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Dielectric relaxation and ionic conduction in 66%Silica/CW229-3/HW229-1 microcomposite polymer

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ABSTRACT

Composites of epoxy resin with high percentage of silica fillers (66%) are designed to improve mechanical and electrical properties of transformers used in railway application. FTIR, (DRX and FE-SEM) and absorption/desorption phenomena are used to investigate the structure, the morphology and the diffusion of water in the microcomposites, respectively. Good dispersion of silica filler with size less than 10 μm was assessed by SEM, although some clustering (agglomerates) of greater than 1 μm was observed. The absorption water in the microcomposite obeys to the first Fickian law and shows saturation water of 0.6%. The calculation of the diffusion coefficient of water leads to a value of $2.9*10^{-12}$ m^2 s^{-1} in the studied system. Relaxation times of α-relaxation and ionic conduction relaxation processes are determined. A correlation is observed between the ionic conductivity and dielectric relaxation processes. The dc-current behavior shows a change in the conduction mechanism from electronic conduction below the T_g to ionic conduction above the T_g. Shallow traps of 0.54 eV and deep traps of 2.21 eV are determined below and above the T_g, respectively. The TSC analysis confirms the VFT behavior of the α-relaxation of the microcomposite as obtained by the dielectric spectroscopy.

1. Introduction

Microparticle filled polymers (thermoplastics and thermosetting) proved advantages over the conventional unfilled polymers because of their flexibility, good processability and tailorable performance by controlling the content of the filler. They provide resistance to degradation and improvement in thermo-mechanical properties without causing a reduction in dielectric strength. The interface structures and the content of microparticles are the main critical parameters in determining the properties of microcomposites [1–7]. According to the content of microparticles loaded in the epoxy resin especially for a high percentage, the interface properties [8] also strongly affect the dielectric behavior because interfaces act as the charge carrier trapping sites, which determine the charge carrier transport and storage. Despite numerous microcomposites research results reported up to now, there is only a little knowledge about understanding of the role of interface in the properties of the material. This is mainly due to the lack of reliable experimental data given by a series of microcomposite with different interface structure [9,10].

Epoxy resin is the conventional material which have been mostly used in a large industrial application, such as dry type distribution transformers, switchgears, rotary machine, coatings, inks, vacuum pressure impregnation of coils, encapsulation of electronic circuit elements, printed circuit board coating and indoor and recently for outdoor electrical insulation material for post insulators. Epoxy resin presents these numerous applications due to their good heat and chemical resistance, superior mechanical and electrical properties, as well as excellent processability. Despite its numerous advantages, the modification of the chemical structure of epoxy resin aiming at improving the dielectric properties is quite necessary in order to increase the service life and operating reliability of the devices used in the desired application. Previous works show that the incorporation of inorganic microparticles into a matrix of epoxy resin with formation of microcomposites has been proved to be an efficient way to enhance and improve the aforementioned properties [9]. Silica is chosen as microfillers because of its low dielectric constant (4 at 1 MHz), low dielectric loss (0.0003 at 0.1 MHz) and low cost. Application of silica as filler in the epoxy resin potting compounds and epoxy resin molding

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compounds results in a decrease of the thermal expansion and an increase of the thermal conductivity [11] which are among desired properties.

In the first part of this work structural characterization of the (silica/epoxy) microcomposite was carried out using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) topography microscopy,Energy-Dispersive X-ray (EDX) analysis and the absorption/desorption behavior of water in the microcomposite. In the second part, the influences of several parameters, such as temperature, frequency and electric field on the dielectric and electrical properties of the microcomposite after inclusion of microfillers were investigated using a broad band dielectric spectroscopy (BDS), thermo-stimulated depolarization current (TSDC), current-time (I-t) behavior and current−voltage (I–V) characteristics.

2. Experimental

2.1. Materials

A commercial DGEBA (diglycidyl ether of bisphenol A) type epoxy resin whose trade name was CW 229-3 (thermal class H) was used in this study with an anhydride hardener (HW 229-1). According to Huntsman [12], Araldite CW 229-3/Aradur HW 229-1 is a good example of a prefilled resin system which provides high crack and thermal shock resistance. It says 20 test cycles were successfully conducted down to temperatures as low as −80 °C. The impregnation capability was proven to be good, with a heat conductivity of 0.7 W/mK. Thermal endurance in long-term aging tests (IEC 60216) resulted in a thermal index of more than 180 °C (class H). Even 200 °C was determined as a relative temperature index (RTI) following UK746B and this system also offers excellent crack resistance and low coefficient of thermal expansion. This epoxy resin type was loaded by 66% of silica to constitute a (66%Silica/*CW229-3*/*HW229-1*) microcomposite. Specimens were formed in the shape of plates (2 mm thick × 50 mm wide × 50 mm long) for the water absorption test and for dielectric and electrical measurements.

Two hours before molding, the resin and the hardener are weighed in equal proportions and are placed in a heating chamber at 60 °C. They are mixed 15 min in a mixer preheated at 60 °C, under a primary vacuum allowing the degassing of the material and the elimination of bubbles. The molds used are constituted by metal plates, the gap being adjusted by means of spacers and bolts. The mold is preheated at 100 °C. The casting of the mixture is realized by gravitation under a light primary vacuum in an autoclave controlled at 90 °C. The mold is then placed in an oven at 100 °C during 16 h for curing and post-curing.

2.2. Structural and morphological characterizations

X-ray diffraction (XRD) analysis for the (66%Silica/CW229-3/HW229-1) microcomposite was performed with a Siemens D 8000 diffractometer using a Co-Kα source at 40 kV and 40 mA. Fourier transform infrared spectroscopy (Nicolet 380 model FTIR Spectrometer in the wavenumber region 400 to 4000 cm^{-1}) was used to characterize the chemical composition of the microcomposite. The morphology of epoxy microcomposites was examined using Field Emission Scanning Electron Microscope (FE-SEM).

2.3. Dielectric and electric analyses

Broadband Dielectric Spectroscopy (BDS) controlled by a Novocontrol was employed in order to measure the dielectric properties in a frequency range from 10^{-2} Hz−10^{6} Hz and a temperature range of 20 °C−170 °C. The sample, 2 mm thick, 50 mm wide, 50 mm long was positioned between two metal electrodes 35 mm in diameter. Both side of the plate were covered by a vacuum sputtering gold. The entire bottom surface is coated with 50 nm of gold and a surface of the top electrode of diameter 35 mm is also coated = with 50 nm of gold. The dielectric and the electrical analysis were carried out on dry films in nitrogen atmosphere to avoid the adsorption of humidity from the air. A ring guard of 0.5 mm thickness is used in these measurements to avoid the effects of surface conductivity. Before any measure, the samples are short-circuited at 80 °C under a primary vacuum condition for 24 h.

2.4. TSC analysis

The TSC analysis was carried with a Keithley 6517A to measure the depolarization current (I_{dep}) coupled with a thermal chamber covering the temperature range from −180 to 350 °C. The surfaces of the 2 mm thick epoxy plates were covered over a diameter of 35 mm (top electrode) and over the entire surface (bottom electrode) with evaporated gold films of 50 nm thickness. The specimen was initially polarized at a given temperature (T_p) in the vicinity of the T_g material (T_g + 10 °C) for the polarization time (t_p) of 15 min under a polarization field (E_p) of 1 kV/mm and after the polarized specimen was frozen by cooling down to a lower temperature T_0 = 0 °C. Then the depolarization current was measured at different constant heating rates varying from 4 to 16 °C/min from T_0 to T_f = 170 °C, where $T_f > T_p$. Before any measure, the specimen is short-circuited at 80 °C under a primary vacuum condition for 24 h.

3. Results and discussion

The composite materials made of a matrix of epoxy resin reinforced with silica fillers have many applications in electrical medium and high voltage, such as isolation transformers. Despite good dielectric and mechanical properties, this insulation is particularly vulnerable to hygrothermal aging. The absorption of water in epoxy resins is the first studied phenomenon in this work. It is highly described in the literature, however, varies depending on the system studied. Some ideas on this topic are given in the following paragraph.

3.1. Water uptake

Before any physicochemical and electrical characterizations on the microcomposite, we have subjected our materials to a drying process. In this part, the material is dried at 80 °C under primary vacuum (10^{-1}–10^{-2}) mbar. Fig. 1(a) shows that the material losses 0.35% of water after about 300 h (stabilization time). Consequently, the material under ambient conditions (20 °C; 50% RH) contains about 0.35% of water. A fraction of the water content in the microcomposite can be created easily during the polymerization process of the resin or during boiling of the silica-filled epoxy resin compounds and another fraction can be created by adsorption of the atmospheric water, after the curing process.

A plate having an initial weight m_0 = 9.4685 g was used for the water absorption test. The diffusion coefficient of water into the polymer may be calculated, assuming Fickian behavior, by plotting the ratio of the weight of water taken as a function of the square root of time. The diffusion coefficient D of the microcomposite is calculated from the model of one phase which has led to the following equation [13–15]: