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Influence of absorbed water on the dielectric properties and glass-transition temperature of silica-filled epoxy nanocomposites

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Abstract: Work on dielectric spectroscopy of epoxy resin filled with nano-SiO_2 at different relative humidities and temperatures is reported. Above the glass-transition temperature (T_g), dc-like imperfect charge transport (QDC or LFD) dominates the low frequency dielectric spectrum. Another mid-frequency relaxation process was found in the non-dried composites. Water also induces glass-transition temperature decreases, which can be measured both by dielectric spectroscopy and DSC.

Both theory and experiment demonstrated that a higher water content could exist in nanocomposites than unfilled epoxy suggesting a bigger free volume when nanostructured. In our system, the hydrophilic surface of silica is likely to cause water to surround and lead to delamination of the epoxy from SiO_2. This is a potential mechanical and dielectric weakness in the nanocomposites, which may lead to an ageing phenomenon. Hydrophobic surface group may reduce the water adsorption in nanocomposites.

Introduction

Because of their length scale and high specific surface area, nanoparticles exhibit novel properties as a filler in composites. A lot of research has been carried out recently incorporating various nanoparticles into existing dielectric systems in a cost effective manner, resulting in improved benefits over conventional filler systems [1]. 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. For example, epoxy resin can absorb up to a few weight percent of water; this may lead to an overall degradation of the dielectric properties. This could be further exacerbated by nanofillers if they cause an increase in free volume (e.g. through cracks, voids or through inhibiting cross-linking). In this paper, the effect of water on the dielectric spectrum of epoxy resin and epoxy nanocomposites was studied.

Experiments

Materials

The resin studied was an epoxy based on diglycidyl ether of bisphenol A (Araldite CY 225 from CIBA Speciality Chemicals) and cured with an accelerator (Hardener HY 227, CIBA Speciality Chemicals) at 100 °C for 2 h and postcured at 130 °C for 16 h. 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 about 50nm, and that of micro-particles is about 40 μm. All samples were cut into the disks with a diameter of 60 mm. The thickness of sample is 0.5±0.1 mm.

Dielectric spectroscopy measurements

Dielectric measurements in the frequency range 10^{-4} to 10^5 Hz were carried out using a Solartron 1255 HF Frequency Response Analyzer, and a Solartron 1296 Dielectric Interface. The temperature of measurements was varied in the range 298-353 K. A sealed electrode clamber was designed to maintain a given relative humidity during the dielectric spectroscopy measurements.

Control of relative humidity

Four humidity conditions were chosen in the testing, which were nominally 0% Relative Humidity (dried and then kept by silica gel, below 5% RH), 30% RH (controlled by saturated $MgCl_2$ solution, between 26-33% RH), 50% RH (NaBr solution, between 51-59% RH) and 100% RH (controlled by de-ionised water). The method used to obtain a given relative humidity was found in reference [2]. Information on that solubility of salts was found in literature [3].

Before dielectric spectroscopy measurement, the samples were kept under the same humid environment as that required for dielectric spectroscopy measurement for one week to come into equilibrium. The sample weights (1.3-3.4g) were monitored with an accuracy of 0.001g to ensure that equilibrium had been reached at that relative humidity and temperature (293K). To measure dielectric properties under 0% RH, the samples were dried in a vacuum oven (10^2 Pa) at 353K for one week before testing. For the 100% RH measurement, epoxy samples were immersed in de-ionised water for one week at room temperature (293K).

Results and discussions

Hydration

The hydration (i.e. the percentage weight increase due to the water uptake) is given in Fig 1. According to

Fig 1, nanocomposites absorb more water than unfilled epoxy and microcomposites under the same humid condition. Also, the absorption of water is increasing with the content of nano-filler. This may be due to the high specific interfacial area (particle area per composite volume) where water may collect and the nanocomposites may increase the free volume [4,5]; this may also allow increased water percolation through the nanocomposite. 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 network polar groups [6] and at the interface.

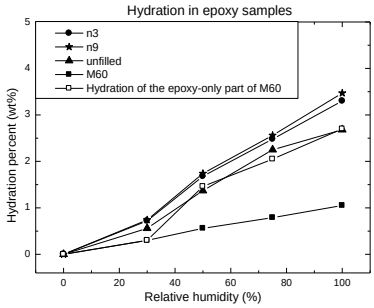

Figure 1: Hydration percentage (wt%) in epoxy samples at various relative humidity after two weeks

In unfilled epoxy, there are fewer cracks or voids formed during processing, hence the space containing water was considerably reduced. In microcomposites, the specific interfacial area is quite low and the proportion of epoxy in the composite (i.e. the part capable of water absorption) is much reduced due to the high filler content [7]. The filler will inhibit percolation. Fig 1 also shows the hydration of the epoxy-only within the microcomposite should be close to that of unfilled epoxy, suggesting that microfillers have little effect on water sorption.

The overall dielectric behaviour

Figs 2 and 3 show the dielectric behaviour (real and imaginary part of capacitance, C´ and C´´) of 3 wt% nanocomposite at 298 and 353 K under 0% and 100% RH. The reproducibility of the data was confirmed by measuring several samples.

At 298K, the dried nanocomposite shows a typical conduction polarization at lower frequency ($C' \propto \omega^0$, $C'' \propto \omega^{-1}$). At 353K, the low-frequency behaviour is not resolved, Fig 2. At 100% RH, and above 333 K, the polarization within the water-saturated nanocomposites at lower frequencies is a typical QDC, or LFD ($C' \propto C'' \propto \omega^{n-1}$), Fig 3.

The very high values of the real permittivity were observed in the regime of high relative humidity at lower frequencies and high temperature. For example, ε' reaches several hundred in saturated epoxy samples at 353 K below 10^{-2} Hz.

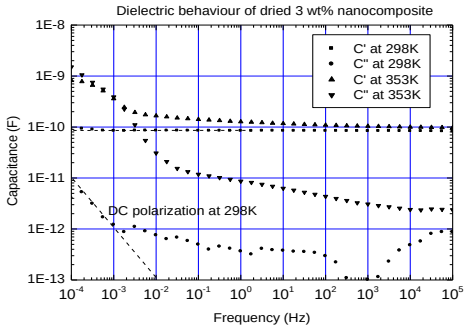

Figure 2: Dielectric behaviour of dried 3 wt% nanocomposite at 298K and 353K

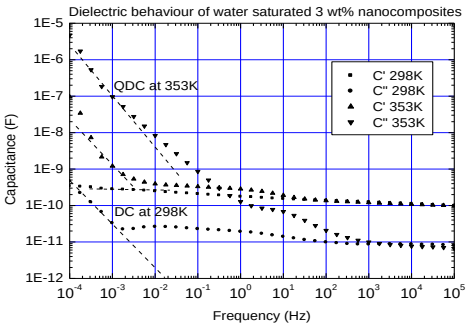

Figure 3: Dielectric behaviour of water-saturated 3 wt% nanocomposite at 298K and 353K

Similar low frequency phenomena were observed in unfilled epoxy. This corresponds to water containing free charges/carriers, forming a percolation network through the material [8]. The activation energy of 3 wt% nanocomposites drops from ~2.5 eV (0% RH) to ~1 eV (100% RH), suggesting the channels in the percolation network are dilated.

The mid-frequency relaxation

Both free and bound water have been observed in epoxy [6,9,10]. Bound water infiltrates the polymer structure, interacts with adjacent bond sites, and forms hydrogen-bonded clusters. Water may also be confined to the particle-epoxy interface layer but free to move through it, at least in a limited way. Free water occupies the free volume holes, cracks and crevices, and is relatively free to move.

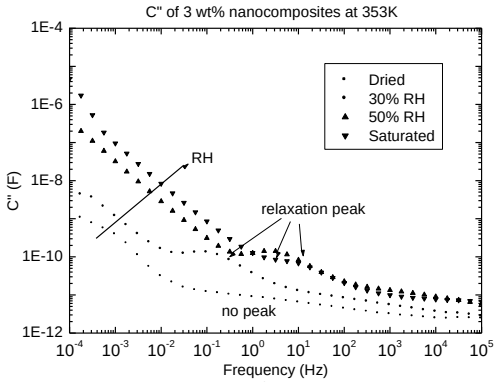

Figure 4: Imaginary capacitance of 3 wt% nanocomposites at 353K

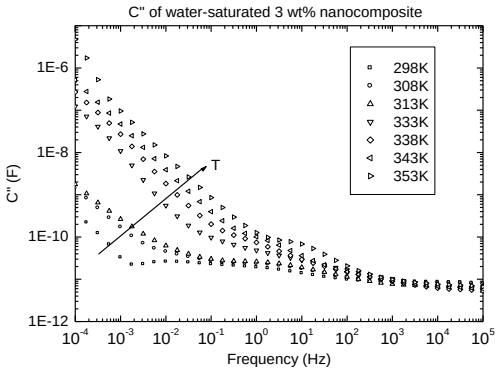

Figure 5: Imaginary capacitance of water-saturated 3 wt% nanocomposites at various temperatures

The relaxation peak in the mid-frequency range, i.e., 10^{-2} to 10^{2} Hz, seems to be linked with the water within nanocomposite or unfilled epoxy samples, since it cannot be observed in any dried sample, as shown in Fig 4. This relaxation process strongly increases with temperature and relative humidity. Fig 5 shows, for water-saturated samples, even at low temperature, i.e., 298K, the mid-frequency relaxation can be observed in dielectric spectrum.

The activation energy of the relaxation process caused by water at the mid-frequency range in water saturated 3 wt% nanocomposites was 0.28 eV. The activation energy reflects the strength of local interactions around a water molecule. The activation energy of H-bond is 0.052 eV, and that of liquid/free water is about 0.21 eV [11]. The number of H-bonds associated with a water molecule is 4. However, in water saturated epoxy specimen, the number of H-bond associated with a water molecule is above 5 (i.e. 0.28/0.052), one more H-bond than liquid water, which is connected with Si. Hence, it is likely the bound water causes the mid-frequency relaxation.

Loss tangent and Glass-transition temperature (T_g)

Figs 6 and 7 show the relation betweeen loss tangent of epoxy materials and relative humidity. The loss at 10^{2} Hz were chosen to avoid the influence of relaxation peak, since this frequency is above the mid-frequency relaxation process caused by water.

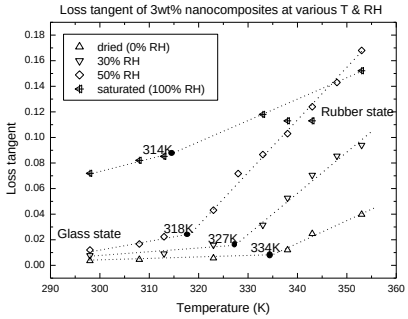

Figure 6: Relation between loss tangents at 10^{2} Hz of 3 wt% nanocomposite and relative humidity at various temperatures

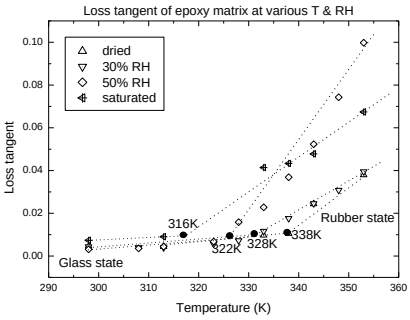

Figure 7: Relation between loss tangents at 10^{2} Hz of unfilled epoxy and relative humidity at various temperatures

In Figs 6 and 7, two linear regions can be delineated in loss tangent/relative humidity curves. The left/lower part is in the lower-temperature region, and so is likely to be associated with glass state. Conversely, the right/upper one is likely to be associated with the rubber state. If this assumption is right, the cross point of those two lines should be the glass transition temperature, T_g. The T_g appears to decrease with increasing relative humidity in epoxy nanocomposites and unfilled epoxy. Moreover, a similar situation was found in unfilled epoxy and microcomposite. Similar findings were observed at 10^{4} Hz.

Most epoxy manufacturers declare that the T_g of epoxy resin does not or only slightly decrease with moisture. Some researchers have claimed that absorbed water molecules forming double hydrogen bonds would cause an increase of T_g [12]. However, other papers reported that the absorbed water in epoxy materials would lead to a decrement of the glass transition temperature due to the plasticizing effect of water [10,12,13-16]. Our loss tangent results support the viewpoint that T_g of epoxy samples is decreasing with increasing relative humidity.

To confirm this finding, DSC experiments also were used. The glass transition temperatures of epoxy materials were tested by a modulated differential scanning calorimeter (TA Instruments, DSC 2920) with a heating/cooling rate 10 °C/min from 20 °C to 100 °C. The results are shown in Fig 8.

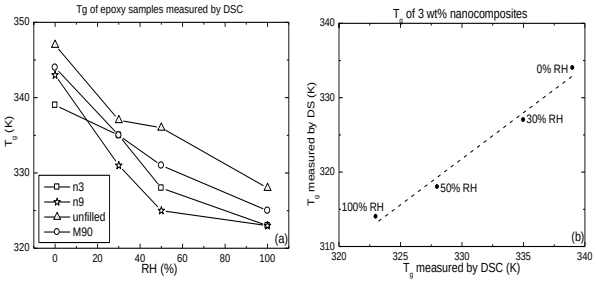

Figure 8: T_g of epoxy samples at various relative humidity, measured by DSC, (a), and dielectric spectroscopy (DS), (b)

DSC results prove that T_g of epoxy samples does indeed decrease with the increasing relative humidity. When humidity varies from 0% to 100 %RH, T_g of epoxy samples decreased by ~20 K. The results are similar with that of loss tangent, though the absolute values of T_g differ by ~10 K for n3 and unfilled epoxy under our current experimental setting.

Polymer composites used above their glass transition temperatures, T_g, present a substantial degradation of physical/mechanical properties [17]. The decrement of glass transition temperature suggests there may be a degradation of mechanical properties of epoxy materials due to water absorption [18].

DSC results also found that the depression of T_g caused by water is recoverable: after drying, the T_g of epoxy samples returns to its dry level. It seems that reversible interactions occurred between water and the resin under our experimental conditions. However, exposure to moisture at elevated temperatures can produce irreversible effects, which can be attributed to the chemical degradation of the matrix and to the attack on the fillers/resin interface. This causes an increase of the internal voids of the entangling polymer chain, promoting as a consequence the chain expansion and the microcracks formation into the polymer matrix [19].

Conclusions

In the present 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. In our system, the hydrophilic surface of silica is likely to cause water to surround the SiO_2 nano-particles and cause delamination of the epoxy from SiO_2. This is a potential mechanical and dielectric weakness in the nanocomposites, which may lead to an ageing phenomenon. A possible solution to this problem could be proposed by using hydrophobic surface groups to replace the hydrophilic surface groups to reduce the water adsorption in nanocomposites. The effectiveness needs to be tested in further testing.

Above glass-transition temperature (T_g), dc-like imperfect charge transport (QDC or LFD) dominates the dielectric spectrum at lower frequencies. Another relaxation process was also found at the mid-frequency range, which might be caused by water. By analysing the activation energy of this relaxation process, it is deduced that this relaxation process is caused by bound water.

The glass-transition temperature was found to be decreased in all epoxy samples with the increasing water content in materials by both loss tangent results and DSC measurements. This shows that the mobility of local main chains in epoxy network is increasing by intervention of water. This also can be inferred from dielectric spectroscopy results.

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