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Preparation and studies on properties of porous epoxy composites containing microscale hollow epoxy spheres

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ABSTRACT

In this work, a series of porous epoxy composites containing microscale, hollow epoxy spheres were synthesized and characterized. First, microscale epoxy spheres were produced using amino-modified silica (AMS) particles with diameters of ~1 μm through a base-catalyzed sol–gel route. The as-synthesized AMS particles were then characterized through Fourier-transform infrared, ^{13}C nuclear magnetic resonance (NMR), and ^{29}Si-NMR spectroscopy. The prepared core–shell particles were immersed into a 1 wt.% of HF solution for 24 h to remove the inner part of the silica core, leading to the formation of hollow spheres of epoxy with a wall thickness of ~100 nm. These hollow epoxy spheres (HES) were characterized by scanning electron microscopy (SEM), Transmission electron microscopy, and thermogravimetric analysis (TGA). Finally, a series of hybrid materials was synthesized by performing thermal ring-opening polymerization reactions of epoxy resin in the presence of as-synthesized HES. Based on SEM observations on the morphology, the HES showed good dispersion capability in the polymer matrices, which led to a significantly reduced thermal conductivity and slightly decreased dielectric constant based on the transient plane source and LCR measurements, respectively. For example, the thermal conductivity and dielectric constant decreased by 49.3% and 12.6%, respectively, in the porous epoxy material synthesized with a final HES loading of about 10%. One possible reason was the large amount of air present in the material. Other physical characteristics such as the thermal and mechanical properties based on the results of TGA, differential scanning calorimetry, and dynamic mechanical analysis were investigated.

1. Introduction

Porous materials are generally used when low, fixed, and well-defined thermal conductivity is required, for instance, in catalyst supports, hot-gas or molten-metal filters, membranes, and gas burners [1]. Neat porous polymeric materials have received much attention because their important characteristics can be applied in versatile fields, and they are often used as core materials in sandwich composites for the aerospace and automotive industries, as well as in marine structures [2]. Typically, foams with inclusion voids under investigation for potential applications are mainly based on the porous structures within thermoplastic polymers [3–6]. On the other hand, porous thermosets are synthesized by reactive encapsulation of suitable solvents using a cross-linking polymerization reaction carried out to completion followed by phase separation [7]. Recently, microscale and nanoscale hollow spheres of polymers have attracted a great amount of attention because of their potential use in encapsulation applications. Hollow microspheres represent a special class of microspheres that are gas-filled spherical particles with diameters between 1 and 1000 nm; they have a range of potential applications as the empty cores allow the encapsulation of a range of materials in high concentration [8]. The inner volume of each hollow microsphere contains an inert gas, which results in some unique properties such as light weight, low thermal conductivity, and a low dielectric constant [9–15]. Most microspheres are made from rigid shell materials such as polymeric materials (i.e., thermoplastic or thermoset resins) [16,17], ceramic, carbon, metal, and glass to obtain excellent end properties [18]; there are reports in the literature on studies to reduce thermal transfer and the dielectric constant of hollow glass microspheres, hollow SiO_2, and hollow TiO_2 in a matrix material [1,9,10,19]. In addition, the hollow polymer spheres were used to produce other materials with low dielectric constant. Recently, Ishizaka et al. used hollow polymer particles as filler material in

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the synthesis of low-dielectric-constant polyimide (PI) films. This strategy provided films in which air voids existed between and within the composite PI particles; as a result, the dielectric constant reached values as low as 1.9 [20]. However, there have not been reported studies on using hollow polymer spheres to reduce a material's thermal conductivity.

In the study reported here, we used hollow epoxy spheres (HES) as a filler to synthesize a porous epoxy material and investigated its thermal conductivity. The hollow epoxy was fabricated by adding an epoxy coating on the surface of amino-modified silica (AMS) particles that were synthesized by performing a conventional base-catalyzed sol–gel reaction of methyltrimethoxysilane (MTMS) in the presence of 3-aminopropyltrimethoxysilane (APTMS) molecules and following with removal of the core particles via chemical etching (1.0 wt.% HF). These HES were incorporated directly into an epoxy solution to synthesize the porous epoxy material. The thermal conductivity of porous epoxy decrease by 50% and the storage modulus remained at 1200 MPa when 10 wt.% of HES was added to the epoxy materials. In this case, the thermal conductivity was again a key property.

2. Experimental

2.1. Instrumentation and measurements

Methyltrimethoxysilane (MTMS; Sigma–Aldrich), 3-aminopropyltrimethoxy-silane (APTMS; Fluka), bisphenol A diglycidyl ether (DGEBA; Fluka), triphenylolmethane triglycidyl ether (TGTPM; Sigma–Aldrich), *N*,*N*-dimethylacetamide (DMAc, Sigma–Aldrich), tris[poly-(propylene glycol) amine terminated] ether (T-403; Sigma–Aldrich), and ammonium hydroxide (28%, Riedel–deHaen), were used as-received without further purification. The surface-modified silica spheres were studied using ^{13}C and ^{29}Si solid-state magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectra. The MAS-NMR spectra were recorded at 9.4 T using a Bruker Avance 400 spectrometer, with zirconia rotors of 4-mm diameter spun at 5 kHz. The ^{13}C spectra were obtained with a Bruker MSL500 spectrometer at 125 MHz using the cross-polarization (CP) technique and tetramethylsilane (TMS) as a reference. Fourier-transform infrared (FTIR) spectra were obtained in the range of 4000–400 cm^{-1} and at a resolution of 4.0 cm^{-1}, using an infrared spectrometer (FT/IR-4100, JASCO) at room temperature. Transmission electron microscope (TEM) images of the HES were obtained with a microscope (200FX, JEOL) operated at an accelerating voltage of 120 kV. The apparatus for the thermal-conductivity measurements was a TPS 500 Thermal Constants Analyzer supplied by Hot Disk Inc. The apparatus consisted of a personal computer with a Keithley 2400 Source Meter, cables, high-temperature test-piece holder, and a number of Hot Disk sensors. The transient plane source (TPS) method covers a range from good thermal insulating materials (k = 0.03 W/mK) to good thermal conductors (k = 100 W/mK). The Hot Disk sensor consisted of an electrically conducting pattern in the shape of a double spiral etched out of a 10-μm-thick sheet of nickel, as shown in Scheme 1a. Nickel foil was chosen because of its high and well-known coefficient of resistivity. The conducting pattern was supported on both sides with a thin electrically insulating material. When performing the measurements, the TPS element was simply sandwiched between two halves of the test specimen, as indicated in Scheme 3b. The dielectric properties of the porous epoxy composite were measured Agilent Precision LCR Meters with model Hewlett Packard 4291B meter at various frequencies (1 MHz–1.8 GHz) and at room temperature.

2.2. Synthesis of amino-modified silica particles

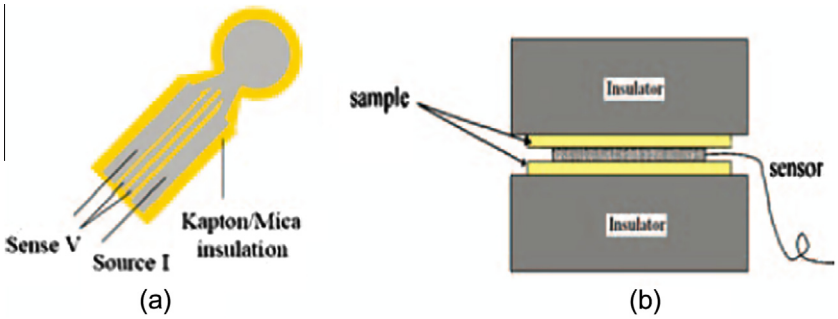
The AMS nanoparticles were synthesized via a conventional base-catalyzed sol–gel reaction of 2.0433 g MTMS in the presence of 0.2689 g APTMS molecules, as shown in Scheme 2. After 0.2 g of surfactant and 0.02 g of polyvinylpyrrolidone (PVP) were first dissolved in 20 mL of de-ionized water, 0.1 mL of an ammonium hydroxide (28%) solution was added to the aqueous medium, and the temperature of the medium was kept at 0 °C. An organo-methoxysilane mixture was slowly added to the aqueous medium over approximately 1 h, and the reaction continued for 6 h at room temperature. Finally, the synthesized particles were washed severed times with ethanol and separated from the aqueous mixture by centrifugal sedimentation to remove the surfactants and then re-dispersed in water.

2.3. Preparation of silica–epoxy core–shell particles

The SiO_2–epoxy particles were synthesized as follows. First, 1 g of AMS particles was dispersed in DMAc with ultrasonic agitation at room temperature. After 1 g of TGTPM was added to the mixed solution and was completely dissolved, 0.48 g of T-403 was added in small portions and the mixture was left to react continuously for about 48 h with agitation at 80 °C. The epoxy-coated silica particles were then isolated by centrifugation and dried at an operational temperature of 140 °C for 6 h. Eventually, silica–epoxy core–shell particles (CSPs) were obtained.

2.4. Fabrication of hollow epoxy spheres

Hollow epoxy spheres were fabricated by etching the as-synthesized epoxy-coated silica CSPs with 1% hydrofluoric acid. Approximately 3 g of CSPs was mixed with 100 mL of 1% HF in a well-sealed vial and then left to react for 24 h. After etching was completed, the resulting HES were washed severed times with de-ionized water. Repetitive centrifugation and re-dispersion were



Scheme 1. (a) Hot disk sensor with Kapton/Mica insulation and (b) test device of Hot Disk thermal constants analyzer.