A Novel Flame Retardant of Spirocyclic Pentaerythritol Bisphosphorate for Epoxy Resins

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ABSTRACT: A novel flame retardant for epoxy resins, bisdiglycol spirocyclic pentaerythritol bisphosphorate (BDSPBP) was synthesized from the reaction of diglycol with spirocyclic pentaerythritol bisphosphorate diphosphoryl chloride, which was obtained from the reaction of phosphoryl chloride with pentaerythritol. Flammability of the cured epoxy resin systems consisted of diglycidyl ether of bisphenol A (DGEBA), low-molecular-weight polyamide and BDSPBP are investigated by vertical burning test (UL-94) and limiting oxygen index test (LOI). The results indicate that BDSPBP has good flame retardance on epoxy. The thermogravimetric analysis (TGA) shows that the epoxy resin containing BDSPBP has a high yield of residual char at high temperatures, indicating that BDSPBP is an effective charring agent. From the SEM observations of the residues of the flame retardant systems burned, the compact charred layers can be seen, which form protective shields to protect effectively internal structure, and inhibit the transmission of heat and heat diffusion during contacting fire. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4978–4982, 2006

Key words: flame retardant; synthesis; epoxy resin; charring agent; TGA

INTRODUCTION

In recent modern industry, epoxy resins play an important role due to their excellent characteristics of great versatility, toughness, low shrinkage on cure, good moisture resistance, solvent and chemical resistance, outstanding adhesion, and superior electrical and mechanical properties. So they are widely applied in surface coating, adhesives, painting and potting materials, composites, laminates, encapsulants for semiconductor and insulating materials for electric devices, etc.[1–3] These good performance and properties are obtained by crosslinking the epoxy resins into a three-dimensional, insoluble, and infusible network by reacting them with a hardener. However, cured epoxy resins have two main disadvantages: one is their inherent brittle nature, and another is their flammability. Several approaches for modifications on epoxy resins have been tried. Thermoplastic materials are being used for toughening the epoxy resins instead of rubbers because mechanical and thermal properties are not sacrificed to the same extent as when rubbers are used. Therefore, more attention has recently been give to the modification of epoxy resins by high performance tough thermoplastics, such as polyethersulfone, polyetherimide, carbopolyimide, and polyamides.[4–6] In this work, polyamide (PA-650-I) is chosen as a curing agent because of no toxicity, good adhesion and flexibility, easy operation and wide ranges of curing temperature, and variable composition. Cured epoxy resins with PA-650-I are widely used in many areas such as adhesion between metal and nonmetal materials, anticorrosive coatings, encapsulating electronic components and chemical grouting, etc. So polyamide is superior to the other common amines as a curing agent. On the other hand, to improve fire resistance of the resins, halogen-containing compounds are commonly used as flame retardants in epoxy resins. However, some halogen-containing flame retardants generate toxic and corrosive fumes during combustion, and the use of some halogen-containing additives will be banned in the future.[3,7–9] For these reasons, epoxy resin suppliers and processors are searching for halogen-free flame retardants that do not affect the processing and properties of materials. Phosphorus compounds have been found to be effective flame retardants, and are usually used as additives or incorporated into the backbone of the epoxy resin or the amine as curing agents.[10–27] Some organic phosphorus flame retardants for epoxy resins have exhibited less toxicity and smoke, better flame retardance and higher thermal stability than the conventional halogen-containing flame retardant systems.[28–30]

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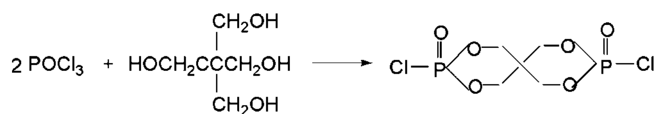


Scheme 1 The structure of SPDPC.

In the present work, a novel flame retardant bisdiglycol spirocyclic pentaerythritol bisphosphorate (BDSPBP) was synthesized and used as the flame retardation of epoxy resins. The flammability of the cured epoxy systems made of BDSPBP/DGEBA/PA-650-I was investigated systematically.

EXPERIMENTAL

Materials

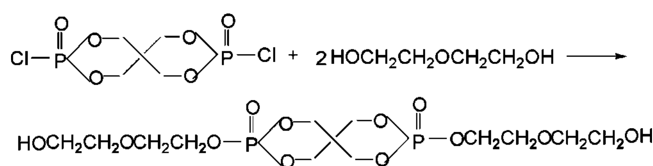
Diglycidyl ether of biphenol-A (DGEBA, E-44) was provided by Wuxi Resin Factory of Xingchen New Chemical Material Co. (Wuxi, China). Polyamide (PA-650-I) was purchased from Haitian Chemical Reagent Co. (Hunan, China). Phosphoryl chloride and pentaerythritol were obtained from Rutejin Chemical Reagent Co. (Tianjin, China) and No. 1 Reagent Company of Shanghai (Shanghai, China), respectively. Diglycol, NaOH, and anhydrous ethyl ether were purchased from Kelong Chemical Engineering Reagent Company (Chengdu, China). All the chemicals used were of reagent grade, except for E-44 and polyamide. Diglycol was distilled before use.

Synthesis of spirocyclic pentaerythritol bisphosphorate diphosphoryl chloride

Spirocyclic pentaerythritol bisphosphorate diphosphoryl chloride (SPDPC) (Scheme 1) was synthesized according to the method reported by Chen et al.[31]

Synthesis of bisdiglycol spirocyclic pentaerythritol bisphosphorate

In a 500 mL glass flask with a mechanical stirrer, a thermometer, and a condenser, SPDPC (29.7 g, 0.1 mol) and diglycol (24 mL, 0.25 mol) were added. The mixture was stirred and gradually heated. The reaction was carried out for 6 h at 80°C, and then the mixture was heated continually upto 130°C. Finally the reaction was completed after about 4 h at 130°C when no HCl could be detected. The reaction system was then cooled to room temperature. The raw product obtained was purified with anhydrous ethyl ether. The purified product was white *viscid dope*. FTIR (KBr) (cm^{-1}): 3362.0 (vs., —OH), 1257 (m, P=O), 1025 and 960 (vs., P—O—C), 1130.1 (w, C—O—C), 2927.0 (m, CH_2). The disappearance of the peak of P—Cl indicated the formation of the product (Scheme 2).



Scheme 2 The structure of BDSPBP.

Preparation of flame-retardant epoxy samples

The cured epoxy resins were obtained via thermal curing. The reactants (E-44, polyamide) were mixed in a 2 : 1 equivalent ratio with epoxy resin. Then different contents (0, 2, 5, 8, 10, 12, 15, and 18 wt %) of BDSPBP were added into the reactants, respectively, to form a series of mixtures during stirring. Finally the mixtures were cured for 5 h at 80°C and for 2 h at 120°C and the solid products were obtained.

Measurements

Oxygen index was obtained from HC-2C Oxygen Index instrument (Jiangning, China) according to ISO 4589:1984. The cured epoxy samples with different contents of flame retardants were cut to a size of $120 \times 6.5 \times 3$ mm^3. The vertical burning test (UL-94) of samples (thickness: 3 mm) was conducted on a CZF-2 instrument (Jiangning).

Thermogravimetric analysis (TGA) was conducted on Q500 V6.4 Build 193 thermal analyzer at a heating rate of 10°C/min. Samples were heated in the temperature range from room temperature to 800°C under air or N_2 at a flow rate of 60 mL/min.

Scanning electronic microscopy (SEM) observed on a JEOL JSM-5900LV was used to investigate the outer surface of residues of the cured systems. The residue samples for SEM were obtained after combustion in their limiting oxygen concentration. SEM graphs of the residual char samples were recorded after gold coating surface treatment.

TABLE I
Flammability Tests of the Cured Resins with Different Flame Retardant Contents According to LOI and UL-94

Content of flame retardant in the cured resin (wt %)	Phosphorus Contents (wt %)	LOI Values (%)	UL-94 ratings
0	0.00	21.7	–
2	0.28	23.9	–
5	0.71	27.9	–
8	1.10	28.2	–
10	1.42	29.0	–
12	1.70	29.1	V-1
15	2.11	29.2	V-1
18	2.56	29.4	V-0

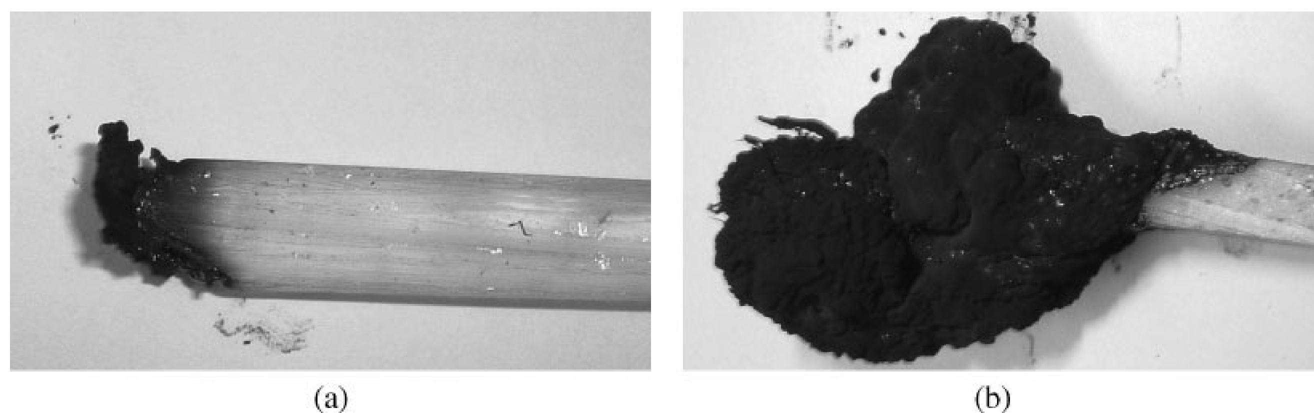


Figure 1 Photos of residues of cured epoxy resin samples containing 0 wt % (a) and 18 wt % BDSPBP (b) after combustion in their limiting oxygen concentration.

RESULTS AND DISCUSSIONS

Flammability of the epoxy systems with different contents of flame retardants

To investigate flame retardancy of polymer materials, we tested the limited oxygen index (LOI) values and vertical burning ratings (UL-94) of the cured epoxy systems with different BDSPBP contents, and the results are given in Table I. During test, the cured resins containing over 5 wt % BDSPBP show good fire resistance. A V-0 and LOI = 29.4 level can be reached when BDSPBP content is increased to 18 wt %, demonstrating that BDSPBP has good flame-retardant effect on the epoxy systems. All the residues of the cured resins containing BDSPBP showed intumescent chars after burning (See [Fig. 1(b)]). Furthermore, when the content of BDSPBP increases, the fire-resistant effect is improved. Although the LOI values do not have an obvious increase when the flame retardant content is over 10 wt %, the UL-94 rating reaches V-0 when the flame retardant content is 18 wt %. From Figure 1, we can see that there is an obvious difference between the morphologies of the residues of cured resins containing 0 and 18 wt % BDSPBP, and the latter exhibits very thick intumescent char layers. The results further proved that BDSPBP has good flame retardancy.

Thermal decomposition behaviors of the cured systems with different contents of flame retardants

TGA curves of cured resins can offer much information on their thermal stability and thermal degradation behavior. The TGA thermograms of the cured resins with 0 and 18 wt % BDSPBP under air and under N_2 atmosphere are shown in Figures 2 and 3, respectively. The temperature, at which the weight

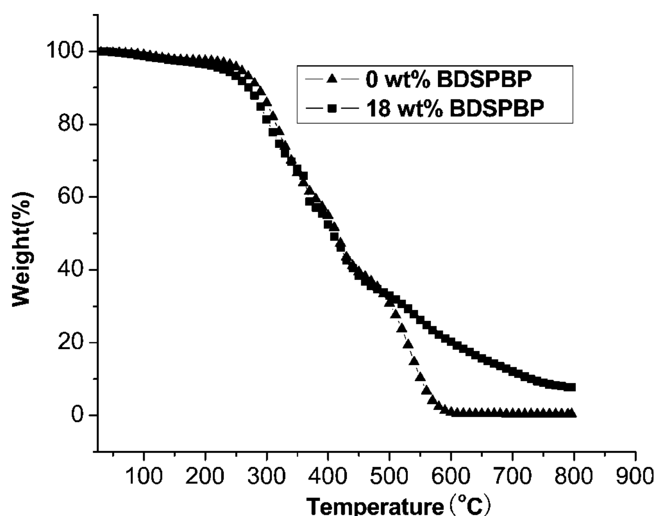


Figure 2 TGA thermographs of cured epoxy resins containing 0 and 18 wt % BDSPBP at a heating rate of 10°C/min in air.

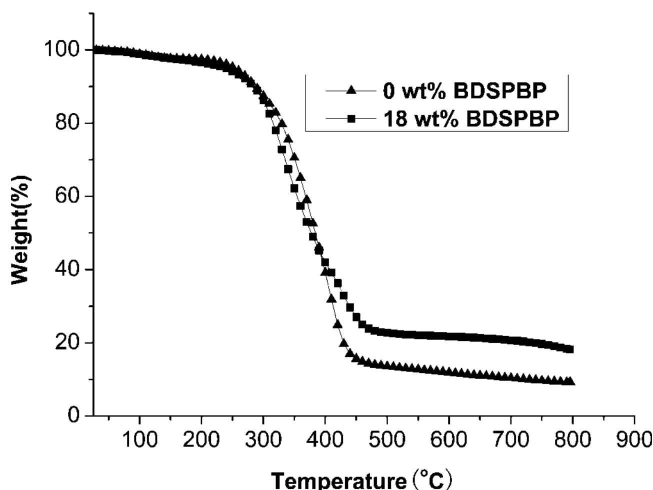


Figure 3 TGA thermographs of cured epoxy resins containing 0 and 18 wt % BDSPBP at a heating rate of 10°C/min in N_2.

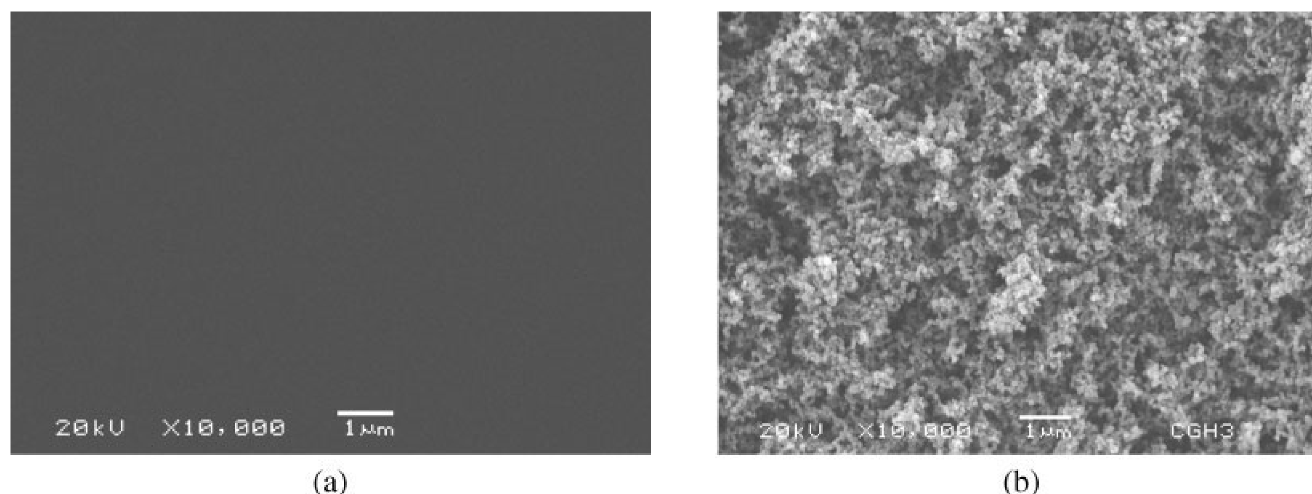


Figure 4 SEM micrographs of surfaces of residues of cured epoxy resins containing 0 wt % (a) and 18 wt % (b) BDSPBP after combustion in their limiting oxygen concentrations.

loss reaches 5%, is lower for the epoxy resin containing 18 wt % BDSPBP than for the epoxy resin containing no BDSPBP, in either air or N_2. This is due to the decomposition of the phosphorus groups at relatively low temperatures, forming a phosphorus-rich layer which can limit the production of combustible gases, decrease the exothermicity of pyrolysis reactions, and inhibit the thermal conductivity of burning materials.[14,15,24] For phosphorylated materials, this plays an important role in fire resistance in the condensing phase.[32–34] At high temperatures, the epoxy resin containing BDSPBP has high char yields, for example, 7.7% in air and 18.2% in N_2 at 795°C, in comparison with the phosphorus-free cured resin (0.4% in air and 9.2% in N_2). The high yield of residual char at high temperatures indicates that BDSPBP is an effective charring agent. As we know, the protective chars can be resistant to even higher temperatures and shield the underlying polymers from attack from oxygen and radiant heat.[34–37] Therefore, the addition of BDSPBP can enhance effectively the flame retardancy of epoxy resin.

Morphology of the residues

SEM micrographs in Figure 4 show the microstructures of residues of cured epoxy systems containing 0 wt % [Fig. 4(a)] and 18 wt % [Fig. 4(b)] flame retardant, BDSPBP. From the SEM observations, we can find that there is the obvious difference between the morphologies of the residues of the two kinds of systems. From Figure 4(a), we can observe nothing on the surface of the residues. However, from Figure 4(b), we can observe cavities and compact charred layers, which can form protective shields to protect effectively internal structure, inhibit the transmission of heat and heat diffusion during contacting fire.

CONCLUSIONS

The flame retardant BDSPBP can improve the flame retardancy of cured epoxy resins effectively. The cured epoxy system containing 18 wt % BDSPBP can obtain LOI value of 29.4 and reach V-0 rating of UL-94. TGA curves indicate that the char yield of the cured resin with 18 wt % BDSPBP is higher than that of the cured resin with no BDSPBP. The SEM observations of the residues of cured epoxy resin containing 18 wt % BDSPBP confirmed the formation of the compact charred layers, which could inhibit the transmission of heat and heat diffusion during contacting fire.

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