



## Novel low phosphorus-content bismaleimide resin system with outstanding flame retardancy and low dielectric loss

Xiangxiu Chen, Aijuan Gu\*, Guozheng Liang\*, Li Yuan, Dongxian Zhuo, Jiang-tao Hu

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Materials Science & Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 178 East Ganjiang Road, Suzhou, Jiangsu 215123, PR China

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### ABSTRACT

A novel modified bismaleimide resin system (BDP) with significantly improved flame retardancy and decreased dielectric loss was successfully prepared by copolymerizing 4,4'-bismaleimidodiphenyl methane (BDM) with 2,2'-diallyl bisphenol A (DBA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Compared with BDM/DBA resin, BDP resin has obviously different crosslinked structure, and thus simultaneously improved dielectric properties and flame retardancy. Most attractively, with a very low content of phosphorus element, the BDP resins show significantly improved flame retardancy. For example, when the content of phosphorus is as low as 0.5 wt%, the flame retardancy of BDP resin is evaluated to be UL94 V-0 level, while that of BD resin is classified as UL94 V-1 level; in addition, the total heat release (THR) of BDP resin reduces to about 61% of that of BD resin, and similar phenomenon is also observed on the weight ratio of CO/CO<sub>2</sub>. This outstanding flame retardancy of BDP resins is attributed to the attractive phosphorus-nitrogen synergistic effect. The main flame retardancy mechanism of BDP resins is evaluated to be condensed phase mechanisms. On the other hand, BDP resins exhibit improved dielectric properties; specifically, the dielectric constant and loss at 1 GHz of BDP resin with 19.7 wt% of phosphorus are 2.90 and 0.0058, only about 92% and 51% of that of neat BD resin, respectively. These interesting results demonstrate that the co-reaction of DOPO with BD resin is important, and the method proposed herein is a new approach to develop high performance resins with attractive flame retardancy and dielectric properties.

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### 1. Introduction

Developing high performance polymers with good flame retardancy is one hot subject of present polymer science and engineering because they are increasingly demanded by many cutting-edge fields including aerospace, micro-electrics, construction, textile, etc. [1–3], but unfortunately, almost all polymers don't have good flame retardancy.

Based on lots of previous investigations, by adding flame retardant to a polymer has been proved to be a common and effective method to endow polymers with good flame retardancy. Flame retardants include many sorts, among them phosphorus-containing flame retardant is regarded as the right alternative of halogen-free flame retardant owing to its high efficiency and low toxicity [4–7]. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is the representative phosphorus-containing flame

retardant, besides the merits of phosphorus-containing flame retardants, DOPO also has good thermal stability, therefore a lot of researches focused on preparing flame retardant polymers by utilizing DOPO and its derivatives [8–11], for example, DOPO based epoxides and curing agents were synthesized [12–18]. These researches obtained some interesting and positive results, however some important topics have not been studied. As we've known that excellent dielectric property (low dielectric constant and loss) is considered to be one key property of high performance resins for micro-electric field; unfortunately, the influence of flame retardant on dielectric properties of polymers is seldom studied. On the other hand, when DOPO and its derivatives were used to prepare flame retardant resins, the content of phosphorus generally should be larger than 2.5 wt% to get desirable flame retardancy (for example, UL94 V-0 level) [19], however, a larger content of phosphorus is not beneficial to maintain the thermal stability of the resin. Therefore, it is of great importance and interesting for studying these topics, this is also the target of our investigation described herein.

Bismaleimide/diallyl bisphenol A (BD), derived from the 2,2'-diallyl bisphenol A (DBA) modified bismaleimide resin (BDM), is

\* Corresponding authors. Tel.: +86 512 61875156; fax: +86 512 65880089.  
E-mail addresses: [ajgu@suda.edu.cn](mailto:ajgu@suda.edu.cn) (A. Gu), [lgzheng@suda.edu.cn](mailto:lgzheng@suda.edu.cn) (G. Liang).

claimed to possess outstanding integrated performance including outstanding thermal and moisture resistance, good processing characteristics, and high mechanical strength [20,21], so BD system has been employed to be high performance matrices for advanced composites, adhesives, and insulating coatings [22–25]. However, the flame retardancy of BD resin is not good, belonging to V-1 order according to UL94 tests. Therefore, BD resin is selected as the model for our investigation.

This paper gives the first presentation on preparing a novel flame retardancy resin system (BDP) based on BD resin and DOPO, and the discussion about the effect of the stoichiometry between BD and DOPO on the properties of BDP resins. This investigation is expected to propose a new approach to develop high performance flame retardant resins with simultaneously improved integrated performance, especially dielectric properties.

## 2. Experimental

### 2.1. Raw materials

4,4'-Bismaleimidodiphenol methane (BDM), was obtained from Institute of Northwestern Chemical Engineering (China). 2,2'-Diallyl bisphenol A (DBA) with a purification of 85% was purchased from Laiyu Chemical Factory in China. DOPO (the content of phosphorus atom is 14 wt%) was purchased from Eutec Chemical Co., Ltd (China).

### 2.2. Preparation of uncured samples for measurements

BDM and DBA was mixed with a molar ratio of 1:1, and then the mixture was put into a polyethylene (PE) bag, and ground into even mixture for differential scanning calorimeter (DSC) tests.

A mixture of BDM and DOPO (the molar ratio is 1:2), the mixture of DBA and DOPO (the molar ratio is 2:1), or the mixture of BDM, DBA and DOPO (the molar ratio is 3:1:2) was also prepared using above procedure for Differential Scanning Calorimeter (DSC) and thermogravimetric (TG) tests.

### 2.3. Preparation of BD and BDP prepolymers

According to Table 1, appropriate quantities of BDM and DBA were placed in a beaker with a mechanical stirrer and a thermometer. The mixture was heated to 125–135 °C and maintained within that temperature with stirring until a clear and brown liquid was obtained. The liquid was maintained at that temperature for additional 25 min to obtain a transparent liquid, which was BD prepolymer.

According to Table 1, appropriate quantities of DBA and DOPO were placed in a beaker with a mechanical stirrer and a thermometer. The mixture was heated to 125–135 °C and maintained within that temperature with stirring until a clear and yellow liquid was obtained (a tiny amount of which was used to record the FTIR spectrum). And then pre-weighted BDM was added into the beaker at 125–135 °C with stirring until a transparent liquid, and kept at

that temperature for 25 min to obtain a homogeneous liquid, which was coded as BDP prepolymer.

### 2.4. Preparation of cured BD and BDP resins

Each prepolymer was thoroughly degassed at 130 °C, and poured into a preheated (130 °C) metal mould, followed by curing per the curing procedure of 150 °C/2 h+180 °C/2 h+220 °C/3 h. After that the cured sample was demolded and postcured in an air oven at 230 °C for 4 h.

### 2.5. Measurements

DSC analyses were done using DSC 200 F3 (Netzsch, Germany) in the temperature range between 50 and 320 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

Fourier Transform Infrared (FTIR) spectra of each resin were recorded between 400 and 4000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  on a Nicolet 5700 infrared spectrometer (USA).

$^{31}\text{P}$  NMR spectra were performed on a Bruker Avance 400 Spectrometer (Germany) at 400 MHz using DMSO- $d_6$  as the solvent.

Dynamic Mechanical Analysis (DMA) scans were performed using TA DMA Q800 apparatus from TA Instruments (USA). Single cantilever clamp geometry was used. DMA tests were carried out from room temperature to 325 °C with a heating rate of 3 °C/min at 1 Hz. The dimensions of each sample were  $(35 \pm 0.02) \times (13 \pm 0.02) \times (1.0 \pm 0.02) \text{ mm}^3$ .

A Scanning Electron Microscope (Hitachi S-4700, Japan) coupled with energy disperse X-ray spectrometer (EDS) was employed to observe the morphologies of the fractured surfaces of the charred layers samples. The resolution of the secondary electron image is 1.5 nm under 15 kV. All samples should be dried at 105 °C for 6 h before tests.

Dielectric constant and loss were performed with an Agilent E4991A measurement system (USA) at 30 °C by a two-parallel-plate mode over a wide frequency from 1 MHz to 1 GHz. The dimensions of each sample were  $(50 \pm 0.02) \times (50 \pm 0.02) \times (1.0 \pm 0.02) \text{ mm}^3$ , and all samples were dried under vacuum at 105 °C for 1 h before tests.

TG analyses were performed using PerkinElmer TGA-7 (USA) at a heating rate of 10 °C/min with a flow rate of 100 mL/min in a nitrogen atmosphere from 50 to 800 °C. The initial decompose temperature ( $T_{di}$ ) was defined as the point of intersection at which the tangent of onset temperature and the tangent of the maximum degradation rate temperature ( $T_{max}$ ).

UL94 tests were performed according to ASTM (D63-77). The dimensions of each sample were  $(125 \pm 0.02) \times (13 \pm 0.02) \times (1.6 \pm 0.02) \text{ mm}^3$ .

Limited Oxygen Index (LOI) values were measured on a Stanton Redcraft Flame Meter (UK) according to ASTM D2863/77. The dimensions of each sample were  $(100 \pm 0.02) \times (6.5 \pm 0.02) \times (3 \pm 0.02) \text{ mm}^3$ .

Flammability of resins was characterized using a cone calorimeter performed in an FTT device (UK) according to ISO 5660 with an incident flux of 35  $\text{kW/m}^2$ . The dimensions of each sample were  $(100 \pm 0.02) \times (100 \pm 0.02) \times (3 \pm 0.02) \text{ mm}^3$ .

**Table 1**  
Formulations of BD and BDP resins.

Resin	Weight ratio		
	BDM	DBA	DOPO
BD	140	70	0
BDP1	140	70	8.1
BDP2	140	70	13.0
BDP3	140	70	16.2
BDP4	140	70	19.7

## 3. Results and discussion

### 3.1. Curing behavior and mechanism of BD and BDP prepolymers

It is known that the curing behavior of a thermosetting resin determines its crosslinking network, and thereby the properties of the cured resin, so the curing behavior is the first issue needing to be investigated on developing any new thermosetting resins and related materials.

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