



Development and mechanism of ultralow dielectric loss and toughened bismaleimide resins with high heat and moisture resistance based on unique amino-functionalized metal-organic frameworks

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ABSTRACT

High dielectric loss is the main factor that leads to easy aging and low service reliability of electronic and insulation products. Herein, novel heat and moisture-resistant bismaleimide (BD) resins with ultralow dielectric loss and high toughness were developed through synthesizing unique amino-functionalized metal-organic framework (sN-MIL) with small pore diameter and low specific surface. The addition of only 0.3 wt% sN-MIL into BD resin effectively improves impact strength and fracture toughness to about 1.70 times; meanwhile significantly reducing dielectric loss to only 0.0004 (100 Hz), which is almost the lowest dielectric loss reported among porous filler/polymer composites. The origin behind these attractive performances of sN-MIL/BD composites was intensively discussed.

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1. Introduction

High performance thermosetting resin (HPTR) has always been the key and base material for the development of cutting-edge industries such as electric information [1], insulation [2], new energy [3], and aerospace [4], etc. The development on products with lighter weight, higher speed and higher power makes great necessity of high service reliability. Lots of studies have pointed out that high dielectric loss is the main reason that leads to easy aging and low service reliability [5], so low dielectric loss becomes the necessary property of new generation HPTRs besides high heat resistance and toughness [1,2].

Up-to-date, the main mechanism of reducing dielectric loss is decreasing polarity intensity [6]. The specific methods include introducing nanopores [7], preparing dipole rapid-polarized polymers [8], improving dispersion of nanofillers [9], and building core-shell nanostructures [10], etc. The method of introducing inorganic

rigid particles with porous structure, by taking the advantage of air (its dielectric loss is 0) [11], may also toughen resins [12] while maintaining good thermal property, and thus attracting attentions of researchers worldwide.

Cyclodextrin (CD) [13], meso-porous silicon (SBA-15) [14], or polyhedral oligomeric silsesquioxane (POSS) [15] was introduced into resins to prepare HPTRs with low dielectric loss. As these fillers did not have good dispersion in resins, surface functionalization of fillers is necessary. However the introduction of reactive groups generally increases polarity, and thus partially counteracts the effect of reducing dielectric loss from pores [14]. Besides, if the volume fraction of voids in a resin exceeds 30 vol%, pores tend to form channels, into which moisture is easy to enter, and thus leading to high dielectric loss [16]; meanwhile too much voids are also easy to form cracks [17], leading to degraded mechanical property.

Metal-organic frameworks (MOFs) synthesized by self-assembly technique are composed of organic ligands and suitable metal cations (Cu⁺, Cu²⁺, Ag⁺, Zn²⁺, Co²⁺, K⁺, etc.) or clusters [18,19]. They have many merits including large porosity, high specific surface, low density, selective adsorption and high thermal stability, etc. [20]. In 2010 Seifert et al. gave the first statement that MOF would replace Si-based materials and become a new interlayer

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insulating material with low dielectric constant in the microelectronic industry [21]. However, only about five articles reported the modification of thermosetting resins by MOFs, and they focused on toughening, but did not related to low dielectric loss.

Manju et al. was the first group of introducing Zn₄O (1,4-benzenedicarboxylate)₃ metal–organic frameworks (MOF-5) into epoxy resin [22], they found that adding 0.3 wt% of MOF-5 increased 68% and 36% in notched Izod impact strength and critical stress intensity factor (K_{IC}), respectively. However MOF-5 is not stable in humid environment and will collapse after stayed in moist air for only 2 days [23]. We fabricated a hybrid (GO/MnMOF) comprised of graphene oxide (GO) and manganese based MOF (MnMOF), and found that the impact strength of modified cyanate ester (CE) resin with 0.5 wt%GO/MnMOF is about 2.3 times of that of CE resin [12]. However, strong oxidizing agents should be used to prepare GO; besides, dielectric constant and loss need to be further reduced.

Notably, available MOFs have ultrahigh surface areas (an extreme case is 7000 m² g⁻¹ [18]) and very large porosity (free volume is as high as 90% or even larger), so they are easy to absorb moisture and form aggregation in resins, and consequently, they are not suitable to prepare materials with low dielectric loss; in other words, special MOFs with small pore size, low surface area and excellent stability should be synthesized for developing new HPTRs.

Bismaleimide (BMI) resin is a representative of HPTRs with significant applications in electronic information, insulation, new energy, aerospace and others [24], so BMI resin is selected as the basic resin of our research reported herein. To meet performance requirements of new generation HPTRs, an amino-functionalized MOF (sN-MIL) with small pore diameter and low specific surface area was synthesized, and then new sN-MIL modified BMI resins with ultralow dielectric loss and high toughness were developed. The mechanism behind was intensively studied through correlating with structure.

2. Experimental

2.1. Materials

4, 4'-Bismaleimidodiphenylmethane (BDM) was supplied by Northwestern Institute of Chemical Engineering Institute (China). 2,2'-Diallylbisphenol A (DBA) was purchased from Laiyu Chemical Factory (China). 2-Aminoterephthalic acid (H₂BDC-NH₂) was obtained from TCI (Shanghai) Development Co., Ltd, China. Aluminum chloride hexhydrate (AlCl₃·6 H₂O) and *p*-phthalic acid (H₂BDC) were bought from Shanghai Chemical Reagent Co., Ltd, China. N, N-Dimethyl formamide (DMF, AR) and ethanol (C₂H₅OH, AR) were commercial reagents. All chemicals were used as received.

2.2. Synthesis of sN-MIL

Amino-functionalized MIL-101 (Al) (sN-MIL) was prepared using a modified procedure based on the method reported earlier [25]. Typically, H₂BDC-NH₂ (0.816 g, 4.5 mmol) was dissolved in 180 mL DMF at 110 °C to get a clear solution, into which AlCl₃·6 H₂O (2.172 g, 9 mmol) was added within 30 min, followed by stirring for 4 h at 110 °C and staying at 110 °C for 12 h without stirring. After cooled to 20–25 °C, the yellow solid was filtered, and washed with 80 mL ethanol, successively, to get crude product. The crude product was put into 150 mL boiling ethanol and maintained for 24 h to get activation. Finally, the solid was dried at 200 °C for 24 h under reduced pressure to get sN-MIL.

2.3. Preparation of prepolymers, cured resins and composites

BDM and DBA with a molar ratio of 1:0.86 were blended and maintained at 140–145 °C with stirring for 15 min to obtain BD prepolymer. sN-MIL and DBA were blended under ultrasonic condition for 30 min, followed by blending with BDM at 140–145 °C for 15 min to obtain a prepolymer, which was coded as xsN-MIL/BD, where x means the weight percent of sN-MIL in the whole prepolymer, taking values of 0.1, 0.3 and 0.7.

Each prepolymer was maintained at 140–145 °C for an additional 15 min to obtain a transparent liquid, which was poured into a pre-heated mold and degassed in vacuum at 140 °C for 20 min. Then the mold was put into an oven for curing and postcuring with procedures of 150 °C/2 h + 180 °C/2 h + 200 °C/2 h + 220 °C/2 h, and 240 °C/4 h, successively, to get cured resin or composite.

2.4. Measurements

Powder X-ray diffraction (XRD) patterns were obtained from a Rigaku D/Max diffractometric (Rigaku Co. Ltd, Tokyo, Japan) with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) at a scanning rate of 2° min⁻¹.

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm⁻¹ at a resolution of 2 cm⁻¹ on a Prostar LC240 infrared spectrometer (Agilent Technologies, Palo Alto, USA).

Specific areas were calculated according to standard Brunauer–Emmett–Teller (BET) method on an automatic surface analyzer (ASAP2020M, USA). The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99.

Differential scanning calorimetry (DSC) tests were performed on a TA calorimeter (Q200, TA) with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Broadband dielectric spectrometer (Novocontrol Concept 80, Germany) was applied to test dielectric properties of samples with dimensions of (25 ± 0.02) mm × (25 ± 0.02) mm × (3 ± 0.02) mm at room temperature. DC volume conductivities were calculated from resistances tested on a Keithley Model 4200 sourcemeter (USA). Silver paste was painted on bottom and upper surfaces of samples.

Thermogravimetric (TG) analyses were performed on a TA instrument (Discovery TGA, USA) with a heating rate of 10 °C min⁻¹ and a nitrogen flowing rate of 10 mL min⁻¹.

Dynamic mechanical analyses (DMA) were conducted on a dynamic mechanical analyzer (TA Q800, USA) under a single-cantilever blending mode with a heating rate of 5 °C min⁻¹ at 3 Hz.

Free volumes were got from positron annihilation lifetime spectroscopies (PALS) which were recorded on a positron lifetime spectrometer (USA) with a time resolution of 300 ps and positron source of ²²Na (20 μ Ci). The dimensions of samples were (10 ± 0.02) mm × (10 ± 0.02) mm × (1 ± 0.02) mm.

Following Chinese Standard GB/T2571-95, impact strengths of each specimen with dimensions of (50 ± 0.02) mm × (6 ± 0.02) mm × (3 ± 0.02) mm were tested using a JGL-5 tester (Shenzhen, China).

K_{IC} was measured using single-edge notched beam specimens under mode I condition. The crack size of original crack (a) was 0.45 $W < a < 0.7 W$ (W is the width of specimens), the displacement rate was 0.5 mm min⁻¹.

According to Chinese Standard GB/T2570-95, flexural strengths were tested on an electronic universal testing machine (WDW, Shenzhen, China) with a cross-head speed of 10 mm min⁻¹ at room temperature. The dimensions of each specimen were (80 ± 0.02) mm × (15 ± 0.02) mm × (3 ± 0.02) mm.

Scanning electron microscope (SEM) (Hitachi S-4700, Tokyo, Japan) equipped with an energy dispersive spectrometry (EDS) attachment and transmission electron microscopy (TEM, Hitachi H800, Japan) were employed to observe morphologies of samples.

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