



# New glass fiber/bismaleimide composites with significantly improved flame retardancy, higher mechanical strength and lower dielectric loss



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## ARTICLE INFO

### Article history:

Received 25 May 2014

Received in revised form 29 September 2014

Accepted 1 November 2014

Available online 8 November 2014

### Keywords:

A. Glass fibers

B. Interface

A. Thermosetting resin

B. Mechanical properties

## ABSTRACT

Novel glass fiber (GF)/bismaleimide composites with significantly improved flame retardancy, higher mechanical strength and lower dielectric loss were developed, of which the resin matrix is a new flame retarding resin system (BDDP) based on 4,4'-bismaleimidodiphenyl methane (BDM), 2,2'-diallyl bisphenol A (DBA) and [(6-oxido-6H-dibenz [c,e] [1,2] oxaphosphorin-6-yl)-methyl]-butanedioic acid (DDP). The influence of the loading of DDP in the matrix on the integrated performances of composites was intensively studied. Results show that GF/BDDP composites not only have significantly improved mechanical and dielectric properties, but also possess excellent flame retardancy. The main flame retarding mechanism of GF/BDDP composites is the condensed phase mechanism. The introduction of DDP significantly strengthens the interfacial adhesion between GF and the resin matrix, this is responsible for the attractive performances of GF/BDDP composites.

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## 1. Introduction

Fiber reinforced resin composites have been one of the most important materials since 1940s owing to their outstanding properties (light weight, high specific modulus and strength) and wide applications [1,2]. Of them, glass fiber (GF) reinforced resin composites have the biggest and widest application fields [3,4]. In recent years, besides mechanical and thermal properties, good flame retardancy and dielectric properties have been increasingly required by many cutting-edge fields including aerospace, electric, insulation, and IT industries [5–7].

It is known that the processing characteristics, dielectric and mechanical properties of a composite are largely controlled by those of the resin [8]. As GF does not burn, so researchers prepared flame retarding GF reinforced composites by developing flame retarding resin matrices. Typically, Yang's groups added aluminum hypophosphite and melamine cyanurate into poly(ethylene terephthalate), the modified polymer was then used to prepare GF reinforced composites; they found that about 10 wt% flame retardants should be added so that the flame retardancy of composites can achieve V-0 rating according to vertical burning UL 94 tests [9]. Similarly, only with the introduction of at least 10 wt% of flame retardants into the matrices, the GF reinforced polyamide [10] or

epoxy resin [11] composites have good flame retardancy (UL 94 V-0 rating). However, such high loading of flame retardants is not beneficial to obtain high mechanical and thermal properties [10–12]. Therefore, it is of great importance and interest to develop new GF reinforced composites with low concentration of flame retardants.

The performance of the matrix is known to be not equal to that of composite [13], especially, to make the super performance of the matrix be fully exhibited in a composite, the interface between the matrix and reinforcement plays a key role [13,14]; however, few literature compared the flame retardancy between the resin and resultant composite, and intensively studied the origin behind.

To make progress on developing flame retarding GF composites, developing resins with outstanding integrated performances including processing characteristics, flame retardancy, dielectric (low dielectric constant and loss) and mechanical properties is necessary for obtaining high performance GF reinforced composites. Bismaleimide (BMI) resin is one of heat resistant resins [15], and has been used as the matrices for advanced fiber reinforced composites. However, being an organic material, BMI does not have good flame retardancy [16]. At present, due to the high efficiency and environmentally friendly feature, the addition of phosphorus-containing flame retardants is the common technique for preparing flame retarding polymers [17]. We reported a modified BMI resin, derived from the 2,2'-diallyl bisphenol A (DBA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

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modified 4,4'-bismaleimidodiphenyl methane (BDM) resin (BDP) [18], the flame retardancy of BDP resin is UL 94 V-0 level. However, BDP prepolymers can only dissolve in solvents with high boiling points (such as N,N-dimethyl formamide and N,N-dimethyl acetamide), and DOPO has low thermal decomposition temperature.

There are two targets for our research reported herein. One is developing new GF composites with significantly improved flame retardancy, higher mechanical strength and lower dielectric loss through preparing new resin based on BDM/DBA and [(6-oxido-6H-dibenz [c,e] [1,2] oxaphosphorin-6-yl)-methyl]-butanedioic acid (DDP); the other is intensive studying the effect of the nature of the matrices on the structures and integrated properties of composites. Especially multi-type techniques including vertical burning UL 94 tests, the limited oxygen index (LOI), thermogravimetric analysis-infrared spectrometry (TG-IR) and cone calorimeter were employed to investigate the flame retardancy. Some attractive performances were obtained, and the nature behind was intensively discussed.

## 2. Experimental

### 2.1. Raw materials

BDM was obtained from Institute of Northwestern Chemical Engineering (China). DBA was purchased from Laiyu Chemical Factory in China. DDP was purchased from Eutec Trading (Shanghai) Co., Ltd. (China). GFs (3313, areal density = 80 g/m<sup>2</sup>, diameter = 0.070 mm) were purchased from Asahi Kasei Chemicals Co. (Japan), which were treated using silane with epoxy groups.

### 2.2. Preparation of BMI and BDDP prepolymers

140 g BDM and 70 g DBA were mixed thoroughly at 145–150 °C until a clear and brown liquid was obtained. The liquid was maintained at that temperature for additional 45 min to obtain a transparent BMI prepolymer.

According to Table S1 in the Supporting Information, appropriate quantities of DBA and DDP were thoroughly blended at 145 °C for 10 min, and then BDM (its weight ratio to DBA was 2:1) was added with stirring and kept at 145 °C for 35 min to obtain a homogeneous prepolymer, coded as BDDPx, where x is 1, 2, 3 or 4 when the loading of DDP in the whole prepolymer is 3, 6, 9 or 12 wt%.

### 2.3. Preparation of cured BMI and BDDP resins

Each prepolymer was thoroughly degassed at 130 °C, and poured into a mould, followed by curing using the 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.

### 2.4. Preparation of GF/BMI and GF/BDDP composites

Each prepolymer was dissolved in acetone (the weight ratio of the resin vs acetone was 65:35) to form a transparent resin solution (varnish). A sheet of GF woven fabric was immersed in the varnish, and then hung up for at least 24 h at room temperature to remove acetone, followed by heating in a hot air convection oven at 130 °C for 10 min to form a prepreg. Sixteen prepreps were stacked one by one, and then put into a metallic mold for molding according to a programmed cycle of 150 °C/2 h + 180 °C/2 h + 220 °C/3 h under a pressure of 100 psi. After that, the sample was postcured in an air oven at 230 °C for 4 h. The resultant composite was coded as GF/BMI or GF/BDDPx (according to the resin used).

The volume fractions of fibers of the composites were measured by an ablation method according to the Chinese Standard GB2577-89. Results show that GF/BMI and GF/BDDPx composites have similar volume fraction (32 ± 1 vol%).

### 2.5. Measurements

Interlaminar shear strength (ILSS) was tested on a universal testing machine (AG-X10KNSTD; Himadzu, Japan) using a three-point short-beam bending mode (ASTM standard D2344) at 25–30 °C with a cross head speed of 2 mm/min. Each reported ILSS value was the average of the results from six specimens.

The morphologies of the fractured surfaces of samples were observed by using a Scanning Electron Microscope (SEM, Hitachi S-4700, Japan). All samples were dried at 105 °C for 6 h before tests.

The reactions of monomers and mixture were evaluated using a Differential Scanning Calorimeter (DSC, Netzsch DSC 200 F3, Germany) with a heating rate of 10 °C/min under a nitrogen atmosphere.

Vertical burning UL 94 tests were performed with ASTM D635-77, the dimensions of each sample were (125 ± 0.02) × (13 ± 0.02) × (1.6 ± 0.02) mm<sup>3</sup>. For each system, five samples were tested. LOI values were measured on a Stanton Redcraft Flame Meter according to ASTM D2863/77. Cone calorimeter tests were performed on an FTT device (UK) with an incident flux of 50 kW/m<sup>2</sup> according to the Standard ISO 5660, the results were reproducible to within about ±10%, and the data reported are the averages of triplicate tests.

Thermogravimetric (TG) analyses were performed using Perkin-Elmer TGA-7 (USA) at a heating rate of 10 °C/min with a flow rate of 100 mL/min in a nitrogen atmosphere. 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 ( $T_{max}$ ).

TG-IR spectra were recorded on a thermogravimetric analyzer TG 209F1 (Netzsch, Germany) coupled with a Fourier Transform Infrared (FTIR) spectrometer (Nicolet 6700) to determine the vapor products of the sample during the decomposition with a heating rate of 10 °C/min in a nitrogen atmosphere.

Dielectric properties were tested on an Agilent E4991A measurement system (USA) at 30 °C with a two-parallel-plate mode. The dimensions of each sample were (50 ± 0.02) × (50 ± 0.02) × (1.6 ± 0.02) mm<sup>3</sup>.

## 3. Results and discussion

### 3.1. The structures of GF/BDDP and GF/BMI composites

The integrated performances of a fiber reinforced polymeric composite are determined by the properties of the individual components and the interfacial adhesion [19]. ILSS is one of the most important properties for composites, which gives information about the interfacial adhesion between the reinforcement and the matrix [20]. Fig. 1a shows the ILSS values of GF/BMI and GF/BDDP composites, the values of GF/BDDP composites are 1.4–1.9 times of that of the GF/BMI composite, and the former increases as the concentration of DDP increases.

To confirm above data, the SEM micrographs of the cross-sections of composites after ILSS tests were observed and provided in Fig. 1b1–b5. For GF/BMI composite, few resins are left on the surfaces of fibers, reflecting that GFs are easily pulled out of the matrix owing to their poor interfacial adhesion with BMI resin. This phenomenon is changed in the GF/BDDP composites. Specially, as the content of DDP increases, more fibers are buried and covered by BDDP resins; besides, fibers tend to be broken

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