Synthesis of a Novel Phosphorus-containing Flame Retardant for Epoxy Resins

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In this study, a novel phosphorus-containing flame retardant copolymer of spirocyclic pentaerythritol di(phosphate monochloride) and bisphenol S (SPD-BS) was successfully synthesized and used as a flame retardant in diglycidyl ether of bisphenol A (DGEBA) epoxy resins. The chemical structure of the SPD-BS was characterized using FT-IR and ^{1}H NMR spectra. The thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The effects of SPD-BS and nano-CaCO₃ on the flame-retardant properties of DGEBA/SPD-BS systems were evaluated by measurement of the burning rate. As a result, the thermal stabilities of the DGEBA/SPD-BS systems were decreased with increasing SPD-BS content. The flame-retardant properties and char yields of the systems were significantly increased when SPD-BS content increased. The synergism of nano-CaCO₃ incorporation on flame retardancy was found for the DGEBA/SPD-BS systems.

Key Words: Phosphorus, Flame retardant, Epoxy resins, Thermal properties, Flame-retardant properties

Introduction

Thermosetting epoxy resins are widely used in various industrial fields because of their advantageous properties.[1,2] However, the flammability of the epoxy resins is one of the major drawbacks in application where high flame retardancy is required. Epoxy resins can be imparted with flame-retardant properties by adding additives or reactive flame retardants into epoxy resins.[3]

Recently, phosphorus compounds have been used as effective flame retardants for many polymers. Phosphorus-containing flame retardants incorporated into epoxy resins generate less toxic gas and smoke than halogen-containing compounds during epoxy resins combustion and also exhibit high flame retardancy.[4] Jeng *et al.* modified epoxy resins with an organosoluble phosphorus-containing bismaleimide. The experimental results indicated that the incorporation of the bismaleimide is an effective way to enhance the thermal properties and flame retardancy simultaneously.[5] Shieh *et al.* synthesized phosphorus-containing flame retardants and investigated the effect of the flame retardant structure on the physical and flame-retardant properties of epoxy resins.[6] Perez *et al.* synthesized a novel phosphorus-modified polysulfone (P-PSu) and employed it as a combined toughness modifier and a source of flame retardancy for epoxy resins. The results showed that the cured epoxy resin can simultaneously be equipped with both an enhanced toughness and improved flame retardancy by adding P-PSu.[7] Toldy *et al.* synthesized efficient organophosphorous compounds and used them in epoxy resins.[8] The results exhibited that the limiting oxygen index (LOI) value is increased from 21 to 28 by addition of the organophosphorous compounds. Liu *et al.* synthesized a nonflammable phosphazene-based epoxy resin and studied the thermal and flame retardancy of the epoxy resin cured with four curing agents.[9]

In this study, a novel phosphorus-containing flame retardant copolymer of spirocyclic pentaerythritol di(phosphate monochloride) and bisphenol S (SPD-BS) was successfully synthe-

sized and used as a flame retardant in diglycidyl ether of bisphenol A (DGEBA) epoxy resins. The chemical structure of the SPD-BS was characterized using FT-IR and ^{1}H NMR spectra. The thermal properties of the SPD-BS were studied by a differential scanning calorimetry (DSC) and a thermogravimetric analysis (TGA). The thermal stabilities of DGEBA/SPD-BS systems were investigated using a TGA. The effects of SPD-BS and nano-CaCO₃ on the flame-retardant properties of the systems were evaluated by measurement of the burning rate.

Experimental

Materials. Conventional petroleum-based epoxy resin used in this study was DGEBA supplied by Feichengdeyuan Chem. of China (E-51), which had an epoxide equivalent weight (EEW) of 185 - 208 g/eq. Pentaerythritol, phosphoryl chloride, bisophenol S, and triethylamine were purchased from Sinopharm Chem., Tianjin Guangfu Chem., Tianjin Damao Chem., and Zhejiang Jiande Jianye Organic Chem. of China, respectively. 4,4'-Diaminodiphenyl methane (DDM) was purchased from Toshiba silicon Co. Nano-CaCO₃ of a mean particle size of 40 - 70 nm and a specific surface of 20 - 30 m²/g was supplied by WINNOFIL'S, Solvay.

Synthesis of spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride (SPBDC). Pentaerythritol (27.23 g, 0.2 mol) and phosphorus oxychloride (153.33 g, 1.0 mol) were mixed in a 500 mL glass flask equipped with a circumference condenser and tail gas absorber. The mixture was heated up to 110 °C gradually and reacted for 6 h. The raw product was filtered and purified with dichloromethane, then dried to constant weight at 80 °C. A white powder was obtained (yield: 63.5%). mp 231.5 °C. FT-IR (KBr) 1307 cm⁻¹ (P=O), 1028 (P-O-C), 854 (P-O), 547 (P-Cl). ^{1}H NMR (DMSO-d_6) 4.0-4.05 ppm (tr, 8H, -CH₂), 3.33-3.36 ppm (tr, 4H, -OH).

Synthesis of copolymer of spirocyclic pentaerythritol di(phosphate monochloride) and bisphenol S (SPD-BS). SPBDC (5.94 g, 0.02 mol), bisphenol S (4.76 g, 0.019 mol), and ace-

tonitrile (40 mL) were added in a glass flask. Then triethylamine (4.01 g. 0.04 mol) was added slowly to a separatory funnel and stirred at room temperature for 30 min. The mixture was gradually heated and reacted at 84 °C for 8 h. The raw product was filtered and washed with acetonitrile. and then dried at 70 °C in a vacuum oven. The product was white powder (yield: 94.9%). mp 236.7 °C. FT-IR (KBr) 3015 cm⁻¹ (C-H). 1248 (Ph-O), 1154 (-SO₂-). 1031 (P-O-C), 591 (-SO₂-). ¹H NMR (DMSO-d_6) 4.0-4.05 ppm (d. 8H. -CH₂). 6.75-7.28 (d. 4H. -CH).

Sample preparation. The weight content of SPD-BS was varied from 0 to 15 wt%, and the weight content of nano-CaCO₃ was 2 wt%. The desired amount of DGEBA. SPD-BS. and nano-CaCO₃ were mixed at 80 °C for 30 min, and then DDM was added into the mixtures. The mixtures were thoroughly stirred by a magnetic stirring bar and sonicated for 30 min. The mixtures were degassed in a vacuum oven to eliminate air bubbles. The preparation of the specimens for combustion tests was as follows: bubble-free mixtures were poured into a pre-heated mold. which was sprayed with a mold release agent. Curing was performed at 120 °C for 1 h, at 150 °C for 2 h. and at 180 °C for 1 h in a convection oven.

Characterization and measurements. IR spectra were recorded with a Bio-Rad Co. digilab FTS-165 spectrometer by using KBr pellets. ¹H NMR spectra were taken on a BRUKER Co. DRX300 spectrometer operation at 300 MHz in DMSO-d_6.

The thermal stabilities of the cured samples were studied with a du Pont TGA-2950 analyzer at a heating rate of 10 °C/min from 30 to 700 °C under a nitrogen atmosphere.

Combustion tests were performed by measurement of the burning rate. The measurements were carried out using Bunsen Burner according to the Plastics-Determination of Burning Characteristics-Horizontal and Vertical Test (GB/T 2408-2008). The sample size was 2 × 13 × 100 mm³.

Results and Discussion

Synthesis and characterization of flame retardant. The synthesis route is shown in Figure 1. SPBDC was synthesized through the reaction of pentaerythritol and phosphorus oxychloride at 110 °C for 6 h. SPD-BS was synthesized by reaction of SPBDC and bisphenol S using triethylamine as a catalyst in acetonitrile at 84 °C for 8 h. The obtained SPBDC and SPD-BS were both white powder. The chemical structures of the SPBDC and SPD-BS were characterized by FT-IR and ¹H NMR spectra.

Figure 2 (a) shows the FT-IR spectra of pentaerythritol and SPBDC. which exhibit characteristic absorption peaks at 3327 and 547 cm⁻¹ due to the hydroxyl and P-Cl groups. In the spectra of SPEC. the disappearance of hydroxyl groups and the formation of characteristic absorption peaks at 1307. 1028. and 854 cm⁻¹ are attributed to the P=O, P-O-C, and P-O groups, respectively. which demonstrates the reaction of pentaerythritol and phosphorus oxychloride.[3,6] Figure 2 (b) shows the FT-IR spectra of SPD-BS. The absorption peaks at 1154. 1031. and 591 cm⁻¹ indicate the -SO₂-, P-O-C, and -SO₂-groups, respectively; however the distinctive absorption peak at 547 cm⁻¹ for P-Cl in SPBDC disappears.[6,10,11]
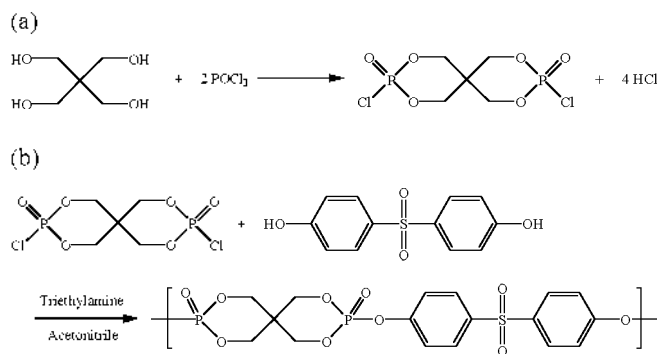

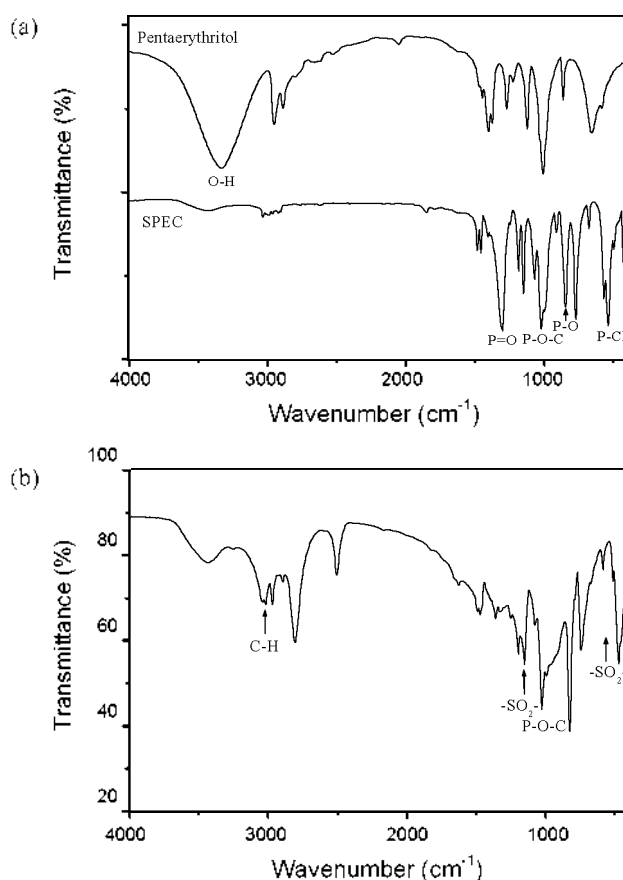**Figure 1.** Schematic outline for the synthesis of SPBDC (a) and SPD-BS (b).

Figure 2. FT-IR spectra of pentaerythritol, SPBDC, and SPD-BS.

Figure 3 (a) shows the ¹H NMR spectra (DMSO-d_6) of pentaerythritol. The chemical shift at 4.18 - 4.21 ppm belongs to the CH₂ protons and the chemical shift at 3.33 - 3.36 ppm corresponds to the hydroxyl protons. Figure 3 (b) shows the ¹H NMR spectra of SPBDC (DMSO-d_6). The chemical shifts of CH₂ protons appear at 4.0 - 4.05 ppm.[3,9] For ¹H NMR spectra of SPD-BS (DMSO-d_6), the chemical shifts at 4.0 - 4.05 and 6.75 - 7.28 ppm belong to the CH₂ protons and the aromatic ring protons.[9,12] Through the structural characterization of FT-IR and ¹H NMR. the chemical structures of the SPBDC and SPD-BS are confirmed in the present work.
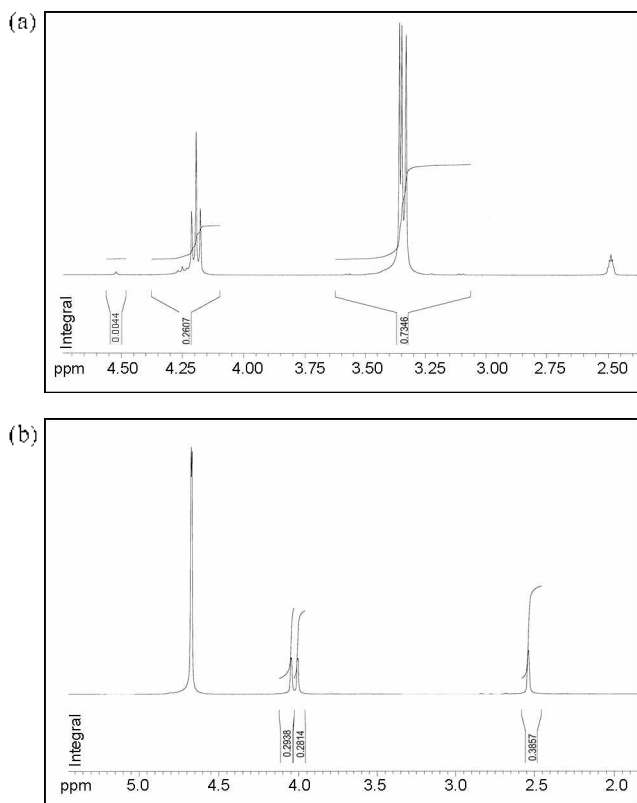
The thermal properties of the SPD-BS were investigated

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(a)

(b)

Figure 3. ^{1}H NMR spectra of pentaerythritol (a) and SPBDC (b).
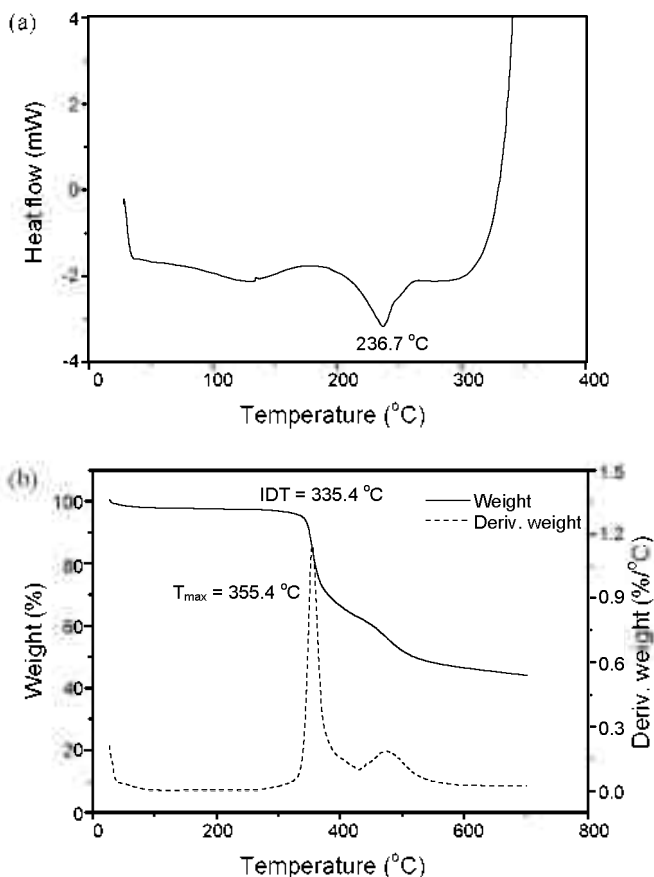
(a)

(b)

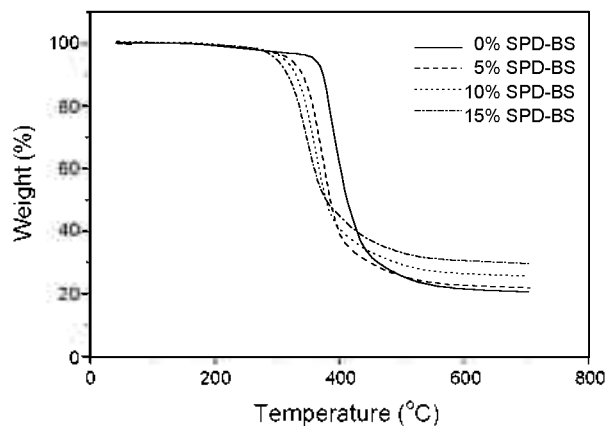**Figure 4.** DSC and TGA thermograms of SPD-BS.

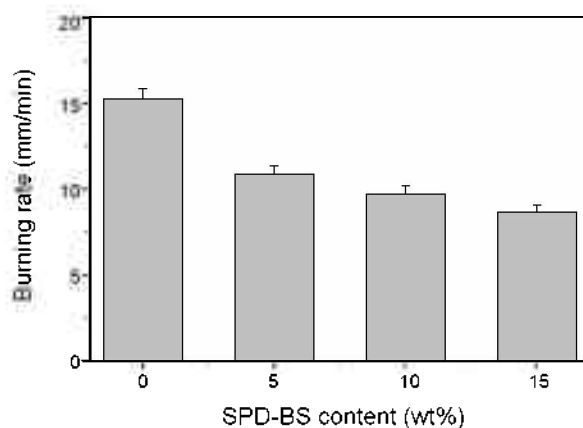**Figure 5.** TGA thermograms of DGEBA/SPD-BS systems at a heating rate of 10 °C/min.

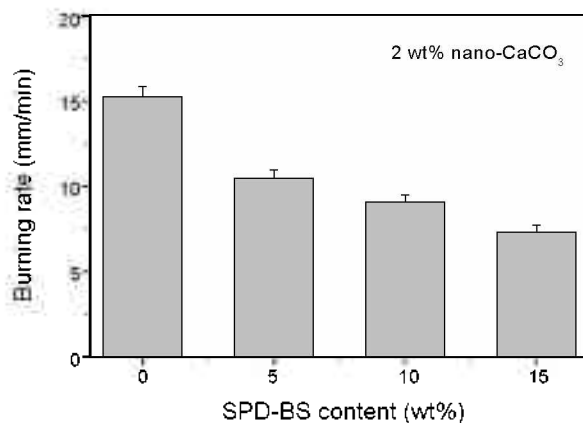**Figure 6.** Burning rate of DGEBA/SPD-BS systems as a function of SPD-BS content.

Figure 7. Burning rate of DGEBA/SPD-BS/nano-CaCO₃ systems as a function of SPD-BS content.

using DSC and TGA. and the results are shown in Figure 4. According to Figure 4, the melting point (mp), the initial decomposed temperature (IDT), and the maximum rate of weight loss (T_{max}) are 236.7 °C, 335.4 °C, and 355.4 °C, respectively.

Thermal stabilities. The effects of SPD-BS content on the thermal degradation behaviors of DGEBA/SPD-BS systems

Table 1. Thermal stability factors of DGEBA/SPD-BS systems obtained from TGA thermograms.

SPD-BS content (wt%)	IDT (°C)	Char ratio at 700 °C (%)
0	354.5	20.6
5	321.7	22.0
10	314.1	25.6
15	300.1	29.6

were studied with TGA at a heating rate of 10 °C/min in a nitrogen atmosphere, and the TGA thermograms are shown in Figure 5. Thermal stability factors, including IDT and char ratio at 700 °C of the systems can be determined from the TGA thermograms.[13-15]

The results of the IDT and the char ratio for the system are listed in Table 1. As a result, the IDT of the systems decreased with increasing SPD-BS content. This is attributed to the poor stability of O=P-O compared with -C-C- bond and the reduced cross-linking density of the epoxy network.[3,16,17] On the other hand, the char ratio of DGEBA/DDM under nitrogen atmosphere was 20.6% at 700 °C, while that of the DGEBA/SPD-BS systems increased to 22 - 29.6% with increasing BS-SPB content. This result indicated that the SPD-BS degraded at an early onset temperature and formed a phosphorus-rich residue during combustion, which correlated to imply the flame retardancy.[5,6,9,17] This was confirmed by the burning rate measurement of the DGEBA/SPD-BS systems.

Flame-retardant properties. Flame-retardant properties of the DGEBA/SPD-BS systems were evaluated by burning rate measurements. Figure 6 shows the effect of SPD-BS content on the burning rate of epoxy resins. Manifestly, the burning rate of the DGEBA/SPD-BS systems was significantly decreased with increasing SPD-BS content. The burning rate of the neat DGEBA was 15.2 mm/min, whereas that of the DGEBA/SPD-BS systems decreased to 10.8 - 8.6 mm/min, which is significantly reduced to 29 - 43%. The result can be attributed to the fact that the SPD-BS forms a carbonaceous char during combustion, which acts as a physical barrier to insulate heat from the flame and to retard the diffusion of combustible gases, thus improving the flame-retardant properties.[3,6,17,18] This result also indicated that incorporating SPD-BS is very effective in improving the flame retardancy of epoxy resins.

The effect of nano-CaCO₃ on the burning rate of the DGEBA/SPD-BS systems was also investigated, and the result is shown in Figure 7. When nano-CaCO₃ content is 2 wt%, the burning rate of the DGEBA/SPD-BS systems decreased from 15.2 mm/min to 10.4 - 7.3 mm/min with increasing SPD-BS content. These results can be caused by the addition of nano-CaCO₃ to the epoxy matrix, which increased the surface contact area between the nano-CaCO₃ particles and the epoxy matrix, which in turn prevented the heat diffusion during decomposition of

the DGEBA/SPD-BS systems.[13,19,20] These results also explain that the SPD-BS and nano-CaCO₃ as flame retardants have a synergistic effect for epoxy resins.

Conclusions

A new phosphorus-containing flame retardant was synthesized and used as a flame retardant in epoxy resins. The chemical structure of the flame retardant was characterized using FT-IR and ¹H NMR spectra. The thermal properties were investigated by DSC and TGA. Flame-retardant properties of DGEBA/SPD-BS systems were evaluated by measurement of the burning rate. When SPD-BS content increased, the thermal stabilities of the DGEBA/SPD-BS systems decreased, whereas the char yields of the systems increased. The flame retardant properties of the systems significantly increased with increasing SPD-BS content. The results also indicated that the synergistic effect was found when SPD-BS and nano-CaCO₃ were incorporated into epoxy resins as flame retardants.

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