

On the volume resistivity of silica nanoparticle filled epoxy with different surface modifications



Pengfei Chu^{a,c}, Hui Zhang^{a,*}, Jun Zhao^a, Feng Gao^a, Yufeng Guo^a, Bin Dang^b, Zhong Zhang^{a,*}

^a CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China

^b State Key Laboratory of Power Systems, Department of Electrical Engineering, Tsinghua University, Beijing 100084, China

^c University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 9 November 2016

Received in revised form 28 March 2017

Accepted 29 March 2017

Available online 30 March 2017

Keywords:

A. Nanoparticle
A. Nanocomposites
B. Interface
B. Electrical properties

ABSTRACT

It was found that metallic oxide nanoparticles may positively influence insulation properties of polymers working under high electric field. Herewith, four kinds of surface-modified silica nanoparticles were employed to fabricate epoxy nanocomposites. The surface properties of nanoparticles were characterized by Fourier-transform infrared spectroscopy, thermogravimetric analysis and contact angles. The effects of surface modification, filler fraction and test temperature on volume resistivity (ρ_v) of epoxy nanocomposites were studied. It was found that, at different test temperatures, the long-alkyl-modified nanoparticles resulted in higher ρ_v values of epoxy and less ρ_v sensitivity to temperature, compared to the short-alkyl-modified and hydroxyl-modified ones. The surface polarity of nanoparticles was found to correlate with the ρ_v values well. The surface modification may cause two possible mechanisms that affect the ρ_v values of the epoxy: (i) to offer the nanoparticles different levels of water absorption; (ii) to change the Maxwell-Wagner-Sillars polarization behaviors of the composites.

© 2017 Published by Elsevier Ltd.

1. Introduction

The epoxy is a kind of electrically insulating material. Owing to its good mechanical, thermal and insulating properties, excellent castability as well as low cost, epoxy shows widespread applications in electronic and electrical engineering [1–4]. For example, epoxy can be used as the packaging of integrated circuits [5,6], insulator materials in gas-insulated transmission lines (GIL) [7,8], insulating barriers for dry-type transformers [9,10], high-voltage generators [11,12] and so on.

In recent years, with the rapid development of ultra-high voltage direct-current (UHVDC) systems in China, highly insulating polymers and polymeric composites are urgently needed. Fig. 1 presents an illustration of GIL (as an important part for UHVDC). As shown, GIL consists of an outer metal tube and an inner aluminum conductor, which is resting on the epoxy-based insulators; the metal tube is filled with an insulating gas mixture of nitrogen (N_2) and sulphur hexafluoride (SF_6) [13,14]. On operation, electrical charges, under high electric field, are prone to accumulate on the surfaces; once the surface charge density reaches a critical

value, flashover happens on the insulators [15,16]. Simulation works suggest that improving the volume resistivity (ρ_v) of epoxy insulators may alleviate the surface flashover problem of GIL for UHVDC power [15,17,18]. On the other hand, insulators with higher ρ_v also reduce the leakage current from the aluminum conductor, thus reducing energy loss. It is worth noting that formation of the accumulated charges is a very complicated phenomenon; the accumulated charges consist of the ‘intrinsic charges’ (from bulk epoxy material) and ‘extrinsic charges’ (from metal particles, foreign dirt as well as ions due to dissociation of SF_6). However, in this work, only the intrinsic charges are considered.

In practice, various inorganic fillers have been usually added into epoxy to tune their properties [19–22]. Recent works have indicated that when the dimensions of the fillers are reduced to nanometers, the volume of filler-polymer interface becomes unnegligible and thus plays an important role in determination of the properties of nanocomposites, especially for the electrically insulating properties [23–25]. Numerous works have reported that the dielectric constant [26], dielectric loss [27], breakdown strength [28], partial discharge resistance [29], electrical voltage endurance [30] and space charge accumulation [31] of epoxy and other insulating polymers can be affected by the inorganic nanoparticles more significantly, as compared to the micron fillers. However, the nanoparticles seem to bring about negative effects to

* Corresponding authors.

E-mail addresses: zhangh@nanocr.cn (H. Zhang), zhong.zhang@nanocr.cn (Z. Zhang).

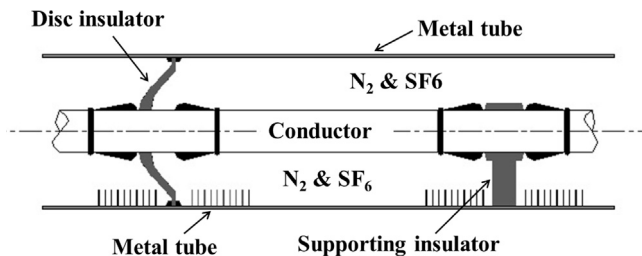


Fig. 1. An illustration of GIL.

the ρ_v of epoxies, as far as we know; i.e. the commonly-used nanoparticles (such as SiO_2 , Al_2O_3 , TiO_2 , ZnO, nano-clay) are found to decrease the ρ_v values of epoxy systems [24,32–36]. The possible reasons causing the ρ_v reduction may be ascribed to the following three major factors:

- (i) *the nanoparticle itself*: the nanoparticles have lower ρ_v values than the epoxy matrix. After purification, the electrical grade epoxies are almost ion-free and show the ρ_v value of the order of magnitude of $10^{16} \Omega \text{ cm}$ or even higher [37], whereas inorganic particles (such as SiO_2 , Al_2O_3 , TiO_2) have ρ_v values of $\sim 10^{15} \Omega \text{ cm}$ [38,39] and ZnO particles have only $\sim 10^{-2} \Omega \text{ cm}$ [40]. In addition, hydroxyl groups or some conductive impurities normally exist on the surface of nanoparticles [41,42].
- (ii) *the matrix*: addition of the nanoparticles (in some cases) may result in incomplete curing level of epoxy (lower crosslink density), leaving some smaller molecules inside the resultant materials [43,44], which can contribute to conduction.
- (iii) *the interface*: around nanoparticles, the loose interfacial zones that would be more conductive than the bulk matrix may form [23,33,45]; the large volume of interface regions may act as electric channels to facilitate the transfer of charge carriers [33,46,47].

Based on the discussion, the interfacial design is an important factor to improve ρ_v of polymer nanocomposites. So far, a few works [42,48] are devoted to this aspect and the related mechanisms are not yet fully understood. In this work we tried to improve the ρ_v values of epoxy composites by surface-modified silica nanoparticles. Special focus was on the relationship between the ρ_v of epoxy samples and the interface properties of nanoparticles.

2. Experimental

2.1. Materials

A solid-like glycidyl ether epoxy (ER113, specific equivalent weight of 220–250 g/equiv., 200–500 mPa·s at 120 °C) and an anhydride hardener (the mixture of methyl-tetrahydrophthalic anhydride and tetrahydrophthalic anhydride, EH314, 40–80 mPa·s at 25 °C) were purchased from DOW Chemical Company. Experiments indicated the epoxy samples showed a good balance between mechanical and electrically insulating performance at a resin-hardener ratio of 100:53 by weight.

Four types of fumed silica nanoparticles (A200, R974, R805, R816) were supplied by Evonik Industries AG. A200 was unmodified silica nanoparticles; R974, R805 and R816 were the surface-modified silica based on A200. The detailed information related to the nanoparticles is listed in Table 1, and the micro-structures of the four kinds of silica nanoparticles are shown in Fig. S1. To clarify the difference of nanoparticles, they were denoted as

OH@SiO_2 , $(\text{CH}_3)_2\text{@SiO}_2$, $\text{C}_8\text{H}_{17}\text{@SiO}_2$ and $\text{C}_{16}\text{H}_{33}\text{@SiO}_2$, respectively, in the following sections.

2.2. Preparation of epoxy/SiO₂ nanocomposites

The fumed silica powder was dried in a vacuum oven at 120 °C for 24 h (the continuous drying process at 120 °C for 24 h by thermogravimetric analysis test ensured that the nanoparticles were fully dried, as shown in Fig. S2), and then mechanically mixed with ER113 at 135 °C by a high-speed dissolver (DISPERMAR AE) at a rotation speed of 4000 rpm for 1 h; the appropriate amount of EH314 was added under mechanical stirring of 1000 rpm and the mixture was further degassed for 30 min. The mixture was poured to mold-release-agent-coated stainless steel molds and thermocured at 105 °C for 15 h, at 150 °C for 15 h, at 155 °C for 5 h and then cooled down to room temperature gradually. The filler contents in the resultant nanocomposites were 0.1, 0.5, 1, 2 and 5 wt%. The cured samples were polished thoroughly using waterproof abrasive papers (No. 2000) and then dried in an oven at 100 °C for 24 h to remove adsorbed moisture. The samples were ~ 1 mm in thickness unless otherwise stated. The samples were stored in a desiccator before any experiments.

2.3. Characterization

Fourier-transform infrared spectroscopy (FTIR, Spectrum One, Perkin Elmer) was used to analyze the surface chemistry of SiO_2 nanoparticles in the wavenumber range from 4000 to 450 cm^{-1} with spectral resolution of 4 cm^{-1} .

The surface grafted density of nanoparticles was analyzed by heating the samples from room temperature to 800 °C in air atmosphere at a heating rate of 20 °C/min using thermogravimetric analysis (TGA, TA Instruments, Q500). The glass-transition temperature T_g was measured by differential scanning calorimetry (DSC, TA Instruments, Q2000). The surface polarity of nanoparticles was determined by a contact angle method [49]. The nanosilica powder was first pressed under a pressure of 20 MPa to form a flat tablet. The contact angle on the tablet was measured via sessile drop method using an equipment DSA 100 (Kruss, Germany). Two liquids, i.e. distilled water (H_2O) and methylene iodide (CH_2I_2) were used, respectively, for testing the surface tension parameters according to Ref. [50]. The contact angle value was the tangent drawn of a spherically fit profile of a liquid droplet sitting on the tablet surface. Five measurements were performed at different positions on the tablet and the average value was reported. Afterwards, the surface polarity of the nanoparticles can be calculated according to the method in Ref. [49].

The dispersion level of silica nanoparticles in epoxy was observed by a field emission scanning electron microscope (SEM, Jeol SM-J7500F, Japan). The samples for SEM were fractured in liquid nitrogen and sputtered with thin gold layer. In addition, 70–100 nm thick specimens were trimmed using a microtome machine and observed by transmission electron microscope (TEM, Hitachi HT-7700, Japan) to characterize the dispersion level of silica nanoparticles in epoxy.

The direct-current (DC) volume resistivity (ρ_v) of the nanocomposite samples was measured by using an electrometer (Keithley Model 6517A) with a resistivity test fixture (Model 8009). Before each test, short-circuit was conducted on each sample for 300 s. The alternating polarity voltage method was used to eliminate the effects of background current [51]. When a test was run, the voltage alternated between +1000 V and –1000 V at a timed interval of 100 s, when the current for samples reached nearly steady state, as illustrated in Fig. S3; the equilibrium current was then measured and used to calculate the ρ_v of the specimen, together with other parameters (the electrode dimensions and specimen

Download English Version:

<https://daneshyari.com/en/article/5439568>

Download Persian Version:

<https://daneshyari.com/article/5439568>

[Daneshyari.com](https://daneshyari.com)