The Influence of Water on Dielectric Behavior of Silica-filled Epoxy Nano-composites and Percolation Phenomenon

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Abstract: The dielectric properties of epoxy resin were studied as a function of hydration by dielectric spectroscopy. The dielectric spectroscopy measurements show different conduction and quasi-DC behaviors at very low frequencies ($<10^{-2}$ Hz) with activation energies dependent on the hydration. These observations lead to the development of a model in which a "water shell" is formed around the nano-particles. The multiple shell model, originally proposed by Lewis and developed by Tanaka, has been further developed to explain low frequency dielectric spectroscopy results in which percolation of charge carriers through overlapping water shells was shown to occur. At 100% relative humidity, water is believed to surround the nanoparticles to a depth of approximately 10 monolayers as the first layer. A second layer of water is proposed that is dispersed by sufficiently concentrated to be conductive. If all the water had existed in a single layer surrounding a nanoparticle, this layer would have been approximately 5 nm thick at 100% RH. Filler particles that have surfaces that are functionalized to be hydrophobic considerably reduce the amount of water absorbed in nanocomposites under the same conditions of humidity. PEA results show that the wetted epoxy specimens have a higher threshold field of space charge accumulation than such dry specimens since water enhances charge decay.

Introduction

Although epoxy is a very popular insulating material, the behavior of epoxy composites under high degrees of humidity has received relatively little attention. Currently the effect of water on the dielectric behavior of epoxy nanocomposites is still far from being well established. In the research presented here, the dielectric behavior of wetted unfilled epoxy resin and epoxy nanocomposites was studied.

Experiments

The epoxy composite specimens were prepared as described in the ref [1]. Epoxy resins with 3 or 9 wt% nanosilica fillers (referred to n3 and n9) were prepared to compare with the epoxy resin without fillers (epoxy matrix). The method for controlling relative humidity and information on the solubility of salts were introduced in [1].

The dielectric measurements in the frequency range 10^{-3}-10^5 Hz were carried out by means of a Solartron 1255 HF Frequency Response Analyzer, and a Solartron 1296 Dielectric Interface. The measurement temperatures were varied in the range 298-353K. A sealed electrode chamber was used to maintain a constant humidity during the dielectric spectroscopy measurements. In order to explore the field required to cause space charge to accumulate within epoxy materials, the following experiment has been carried out using a pulsed-electroacoustic (PEA) space charge measurement system. The field across a plate specimen, ~0.5 mm thick, was gradually increased from 2 to 24 kV/mm in steps of 0.5 or 1 kV/min. The threshold field of space charge accumulation can be observed when the electrode charge deviates from the linear relation with the increasing applied field. This method has been used frequently by G. C. Montanari [2].

Results

Morphology of epoxy nanocomposites: The specimens were inspected by eye (for obvious defects) and then by ESEM (Phillips XL30 ESEM, FEI Company, Hillsboro, Oregon, USA) to check for adequate dispersion of the particles. Figure 1a shows a typical micrograph for the n3 system indicating good dispersion. The n9 system was also generally well dispersed, although figure 1b shows a region in which there is more agglomeration than usual.
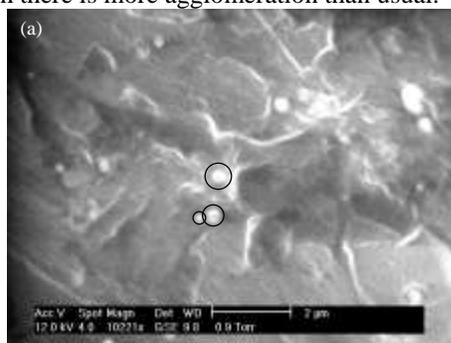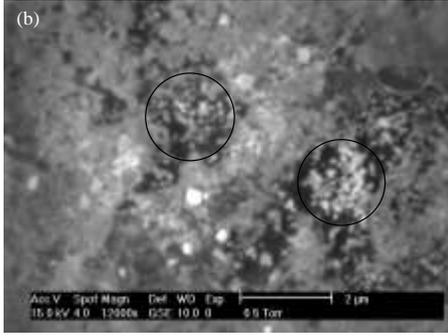
Figure 1: SEM photographs of epoxy nanocomposites. (a) n3 with some of the nanoparticles circled. (b) n9 with some of the regions of nanoparticles circled [3]

Swelling and density change: The degree of swelling (%) and density change (%) of wetted epoxies (water-saturated) are shown in table 1.

Table 1: The swelling and density change of water saturated epoxy specimens (%)

Specimens	Swelling	Water sorption	Density change
Matrix	2.75±0.5	2.68±0.15	-0.06±0.50
n3	3.97±0.8	3.33±0.19	-0.61±0.95
n9	5.89±1.2	4.47±0.26	-1.33±1.29

For the matrix, there is a little swelling but little change in density. This suggests water occupies both some free volume within epoxy and the expansion of nascent cracks. In the case of the nanocomposites there appears to be considerably enhanced swelling with the 9% nanocomposites (n9) showing approximately three times more swelling over and above that of the matrix of n3. Similarly the densities appear to be reduced. This confirms the deduction that the extra swelling in nanocomposites caused by incorporating inorganic fillers is reliable.

The relaxation process at low frequencies: The dielectric spectra of epoxy specimens at various temperatures and relative humidities were measured and have been reported previously [1]. The dielectric relaxation of epoxy nanocomposites at low frequencies changes from conduction to QDC with increasing hydration and temperature [1]. With increasing concentration of nanofillers, a lower temperature and relative humidity environment is required for the transition from conduction current to QDC [1].

Space charge accumulation within epoxy specimens: Both the space charge behavior of dry and wetted (at 75% RH) epoxies were measured by PEA. The profiles of space charge with epoxy materials were quite complicated, figure 2. Usually, build up of space charge within the polymer is not

desirable. The threshold field of space charge accumulation is quite important as an indication of aging [4]. The threshold fields of space charge accumulation within unfilled epoxy resin both at anode and cathode, at 0% RH and 75% RH are shown in figures 3 a and b respectively.
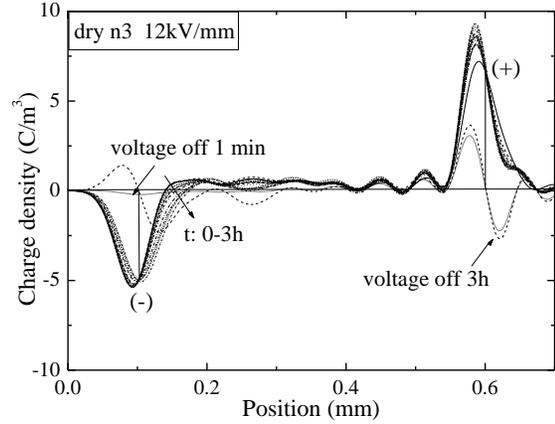
Figure 2: Profile of space charge in dry n3 under 12 kV/mm
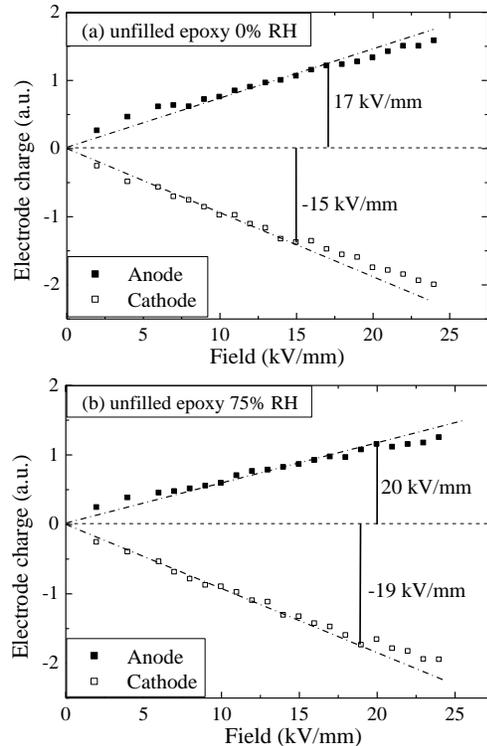
Figure 3: Space charge threshold characteristic of unfilled epoxy at electrodes under various humidities, (a) 0% RH, (b) 75% RH

These threshold field results are not nearly as clear as they are for XLPE [5], this is possibly because the charge decay in the epoxy is much faster. However, possible threshold fields at electrodes of space charge accumulation in epoxies at 0% and 75% RH are shown in table 2.

Materials	Threshold Field (kV/mm)			
	Anode 0% RH	Cathode 0% RH	Anode 75% RH	Cathode 75% RH
Matrix	17	15	20	19
n3	19	17	24	20
n9	24	19	24	22

According to table 2, with increasing concentrations of nanofillers, the threshold fields for space charge accumulation within epoxy nanocomposites increase. In general, the threshold fields of space charge accumulation within these wetted materials were higher than that within dried materials. It is more difficult to build up space charge within the wetted epoxy materials since they are more conductive.

Discussion

Water shell model: According to the hydration of the epoxy matrix and nanocomposites [1], if all the water were to surround the particles as a continuous water layer, then for both the n3 and n9 materials, this layer would increase to 5.3±0.3 nm at 100% RH. However, it is likely that this "water shell" becomes fragmented away from the particle and some of the water is dispersed into the surrounding polymer [6]. This deduction is confirmed by Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectra by Nguyen [7] and Bowden and Throssell [8]. To describe the real situation describing how water exists in epoxy nanocomposites, a "water shell" model is developed. In the model, originally proposed by Lewis [9] and developed by Tanaka [10], a nanoparticle plays a role of "core". To cover the "core", the water in a nanocomposite can be divided into three layers. The first layer of water (5~10 water molecules) may be firmly bound to the nanoparticle. Beyond that, water may be loosely bound by van der Waals Forces as the second layer. The concentration of water in this second layer may be sufficient to allow this to be conductive. The rest of the water will be "free" and exists in the bulk of the matrix. The first and second water layers are likely to provide a channel for charges and carriers. Outside this, the water is in a lower concentration which may not be conductive. At high temperatures, especially above the T_g of epoxy materials, water (and charge carriers in the water) may move through a bigger region. Once the water shell around one nanoparticle can overlap with the others, charges and carriers may move through the interaction zone between neighboring particles.
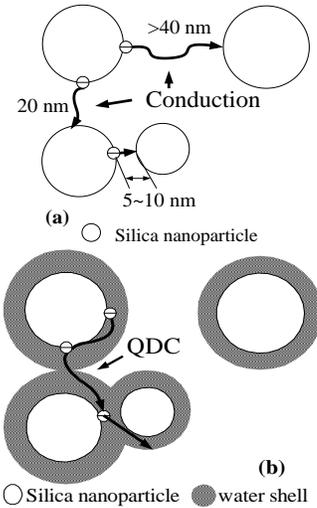

Figure 4: Explanation of dielectric behavior by water shell model

For charge carriers to percolate through overlapping shells, the volumetric concentration of zone and particle must exceed a critical value (19% for spheres) [11]. For dry nanocomposites, figure 4 (a), the situation in nanocomposites is that the shell will be too thin for overlap to be likely. However, once enough water enters the nanocomposites to provide overlapping water layers surrounding nanoparticles, figure 4 (b), these can provide the paths for charges and carriers, and QDC behavior will occur at low frequencies. The higher the content of nanoparticles, the shorter the distance between particles, and the lower the hydration and temperature are required to be to make the water shells around nanoparticles overlap.

Surface modification: There is a great body of evidence supporting the accumulation of water at the interface/surface in composites [12]. According to the hydration of epoxy materials [1], the commercial nanosilica filler enhances the water sorption in epoxy nanocomposites, which is unwanted in most cases. To solve this problem, there are two apparent solutions. One is to establish a better/stronger interfacial adhesion between the blend matrix and the particles by choosing appropriate inorganic fillers. This may result in a higher density composite, less free volume around the particles, so that less water can be stored in the composites. However, sometimes the appropriate filler is difficult to find or uneconomical. The other possible solution is to prevent water from reaching the interface between the matrix and fillers in sufficient quantities. Normally, the commercial silica filler is slightly hydrophilic and tends to adsorb water on the surface. When epoxy resin is filled with silica nanoparticles,

the situation will be worse. According to ref [1], epoxy nanocomposites can absorb more water than unfilled epoxy matrix. This suggests that nanofillers enhance the water sorption in epoxy materials. However, once the surface of the nanosilica is changed to hydrophobic, it is likely to push water out from epoxy material. If that happens, it should be possible to improve the water sorption behavior considerably. A surface hydrophobic nanosilica was chosen for testing, kindly provided by Degussa Gmbh, Germany. Using 3 wt% of surface hydrophobic nanosilica (referred as "bn3"), the hydration in water saturated these epoxy nanocomposites is ~1.5%, which is much less than that of epoxy nanocomposite filled with 3 wt% normal nanosilica (~3.33%); indeed it is even less than the hydration in epoxy matrix (~2.48%). This shows that surface modified nanoparticle reduces the water sorption in such materials.
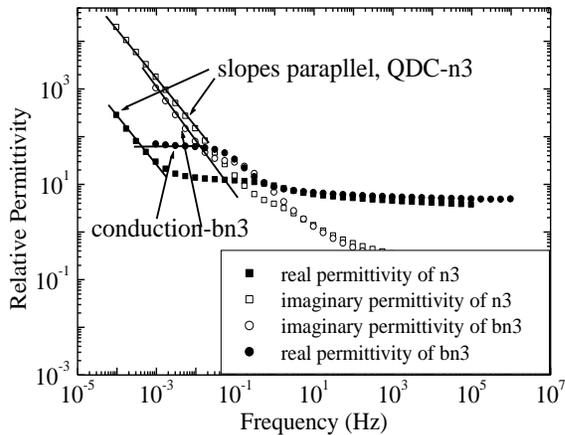
Figure 5: The relative permittivity of water saturated n3 and bn3 at 343 K

No QDC was observed in the dielectric spectroscopy of "bn3" above 10^{-3} Hz, under the conditions of 343K and 100% RH, figure 5. A possible explanation is that the low hydration in "bn3" cannot provide a thick enough "water shell" to realize the required overlap for percolation to occur.

Conclusions

The effect of hydration on the dielectric properties of epoxy materials has been studied. The results of swelling and density change between dried and water saturated epoxy materials indicate that the extra water in nanocomposites surrounds the inorganic particles rather than existing in epoxy matrix. A 'water shell' model was developed using a percolation model to explain the transition from conduction to QDC at low frequencies within wetted epoxy nanocomposites.

The percolation of water shell around nanoparticles causes QDC in wetted epoxy nanocomposites.

The effect of water on space charge accumulation in epoxy materials also was studied. Since water enhances the mobility of charge carriers in epoxy materials, the space charge threshold field of wetted material was higher than that of dried specimens.

The hydration of nanosilica epoxy composite can be considerably reduced by using the filler particles that have surfaces that are functionalized to be hydrophobic. PEA results showed the wetted epoxy specimens have a higher threshold field of space charge accumulation than dry specimens.

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