Influence of relative humidity on the dielectric properties of epoxy resins

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***Abstract*- The dielectric response of two bisphenol-A epoxy resin systems Araldite CY1301 (Tg ~ 50°C) and Araldite CY1311 (Tg ~0°C) was studied at different levels of relative humidity. The dielectric measurements were carried out over the frequency range 1 mHz to 100 kHz and the results were characterised in terms of conduction and relaxation processes. The characteristic parameters (frequency and magnitude) of all processes have found to be moisture dependent. The experimental data were fitted to a Dissado-Hill model and the form of the water dependence was characterized for all components of the dielectric response. The influence of possible interfacial features on the measured results is discussed.**

I. INTRODUCTION

Absorbed moisture has been found to affect the electrical tree growth in epoxy resin systems [1]. Therefore, it is of considerable interest to study its influence on the dielectric properties of the polymers and to relate these properties to possible electrical degradation mechanisms [2].

Carter and Kibler [3] have demonstrated that epoxy resins show non-Fickian kinetics of water absorption. Hence, in terms of diffusion kinetics, two types of water species were identified as present in the epoxy matrix – 'mobile' and 'bound'. The results of a recent investigation of water absorption in epoxy adhesives using nuclear magnetic resonance (NMR) [4] have suggested that the 'mobile' water molecules initially diffuse into the polymer matrix through interactions with the polymer chains such as, secondary bonding, van der Waals interactions, or polar interactions with polar sites within the polymer. Therefore, the 'mobile' water affects the mechanical properties of the polymer and may cause plasticisation, swelling, and lowering of the elastic modulus and T_g of the polymer. The 'bound' fraction is formed after all 'bonding' sites along the polymer chains are filled and water molecules form clusters in microvoids within the polymer matrix. These clusters are large and the water within them is effectively bound in terms of diffusion kinetics, with the inner molecules of the cluster having weak interactions with the polymer matrix. Their existence is also important for the electrical properties of epoxy resins. Cluster formation is essential for quasi-dc (QDC) charge transport [5-7]. QDC occurs in carrier dominated systems, where ion transport between the clusters is possible at times longer than ω_c^{-1}, where ω_c is the characteristic frequency of the process. However, this transport is limited to the neighbouring clusters and there is no complete percolation path to connect the two electrodes. This is the major difference between dc conduction and QDC. It was suggested in [8] that in epoxy nanocomposites overlapping water shells surrounding the filler particles facilitate the charge transport and an ageing model was proposed that explained the observed QDC behaviour at low frequencies. In this work, the moisture dependence of the dielectric response spectra of two bisphenol-A epoxy resin systems Araldite CY1301 and Araldite CY1311 is investigated, and we will demonstrate that QDC can also be observed in a 'neat' epoxy resin (without any filler particles) above the glass transition temperature of the resin and in the presence of absorbed moisture.

II. Experimental

A. Sample preparation

The samples for the dielectric spectroscopy measurements were cast from diglycidyl ether of bisphenol-A (DGEBA) epoxy resins Araldite CY1301 and Araldite CY1311, the latter being a modified version of the former with added plasticizer and having a glass transition temperature of 0°C. The glass transition temperature of Araldite CY1301 is about 55°C. An aluminium mould was used to produce epoxy resin sheets in thicknesses of approximately 0.8 mm and 1.7 mm. The thickness of the samples was measured with a micrometer. The sample to sample variation was within ±0.05mm. The epoxy samples were left to cure for two days in the mould. Afterwards, they were post-cured for an hour in a vacuum oven at 100°C and slowly cooled down to room temperature. All samples were kept in the vacuum oven for a period of several days at room temperature in order to determine the 'dry' mass of the samples. The samples were periodically weighed and shown to decrease in mass while in the vacuum oven, suggesting the existence of some initial moisture in them. In order to accelerate the 'drying' process two samples (one of each type of resin) were kept in another vacuum oven at 100°C. After two days the CY1301 sample showed no further mass decrement, however, the CY1311 sample was still losing mass even after two weeks in the oven at 100°C. This was attributed to the different chemical composition of the two resins and indicated possible chemical changes in the CY1311 epoxy resin as a result vaporization of some volatile additives, most likely the plasticizer. Both samples had changed their colour during this period showing signs of oxidation, although this was more pronounced in the CY1311 sample. No further chemical analysis was undertaken to characterise the signs of thermal ageing observed. The rest of

the samples have not been subjected to the drying procedure described above. They were left in the vacuum oven for 10 days and then weighted with an electronic balance with accuracy ±0.1mg. These weights were accepted as the 'dry' masses of the samples. However, it has been found that even after 10 days in a vacuum, there was some residual moisture in the samples resulting in an uncertainty in the calculated mass uptake of the samples. The samples were stored in sealed containers under controlled temperature and humidity conditions. The relative humidity in the containers was maintained by saturated salt solutions of LiCl, $MgCl_2$, NaCl or immersed in de-ionised water, giving values of the RH of 12, 33, 75 and 100%, respectively at 20°C [9]. The mass uptakes of the samples were periodically recorded by gravimetric measurements with the same electronic balance. The dielectric measurements were undertaken once the relative mass uptake of the samples reached near saturation value.

B. Dielectric spectroscopy

A special electrode cell was implemented for the dielectric measurements, which allows stable values of temperature and relative humidity to be maintained and monitored during the experiments. The temperature and humidity lags of the system were measured and care was taken to ensure enough time for reaching the equilibrium temperature and humidity before measuring the impedance of the sample. The electrode cell is shown in Fig.1. A standard three electrode configuration was used with a guard electrode. The function of the guard electrode is to prevent detection of surface currents which may obscure the bulk response of the material. A compression spring was loaded by the weight of the guard electrode so that good contact was provided between the measuring electrode and the epoxy sample. In this way, the volumetric expansion of the epoxy sample, resulting from the increased temperatures, was accommodated. A temperature and humidity probe was placed in the cell to monitor the values of the temperature and relative humidity during the experiments. The dielectric measurements were taken using a Solartron 1255HF frequency response analyser (FRA) and Solartron 1296 dielectric interface. In this technique, the electric current (amplitude and phase) flowing through the bulk of the sample is measured with respect to an applied AC electric field between two parallel plate electrodes. The applied voltage was scaled with the sample thickness, so that all samples were measured at approximately equal magnitudes of the applied electric field. The voltage levels were 1.5V rms for samples with thickness 1.7mm and 0.6V rms for samples with thickness 0.8mm. The frequency range was 3.7×10^{-4} to 1.0×10^{5} Hz. The dielectric properties of CY1301 samples were measured in the temperature range 20 to 80°C, and the corresponding temperature range was 20 to 60°C for CY1311 samples. Therefore, the CY1301 samples were tested below and above their glass transition temperature, while the CY1311, were tested at least 20°C above it.

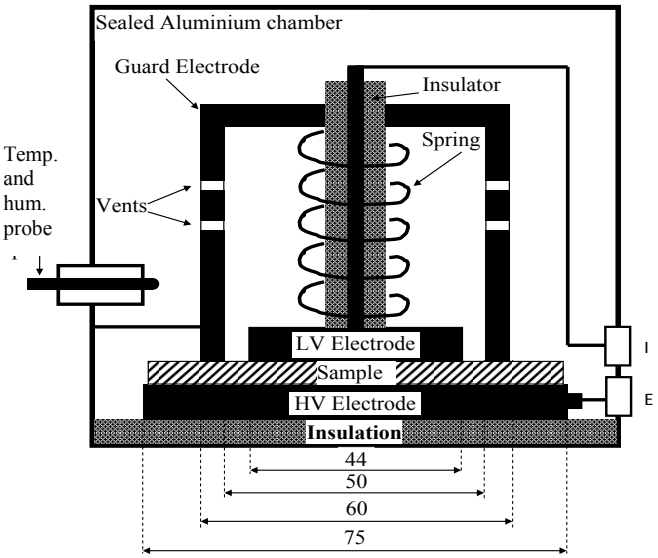

Fig. 1. The electrode system for dielectric spectroscopy

III. Results and Discussion

The dielectric responses of four CY1301 samples below the glass transition temperature are shown in Fig.2. All samples were measured at constant temperature 20°C. The samples were stored in containers with different relative humidities and the corresponding mass uptakes were 0.21, 0.46, 1.3 and 2.0%. The real component of the relative permittivity is almost "flat" in a log-log plot and the imaginary component is dominated by instrumental noise. Both real and imaginary parts of the permittivity increase in magnitude as the moisture content of the samples increases. The peak of the imaginary component that occurs at highest frequencies observed was ascribed to be an instrumental response. However, at low frequencies (< 1 Hz), another loss process occurs which is mostly pronounced in the dielectric spectra of the sample kept in de-ionised water. In order to determine the nature of this low frequency process, the response above the glass transition temperature was investigated. The dielectric spectra measured at 80°C for the same set of samples are shown in Fig. 3. Above the glass transition temperature two distinct processes can be identified, a mid-frequency dispersion (D) and quasi-dc (QDC) charge transport process. The effect of the absorbed moisture is to shift the spectra to the right, towards higher frequencies. A similar shift has been found with temperature in [10] where the QDC process was identified as a bulk material response and the mid-frequency dispersion as an interfacial effect. An equivalent circuit was proposed in [10] containing four components: a frequency independent capacitance, dc conduction, mid-frequency dispersion and QDC. The experimental data were fitted to the model and they have shown good agreement.

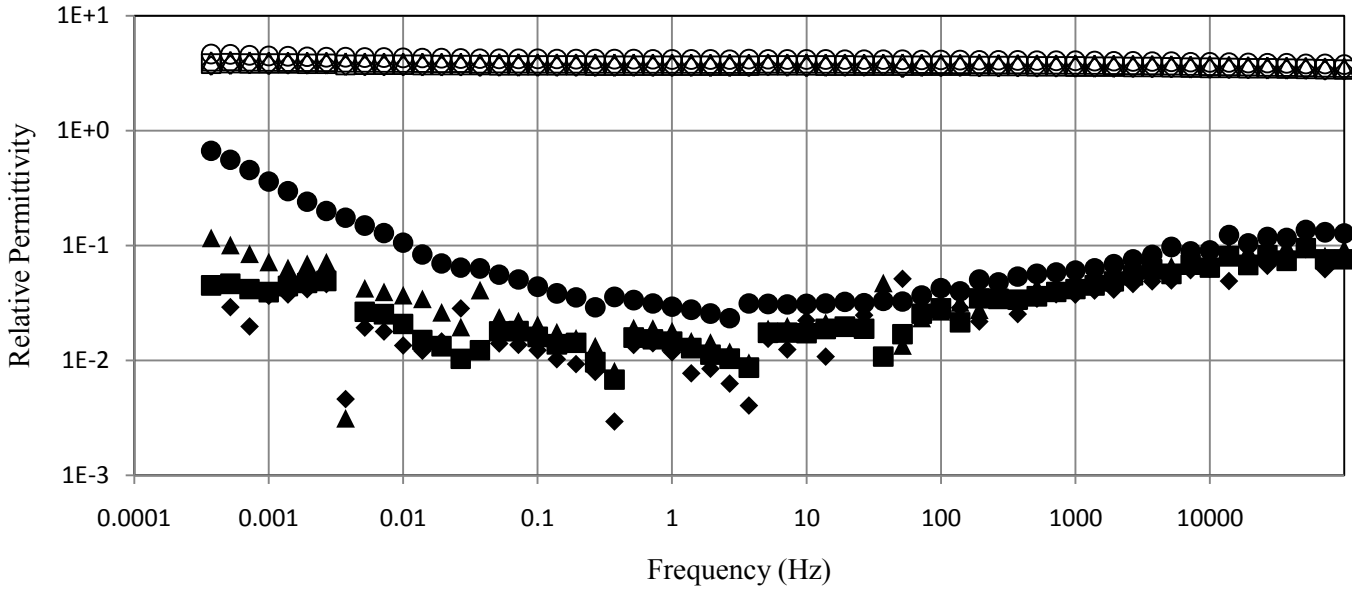

Fig. 2. Imaginary (solid markers) and real (open markers) parts of the relative permittivity of epoxy resin CY1301 for mass uptake 0.2 %(■), 0.5 %(◆), 1.3 %(▲) and 2.0 %(●), sample thickness 1.7mm, temperature 20°C

The influence of the absorbed moisture on the relaxation processes observed in the case of CY1301 epoxy resin above the glass transition is shown in Fig.4 in log-linear plot. Similar results were obtained in the case of CY1311 epoxy resin but they are not shown here for brevity. The increased water content enhances the charge transport between the clusters due to the increased number of clusters and/or greater cluster sizes. Hence, it can be assumed that the water molecules participate in the cluster formation. The values of the characteristic parameters (frequency and dc conductance) were calculated from a fitting programme using the least squares method in accordance with the model proposed in [10]. The characteristic frequency of the mid-frequency dispersion D and the dc conductance process show an exponential dependence on the moisture absorbed in the sample. However, a power law relationship has been found to be a better fit for the characteristic frequency of the QDC process. A power law dependence can be expected if absorbed water molecules form clusters and these clusters are responsible for the observed QDC charge transport. Further work is necessary to investigate the exact mechanism and charge species involved in the QDC process.

The combined effect of temperature and absorbed moisture on the dielectric responses of Araldite CY1311 samples is shown in fig. 5. The two extreme limits of the dielectric response observed were obtained from a sample measured at 20°C and low moisture content (<0.2%) and another sample measured at 60°C and high moisture content (~7%). The frequency shift is about six orders of magnitude to higher frequency with

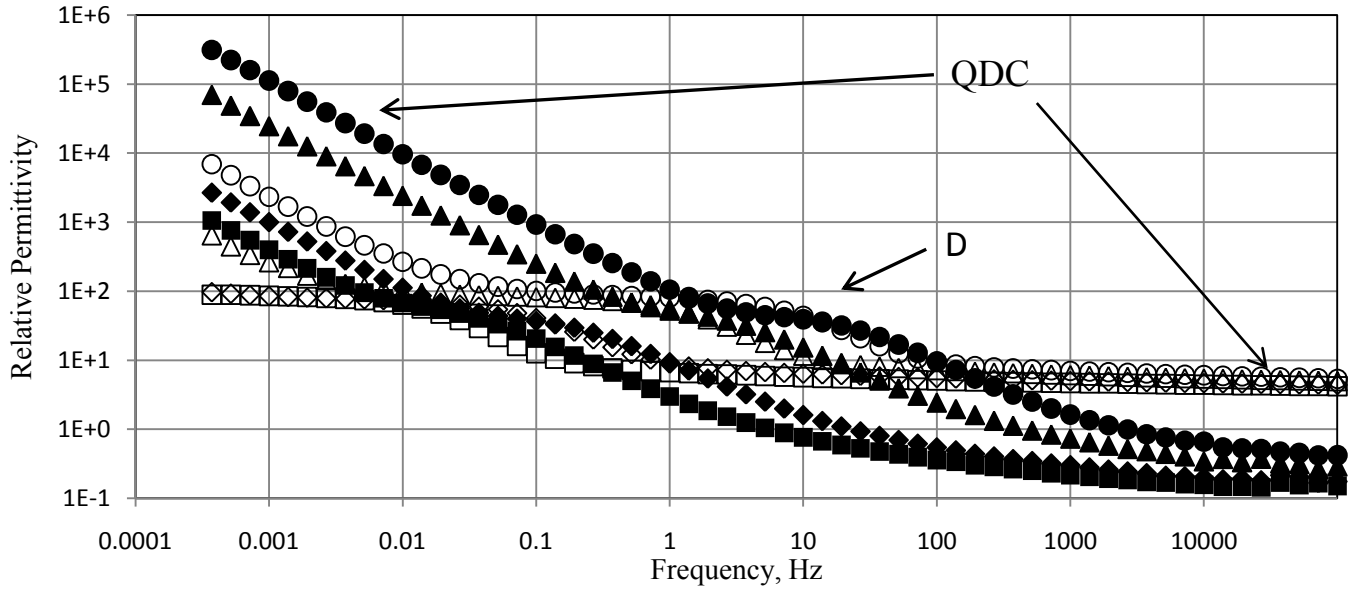

Fig. 3. Imaginary (solid markers) and real (open markers) parts of the relative permittivity of epoxy resin CY1301 for mass uptake 0.2 %(■), 0.5 %(◆), 1.3 %(▲) and 2.0 %(●), sample thickness 1.7mm, temperature 80°C

increasing humidity and temperature values. The spectra

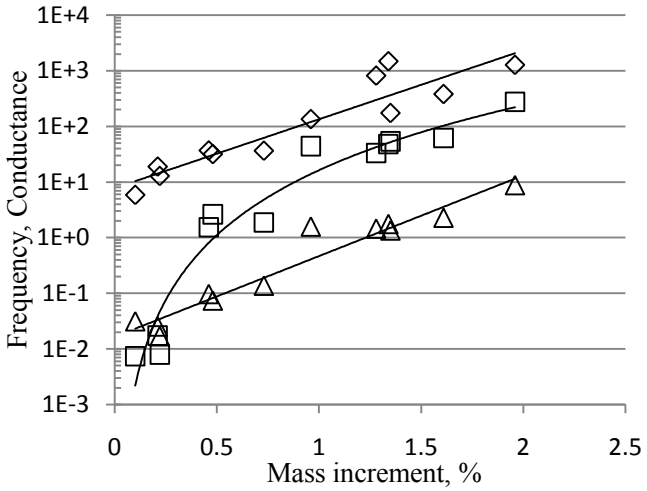

Fig. 4. Moisture dependence of the dc conductance and characteristic frequency of the dielectric processes in CY1301 at temperature 80°C: f_c D(Δ), f_c QDC(□), dc conductance (◊)

appear almost identical to those found in Araldite CY1301 above the glass transition temperature (fig. 3). However, at high moisture content (> 2%) a second dispersion process (D1) occurs at a characteristic frequency below that of the mid-frequency dispersion (D). The dielectric increment of D1 is several orders of magnitude and the slope of the real permittivity is greater than -1 (in the log-log plot), which indicates an equivalent circuit in which a transport process charges a blocking capacitance and thus closely resembles a Maxwell-Wagner-Sillars (MWS) interfacial polarization. The imaginary part of the permittivity is dominated by a dc conductance at high moisture contents and its slope (in the log-log plot) approaches -1. Also, it has been found that D1 has a weak temperature dependence unlike the other processes, which have shown near Arrhenius behaviour [10]. Further investigation is necessary to ascertain the precise nature of the dispersion D1 however the experimental

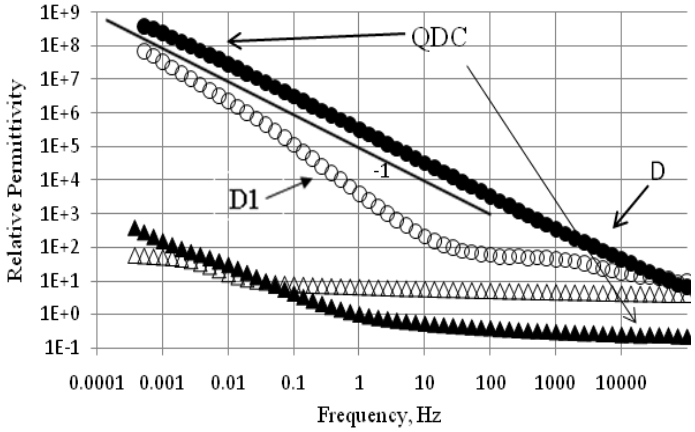

Fig. 5. Imaginary (solid markers) and real (open markers) parts of the relative permittivity of epoxy resin CY1311 for mass uptake 0.20%, temperature 20°C (▲)and 7.2%, temperature 60°C (●), sample thickness 1.7mm

evidence suggests that it is an interfacial phenomenon associated with the higher moisture uptake of the samples.

IV. Conclusions

The dielectric spectra of epoxy resins are comprised of several dielectric phenomena including charge transport in the bulk of the material and interfacial polarization. Both resins Araldite CY1301 and Araldite CY1311 show similar responses above the glass transition temperature, although CY1311 is a chemically modified version of CY1301 with added plasticizer. All dielectric response processes were found to be thermally activated processes that can be observed above the glass transition temperature of the corresponding resin. Also, all processes were found to be dependent on the moisture content in the samples. Relationships between the moisture content of the samples and the characteristic parameters of the processes have been established, with the dc conductance and interfacial loss peak being exponentially dependent upon water content and the QDC exhibiting a power-law dependence. The work demonstrates that QDC charge transport can occur in 'neat epoxy' resins without any filler particles in the presence of absorbed water molecules.

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