



High performance cyanate ester resins/reactive porous polymeric microsphere systems with low-temperature processability



Chao Lin, Li Yuan*, Aijuan Gu, Feng Chen, Guozheng Liang

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

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ABSTRACT

Porous cross-linked poly(phenylene oxide)–epoxy polymer microspheres PPO-EPMS) with reactive hydroxyl(-OH) and amine groups were applied to bisphenol A dicyanate ester (BADCy) resin to develop a novel high performance resin system with low-temperature processability. The effects of PPO-EPMS on the reactivity of BADCy, the mechanical properties, the thermal properties and the dielectric properties of cured BADCy were discussed in detail. Results indicate that PPO-EPMS can catalyze the polymerization of BADCy owing to the -OH and amine groups in MS. BADCy systems with appropriate PPO-EPMS content cured at low temperature show better mechanical property and higher glass transition temperature (T_g) than the pure BADCy cured at high cure temperature. The dielectric property of BADCy/PPO-EPMS systems cured at low temperature is very close to the dielectric property of BADCy cured at high temperature in the frequency range of 10–10⁶ Hz between 50 and 150 °C.

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1. Introduction

Cyanate ester (CE) resins can polymerize in the presence of heat and catalysts to form three-dimensional networks of oxygen-linked triazine through the cyclotrimerization reaction of three cyanate ester (-OCN) groups. The cured CE resins possess many outstanding properties including good mechanical property, outstanding thermal stability, superior dielectric property, excellent adhesive properties and good moisture resistance [1–4]. These unique properties of CE resins make them excellent candidates for many applications such as printed circuit boards, radomes, adhesives and structural materials. However, highly crosslinked CE is brittle and the cure temperature for CE is relatively high (>220 °C), which lead to the poor resistance to crack propagation and high internal residual stress in the matrix [2,5–7]. To overcome the weaknesses of CE, many methods have been developed to toughen the matrix and decrease the polymerization temperature of the resin. For instance, the addition of thermoplastics [8], rubbers [9,10], organic or inorganic fillers [11,12], thermosetting resins [13], and the incorporation of variable length spacer groups between the reactive ends of CE resins [14,15] can improve the

toughness of CE matrix. Small additions of catalysts such as organometallic [16,17] and impurities [2] can significantly reduce the polymerization temperature of CE. So, a combined method of toughening matrix and reducing polymerization temperature is very practical for fabricating CE composites.

Studies have shown that porous (or hollow) microspheres (MS) can improve the toughness of polymer matrix due to the stress transfer from matrix to elastomer particles, the crack-pinning-bowing mechanism and debonding mechanism. For example, reactive epoxy MS could slightly enhance the fracture toughness of polymer with effectively improved glass transition temperature (T_g) [18]. The fracture toughness of epoxy resins filled with urethane MS could be increased 5.7 times, and the shear strength and T-peel strength of the modified resin system were higher than that of unmodified resin system [19]. The impact strength of CE filled with 30 wt% hollow glass MS was 26% higher than that of pure CE [20]. Since porous structure MS can carry catalyst to control the reaction [21,22] and the polymerization of CE is very sensitive to catalysts [2,16,17], porous MS with catalyst can be served as function particles to improve the mechanical property of CE polymer composites, decrease the polymerization temperature, etc.

Recently, porous crosslinked poly(phenylene oxide)–epoxy polymer MS(PPO-EPMS) have been prepared in our laboratory [23]. During the synthesis process of the MS, reactive hydroxyl(-OH) and amine groups resulting from the materials such as the crosslinked PPO, epoxy polymers and catalysts can be

* Corresponding author at: Department of Materials Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, PR China. Tel.: +86 512 65880967; fax: +86 512 65880089.

E-mail address: yuanli@suda.edu.cn (L. Yuan).

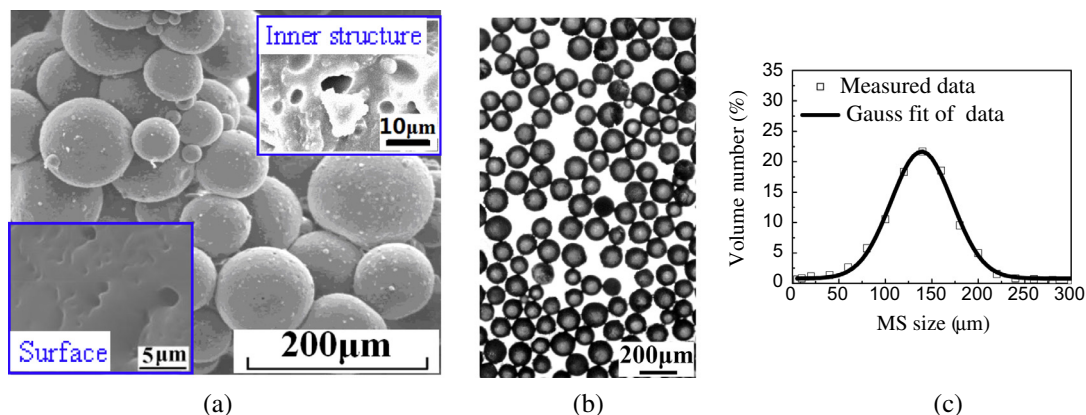


Fig. 1. SEM and OM images and the size distribution of PPO-EPMS. (a) SEM image. (b) OM image. (c) Size distribution.

contained in MS, then the MS can catalyze the polymerization of CE [3,11,15,24,25]. In this study, we developed a novel high performance CE/MS system with low temperature processability. The effects of MS on the reactivity of CE, the mechanical property, thermal property and dielectric property of the cured CE were systematically investigated.

2. Experimental

2.1. Materials

Bisphenol A dicyanate ester (2,2'-bis(4-cyanatophenyl)isopropylidene, BADCy) was bought from Zhejiang Shangyu Shengda Biochemical Co. Ltd. Epoxy resins (diglycidyl ether of bisphenol A: DGEBA) were obtained from Wuxi Resin Plant. 2,6-dimethyl phenol(DMP) was purchased from Rising Chemical Co. Ltd. Surfactant sodium dodecylbenzene sulfonate (SDBS) was supplied by Tianjin Chemical Regents Factory. Cuprous chloride (CuCl) was brought from Shanghai Guanghua Technology Co., Ltd. Ethylenediamine (EDA) was obtained from Shanghai Sunheat Chemicals Co., Ltd. Copper-ethylenediamine(Cu-EDA) complex was prepared by dissolving CuCl and EDA in water. Porous crosslinked poly(phenylene oxide)(PPO)-epoxy polymer MS(PPO-EPMS) with reactive —OH and amine groups were synthesized in our laboratory.

2.2. Synthesis of MS

MS can be synthesized according to Refs. [23,26]. At room temperature(around 25 °C), 30 g DMP and 100 ml deionized water were mixed in 500 ml three-neck round bottom flask equipped with a mechanical stirrer, the pH of mixture system was adjusted to about 13 with NaOH aqueous solution. When DMP completely dissolved in water, 100 ml 1.0%SDBS water solution and a slow stream of 36 g DGEBA were added to the solution to form oil-in-water emulsion under agitation, then the mixture was vigorously stirred at fixed agitation rate (430 rpm) under oxygen condition and 15.6 g Cu-EDA complex catalyst was added to the mixture. After 3 h, the reaction was complete. The obtained PPO-EPMS suspension was rinsed 2 times with deionized water and acetone, filtrated and air-dried for 24 h.

2.3. Preparation of BADCy/MS system

BADCy was heated at 120 °C, when it melted to a clear liquid, a fixed content of MS was added with stirring, keeping at 120 °C for 30–40 min, then the mixture was poured into a glass mould. After out-degassed, BADCy/MS system was cured via the following pro-

cess of 150 °C/2 h + 180 °C/2 h + 200 °C/2 h. The pure BADCy was cured via temperature process of 150 °C/2 h + 180 °C/2 h + 200 °C/2 h and postcured at 220 °C for 4 h.

2.4. Characterization

The impact strength of the cured resin system was determined according to GB/T 2571-1995 using a Charpy Impact Machine Tester. The flexural strength was measured according to GB/T 9341-2008 using an electronic universal testing machine.

The morphologies of MS and the fracture surface of cured BADCy/MS samples were observed using a scanning electron microscope (SEM, Hitachi S-4700) or optical microscope(OM, SMZ-B2, Chongqing Aote Optics Instrument Co., Ltd.). All samples for SEM experiments were sputter-coated with a thin gold layer under vacuum situation.

The size distribution of MS was analyzed using Malvern MasterSizer 2000 particle analyzer. The mean diameter of MS was determined from data sets of at least 250 OM measurements.

The surface area of MS was determined by Quantachrome instruments (OCCHIO FC200S+).

Fourier-transform infrared (FTIR) spectrum of MS was performed using a FTIR spectrometer (NICOLET 5700) to identify the chemical structure.

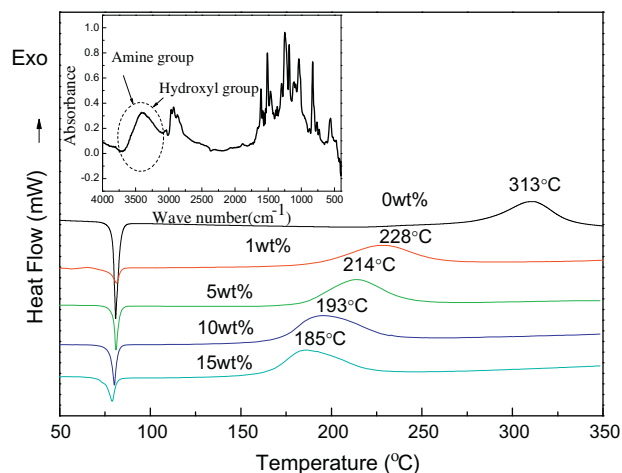


Fig. 2. DSC curves of BADCy/MS systems with different MS content along with the FTIR spectrum of MS.

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