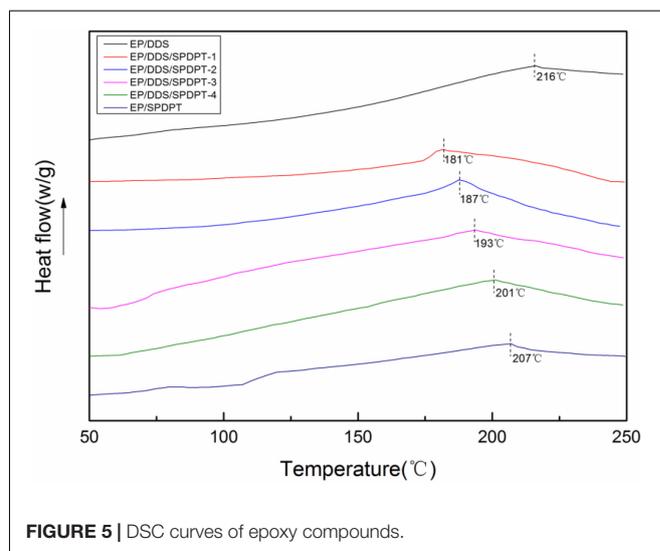


appear at 8.31 and 6.38 ppm, respectively; and the chemical shifts of methylene hydrogen, methyl hydrogen, and methine hydrogen on the piperidine ring appears at 4.22, 3.27–3.33, and 1.29–1.38 ppm, respectively. According to the <sup>1</sup>H NMR spectrum of SPDPC, the methylene hydrogen in the spiro ring is at –0.02 ppm and is present in the NMR spectrum of SPDPT, indicating that SPDPC reacted with triacetone diamine to produce SPDPT.

**Figure 4** shows the <sup>31</sup>P NMR spectra of the intermediate product (e.g., SPDPC) and the final product (e.g., SPDPT). The two spectra differ significantly. The signal peak of SPDPT appears at 5.22 ppm, whereas that of SPDPC appears at –7.29 ppm, indicating that SPDPT and SPDPC are two different P compounds. This finding further points to the fact

**TABLE 2** | Elemental analysis of SPDPT.

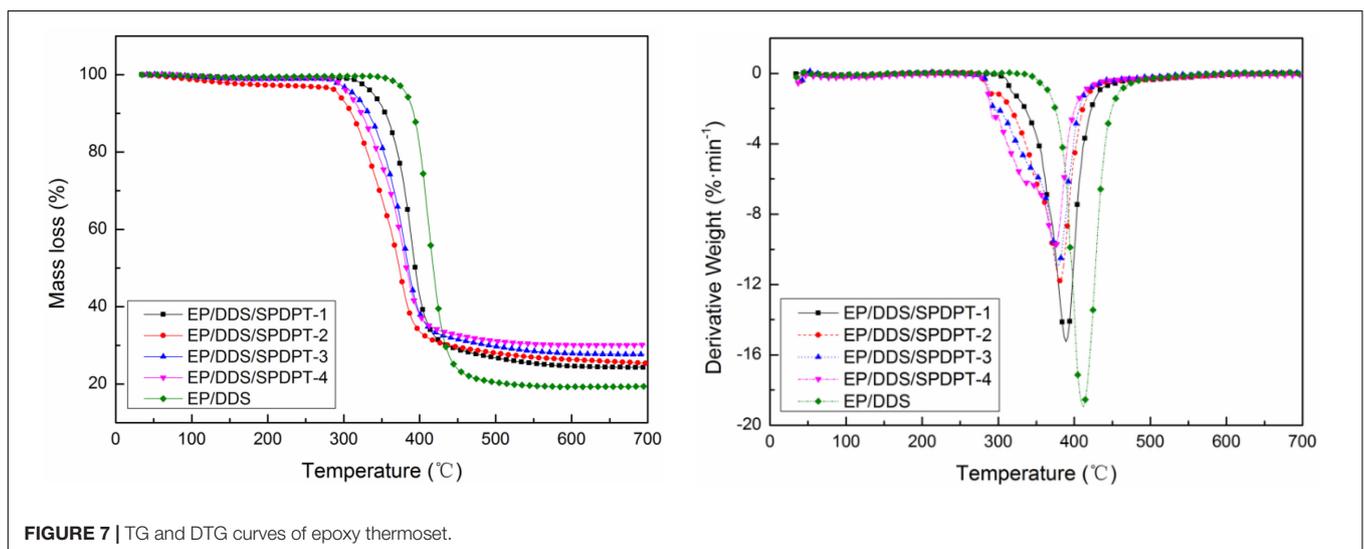
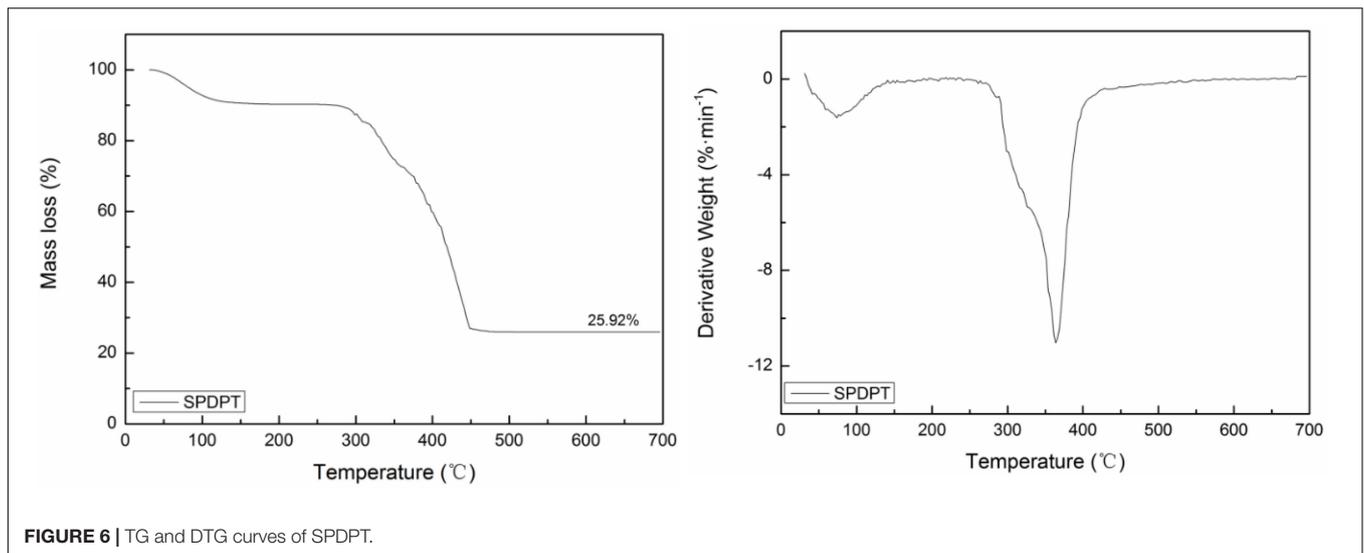
Element	C	H	N	ratio
Calculate	42.12	6.89	8.77	6:1:1
Found	51.49	8.58	10.45	6:1:1



that SPDPC and triacetone diamine reacted to form a new compound of SPDPT.

### SPDPT Elemental Analysis

The chemical structure of SPDPT was further confirmed through elemental analysis, and the results of which are shown in **Table 2**. **Table 2** shows that the measured actual contents of C, hydrogen, and N in SPDPT are almost the same as the theoretical contents.



## Reactivity of Epoxy Compound

The curing behavior of the epoxy compounds was measured through DSC. **Figure 5** shows the DSC curves of the EP/DDS, EP/DDS/SPDPT, and EP/SPDPT epoxy compounds. Only one curing exothermic peak appears on each curve. **Figure 5** shows that a significant curing exothermic peak appears on the DSC curve of the EP/SPDPT compound at approximately 207°C, indicating that the imino group in the SPDPT can react with the epoxy group in the EP. That is, SPDPT can cure EP. Moreover, the peak temperature at the curing exothermic peak of the EP/SPDPT compound is apparently lower than that of the EP/DDS compound. The peak temperature at the curing exothermic peak of the EP/DDS/SPDPT compound increases with the SPDPT content because the introduction of the rigid phenanthroline group in the SPDPT enhances the steric hindrance of the SPDPT molecule, thereby weakening the curing activity of SPDPT.

## Thermal Stability

The thermal stability of SPDPT and the epoxy thermoset was evaluated under N<sub>2</sub> atmosphere using TGA. The TGA and DTG curves of the SPDPT, EP/DDS, and EP/DDS/SPDPT thermosets are shown in **Figures 6–9**. The characteristic data, such as the 5% mass loss ( $T_{5\%}$ ), the maximum degradation at maximum rate of mass loss ( $T_{max}$ ), and the C residue yield at 700°C ( $Y_c$ ), are provided in **Table 3**.

**Figure 6** shows that during the decomposition of SPDPT, the  $T_{5\%}$  of SPDPT is 285°C, and the residual C of SPDPT at 700°C is 26%, indicating that SPDPT decomposes during combustion and produces a large amount of volatile matter.

For the EP/DDS and EP/DDS/SPDPT thermosets (**Figure 7**), the DTG curve has only one weight loss peak.  $T_{max}$  of the EP/DDS/SPDPT thermoset decrease gradually with the increase in the SPDPT content. The residual C yield of the EP/DDS/SPDPT thermoset increases at 700°C with the addition of SPDPT.

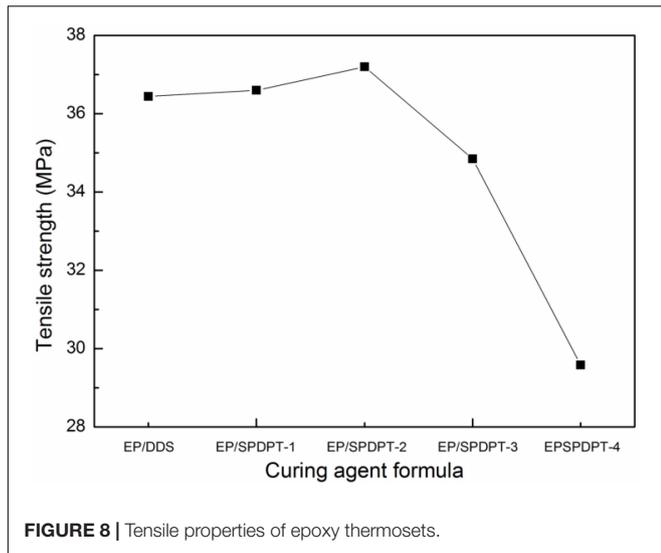


FIGURE 8 | Tensile properties of epoxy thermostets.

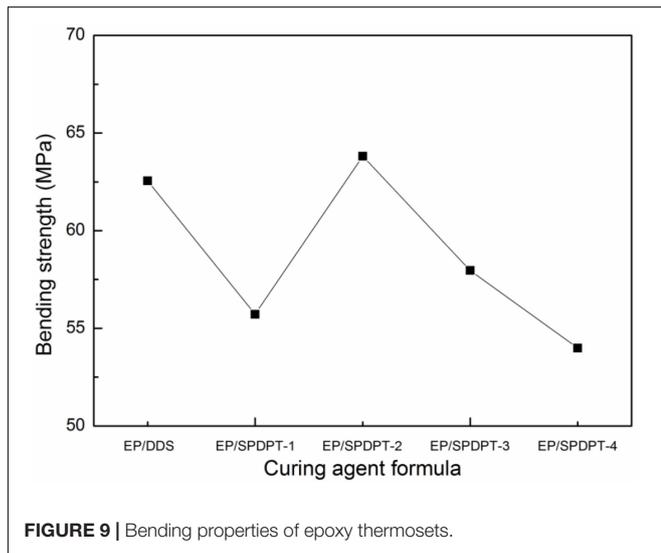


FIGURE 9 | Bending properties of epoxy thermostets.

TABLE 3 | Thermal degradation characteristics of SPDPT and epoxy thermostets.

Sample	T5% (°C)	T <sub>max</sub> (°C)	Y <sub>c</sub> (%)
SPDPT	285.5	–	26.0
EP/DDS	361.6	412.4	19.3
EP/DDS/SPDPT/0.25%	322.9	389.4	24.0
EP/DDS/SPDPT/0.5%	284.3	379.8	25.4
EP/DDS/SPDPT/0.75%	297.5	377.2	27.8
EP/DDS/SPDPT/1%	289.1	374.8	30.1

### Burning Test

The flammability of the epoxy thermostet was evaluated by LOI and UL-94 vertical burning experiments. Table 4 shows the corresponding test results.

Table 4 shows that the LOI value of the epoxy thermostet significantly increases from 20.2 for EP/DDS to 26.4 for EP/DDS/SPDPT, with the P content being only 1%. The EP/DDS

TABLE 4 | LOI and UL-94 test results of epoxy thermostets.

Sample code	P (wt%)	LOI (vol%)	UL94 (3 mm)	Dripping
EP/DDS	0	20.2	Failed	Yes
EP/DDS/SPDPT-1	0.25	23.4	V-1	No
EP/DDS/SPDPT-2	0.5	24.1	V-1	No
EP/DDS/SPDPT-3	0.75	25.2	V-0	No
EP/DDS/SPDPT-4	1	26.4	V-0	No

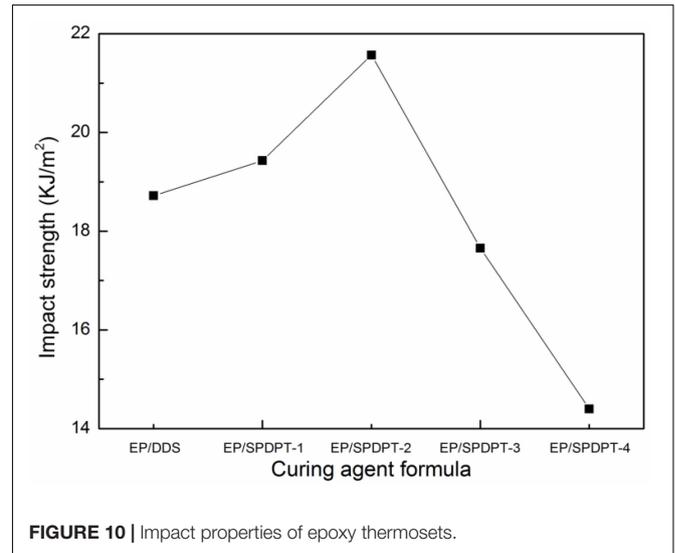


FIGURE 10 | Impact properties of epoxy thermostets.

thermostet failed to pass the UL-94 test, whereas EP/DDS/SPDPT-3 and EP/DDS/SPDPT-4 reached the V-0 rating, and all the EP/DDS/SPDPT thermostets did not show dripping.

### Mechanical Properties of Epoxy Thermostets

Figure 8 shows the tensile property of the epoxy thermostets. Among the EP/DDS/SPDPT thermostets, EP/DDS/SPDPT-2 (P content = 0.5%) produces the best tensile property of 37.20 MPa.

Figure 9 shows the flexural property of the epoxy thermostets. EP/DDS/SPDPT-2 (P content = 0.5%) demonstrates the best flexural property of 63.82 MPa.

Figure 10 shows the impact property of the epoxy thermostets. EP/DDS/SPDPT-2 (P content = 0.5%) demonstrates the best impact property of 24.57 KJ·m<sup>-2</sup>.

Figures 8–10 show that the addition of the flame-retardant curing agent SPDPT exerted a certain impact on the mechanical properties of the epoxy thermostets. The tensile, flexural, and impact properties of the EP increased first and then decreased with the increase in the P content in the EP, indicating that the addition of SPDPT can improve the mechanical properties of the EP system.

The tensile property, the flexural strength, and the impact property reached 37.20 MPa, 63.82 MPa, and 21.57 KJ·m<sup>-2</sup>, respectively.

## CONCLUSION

A novel flame-retardant curing agent that contained piperidine groups was successfully synthesized and used as a reactive flame-retardant curing agent to prepare the desired flame-retardant epoxy thermosets. The EP/DDS/SPDPT epoxy thermosets showed a higher C residue yield at 700°C than the EP/DDS sample. The flame retardancy and mechanical properties of the epoxy thermoset will be improved significantly by adding SPDPT at a low P content. As an EP curing agent, the SPDPT can be prepared easily, and the raw material can also be obtained easily. Therefore, SPDPT boasts great application prospects.

## DATA AVAILABILITY STATEMENT

All datasets presented in this study are included in the article/supplementary material.

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## AUTHOR CONTRIBUTIONS

YC and YP: conceptualization. LY: methodology, formal analysis, and writing – original draft preparation. YC: software, resources, supervision, project administration, and funding acquisition. LY and ZH: validation. ZH: investigation. YP: data curation and writing – review and editing. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer BY declared a shared affiliation, with no collaboration, with one of the authors to the handling editor at the time of review.

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