City Research Online

City, University of London Institutional Repository

Citation: Fothergill, J., Zou, C. & Rowe, S. W. (2007). A "water shell" model for the dielectric properties of hydrated silica-filled epoxy nano-composites. Paper presented at the 2007 International Conference on Solid Dielectrics, Winchester, UK.

This is the unspecified version of the paper.

This version of the publication may differ from the final published version.

Permanent repository link: https://openaccess.city.ac.uk/id/eprint/1363/

Link to published version:

Copyright: City Research Online aims to make research outputs of City, University of London available to a wider audience. Copyright and Moral Rights remain with the author(s) and/or copyright holders. URLs from City Research Online may be freely distributed and linked to.

Reuse: Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

City Research Online: http://openaccess.city.ac.uk/ publications@city.ac.uk

A “Water Shell” Model for the Dielectric Properties of Hydrated Silica-filled Epoxy Nano-composites

Chen ZOU[1], John FOTHERGILL[1], Stephen ROWE[2]
[1]Engineering Department, University of Leicester, UK [2]Schneider Electric Industries S.A.S., France

Abstract: The electrical properties of epoxy resin have been studied as a function of hydration. The epoxy was studied in an un-filled state, filled with 40 µm SiO_2 particles, and filled with 50 nm SiO_2 particles. The relative humidity was controlled by saturated salt solutions at ambient temperatures from 298-353 K. Measurements were made using dielectric spectroscopy over the frequency range 10^{-3}-10^{5} Hz. The hydration isotherm (i.e. the mass uptake of water) was established by measuring the mass as a function of relative humidity (RH).

It was found that the nanocomposites absorb up to 60% more water than the unfilled and micro-filled epoxies. Dielectric spectroscopy shows different conduction and quasi-DC behaviours at very low frequencies ($<10^{-2}$ Hz) with activation energies dependent on the hydration and temperature. These observations have led to the development of a “water shell” model to explain this phenomenon.

Introduction

Polymeric nanocomposites are one of the most attractive research subjects in the field of solid electrical insulation. Currently, most of the research is carried out incorporating various nanoparticles into existing dielectric systems in a cost effective manner, resulting in improved benefits over conventional filler systems. However, the effect of water on nanocomposites is still far from being well established. The potential weakness caused by water may have a detrimental effect on the improved mechanical and electrical behaviours of nanocomposites. In this work, the effect of water on the dielectric spectrum of epoxy resin and epoxy nanocomposites was studied. Epoxy was chosen since water is known to have a profound effect on its dielectric properties.

Experiments

The resin studied was an epoxy based on diglycidyl ether of bisphenol A (Araldite CY 225 from Huntsman) and cured with a hardener (HY 227, Huntsman). The epoxy nanocomposites were prepared under the conditions given in ref [1]. Epoxy resins with 3 or 9 wt% nano-Silica fillers (referred to as n3 or n9) were prepared to compare with the unfilled epoxy resin and with 60 wt% micro-Silica fillers (M60). The average diameter of nano-particles is 50nm, and that of micro-particles is 40 µm. All samples were cut into the disks with a diameter of 60 mm and a thickness of 0.5±0.1 mm. Dielectric measurements in the frequency range 10^{-3} to 10^{5} Hz were carried out using a Solartron 1255 HF Frequency Response Analyser, and a Solartron 1296 Dielectric Interface in the temperature range 298-353 K. A sealed electrode chamber was designed to maintain the given relative humidity during the dielectric spectroscopy measurements. The method to control relative humidity was introduced in ref [1].

Results

Hydration: The hydration (i.e. the percentage weight increase due to the water uptake) is given in Figure 1. The heavily “micro-filled” composite (M60) appears to absorb far less water. However, the water uptake by the epoxy part of this composite is indistinguishable from unfilled epoxy. Nanocomposites absorb more water than unfilled epoxy and microcomposites under the same humidity condition. Hydration also increases with nano-filler concentration. This may be due to the high specific interfacial area (particle area per composite volume) where water may congregate and that the nanocomposites may increase the free volume [2], which may allow increased water percolation. Moreover, the equilibrium water content depends not only on the free volume in the matrix, but also on the concentration of hydrogen bonds formed between water and polar groups [3] and at the interface.

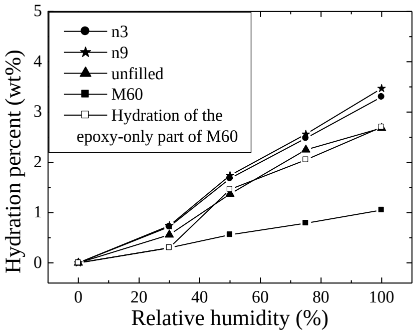

Figure 1: Hydration percentage (wt%) in epoxy samples at various RH after two weeks

Water diffusion in epoxy samples: The water diffusion behaviour in epoxy samples is shown in Figure 2. Before reaching equilibrium, the hydration percent can be plotted as linear hydration versus the square root of time (hours); predicted by Fick's law [4]. The diffusion coefficient, which depends on the material properties and is directly proportional to the slope of the beginning part in the curve, is bigger in nanocomposites than in the microcomposite. This might be caused by the lower hydration in microcomposites, or that water molecules have to diffuse a longer path in M60. One more possible explanation is that some capillaries might be formed at the interfaces between nanoparticles and the matrix, which could pump the water into the bulk of epoxy materials much more easily.

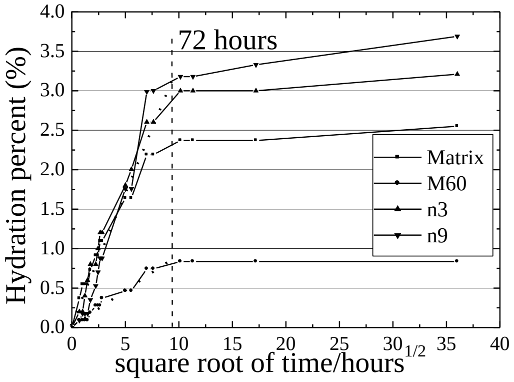

Figure 2: Water diffusion in epoxy samples (75% RH, 298K)

The dielectric behaviour at low frequencies: Figure 3 shows the dielectric behaviour (real and imaginary part of capacitance, C´ and C´´) of n3 at 298 and 353 K under 100% RH. The reproducibility of the data was confirmed by measuring several samples.

When the frequency is below 10^{-2} Hz, true conduction can be observed in all dry epoxy samples, i.e., $C' \propto \omega^{0}$, $C'' \propto \omega^{-1}$. This is typical of a material possessing mobile charge carriers. However, with increasing temperature, once the hydration in nanocomposites reaches a certain level, the dielectric behaviour at low frequencies will change into a quasi-DC/LFD process, i.e., $C' \propto C'' \propto \omega^{n-1}$, Figure 3. This behaviour is typically observed when charge carriers have some limited freedom of movement and, under the influence of the electric field, follow tortuous paths that do not allow transport right through the material. It seems likely that the carriers are moving through partially interconnected interaction zones that surround the particles.

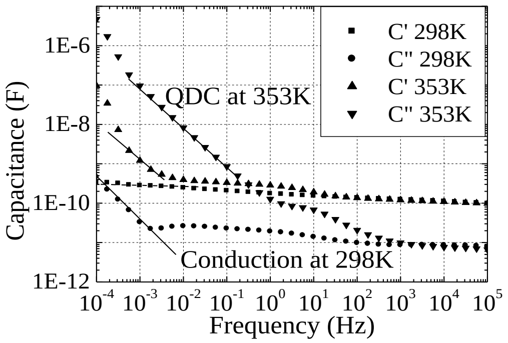

Figure 3: Dielectric behaviour of water-saturated n3 at 298K and 353K

A similar low frequency phenomenon was observed in unfilled epoxy, M60 and n9. However, at the same relative humidity, the start temperature that QDC occurs in n9 is lower than that in other samples. Also, at a temperature beyond the threshold, QDC could occur in n9 at a lower relative humidity than other epoxy samples.

The activation energy values of the relaxation process in epoxy materials at low frequency (below 10^{-2} Hz) and above 338 K are given in Table 1.

Table 1: Activation energy of epoxy samples at low frequencies/high temperatures (above T_g)

RH (%) \ Ea (eV)	Matrix	M60	n3	n9
0 (Dried)	2.5	1.17	2.34	1.01
30	2.2	0.89	1.93	0.83
50	1.9	0.62	1.37	0.84
100 (Saturated)	1.3	0.57	0.94	0.58

Activation energy of the relaxation process at the low frequencies drops with increasing humidity, suggesting the channels in the percolation network are dilated, or the degree of interconnection becomes higher so that the width of barriers to jump over is thinner. As more water enters the composite, the epoxy become more flexible, it contains more "free water". This is reflected by a drop in the activation energy. Moreover, the activation energy of composites with fillers is lower than that of matrix. This might suggest that free volume in composites with fillers is increased by incorporating inorganic fillers, and the more filler is added, the bigger free volume in the composites. Such results are confirmed by the results from saturated samples.

In n9 (20 vol%) and M60 (55 vol%), the particle concentrations are much higher than that the percolation limit (~19 vol%), at which there are continuous paths of touching particles from one side of the material to the other. One would therefore expect that, at least at higher hydration, the activation energies E_a for these two composites to be similar.

However, except at very high hydration, water-mediated pathways around the particles in the n3 (6.6 vol%) composites will not be continuous; in some regions, charges/carriers will need to move through the much more insulating epoxy matrix. One would therefore expect E_a of the epoxy matrix and n3 to show similar trends, as shown in Table 1.

The glass-transition temperature (T_g): DSC results show that T_g of epoxy samples does indeed decrease with the increasing relative humidity, which was observed previously [1]. T_g of epoxy samples decreased by ~19 K when humidity of the atmosphere in which they were prepared varies from 0% to 100 %RH.

Polymer composites used above their T_g, present a substantial degradation of physical/mechanical properties. The decrement of glass transition temperature suggests there may be a degradation of mechanical properties of epoxy materials due to water absorption. Exposure to moisture at elevated temperatures can produce irreversible effects, which can be attributed to the chemical degradation of the matrix and the attack on the fillers/resin interface. Both cause an increase of the internal voids of the entangling polymer chain. This situation will be promoting as a consequence chains expansion and microcrack formation in the polymer matrix.

Discussion

Nanofillers and QDC: Conventional composites use high concentrations (of the order of 50% volume/volume) fillers with dimensions in the tens or hundreds of microns range. The dielectric properties of composites are, at least partly, defined by processes on the surfaces of the particles [5] and the specific area of the fillers in nanocomposites is much greater than that of microcomposites. The greater specific area in nanocomposites provides the source of charges and defects.

For n3, under the assumption that all particles (~50 nm of average diameter) disperse into the bulk uniformly, the average distance between nanoparticles is about 100-150 nm, which is on the brink of the “Debye shielding interaction zone” [6]. As to n9 and M60, the distance between many particles will be much less than 40 nm. Charges and carriers may move through the interaction zone between neighbouring particles. However, for any microcomposite with low filler concentration, the average distance between particles may be microns. This is a huge gap for charges to jump over even under the promotion of the external applied field. Hence, the typical direct current is observed in low concentration microcomposites and unfilled epoxy, because such charges have to go through the high insulating matrix to reach the other side of the sample. Conversely, in n9 and M60, such charges might reach the other side of the sample by jumping from the interfacial zone of one nanoparticle to the other if the gap between the two nanoparticles is not too great. At this situation, the Quasi-DC phenomenon occurs.

Water shell model: As mentioned above, unlike metals and ceramics, epoxies cannot provide hermetic encapsulation. Sensitivity of epoxy composites to humidity is a serious matter of concern. Sorption of water may cause irreversible damage to the material. The hydration test has shown that up to several weight percent of water can be absorbed in epoxy silica nanocomposites. However, it is necessary to establish the state of such water and where it exists. Since the decrement of the glass-transition temperature caused by water absorption is similar in the different composites, it suggests the change of free volume in the epoxy component of the composites is similar too. Hence, it is unlikely there is an extra space in nanocomposites for water unless at a very high hydration. At the lower relative humidity or lower hydration, water surrounds the nanoparticles and forms a thin water shell. Under the assumption that all water is distributed between the surfaces of each particle evenly, the average thickness of water shell is easy to calculate. Obviously, the higher concentration in composites, the thicker water shell is. The results show that the thickness of water surrounds nano-particles is tens of nm under saturated conditions. However, at low RH (not water saturated), the thickness of water layer in n3 is only 1-3 nm by calculating the weight difference of dried and wetted samples. Since the size of water molecule is 0.278 nm, the thickness of water layer is about 5-10 water molecules. This deduction is confirmed by Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectra by Nguyen [7]. To describe the real situation that water exists in epoxy nanocomposites, a “water shell” model is built up. In this model, a nanoparticle plays a role of “core”. To cover the “core”, the water in nanocomposites 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 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. This situation is described in Figure 4.

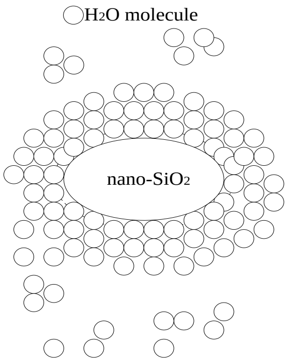

Figure 4: Water shells around nanoparticles

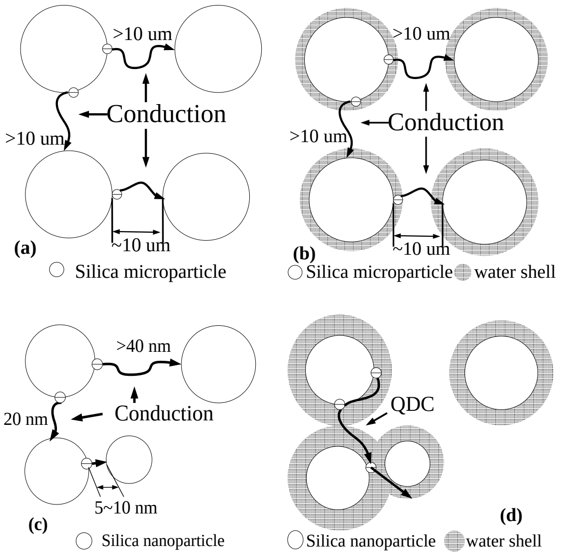

Figure 5: Explanation of dielectric behaviour by water shell model

In low concentration microcomposites (<20 vol%), Figure 5 (a, b), the gap between two particles is too big for the interaction zone to overlap, and only conduction current can be found in microcomposites by charges/carriers going through the matrix. As to nanocomposites, Figure 5 (c, d), under the dry condition, the situation in nanocomposites is similar with that in microcomposites; however, once enough water enters the nanocomposites, the water layers surrounding nanoparticles might overlap and provide the paths for charges and carriers. This causes the QDC behaviour at low frequencies. The higher content of nanoparticles, the shorter distance between particles, and the lower hydration required making the water shells around nanoparticles overlap.

Conclusions

In this work, the effect of water uptake on the dielectric properties of epoxy materials was studied. Both theory and experiment demonstrated that greater water content could exist in nanocomposites than unfilled epoxy because of the bigger free volume when nanostructured.

With increasing temperature, once the hydration in epoxy nanocomposites reaches a certain level, the dielectric properties at the low frequencies will transform into a quasi-DC/LFD process from conduction. This phenomenon was explained by a “water shell” model, which assumes that a water shell around nanoparticles provides a channel for charges.

The dielectric behaviour of epoxy composites are influenced by low concentration of nano-fillers, small amount of fillers can be used to tailor the properties of composites. In epoxy composites, it is important to control hydration in epoxy materials. The influence of water on the dielectric properties of epoxy composites can be explained by a “water shell” model.

The further work will focus on these aspects below,

i. Nanocomposites filled with silane coated nano particles. Surface functionalization of nanoparticles was proven as an efficient method to modify and control the properties of nanocomposites. For example, hydrophobicity of nanoparticles surface may enhance the hydration of epoxy nanocomposites;
ii. Mechanical strength and ageing tests on humid and dry sample;
iii. Electrical breakdown tests on humid and dry sample.

This work is supported by EPSRC (contract number GR/530672/01), UK, and Schneider Electric, France.

References

[1] C. Zou, M. Fu, J. C. Fothergill and S. W. Rowe, “Influence of absorbed water on the dielectric properties and glass-transition temperature of silica-filled epoxy nanocomposites”, *CEIDP*, USA 2006

[2] S. S. Sternstein, A. J. Zhu, “Reinforcement mechanismof nanofilled polymer melts as elucidated by nonlinear viscoelastic behavior”, *Macromolecules* 35 7262–73 2002

[3] Liang Li, Shuyong Zhang, Yuehui Chen, Mojun Liu, Yifu Ding, Xiaowen Luo, Zong Pu, Weifang Zhou and Shanjun Li, “Water Transportation in Epoxy Resin”, *Chem. Mater*., 17, 839-845, 2005

[4] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, 2nd Edition, *Cambridge University Press*, 1997

[5] C Zou, J C Fothergill, M Fu J K Nelson, “Improving the Dielectric Properties of Polymers by Incorporating Nano-particles”, *10th International Electrical Insulation Conference – INSUCON*, Birmingham, UK, May 2006

[6] Toshikatsu Tanaka, Interpretation of Several Key Phenomena Peculiar to Nano Dielectrics in Terms of a Multi-Core Model, *CEIDP*, USA 2006

[7] T Nguyen *et al*, In situ measurement of water at the organic coating/substrate interface, *Prog .in Organic Coatings*, 27, 181-193, 1996