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Preparation and properties of polymer microspheres filled epoxy composite films by UV-curable polymerization

Qiong Tian [a], Demei Yu [a,b,*]

[a] School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China
[b] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China

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ABSTRACT

Interfacial adhesion between fillers and matrix is important to the properties of their composites. In this study, hollow and solid polymer microspheres/epoxy composite films were prepared via powder mixing method and UV-curable polymerization. Interfacial adhesion was established by chemical bonding among the epoxy groups of the microspheres and epoxy matrix. The tensile strength and modulus of polymer microspheres/epoxy composite films first increased and then decreased with increasing the content of fillers. The specific tensile strength and modulus of hollow microspheres/epoxy composites were higher than those of solid microspheres/epoxy composites. The fracture mode of the composite films changed from crack of the polymer microspheres to interfacial debonding with increasing the filler's content. Characteristics of shear yielding deformation, particle bridging and crack bowing mechanisms were identified from the microscopic image of tensile fracture surfaces. The improvement of tensile properties compared with neat epoxy resin was discussed on the basis of percolation mechanism. The hollow polymer microspheres/epoxy syntactic foam films retained high electrical resistivity and UV-shielding property. The UV-curable hollow polymer microspheres/epoxy syntactic foam films with good strength could be used as electrical insulating materials.

1. Introduction

In recent years, hollow particles have attracted considerable attention due to their inner voids [1]. In particular, the fabrication of light-weight syntactic foams has emerged as one of the important applications of such particles. Polymer syntactic foams are composite materials obtained by dispersing hollow particles into the polymer matrix [2]. They are widely used in submarines, aerospace and acoustic applications due to their light-weight, good sound absorption, low moisture absorption and thermal insulation [3–5].

Hollow particles in the syntactic foams can be made from various materials, such as polymer, glass, carbon and metal. Hollow glass and carbon microspheres have been studied for decades. L. Zhang et al. [6] prepared syntactic carbon foams containing hollow carbon microspheres and studied the effect of heat-treatment on the properties of carbon foams. A. Das et al. [7] prepared cenosphere filled polypropylene composites and studied their mechanical properties. F. Altuna et al. [8] fabricated hollow glass microspheres filled copolymers based on epoxidized soybean oil and evaluated their compressive, flexural and thermo-mechanical properties. M. Yu et al. [9] investigated the effect of particle clustering on the tensile properties and failure mechanisms of hollow ceramic microspheres filled syntactic foams. R. Huang and P. Li [10] also detected the effect of hollow glass microsphere's fractions on the elastic behavior and failure mechanism in epoxy syntactic foams. However, the incompatibility between hollow particles and polymer matrix often deteriorates the mechanical properties of syntactic foams. Fibers are often introduced to compensate this loss [11,12], but the density of syntactic foams is dramatically increased. Many researchers concentrated on the surface treatment of hollow particles. S. N. Patankar et al. [13] found that the hollow glass microspheres grafted with polymer compatibilizer behaved better in the improvement of tensile properties of hollow glass microsphere/HDPE composites. L. Zhang [14] reported the effect of coupling agent on the mechanical properties of hollow carbon microsphere/phenolic resin syntactic foam and noted that the interfacial adhesion between microspheres and matrix was improved after treating with coupling agent. However, the complicated treatment before processing not only caused defects of the surface of the hollow microspheres but also induced the waste of chemicals. Recently, L. Zhang et al. [15] reported a facile and environmentally friendly surface modification method, which didn't cause defects of the surface of the hollow microspheres. But the high cost of polydopamine limited the wide application.

Hollow polymer microspheres have many advantages in the fabrication of syntactic foams. First, they exhibit better compatibility with

* Corresponding author at: School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, People's Republic of China.
E-mail address: dmyu@mail.xjtu.edu.cn (D. Yu).

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polymer matrix than the other inorganic hollow microspheres. Second, they can be easily fabricated through developed methods, like emulsion polymerization and template methods [1]. Finally, the size and functional groups of hollow polymer microspheres can be changed according to the different applications. A few investigations about syntactic foams using hollow polymer microspheres have been reported. The specific properties and fracture toughness of hollow phenolic microspheres/epoxy syntactic foams have been researched by Erwin M. Wouterson et al. [16]. However, the effect of interfacial adhesion between hollow polymer microspheres and matrix on the properties of polymer syntactic foams was not fully researched.

In general, syntactic foams usually appear as compacted chunks, and syntactic foam films are merely studied. The fabrication of epoxy syntactic foam films are urgently desired by the material community. UV-curable method is widely used in the field of film preparation. Our previous work [17] has investigated UV-curable epoxy syntactic foam films using hollow polymer particles, but the interfacial adhesion is weak and the strength is relatively low. In this paper, hollow polymer microspheres functionalized with epoxy groups are used to prepare epoxy syntactic foam films by cationic photo-polymerization. For comparison, solid polymer microspheres/epoxy composite films are also prepared. Both hollow microspheres (HMs) and solid microspheres (SMs) are prepared from seeded emulsion polymerization. The tensile, electrical and optical properties of composite films are investigated. The fracture mechanism is concluded from the SEM images of tensile fracture surfaces. The effects of the microspheres' structure and the interfacial adhesion on the properties of composite films are discussed. The electrical and optical properties of HMs/epoxy syntactic foam films are also investigated.

2. Materials and methods

2.1. Materials

The epoxy resin used as the matrix was SKD004, a kind of epoxy resin modified by siloxane, obtained from Pinxiu (Shanghai) Trading Co., Ltd. The cationic photo-initiator, triphenylsulfonium hexafluoroantimonate (Chivacure 1176) was purchased from Foresight Chemicals (Shanghai) Co., Ltd. Sodium dodecyl sulfate (SDS) and toluene were purchased from Tianjin Chemical Industry. Divinylbenzene (DVB) and glycidyl methacrylate (GMA) were purchased from Aladdin Industrial Inc. and was used as received. Benzoyl peroxide (BPO) were purified by recrystallization. Analytical-grade ethanol was obtained from Fuchen Company.

2.2. Preparation of polymer microspheres

P(DVB-GMA) microspheres were prepared by seeded emulsion polymerization [18]. P(DVB-GMA) denotes poly(divinylbenzene-*co*-glycidyl methacrylate). Polystyrene microspheres which were obtained by dispersion polymerization [19] (0.5 g) were dispersed into deionized water (100 mL) dissolving SDS (0.2 g) with the help of ultrasonication for 30 min. Then the mixture of toluene, DVB, GMA and BPO were introduced and stirred continuously at 250 rpm. After swelling process, purified N_2 was bubbled through the mixture for 30 min to remove the oxygen solvated in the system. Then the system was heated to 70 °C. The polymerization was carried out for 12 h. The obtained slurry was centrifuged at 5000 rpm for 10 min and washed by ethanol for three times. The product was vacuum-dried at 50 °C. Hollow and solid P(DVB-GMA) particles were obtained with swelling time of 12 h and 6 h, respectively.

2.3. Manufacture of UV-cured microspheres/epoxy composite films

The mixture of microspheres and epoxy matrix were obtained via powder mixing method as follows: the cationic photo-initiator, Chivacure 1176 was added at 3 wt% by ratio of the resin. Polymer particles were added into the epoxy resin with 0, 1, 5, 10, 15, 20 wt% polymer microspheres by ratio of the resin. The mixture was first sonicated for 15 min, and then mechanically stirred for 30 min at 50 °C. The mixture was degassed in vacuum at 60 °C for 30 min. Then the mixture was coated on teflon substrates evenly and placed under a high pressure Hg lamp (1 kW) for 120 s at room temperature. The films were transferred to an oven and thermo-cured at 80 °C for 4 h. The thickness of the cured films was controlled in the range of 100 ~ 200 μm. The cured composite films were peeled from the substrates and then cut according to China standard, GB/T 13022-1991 for testing.

2.4. Density measurements

Densities of the polymer microspheres and composite films were measured by water displacement method. The theoretical density (ρ_t) of the composite film was calculated from the following equation:

$$\rho_t = \frac{(1+w)\rho_m\rho_0}{w\rho_m + \rho_0} \quad (1)$$

where w is the weight ratio of the microspheres to the epoxy matrix, ρ_m is the density of neat epoxy resin, and ρ_0 is the density of polymer microspheres.

The void content was derived from the theoretical density (ρ_t) and experimental density (ρ_e) according to ASTM D-2734 as the following equation:

$$\text{Void}\% = 100 \times \frac{\rho_t - \rho_e}{\rho_t} \quad (2)$$

2.5. Tensile testing

The tensile tests were conducted on a testing machine, Shenzhen SANS, China., according to a modified China Standard, GB/T 13022-1991, at a cross-head rate of 2 mm/min. Dumbbell-shaped specimens for the tensile testing with effective dimensions of 30 mm × 5 mm × 0.1 mm were prepared by cutting the films on a sample cutting machine, Shanghai Qingji QJZY-36, China. At least four specimens were tested for each sample.

2.6. Characterization

FT-IR spectrophotometer (Nicolet AVATAR-IR 360) was used to characterize the composition of the polymer microspheres. The size distribution measurements were performed on Dynamic Light Scattering (DLS) Instrument (Zetasizer Nanoseries ZS90, Malvern). The *Z*-average diameter and polydispersity index (PDI) were obtained. The morphology was observed by SEM (KEYENCE VE-9800) and optical microscope (OM) (Nikon Eclipse 80i). The electrical resistivity was measured on an impedance analyzer (Concept 80) in the frequency range of 10^6–10^{-1} Hz. The UV–vis transmitting spectroscopy was measured on UV-2550, Shimadzu.

3. Results and discussion

3.1. Characterization of polymer microspheres

The morphology of solid and hollow P(DVB-GMA) microspheres is observed by SEM and OM as shown in Fig. 1. The SMs and HMs are smooth and spherical in Fig. 1a and c. As observed from the OM images, the hollow space is found inside each microspheres in Fig. 1d while the microspheres in Fig. 1b are all solid. The particle size distribution is shown in Fig. 1f. The size and density of HMs and SMs are 2.574 μm and 0.488 g/cm^3, 2.536 μm and 0.967 g/cm^3, respectively (Table 1).