Dielectric Spectroscopy of Epoxy/Glass Composite Materials

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Abstract: *Glass fibre reinforced epoxy (GFRE) material is used in pressboard transformers for optical telecommunication systems, typically at voltages between 1 to 2kV. A programme has been set up to follow the electrical ageing of the GFRE through dielectric and space charge (PEA) measurements. Here we report on the characterisation of the GFRE prior to ageing made by means of linear dielectric spectroscopy. Preliminary results for the aged samples show differences in dielectric response that could be related to de-bonding at the epoxy-fibre interfaces observed in some failed samples.*

Introduction

In recent years the power feed line for optical telecommunications systems has moved over to the use of copper track transformer coils embedded in an epoxy laminate. This gives considerable saving in space. They are currently operated at voltages of about 500Vac/300dc and temperatures of 70-90C. It is expected that in the near future the voltages will rise. Previous experience can no longer be used as a guide to their reliability. Instead it is necessary to develop a better physical understanding of the processes that cause electrical ageing and failure in the insulation system so that its reliability may be estimated with confidence, and limits be set on the degree to which the stress levels may be raised. The current programme is designed to ascertain the way in which thermo-electrical stress causes deterioration of the insulation system that may eventually lead to failure.

The starting point is a characterisation of the insulating material itself. This is a glass fibre mat impregnated with a an epoxy resin cured under pressure at 140ºC for 4 hours and ~180 °C for 1 hour [1]. The glass transition of the composite occurs at T_g = 140 °C A large number of samples have been made and characterised by means of their dielectric response, dynamimic mechanical response, space charge measurements, DSC and SEM analysis. Measurement of the dielectric response of both the composite and the fibre mats has resulted in a qualitative understanding of the physical origin of its main features in the frequency range under investigation.

A number of the samples are currently undergoing ageing at a number of dc voltages and at both 20 °C and 90 °C. These samples are removed periodically and their dielectric response and space charge behaviour measured. The ageing has now extended to three months. During this period one sample broke down at 50kV/mm and room temperature. An investigation of this sample showed evidence of de-bonding at the fibre-epoxy interface. Changes in the dielectric response of the other samples as they aged could also be associated with such de-bonding.

Experimental Results

The measurements were performed on disc samples of 54 mm diameter ranging in thickness from 200 to 400 μm. The dielectric experiments were carried out using a Solartron FRA system with a custom built temperature control accurate to ± 0.1C. Capacitive and loss components were measured over a frequency range from 1 mHz to 100 kHz and from T= 20 C to 100 °C. The results for the composite are shown in Fig 1 in the form of a master plot constructed by translating the data along the log {frequency} axis to bring them into coincidence. A broad loss peak was found at high frequencies that were assigned to the β-process of the glassy epoxy. The activation energy of ~0.3 eV found for the characteristic frequency is typical of such processes. A low frequency process was also found that possessed a constant phase angle (CPA) behaviour (i.e. $C'' \propto C' \propto f^{-p}$ with $p \approx 0.8$. This type of process has been termed a quasi-dc transport [2]. A characteristic activation energy of ~ 1.1 eV was found, but it is not possible to separate this into independent carrier concentration and mobility components. The dielectric response of a glass fibre mat showed a dc conductance at very low frequencies ($f < 1.3*10^{-2}$Hz), which transformed into a quasi-dc conductance (CPA) at higher frequencies, Fig 2. Both processes have the same activation energy of 0.46eV implying that the barriers to charge transport are the same in both cases. Measurements were made with two fibre mats as well as one. The results showed that the q-dc process varied with an inverse power of the thickness rather than inversely with the thickness. This result shows that the response observed is truly a bulk response and is what would be expected of a q-dc response originating with a percolation system. [2]. Although the activation energy is much lower than in the q-dc response of the

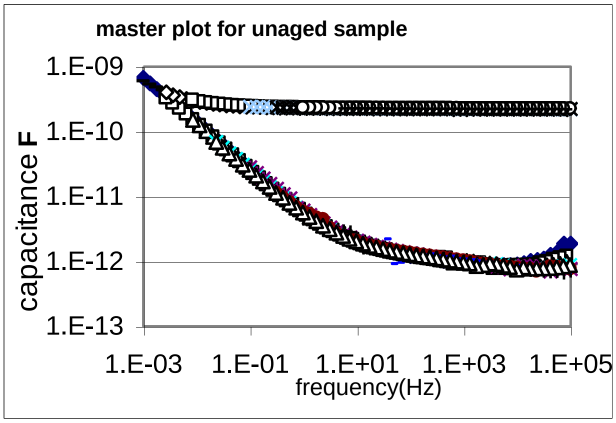

Figure (1), Master plot of the dielectric response of composite, for real (upper) and imaginary (lower) parts of capacitance, for 8 temperatures from 20-90 C

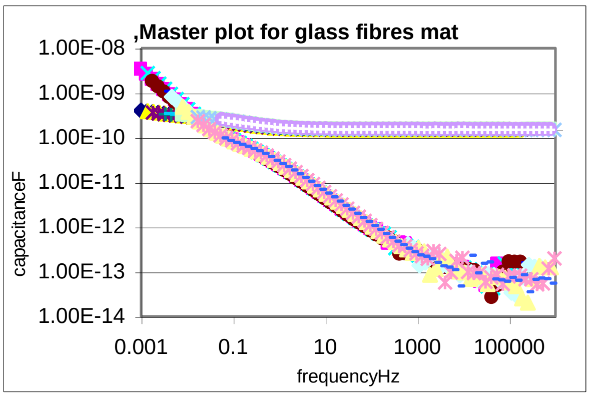

Figure 2. Master plot of the dielectric response of the glass fibre mat, Cr and Cim are real and imaginary parts of the capacitance respectively for the temperatures noted..

composite and the process is moved to higher frequencies it is reasonable to assume that they originate with the same kind of mechanism.

Dielectric measurements made on samples removed temporarily from ageing at 5 weeks, and 3months (at E=62.5kV/mm DC, T=15±5ºC) and on the sample that failed show the same form of response as for the unaged composite. However, the q-dc process had moved to higher frequencies. Arrhenius plots for the set of samples measured are shown in Fig 3. It can be seen from this plot that except for the high temperature region of the failed sample, the activation energy has not changed with ageing. There is, however, a displacement towards higher frequencies, i.e. the process moves towards the behaviour observed on the fibre mat alone. This is even more marked in the failed sample where the activation energy changes at high temperatures to a value (0.53eV) close to that of the mat.

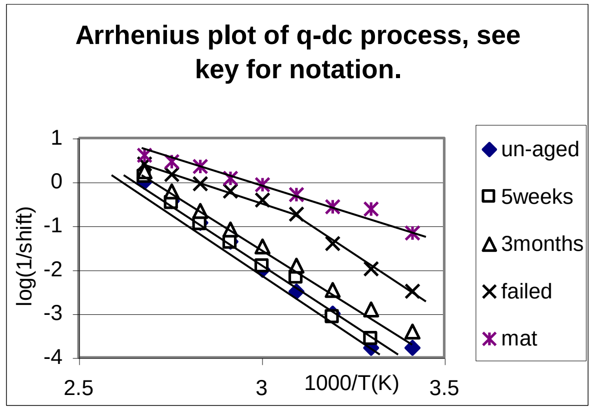

Figure 3, Activation energy of dielectric q-dc response in a range of samples as shown.

The failed sample was noted to have many 'black lines' in the plane of the sample (i.e. perpendicular to the field direction) and well away from the breakdown site. It proved impossible to resolve these under the optical microscope, so an SEM analysis was attempted. Figure 4 shows a view of a black line from above and there is little to see. Figure 5 shows the view of such a line in a region where the surface has been removed to expose it to view. The line can be seen to be a 2.5μm void running alongside the glass fibre for millimetres. Figure 6 shows an elemental analysis obtained on a sample prior to ageing using an SEM. The carbon peak is quite strong, as are peaks associated with the elemental content of the glass fibres (e.g Si, Ca, Al). The same analysis taken around the 'black line' in the failed sample, Figure (7), showed a strong reduction of the carbon peak with respect to the aluminium peak. This indicates that the black lines are not carbonised tracks such as may be produced by partial discharges.

Discussion

The feature in the dielectric response that reflects the

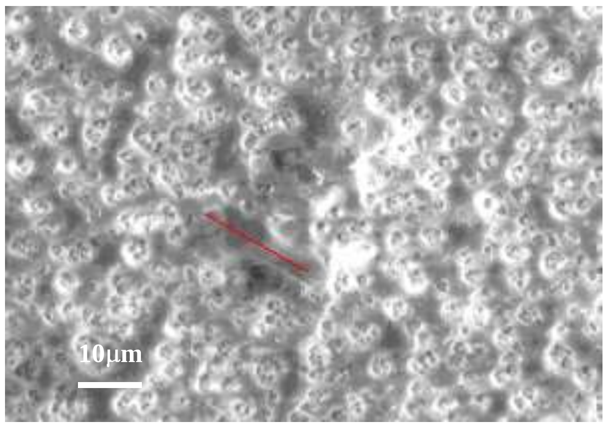

Figure 4, Shows the area near a black line that is indicated by the bar.

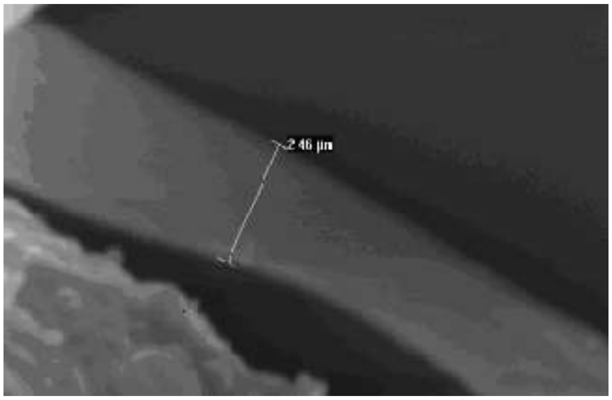

Figure 5 shows the voids (black lines) between the fibres and epoxy. The white line is 2.46 μm long

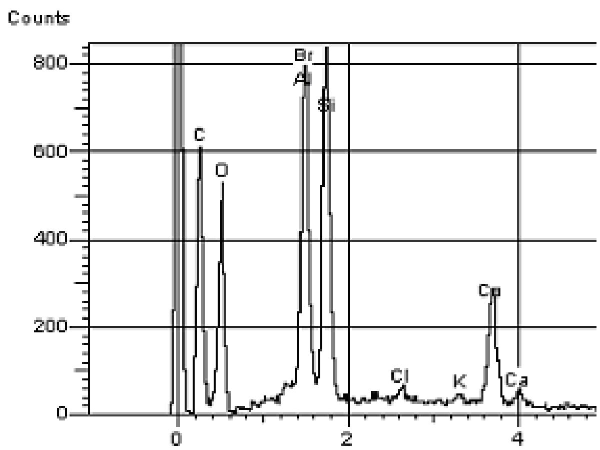

Figure 6 Elemental analysis of un-aged sample (cps vs. keV)

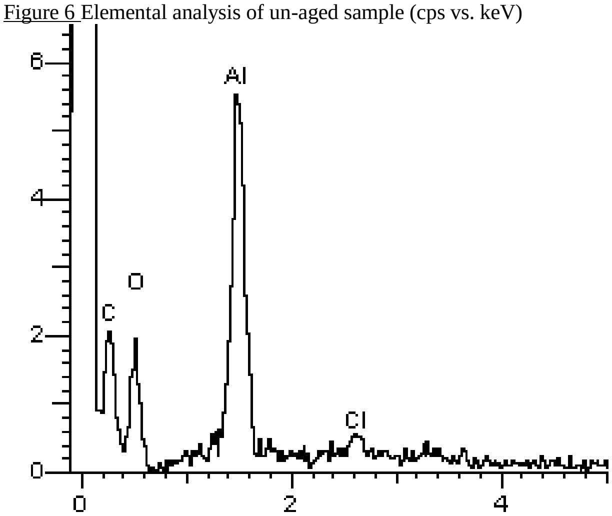

Figure 7. Shows elemental analysis of black line region (cps vs keV).

effect of ageing is the q-dc (CPA) response observed at low frequencies. This form of dielectric response has been associated with equivalent circuits that exhibit self-similarity, i.e possess a scaling relationship between sub-circuits of different size [2,3]. Percolation systems lie in this class and a model for them has been developed [2] in the form of a scaled circuit hierarchy, Fig 8. Repeated embeddings of the generator circuit, as shown in Fig 8 gives the macroscopic system. The derived response [2] has a CPA form with an exponent p whose value is determined by the arrangement of capacitors and resistors in the generator circuit, i.e. the system geometry. The CPA behaviour corresponds to the increasingly tortuous paths needed to achieve transport over ever-longer distances. At very low frequencies the conducting paths that cross the sample

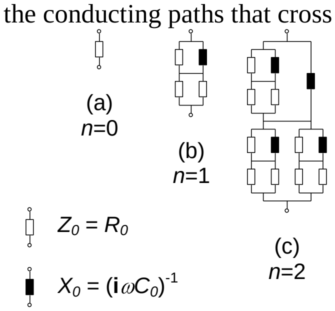

Figure 8. Three embeddings of a simple scaled circuit representation of a percolation system. Taken from [2].

yield a limiting dc conductance. The capacitance and conductance contributions to the system response are inversely dependent upon a power of the sample thickness. Our results can be interpreted on the basis of this model if we assume that charge transport takes place on the surface of the glass fibres, with contacts between fibres acting as blocking capacitors. In the case of the fibre mats a direct contact to the electrode occurs and so the limiting dc-conductance is observed. The fibres will perform the same function in the composite, but now the epoxy on their surfaces increases the activation energy for charge transport. A layer of epoxy resin will also block access to the electrode, preventing the observation of a limiting dc-conductance. It is probable that the charge carriers involved in the transport are supplied by water molecules adsorbed on the fibre surfaces [4], though other ionisable molecular species produced during the curing procedure may also be involved.

The above picture allows an interpretation of the dielectric response measurements in terms of the physical changes introduced by thermo-electric ageing. Those samples that have not yet failed show a consistent trend towards a bigger response without any significant change in activation energy, or exponent p. This implies that the circuit geometry remains the same, but that the resistance and/or the capacitances of the components have reduced. This would be achieved if some portion of the capacitive areas were to become conducting. This is just what would happen if the epoxy became de-bonded from the fibres in some places. The SEM analysis of the failed sample suggests that this in fact has taken place during ageing.

The dielectric response of the aged sample showed other features in addition to the q-dc behaviour. In part this may be due to the presence of the bored-out breakdown channel. The activation energy plot shows two regions of behaviour: one at low temperatures that paralleled that of the composite and one at higher temperatures that followed the fibre mat behaviour. A possible explanation is that the response is contributed by two systems in series. In this case the one with largest impedance will dominate. Thus the one with the smallest activation energy will dominate at high temperatures, and vice-versa the one with the largest activation energy will dominate at low temperatures. The values of the activation energies obtained indicate that the two systems correspond to regions where the fibre mate has become substantially de-bonded and regions where the fibre mat is still mainly bonded to the epoxy.

Electrical Ageing

All the samples investigated so far have been aged electrically only at room temperature. During the period of stress progressive development of de-bonding between the epoxy and the fibres has been shown to occur. Since the epoxy-fibre interface is the region where the percolative charge transport takes place it is possible that the heating effects of local currents may have caused the de-bonding. However, there is no sign of carbonisation in the de-bonded regions investigated via SEM. It is possible therefore that the de-bonding may have occurred as a result of differential thermal expansions of fibres and epoxy under the local temperature rise caused by Joule heating. Alternatively the de-bonding may be the result of mechanical stresses produced by interface fields [5].

The generation of the interface voids is likely to be the cause of dielectric breakdown [6] as long as they are aligned with their long axis in the direction of the electric field [7]. Because of the weave of the mat most such voids will be aligned perpendicular to the field direction with a width of around 2-3μm, which is insufficient to support discharges at the fields applied [7]. At some stage, however, such voids can be expected to join together to provide a gap in the field direction long enough to support discharges. Once discharges can occur failure will follow rapidly. We believe that this is what happened in the sample that broke down.

Conclusions

The dielectric behaviour of the material was shown to exhibit a quasi-dc charge transport process at low frequencies. This could be associated with limited range charge transport along the epoxy-fibre interface. Electrical ageing was found to cause de-bonding of the epoxy and fibre resulting in interface voids, mostly aligned perpendicular to the field direction. Progressive changes in the dielectric response were observed that could be attributed to the increase in de-bonding, and therefore provide a measure of the extent of the ageing that has occurred. Ultimate failure is expected to be caused be discharges when voids aligned with the field are formed by coalescence.

Acknowledgements

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