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Influence of water absorption in flexible epoxy resins on the space charge behaviour

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Abstract- **The aim of the current work is to achieve a better understanding of the influence of water uptake in flexible epoxy resins on the space charge dynamics at high electric fields. The space charge behaviour was studied using pulsed electroacoustic (PEA) technique. The samples were prepared from Araldite CY1311, which is a bisphenol-A epoxy resin. This particular resin was chosen because its glass transition is 0°C and hence it is in a flexible state at room temperature. All samples were conditioned in containers with saturated salt solutions or de-ionised water so that various water uptake levels were obtained. It was found that the space charge dynamics was correlated with the amount of absorbed water in the samples and this is consistent with the dielectric measurements made on the same material where ion transport was identified as the main charge transport process from the observed QDC behaviour.**

I. INTRODUCTION

Epoxy resins are amorphous polymers often used for electrical insulation. Their dielectric properties at low applied electric fields have been found to be dependent on the environmental conditions such as ambient temperature and the level of absorbed moisture [1, 2]. Above the glass transition temperature, i.e. when the resin is in a flexible state, a quasi-dc (QDC) charge transport was identified from the dielectric spectra at low applied electric fields as the main charge transport mechanism even at low levels of absorbed moisture. The QDC process usually involves ion hopping within and between clusters, although electrons can also be involved. It is characterized by two successive fractional power law responses (sometimes called constant phase angle (CPA) response) converting from one to the other at a characteristic frequency, ω_c [3]:

$$\begin{aligned} \chi''(\omega) \propto \chi'(\omega) \propto \omega^{n-1} \qquad & \text{for } \omega > \omega_c \\ \chi''(\omega) \propto \chi'(\omega) \propto \omega^{-p} \qquad & \text{for } \omega < \omega_c \end{aligned} \qquad (1)$$

The long range charge transport occurs when the frequency of the applied voltage is lower than the characteristic frequency of the process, ω_c. This implies that under DC condition the long range charge transport will be allowed since ω_c is always greater than 0, $\omega_c > 0$. In the case of epoxy resins, proton hopping was suggested as the main mechanism that gives rise to the observed QDC behaviour [4]. In addition if the hypothesis that charges involved in the QDC process are ions (protons) then it can be envisaged that significant amounts of heterocharge can build-up at the resin-electrode interfaces under DC conditions. The presence of heterocharge will modify the local electric fields at the interface which may cause certain breakdown or prebreakdown phenomena to occur.

The aim of this work was to investigate the space charge behaviour in flexible epoxy resin samples at various levels of absorbed moisture using a standard pulsed electroacoustic (PEA) system. The results were compared with a previous dielectric spectroscopy study on the same material and certain conclusions are drawn regarding the space charge formation and its dependence on the level of absorbed moisture.

II. EXPERIMENTAL

All samples used in this work were produced from Araldite CY1311 resin, which is in a flexible state at room temperature. The curing reaction involved amine hardener HY1300GB. The liquid resin and hardener were initially degassed in a vacuum oven at 40°C for 10 min. Then the two reactants were mixed together with a ratio 100 parts resin to 30 parts hardener on a hot plate using a magnetic stirrer for 10 min. Afterwards the mixture was degassed in the vacuum oven at 40°C for a second time in order to reduce the number of air bubbles in the final cured resin. The mixture was poured into two steel moulds which allowed three identical thin film samples to be produced at a time. The samples were left at room temperature (RT) to cure for 2 days and afterwards they were post-cured for 1h at 100°C in the vacuum oven and then slowly cooled down to RT. The sample thickness was measured with a micrometer and the thickness of the thin films was in the range 200 μm to 225 μm. Afterwards all samples were kept in the vacuum oven at 40°C for a couple of days in order to remove the moisture absorbed during the opening of the mould. Then the sample weights were measured on an electronic balance with a precision ±0.1 mg and these values were assumed to be their dry masses.

Two samples were stored in containers with saturated salt solutions of K_2CO_3 and NaCl for more than a week. The relative humidity in the containers was 43% and 75%. The samples were measured periodically on the electronic balance to estimate the moisture uptake. The storage period of one week was enough for the absorbed water to reach near saturation value in all samples. The corresponding mass uptakes were 1.2% and 3.4%. One sample was tested on the

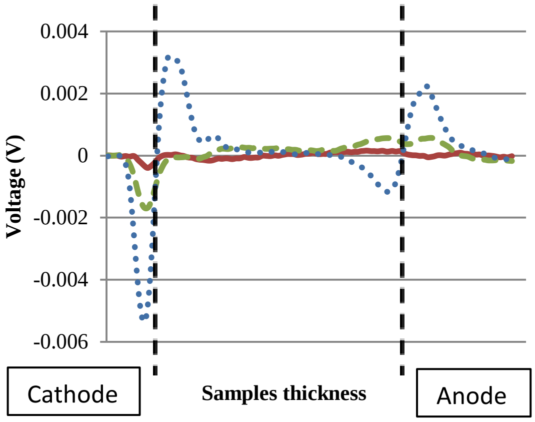

Fig. 1. Voltage waveforms immediately after voltage application for three samples with different level of absorbed moisture, applied field 10MV/m: 0% water content (solid line), 1.2% (dashed line), 3.4% (dotted line). The approximate positions of the cathode and the anode are shown by the vertical dotted lines.

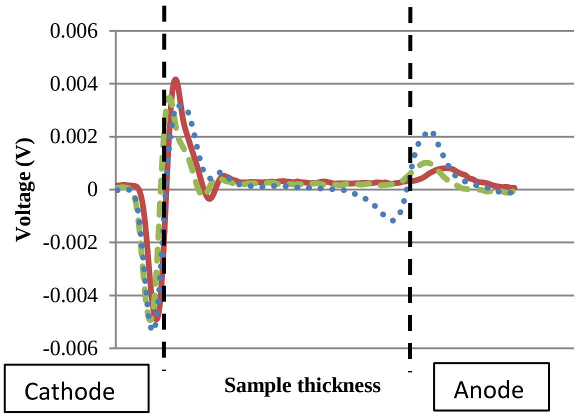

Fig. 2. Voltage waveforms for three samples with different level of absorbed moisture and times, applied field 10MV/m: 3h, 0% water content (solid line), 1h, 1.2% water content (dashed line), 0min 3.4% water content (dotted line). The approximate positions of the cathode and the anode are shown by the vertical dotted lines.

PEA system immediately after it was taken from the vacuum oven without any prior conditioning. This sample is regarded as a 'dry' sample containing 0% water.

The samples were subjected to a standard measurement procedure. A sample was placed on the aluminium base electrode in the PEA system and a semiconducting polymer layer was inserted between the sample and the top electrode. The space charge profiles were obtained under applied positive electric stress of 10MV/m for 24h by application of voltage +2 kV to the top electrode with the aluminium base electrode at 0V. At the end of the poling period the applied field was set to zero and the space charge decay was measured.

III. RESULTS AND DISCUSSION

The raw data profiles obtained from the PEA system, from three different samples taken immediately after the voltage application, are shown in Fig. 1. The samples had levels of absorbed moisture 0%, 1.2% and 3.4%, respectively. In the dry sample (0% water content) the surface charge due to the applied voltage on the electrodes is very small and only the cathode is well defined. In the sample with 1.2% moisture, the two electrodes are clearly pronounced and there is an evidence of positive space charge situated near the anode. The apparent magnitudes of the charges induced on the electrodes in the latter case are approximately 4 times bigger than in the dry sample. In the sample with high moisture content (3.2%) significant amounts of heterocharge was observed at both electrodes. The apparent magnitudes of the induced charges on both electrodes are about order of magnitude higher than in the case of a dry sample, i.e. that due to the application of the applied voltage.

The space charge formation immediately after the voltage application makes the calibration of the system a complicated task. One of the assumptions in the calibration procedure is that there is no space charge in the sample at low electric fields and only peaks due to the surface sheet charges on the electrodes occur in the PEA profile as a result of the applied electric field [5]. In the case of flexible epoxy resins, however, this condition is violated. Previous studies using dielectric spectroscopy suggest that space charge will be formed even at very low electric fields as a result of QDC charge transport, e.g. at applied fields less than 1 kV/m [1, 2]. Therefore the data reported here are plotted as voltage waveforms in volts rather than charge profiles in units of charge density, μC/cm^3. Still the underlying assumption is that the voltage waveform is proportional to the space charge profile, however the exact value of the proportionality constant is unknown.

In Fig. 2 are shown three profiles obtained at different times and levels of absorbed moisture in the samples. The profiles were selected in a way that magnitudes of the heterocharge formed at the cathode were of similar value. The corresponding times were 3h, 1h, and immediately after the voltage application for samples with water content of 0%, 1.2% and 3.4%, respectively. In the latter profile heterocharge is formed near both cathode and anode, while in the former two profiles heterocharge exist only at cathode. Fig. 2 shows

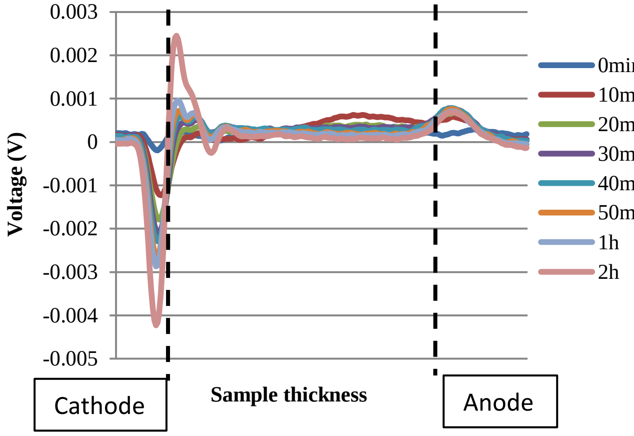

Fig. 3. Voltage waveforms at different times obtained from the dry sample, applied field 10MV/m (For the sake of clarity, the cathode (left-hand side) responses correspond to 2 hours with a maximum of -43 mV decreasing monotonically to 0 min with the minimum response. The approximate positions of the cathode and the anode are shown by the vertical dotted lines.

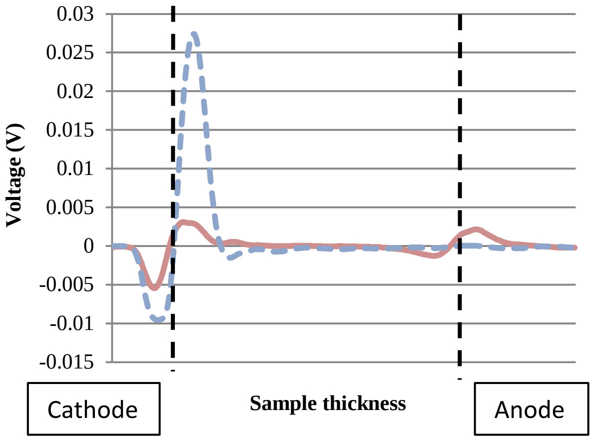

Fig. 4. Voltage waveforms obtained from the sample with 3.4% water content, applied field 10MV/m: 0 min (solid line), 1h (dashed line). The approximate positions of the cathode and the anode are shown by the vertical dotted lines.

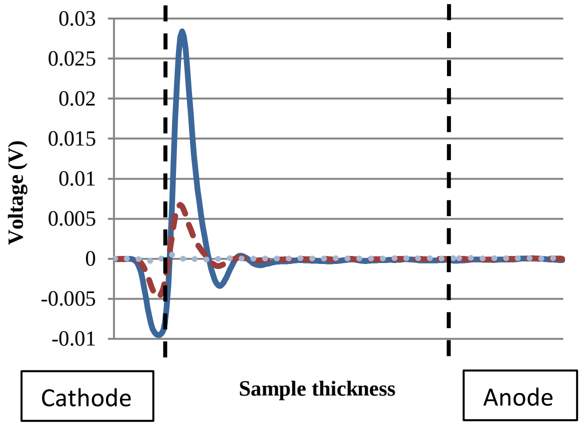

Fig. 5. Charge decay waveforms, dry sample, voltage off: 0s (solid line), 10s (dashed line), 70s (dotted line). The approximate positions of the cathode and the anode are shown by the vertical dotted lines.

that the space charge dynamics scales with the amount of absorbed moisture in the samples.

Figure 3 shows the time evolution of the space charge in the dry sample. At time t = 10 min there is a substantial amount of homocharge near the anode. The positive charges appear to travel across the sample and to accumulate at the cathode at later times. Two hours after the voltage application, a substantial amount of heterocharge is formed at the cathode with almost no evidence of space charge within the sample. This is consistent with the experimental data presented in [6].

In Fig. 4 are shown two profiles obtained from the wet (3.4% water content) sample, immediately after the voltage application and 1h thereafter. The time evolution of the space charge follows a similar pattern as in the dry sample. Positive space charge builds up at the cathode with time while the heterocharge next to the anode and the charge induced on it are neutralised. This shows that the electric field is zero outside the interface region at the cathode. The interface region is created as a result of the blocking effect of the electrode. The electric field in this region is very high, ~40MV/m.

The charge decay measurements obtained from the dry sample are shown in Fig. 5. After approximately 70s the space charge is completely neutralised. Again the data are consistent with [6].

It is tempting to relate the space charge measurements presented here to the dielectric measurements on the same type of epoxy resin published in the literature [1, 2]. At low electric fields QDC was identified as the main charge transport mechanisms. The space charge formation may be related to cluster polarisation at frequencies (times) below (longer than) the characteristic frequency (time) of the QDC process. This can explain the observed heterocharge at both electrodes in the sample with high moisture content immediately after the voltage application (see Fig. 1). The characteristic frequency, ω_c, is known to increase with increasing level of moisture in the samples and in Table 1 is given its dependence on the percentage of absorbed moisture (the data are taken from [4]). The value of the characteristic frequency changes by several orders of magnitude from almost dry (0.1% water content) to wet (7.2% water content) samples. In order to relate the space charge measurements to the dielectric measurements, the data in Table 1 are given at temperature 20°C since all space charge measurements presented here were done at room temperature, 18±5°C. From Table 1 it can be seen that the characteristic frequency for a sample with moisture content 2.4% is 490Hz, and hence the characteristic time constant of the process, τ_c, is approximately 2 ms. Therefore, for a sample with water content 3.4% the formation of space charge due to cluster polarisation will occur faster than 2 ms (depends also on the ambient temperature and applied field), which is much faster than the data acquisition period (~ 10s) for the space charge measurements. This is consistent with the data shown in Fig. 1 where heterocharge is present at both electrodes immediately after the voltage application. Due to the proton hopping involved in the QDC process with time (depending on the water content) the positive charges will migrate towards the cathode and accumulate at the sample-electrode interface, which can be seen in Fig. 2 to 5. When the applied field is set to zero, the space charge decays very fast (less than 2 minutes), and ion diffusion may account for the fast charge neutralisation and cluster depolarisation (see Fig. 5).

TABLE I

CHARACTERISTIC FREQUENCY [HZ] OF THE QDC CHARGE TRANSPORT PROCESS AS A FUNCTION OF THE LEVEL OF ABSORBED MOISTURE IN CY1311 EPOXY RESIN SAMPLE AT 20°C [4]

Moisture level	Characteristic frequency [Hz]
0.1%	0.0120±0.0026
0.7%	2.0±0.1
2.4%	490±21
7.2%	8500±910

Although most space charge data presented here appear to be consistent with a QDC response that was previously found using dielectric spectroscopy on the same material at low electric fields, the data obtained at low moisture content and early times suggests that other processes may occur at high applied electric fields. For example, the homocharge formation at the anode immediately after the voltage application in the dry sample suggests charge injection/extraction rather than cluster polarisation. The low moisture content data also suggests that the time required for the positive charge to cross the sample is much longer than the characteristic time constant of the QDC process for similar levels of absorbed moisture and temperature. In the case of the dry sample, significant heterocharge starts to build up at the cathode 20 min after the voltage application, while τ_c in this case is approximately 80s. However, the time required for the space charge to cross the sample also depends on the percolation backbone along which charges move and which structure is currently unknown. Further work is required to ascertain all parameters involved in the QDC process in order to make direct comparison between the dielectric and the space charge measurements.

IV. CONCLUSIONS

The work shows the intrinsic difficulty to calibrate the PEA system in the case of flexible epoxy resins where space charge is expected to form immediately after voltage application regardless of the level of applied electric stress. An alternative calibration has to be sought in this place, which is currently unavailable. The PEA data show significant build up of positive heterocharge near the cathode with time, which can be related to a QDC process, previously found in the same material using dielectric spectroscopy. Proton hopping has been suggested as the main charge transport mechanisms involved in the QDC process, which is consistent with the observed space charge behaviour. Further work is required in order to obtain a quantitative relationship between the space charge and the dielectric measurements.

REFERENCES

[1] S. J. Dodd, N. M. Chalashkanov, L. A. Dissado, and J. C. Fothergill, "Influence of Absorbed Moisture on the Dielectric Properties of Epoxy Resins," presented at the 2010 CEIDP, West Lafayette, Indiana, USA, 2010.

[2] S. J. Dodd, N. M. Chalashkanov, J. C. Fothergill, and L. A. Dissado, "Influence of the Temperature on the Dielectric Properties of Epoxy Resins," presented at the IEEE ICSD 2010, Potsdam, Germany, 2010.

[3] M. Shablakh, L. A. Dissado, and R. M. Hill, "Nonconductive Long-Range Charge Transport in Hydrated Biopolymers," Journal of Biological Physics, vol. 12, pp. 63-78, 1984.

[4] N. Chalashkanov, "INFLUENCE OF WATER ABSORPTION AND TEMPERATURE ON CHARGE TRANSPORT AND ELECTRICAL DEGRADATION IN EPOXY RESINS," PhD thesis, Department of Engineering, University of Leicester, 2011.

[5] Y. Li, M. Yasuda, and T. Takada, "Pulsed Electroacoustic Method Measurement of Charge for Accumulation in Solid Dielectrics," IEEE Trans. Dielectrics and Electrical Insulation, vol. 1, pp. 188-195, 1994.

[6] J. V. Champion, S. Dodd, J. M. Alison, and L. Askew, "Electrical tree growth and space charge behaviour of epoxy resin blends " presented at the 1998 IEEE International Conference on Conduction and Breakdown in Solid Dielectrics, Vaesteras, Sweeden, 1998.