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Synthesis of a fully capped mesoporous silica and its hybrids with extremely low dielectric constant and loss

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ABSTRACT

A novel fully capped mesoporous silica (FCMPS) was synthesized by producing a layer of linked polyhedral oligomeric silsesquioxanes (LPOSS) on the surface of a typical mesoporous silica (SBA-15). The structure of FCMPS was characterized using Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (^{29}Si NMR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM), Nitrogen adsorption–desorption and thermogravimetric (TG) analyses. Compared with SBA-15, FCMPS has not only high surface area, pore volume and size, but also remarkably improved thermal stability, the initial degradation temperature (T_{di}) of FCMPS increases about 194 °C. In addition, FCMPS overcomes the drawback of SBA-15, exhibiting much lower and stable dielectric constant and loss. Based on the synthesis of FCMPS, the FCMPS/bismaleimide resin (BD) hybrids with different contents of FCMPS were prepared, and their dielectric properties were investigated. Results show that FCMPS/BD hybrids have much lower and stable dielectric constant and loss than SBA-15/BD hybrids owing to the special structure of FCMPS. With the addition of 1 wt.% FCMPS into BD resin, the dielectric constant of the resultant hybrid is as low as about 2.50 over the whole frequency from 10 to 10^6 Hz; moreover, the dielectric loss of the hybrid is almost independent on the frequency, and the dielectric loss at higher frequencies (>10^3 Hz) is even lower than that of BD resin. These attractive features make FCMPS have obvious advantage in developing materials with low dielectric constant and loss.

1. Introduction

Low dielectric constant (low-*k*) materials have shown great potential in microelectronic industry owing to the continuously increasing requirements of fabricating devices with smaller size and faster speed [1–4]. Nowadays, one leading approach for preparing low-*k* material is to introduce porous materials into a polymer by taking the advantage of the low dielectric constant ($\varepsilon \approx 1$) of air in the pores [5–8].

Mesoporous silica (MPS) is a kind of porous material [9], however it has several tricky problems that restrict the application in fabricating low-*k* polymeric hybrids. First, MPS is very easy to adsorb water (moisture) owing to the existence of rich polar and hydrophilic silanol groups in the inner channels of MPS, as the dielectric constant of water is as high as about 80, so MPS usually shows a very high dielectric constant. Second, the size of the inner channels of MPS is generally so large that the resin molecule can enter into the channels [10]; hence the dielectric constant of the resultant hybrids is not as low as predicted.

In order to fully take the advantage of MPS in preparing low-*k* materials, Yamauchi et al. tried to block (cap) the entrance of MPS [11,12], however they found that it was not possible to eliminate silanol groups in the inner channels if the entrance of MPS had been fully blocked, so they prepared partly (or incompletely) capped MPS, and introduced small molecules into the inner channels of MPS to eliminate the silanol groups. After that, they added the partly capped MPS into epoxy resin, and found that the dielectric constant at around 1 GHz of the hybrid with 20 wt.% partly capped MPS is as low as 2.60.

Unfortunately, above partly capped MPS is not suitable for real applications owing to following reasons. First, the mechanism for capping is the co-reaction between Si-OH and active groups of capping materials, hence the dimensions of the capping material determine the capping degree of the capped MPS. If the dimensions of the "capping material" are small, then macromolecules can enter the entrance of the partly capped MPS, this means that the dimensions of the "capping materials" should be enlarged as the porosity of MPS increases, so the selection range of the suitable "capping" materials is limited. Second, some polar compounds can still enter the inner channels of incompletely capped MPS owing to the large entrance, and thus resulting in high dielectric constant. Therefore, how to overcome these problems is a challenging

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and meaningful topic. The aim of this work is to synthesize a new and fully capped MPS, which is then used to develop low-*k* polymeric hybrids.

Polyhedral oligomeric silsesquioxane (POSS) is composed of an inorganic cage-like silicon and oxygen framework (Si_8O_{12}) surrounded by organic corner groups [13–18]. The organic corner groups provide a great possibility to combine many POSS particles together to form a new kind of MPS that is named as linked POSS (LPOSS) [19,20]. Besides the chemical structure, LPOSS has lots of porosities, so LPOSS exhibits low dielectric constant. Note that the size of LPOSS can be easily adjusted [21,22], hence LPOSS may be a potential material for capping MPS, but no work has been reported.

Lots of investigations have proved that the properties of the hybrids are determined by the nature of either inorganic or organic phase as well as the interface between the two phases, demonstrating that inorganic and organic phases should be carefully selected to meet the requirements of applications.

Besides the porous materials, the nature of the polymer is also the key factor for preparing low-*k* materials. In this study, diallyl bisphenol A modified bismaleimide (BD) resin, one typical kind of heat resistant thermosetting resin, is chosen as the organic phase for developing low-*k* hybrids owing to its outstanding integrated performance (such as good processing characteristics and diversity of reactivity, high strength and toughness, good thermal and dielectric properties, etc.) and wide applications [23,24].

In this work, a fully capped mesoporous silica (FCMPS) with a core–shell structure was designed and synthesized, of which the core is SBA-15 that is a typical MPS and has been widely used in fabricating low-*k* materials [8,10,25], and the shell is LPOSS. Based on the synthesis of FCMPS, new hybrids based on FCMPS and BD resin were prepared, and the dielectric properties of FCMPS/BD hybrids were investigated. The corresponding properties of SBA-15/BD hybrids were also studied comparatively. Results show that FCMPS has superior advantage in fabricating low-*k* materials.

2. Experimental

2.1. Raw materials

4,4′-Bismaleimidodiphenol methane (BDM) was obtained from Institute of Northwestern Chemical Engineering (China). 2,2′-Diallylbisphenol A (DBA) was purchased from Laiyu Chemical Factory (China). Tetramethylammonium hydroxide pentahydrate (AR) was purchased from Rudong Zhenfeng Yiyang Chemical Co., Ltd., China. SBA-15 was received from Department of Chemistry, Fudan University, China. Toluene (AR) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Tetraethoxysilane (AR), anhydrous methanol (AR), anhydrous acetone (AR) and dimethyldichlorosilane (DMDCS, AR) were all commercial products made in China, and used as received.

2.2. Synthesis of octameric silicate anion

20.8 g (0.1 mol) tetraethoxysilane were added dropwise into a reactor containing 0.1 mol tetramethylammonium hydroxide and 91 mL (5.05 mol) water. The reaction mixture was vigorously stirred at 23 ± 2 °C for 24 h, and then 60 °C for 10 h. After that, the mixture was concentrated by distillation under a reduced pressure. The concentrated product was cooled to 4 °C, and microcrystalline was precipitated from the cool solution. The crystal was separated by filtration, washed with acetone, and dried in vacuum to get cubic octameric silicate anion, $(Me_4N)_8Si_8O_{20}$.

2.3. Preparation of FCMPS

FCMPS was prepared following three stages. First, DMDCS (10.75 g) was added slowly into a reactor containing anhydrous toluene (150 mL) and dry mesoporous silica SBA-15 (5 g). The reaction mixture was vigorously stirred at 40 °C for 6 h, and then anhydrous toluene and residual DMDCS were removed to get a crude product. The crude product was washed with anhydrous acetone and dried at 50 °C in the vacuum, the resultant product was coded as Cl-SBA-15.

Second, from the literatures, it can be known that the surface area of SBA-15 can be up to 960 m^2/g [26], and POSS nanostructures have diameters ranging from 1 to 3 nm [13]. According to these data, the weight ratio between POSS and Cl-SBA-15 was set as 10:1, which guarantee the blocking of the entrances of Cl-SBA15 particles. Specifically, Cl-SBA-15 (0.3 g) and anhydrous acetone (30 mL) were blended to form Solution A. $(Me_4N)_8Si_8O_{20}$ (0.3 g) and anhydrous methanol (10 mL) were mixed to form Solution B. Solution A was added into the Solution B, and then reacted at 40 °C for 15 min under sonication to form Solution C. $(Me_4N)_8Si_8O_{20}$ (2.7 g) and anhydrous methanol (20 mL) were mixed to form Solution D. The solution D and DMDCS (1.2 mL) were slowly added into the Solution C, successively, to form a mixture, which were vigorously stirred at 40 °C for 30 min. By removing anhydrous solvent and residual DMDCS, white powders were obtained, which were then washed with anhydrous methanol to remove the free POSS particles and their aggregates, followed by being dried at 50 °C in the vacuum. The resultant product was coded as POSS-SBA-15.

Third, POSS-SBA-15 was heated to 250 °C and maintained at that temperature for 1.5 h. After naturally cooling to room temperature, the resultant product was the fully capped MPS, designed as FCMPS.

2.4. Preparation of BD prepolymer and cured resin

BDM and DBA with a weight ratio of 1:0.85 were put into a reactor. The mixture was heated to 140 °C and maintained at that temperature for an additional 30 min with mechanical stirring to get the BD prepolymer.

The BD prepolymer was poured into a preheated glass mold for degassing under vacuum at 140 °C for 30 min. After that, the mold was put into an oven for curing and postcuring via the procedures of 150 °C/2 h + 180 °C/2 h + 200 °C/2 h + 220 °C/2 h, and 230 °C/4 h, successively. The resultant resin was cured BD resin.

2.5. Preparation of SBA-15/BD prepolymers and cured hybrids

BDM and DBA with a weight ratio of 1:0.85 were placed in a reactor. The mixture was heated to 140 °C and then appropriate quantity of SBA-15 was added into the mixture. After that, the mixture was maintained at that temperature for an additional 30 min with mechanical stirring stirring to get a prepolymer, coded as nSBA-15/BD, where n represents the mass of SBA-15 per 100 weight of BDM and DBA, taking values of 1.0 and 2.0.nSBA-15/BD prepolymer was poured into a preheated glass mold for degassing under vacuum at 140 °C for 30 min. After that, the mold was put into an oven for curing and postcuring via the procedures of 150 °C/2 h + 180 °C/2 h + 200 °C/2 h + 220 °C/2 h, and 230 °C/4 h, successively, to get a cured nSBA-15/BD hybrid.

2.6. Preparation of FCMPS/BD prepolymers and cured hybrids

Using above procedure for preparing the SBA-15/BD prepolymer, the prepolymer based on BD resin and FCMPS was also prepared except that the SBA-15 was replaced by FCMPS. The