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# Tailoring of thermal and dielectric properties of LDPE-matrix composites by the volume fraction, density, and surface modification of hollow glass microsphere filler

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ABSTRACT

Hollow glass microsphere (HGM) filled low-density polyethylene (LDPE) composites were prepared, and the effects of density, content, and surface modification of HGM on the thermal and dielectric properties of the composites were investigated. It is found that the thermal conductivity of the composites decreases with increasing HGM content or decreasing HGM density. At the same HGM content and density, the composites filled with suitable amount of silane coupling agent (KH570) modified HGM exhibit higher thermal conductivity than unmodified-HGM filled composites. The dielectric constant at 1 MHz of the composites also decreases with increasing HGM content or decreasing HGM density, but their dielectric loss increases with increasing HGM content or increasing HGM density. By modifying the surface of HGM with suitable amount of KH570, the dielectric constant and loss at 1 MHz of the composites can be decreased at the same time. The results of microwave dielectric properties of the composites indicate that the dielectric constant decreases with increasing HGM content or decreasing HGM density, the quality factor ($Q \times f$) decreases with increasing HGM content or increasing HGM density, but both dielectric constant and quality factor are slightly affected by the surface modification of HGM. Due to lower intrinsic thermal conductivity and dielectric constant but higher dielectric loss of HGM than LDPE, the thermal conductivity and dielectric properties of the composites can be controlled with adding HGM and varying its volume fraction. The surface modification of HGM improves the interface contact between HGM and LDPE in the composites, which is confirmed by the SEM observation, and thus the heat conduction and dielectric properties at low frequency are improved. Based on calculated thermal conductivity and dielectric constant of HGM, the experimental trends of thermal conductivity and dielectric constant at 1 MHz of the composites are analyzed by using different models, including typical models for particles-filled composites and special models developed for hollow microsphere filled composites. The results from suitable models show close correlation with the experimental values.



## 1. Introduction

Hollow glass microsphere (HGM) has unique structure, which results in some superior characteristics such as light weight, low dielectric constant, excellent thermal insulation and sound insulation. Based on light weight, HGM filled polymer–matrix composite has been developed for marine, aeronautic and building materials, and this kind of composite is usually named as syntactic foams. At present, most works had been focused on the mechanical properties of the syntactic foams, including tensile, compressive, flexural, and impact properties, in which the compressive properties are specially concerned in order to obtain high specific compressive strength of the syntactic foams [1–7]. The effects of HGM content and density on the mechanical properties of the syntactic foams have been systematically investigated. Recently, the effects of surface modification and polydispersivity of HGM are also investigated [7,8].

Considering the low thermal conductivity and dielectric constant of HGM, the thermal conductivity and dielectric properties of HGM filled polymer–matrix polymer composites are also investigated to develop thermal-insulating materials and low-dielectric-constant materials [9–14], respectively. It is specially pointed out that low-dielectric-constant composites are very important for application in the microelectronic industry in order to increase the velocity of signal propagation and reduce signal attenuation, especially as the working frequency of electronic appliances increases [15–17]. With regard to the thermal conductivity and dielectric properties of HGM filled polymer–matrix composites, there are relatively few reports. Recently, Liang et al.

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measured the thermal conductivity of HGM filled polypropylene (PP) composites, in which the HGM density is 0.21 and 0.68 g/cm$^3$ and its volume fraction is 0–20% [9,10]; Gupta et al. measured dielectric constant and loss as well as electrical impedance for four syntactic foam compositions with respect to temperature and frequency, in which the HGM density is 0.22–0.46 g/cm$^3$ and its volume fraction is 30–65% [12]; Park et al. investigated the dielectric constant at 1–10 GHz of HGM filled epoxy-matrix composites (weight content of HGM varying from 0% to 2%) [13]. In our previous work, the dielectric and thermal properties of HGM filled epoxy-matrix composite as HGM content from about 10–50 vol.% had been studied [14].

It can be seen that the effect of HGM characteristics, especially the surface modification of HGM, on the thermal and dielectric properties of the composites is not systematically and extensively studied. Previous researches have indicated that the surface modification of filler is an effective method to modify the properties of the composites [18–22]. On the other hand, most common polymer matrix used for the fabrication of electronic packages is brominated bisphenol epoxy resin. The bisphenol epoxy resin is a good choice at low frequency region but too lossy to use at frequency higher than 1 GHz [23,24]. The matrix materials with low dielectric constant and loss are demanded for packaging and/or substrate materials with fast growing high-frequency appliance markets. In this paper, low density polyethylene (LDPE) with low dielectric constant and loss is chosen as the matrix. The effects of content (10–50 vol.%), density (0.38 and 0.60 g/cm$^3$) and surface modification with silane coupling agent of HGM on the thermal and dielectric properties, including thermal conductivity, dielectric constant and loss at low frequency (1 MHz), and dielectric constant and quality factor at microwave frequency, of HGM filled LDPE–matrix composites were systematically investigated. The results will provide the reference for application of HGM filled polymer–matrix composites, especially in microelectronic industry.

## 2. Experimental procedures

### 2.1. Materials

The LDPE was bought from Qilu Petrochemical Corporation of China. Two types of HGM with trade name of S38HS and S60HS were purchased from 3 M China Ltd. The physical properties of HGM are listed in Table 1, in which the density, particle size distribution, and compressive strength are provided by the provider. From the particle size distribution, the HGM size shows a lower polydispersivity and its mean outer diameter is 40 and 30 μm for S38HS and S60HS, respectively. The wall thickness of HGM is calculated based on its mean outer diameter and glass density of 2.54 g/cm$^3$. The coupling agent was γ-methylacryloxypropyl trimethoxy silane (trade name: KH-570), purchased from Jiangsu Chenguang Coincident Dose Co., Ltd.

### 2.2. Procedure for composite preparation

The composites were fabricated by firstly pretreating the surface of the HGM with KH-570 coupling agent by the following steps: (i) making an ethyl alcohol aqueous solution at a selected concentration, (ii) adding appropriate amount of KH-570 (1–5 wt% based on the weight of HGM filler) to the solution and stirring for 10 min by using a magnetic stirrer, (iii) adding HGM particles to the solution made in (ii) and stirring for 20 min, (iv) heating to 80 °C and refluxing for 30 min while stirring and then cooling to room temperature, (v) rinsing with alcohol by filtration, and (vi) drying at 110 °C for 12 h. Then, two types of HGM (S38HS and S60HS) with and without surface modification were weighted out according the following equation:

$$W_{HGM} = \frac{V_{HGM} \cdot \frac{\rho_{HGM}}{\rho_m}}{1 - \left(1 - \frac{\rho_{HGM}}{\rho_m}\right) V_{HGM}} \quad (1)$$

where $W_{HGM}$ was the weight fraction of HGM in composite samples; $V_{HGM}$ was the volume fraction of HGM in composite samples, and it was designed as 10–50% with 10% interval; $\rho_{HGM}$ and $\rho_m$ were the densities of HGM and neat LDPE (0.93 g/cm$^3$), respectively. Subsequently, HGM and LDPE powders were mixed for 240 min to obtain a homogeneous mixture, and then the mixed powders were placed in a die and melted at 140 °C under 10 MPa pressure. After cooling and solidification under pressure, the samples in shape of plate with 30 mm in diameter were taken out from the die.

### 2.3. Characterization

#### 2.3.1. Thermal conductivity measurement

The thermal conductivity measurements were carried out using a thermal conductivity meter (DRL-II, Xiangtan City Instrument & Meter Co., Ltd.), which is fabricated according to ASTM D-5470 standard. Quartz was used as the standards in calibration of the instrument. Thermally conductive silicone grease was used to minimize the contact resistance between the sample and the hot/cold poles of the instrument. During measurement, the temperatures of hot and cold poles were 60 and 20 °C, respectively. The measured samples had diameter of 30 mm and thickness of 2.5 mm.

#### 2.3.2. Low frequency dielectric properties measurement

Dielectric constant and loss at low frequency were measured by Agilent-4284A impedance analyzer with an applied AC voltage of 500 mV and the frequency of 1 MHz. The measured samples had dimension of 10 × 10 × 2.5 mm$^3$ for length, width and thickness, respectively, and both sides of the samples were coated with silver paste. The dielectric constant was calculated from capacitance ($C$) by $Ct/\varepsilon_0 A$, where $t$ was the thickness of the discs, $\varepsilon_0$ the vacuum dielectric constant, and $A$ the disc area.

#### 2.3.3. Microwave dielectric properties measurement

The dielectric constant and quality factor ($Q \times f$, in which $Q$ is reciprocal of the dielectric loss and $f$ is the frequency) at microwave frequency region (about 8 GHz) were measured in the TE011 mode by the Hakki and Coleman method [25] using an Advantest R3767C network analyzer (Advantest Corporation, Tokyo, Japan). The measured samples had diameter of 30 mm and height of 16 mm.

#### 2.3.4. SEM analysis

To study the interface state between HGM filler and LDPE matrix, the composite was broken in liquid nitrogen and images of fractured surface were observed by a Field Emission Scanning Electron Microscope (FE-SEM; Nova 400 NanoSEM, FEI). The samples with fractured surface were mounted on an aluminium stub using a conductive paste (silver) and were coated with gold before SEM observation.

#### 2.3.5. FT-IR analysis

Infrared transmittance spectra of the samples were measured using an FT-IR spectrometer (Vertex70, Bruker Optics). The KBr slice technique was employed with resolution of 0.4 cm$^{-1}$. The dry KBr powders were mixed with the powders of the samples by grinding for homogenization. The mixed powder was then pressed into a transparent and thin slice. These thin slices were used for the IR spectral measurements.