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Dielectric relaxation dynamics of Al/epoxy micro-composites

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ABSTRACT

The dynamic dielectric properties of the Al/epoxy composites were investigated by means of broadband dielectric spectroscopy spectrometer with the frequency range 1–10^7 Hz at the temperature of −20 −200 °C. Three relaxation processes are detected in the dielectric spectra as a function of temperature and frequency: (1) Maxwell interfacial polarization (IP) at low frequencies and high temperatures; (2) a primary α-relaxation process near T_g at the middle frequencies; and (3) Intermediate dipolar effect (IDE) relaxation at high frequencies above −20 °C. The dynamics of all the recorded processes include contributions from both polymer and the inorganic reinforcing phases. The analyses of loss tangent and electric modulus spectrum of the composites indicate that the chain segmental dynamics of the polymer are accompanied by the absorption of energy given to the system. Finally, the alternating current (AC) conductivity spectra support the hopping type of conduction in the composites and the ionic conduction relaxation processes are observed also.

1. Introduction

As a kind of functional materials, polymer matrix composites (PMCs) with high dielectric constant (k), breakdown strength, energy density, and low dielectric loss, have attracted the attention of researchers as advanced technological materials such as artificial muscles, energy storage, flexible electronics, embedded capacitor and sensors [1–4]. However, their major drawback for electronics applications is their low value of permittivity (i.e., <10) [5,6]. Therefore, a key issue is to enhance the dielectric constant of polymers while retaining other excellent performances. To solve this problem, one common strategy is to add high k ceramic fillers such as $BaTiO_3$ or $PbTiO_3$ into the polymer matrix. Generally, the k of the composites could be obviously improved only by adding up to 50 vol % of these fillers. Unfortunately, the mechanical and processing properties are greatly deteriorated owing to the high loading of fillers, and it is difficult to control the dielectric constant by precisely adjusting the filler content [5–9]. Another widely used strategy is to prepare percolative polymer composites by introducing high electrical conductivity particles such as metal (i.e., Aurum, Silver, Copper, Aluminum) [10–17] and carbon fillers [18–23] into a polymer. Based on the percolation theory and mini-capacitor model, when the volume fraction of conductive filler increases to the percolation threshold, dielectric constant of the composites can be dramatically enhanced [24,25]. However, a critical problem of this kind of composites is that they generally have very high dielectric losses, bringing about huge energy wastage and low reliability in service [26]. Therefore, the development of polymer composites with high dielectric permittivity but low dielectric loss is important for practical engineering applications [15,17,27,28].

To solve this problem, some useful strategies have been proposed. Nowadays, commonly used one is preparing the conductor-insulator core-shell structured particle to avoid the connection of conductors and thus reduce the dielectric loss. As previously reported, surface self-passivated aluminum (Al) particles are often chosen as the filler to fabricate the core-shell structured Al ($Al@Al_2O_3$)/polymer composites with high permittivity but low dielectric loss [13,20,29–32]. The metal core is used to increase the dielectric constant owning to its interfacial polarization or Maxwell-Wagner-Sillars effect (MWS), while the insulator shell serves as a barrier layer to control the dielectric loss efficiently

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through blocking the electron transfer between adjacent metal cores [10,11,20,31,32]. Due to this special structure, a low dielectric loss and conductivity can be obtained compared with that of a neat epoxy resin [17]. The obtained Al/polymer composites have combined the advantages of ceramics/polymer system and percolative composite, presenting a high dielectric constant and a low dielectric loss [20].

Most of the researches on Al/polymer composites done so far have focused on the study of their dielectric behavior as a function of Al filler content and the percolation threshold (P_C) critical behavior in the vicinity of metal-insulator transition process. Up to now, the investigation on the dynamic dielectric properties of Al/polymers has been rarely investigated, and it is as important as dielectric properties at room temperature from the application point of view and requires serious attention. This has motivated us to conduct a systematic study on the dynamic dielectric behavior of core-shell structured Al/epoxy composites, and on how the presence of filler concentrations of particles, temperature as well as frequency affects the dielectric properties in a complex polymer matrix. Broadband dielectric spectroscopy with wide temperature (from −20 to 200 °C) and frequency ($1-10^7$ Hz) ranges provides a highly accurate and powerful measurements for the investigation of molecular mobility, electrical conductivity mechanisms, interfacial effects and dielectric properties in polymers and complex systems. Therefore, the present research is expected to provide a deeper insight into the dynamic thermal and dielectric behavior of the Al/epoxy composite.

2. Experimental

2.1. Materials

A diglycidyl ether of bisphenol A-type epoxy resin (D.E.R.-331, Dow Crop.) with an epoxy value of 0.52–0.54 was chosen as the polymer matrix in this study. Epoxy resin and curing agent with trade names D.E.R-732 (Dow Crop) and methylhexahydrophthalic anhydride (MeHHPA) (Shanghai Shengyuan, China), were used for the preparation of the composite systems. Besides, 2,4,6-tri(dimethylaminomethly) phenol (DMP30) (Shanghai Haitai, China) was selected as the cure accelerator. The average diameter of 1–2 μm aluminum particles was purchased from Xuzhou Hong wu Nano Co. (Jiangsu, China). Besides, in this study, the silane coupler was γ-glycidoxypropyl-trimethoxysilane, which had an epoxide as one of its end group, supplied by Nanjing Xiangfei, Chemical, China.

2.2. Surface modification of Al particles

The surface treatment for Al particles by using the silane couplers γ-glycidoxypropyl-trimethoxysilane were carried out as the following steps [33]: (i) Ethanol aqueous solution (95 wt% concentration) and silane coupling agent (1.0 wt% of the Al mass) were added into a bottom flask with reflux setting. (ii) The mixture was followed by sonnication and addition of diluted hydrochloric acid to adjusting the ethanol aqueous solution pH to 3–5 and stirring for 20 min (iii) And the Al particles were added into the solution by ultrasonicating for 60 min (iv) The mixture was heated to 80 °C and refluxed for 6 h while stirring and then cooling to room temperature, setting for 2 h. (v) The products were filtered by ethanol least three times and dried under vacuum at 110 °C for 10 h.

2.3. Preparations for the Al/epoxy composites

The preparations for Al/epoxy composites were carried out as follows [33]. For the preparation of Al/epoxy composites, the main epoxy, curing agent (MeHHPA), and the accelerator (DMP30) were mixed according to the weight ratio of 100:85:1, while the main epoxy matrix is made of D.E.R-331 and D.E.R-732 with a weight ratio of 7/3. Then, the blended mixture was ultrasonicated for 30 min at 40 °C and stirred vigorously for 1 h, and the obtained homogeneous mixture was degassed for about 30 min in a vacuum condition to get rid of bubbles. After that, the liquid mixture was poured into a clean glass plate mold kept at 60–80 °C, and then cured in an oven at 110 °C for 1 h and 150 °C for 5 h, respectively. Afterwards the cured sample was left to cool down slowly to room temperature. Thus, the epoxy-based composites with Al particles concentrations ranging from 5 to 70 wt% were prepared.

2.4. Characterizations

The dielectric measurements of the samples were recorded by using a broadband dielectric spectrometer (Novocontrol Technology Company, Germany) with the frequency range $1-10^7$ Hz at the temperature from −20 °C to 200 °C. The specimens for dielectric measurements were molded in the form of circular disk (diameter = 20 mm and thickness ~1 mm). A layer of Al foil was placed on the upper and lower surfaces of the specimens prior to measurements.

The morphology of the prepared samples as well as the dispersion of fillers in the composites was studied using a scanning electron microscopy (SEM, JSM-7000F, JEOL, Japan). The fractured surfaces were prepared in liquid N_2 and were sputtered with gold in vacuum prior to observation.

Differential scanning calorimetry (DSC) (DCS 200PC, Netzsh Crop., Selb, Germany) measurements were performed in order to evaluate the glass to rubber transition temperature (T_g) for the sample. Measurements were conducted in a nitrogen atmosphere, from −20 °C to 200 °C, at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Surface morphology

The SEM picture in Fig. 1 presents the morphological characteristic of the produced system. The surface untreated 50 wt% Al/epoxy composite is shown in Fig. 1 (b) and the surface modified 50 wt% Al/epoxy composite is given in Fig. 1(c). It can be clearly seen that the untreated composite has rounded smooth pits which were formed after Al particles had been pulled off from the matrix, while in Fig. 1(b), the homogeneous distribution of Al particles in the polymer matrix with small trails of agglomeration. This can be attributed to the use of coupling agents improving the interfacial bond strength between Al particles and epoxy resin, and decreasing the voids and defects at the phases interfaces. It was reported that good dispersion along with homogeneous packing of ceramic filler is likely to exhibit higher dielectric constant [34].

3.2. Dielectric permittivity and loss

Broadband dielectric spectroscopy (BDS) was employed for investigation on different molecular relaxation processes in epoxy composites. All the samples were examined by means of BDS over a wide temperature from −20 °C to 200 °C and frequency from 1 to 10^7 Hz. Fig. 2 presents three dimensional plots of the real (ε') part of the dielectric permittivity and the dissipation factor (tanδ) as a function of frequency and temperature for 50 wt% Al/epoxy composites. Polymer matrix composites are expected to exhibit relaxations originating from both the polymer matrix and the filler. Fig. 2(a) reveals that the dielectric permittivity diminishes with frequency, as a result of the inertia of the dipolar moments in the system to follow the alternation of the applied field, reflecting the