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Influence of particle surface properties on the dielectric behavior of silica/epoxy nanocomposites

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Abstract

Silica/epoxy composites have been widely used in functional electric device applications. Silica nanoparticles, both unmodified and modified with the coupling agent KH-550, were used to prepare epoxy composites. Dielectric measurements showed that nanocomposites exhibit a higher dielectric constant than the control sample, and had more obvious dielectric relaxation characteristics. Results showed that particle surface properties have a profound effect on the dielectric behavior of the nanocomposites. These characteristics are attributed to the local ununiformity of the microstructure caused by the large interface area and the interaction between the filler and the matrix. This phenomenon is explained in terms of prolonging chemical chains created during the curing process. The mechanism is discussed with measurements of X-ray diffraction (XRD) and Fourier transform infrared (FTIR).

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1. Introduction

Silica/epoxy composites have been widely used in functional electric device applications such as electrical cable insulation, electronic packing materials and high-performance capacitors. These kinds of organic–inorganic composites represent a new class of materials that combine the desirable physical and chemical properties of both organic and inorganic components. In the dielectrics and electrical insulation field, the paper entitled "Nanometric Dielectrics" published by John Lewis [1] in 1994 opens a new field of dielectrics.

Polymer nanocomposites are structured in the form of a polymer matrix with several wt% nanofillers homogeneously dispersed. Research interests in epoxy–silica composites can be mainly divided into studies on the mechanical [2,3], thermal [4,5] and dielectric properties [6,7]. The research presented in this paper concerns dielectric properties of the composites.

Most research in the dielectric properties of epoxy–silica composites appeared since the 1990s. Gonon and Sylvestre have published a series of papers on their research in the dielectric properties of epoxy–silica composites. They found that the dielectric constants were in the range of 3.7–4.3, varying with frequencies, temperatures and with or without carbon black [6]. They also studied the effects of humidity and thermal stress on the dielectric properties of epoxy–silica composites [7], post-curing influence on electrostatic charges deposited on epoxy–silica composites [8] and effects of hydrothermal aging on the dielectric properties [9]. These results, together with the studies by other researchers [10,11], have explained the dielectric properties of epoxy–silica composites for traditional microfilled composites.

The appearance of nanofillers for epoxy resins has provided a new research field in recent years. Nanoparticles tend to affect composite resins differently from

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microparticles and could change the properties unexpectedly. Early in 1994, Lewis [1] pointed out that the pursuit of interfacial properties, especially at the nanometric level, would offer new opportunities for designing a different field of dielectrics. He concluded that the interface was the dominant feature of dielectrics at the nanometric level [12,13]. Nelson [14] investigated the dielectric properties of epoxy–TiO_2. When 10% Ti microparticles were used, the relative permittivity increased from 5.68 to 6.01 for the base resin. However, when the same amount of nanoparticles was used, the permittivity dropped to 4.5. Different findings were observed in different composites on glass transition temperature (T_g), with some showing a decrease when nanoparticles were added [15,16], and others showing an increase [17,18].

This paper presents an investigation of the influence of the surface chemistry on the microstructure and dielectric properties of the nanocomposites. Repeated experiments were performed using silica nanoparticles of different surface properties to form composites and their dielectric properties were measured. The investigation finds that the particle surface property has an obvious effect on the dielectric property of composites and on glass transition property. The experimental results are presented and discussed in detail in terms of the chemical structure of the composites.

2. Experimental details

Silica nanoparticles (average diameter 20 nm, from Nanjing High Technology Nano Co. Ltd., China) both unmodified and modified by KH-550 (a polar silane coupling agent: γ-aminopropyl-triethoxysilane, $NH_2CH_2CH_2Si(OC_2H_5)_3$, from Nanjing High Technology Nano Co. Ltd., China), were used. The epoxy was diglycidyl ether of Bisphenol-A (from Shanghai Resin Co. Ltd.). The hardener was *m*-phenylenediamine $C_6H_4(NH_2)_2$ (from Sinopharm Chemical Reagent Co. Ltd.). All of the raw materials used were of analytical grade. The composition of the hardener and the epoxy was in the weight ratio of 0.14:1 calculated on the basis of epoxy value and on the active hydrogen number of the hardener. The filler loaded was 3 wt.% of epoxy. A blank epoxy formulation was used as the control sample.

The silica powders were dried at 120 °C in an oven for 6–8 h to remove the adsorbent water before use. The preparation was carried out as follows: The silica powders were well dispersed in acetone with the help of a high-speed magnetic blender, ultrasonicated, and then the required quantity of epoxy (pre-heated at 80 °C) was slowly added in. The resultant transparent mixture was heated to 80 °C with magnetic blending until the acetone was almost removed and then degassed in vacuum. Afterwards, the hardener was mixed manually and degassed again. Finally, the homogeneous and degassed mixture was sandwiched between two smooth armor plates coated with a thin film of a mold release agent and was preheated. The curing process was carried out by first keeping it at 80 °C for 0.5 h, then at 100 °C for 0.5 h and at 130 °C for 2 h. Finally the casts were cooled overnight to room temperature. The samples produced were of good quality, exhibiting no visible flaws or voids. The samples were stored in a desiccator to avoid the influence of moisture.

Infrared spectra of silica particles were taken with a Thermo Nicolet Fourier transform infrared (FTIR) spectrometer. X-ray diffraction patterns of the blank epoxy and nanocomposites were obtained at ambient temperature using a Rigaku D/max2500 diffractometer (Cu Kα radiation, $\lambda = 1.54056$ Å, 40 kV/200 mA). The 2θ ranges of all the data sets are from 5° to 70° with a step size of 0.02°.

For electrical measurements, the specimens were coated with vacuum-sputtered gold film to ensure a good contact. Dielectric measurements were carried out using a Hewlett-Packard 4294 impedance analyzer at frequencies 10, 100, 500 and 1000 kHz, respectively. The samples were put in a shielded cell connected with a temperature conditioner and dielectric measurements were corrected from the cell capacity and electrode contact effects.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the FTIR transmittance spectra of the unmodified and modified silica nanoparticles. The two curves are similar but differ in the absorption intensity. There are two absorption bands located at 3440 and 1630 cm^{-1} in both transmittance curves. The weaker intensity of the modified particles indicates that the surface modification leads to a good hydrophobic property. The absorption band at around 3440 cm^{-1} is attributed to the O–H stretching vibration of surface hydroxyl groups involved in hydrogen bonds. The absorption band at 1630 cm^{-1} corresponds to the O–H bending vibration of

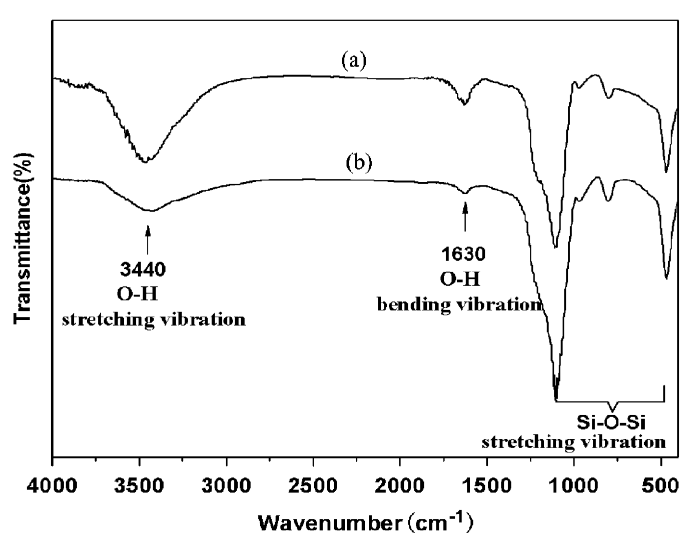

Fig. 1. Fourier transform infrared (FTIR) spectra of nanoparticle (a) unmodified; (b) modified.