"Sub-Hertz" Dielectric Spectroscopy

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ABSTRACT

Dielectric spectroscopy measurements below 1 Hz are often dominated by "conduction-like" effects. For this reason, they often appear to be dismissed as being of little interest. In this paper two "sub-hertz" responses are considered that give insights into the insulating systems concerned. The first system is that of cross-linked polyethylene, taken from a power cable system. Measurements at temperatures between 60˚C and close to melting at 100˚C show a change in characteristic from a percolation process to a "true" DC conduction at close to the melting point. Using DC conductivities, it appears to be possible to show whether the cable has been subjected to thermo-electric ageing. This might give insights into where the conduction and hence the ageing in the XLPE is occurring. The second system is an epoxy composite. By considering the sub-hertz response, it is possible to demonstrate the effect of the interface between the filler and the epoxy matrix. In this system, ageing, resulting in delamination between the glass fiber filler and the epoxy, is clearly detected by sub-hertz dielectric spectroscopy. This process is likely to be facilitated by the presence of water, which is known to lead to mechanical failure in such systems, and which can also be detected by "sub-hertz" dielectric spectroscopy. The implications for nano-dielectrics are then briefly considered.

EXPERIMENTAL

The measurements presented here were made using a Solatron dielectric spectrometer comprising a 1255 frequency response analyzer with a 1296A CDI dielectric interface. An excitation voltage of 1 V RMS was used. The measurement cell comprised a guarded electrode system formed by slightly adapting a Keithley 6165 "resistivity adapter" cell. The diameter of the guarded electrode was 50.8 mm (2 in). Measurements were made by averaging at least four readings at each frequency. The cell was maintained at the desired temperature to within 0.2˚C. This guard ring cell was used as the specimens were expected to have extremely low losses. However, considerable noise was observed when the loss tangent was $<10^{-3}$.

Measurements on XLPE

Measurements were made on XLPE (cross-linked polyethylene) tapes that had been peeled from power cable insulation. The tapes were 150 μm thick and the surface RMS roughness was approximately 1 μm. Cables from different manufacturers were tested both "as made" and after electro-thermal ageing.

Measurements on Epoxy Resin

Measurements were also made on a commercially produced epoxy – glass composite used for printed circuit boards (PCBs); a standard "FR4" printed-circuit board material, type N4000-2 made by Park-Nelco. This was 400 μm thick comprising approximately: 50 μm epoxy, 100 μm epoxy impregnated e-glass mat, 100 μm epoxy, another 100 μm epoxy impregnated e-glass mat, and 50 μm epoxy.

RESULTS AND DISCUSSION

Cross-Linked Polyethylene

Low frequency measurements dielectric relaxation measurements on XLPE are shown in Figure 1.

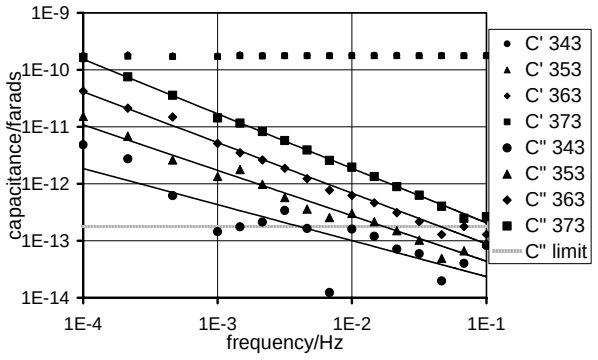

Figure 1: Low Frequency Dielectric Spectroscopy on XLPE cable samples. 'C" limit' is the noise floor of the instrument.

Measurements were made in 10˚C steps from 293 K (20˚C) to 373 K (100˚C). However, only results from the highest four temperatures are reported here as there was significant noise in the *C"* results at lower temperatures. It can be seen that the *C'* values are virtually

identical and independent of frequency. The *C″* values form straight lines on this Bode plot indicating

$$C''(\omega) \propto \omega^{-n} \qquad \textit{(Equation 1)}$$

The temperature dependence of *n* is shown in Figure 2.

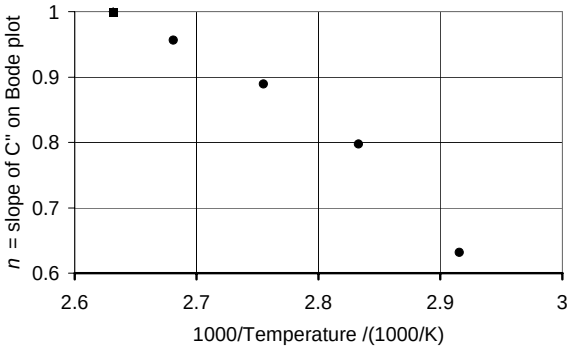

Figure 2: Slope of C″ vs. frequency Bode plot at different temperatures – the square symbol indicates a hypothetical point described in the text.

The magnitude of the slope increases with temperature. A slope of $n = 1$ would indicate a true DC conductivity since *C′* is independent of frequency. To see this, consider the admittance of a complex capacitor to be equivalent to the simple parallel combination of *R* (=1/*G*) and *C*. Then $j\omega C^* = G + j\omega C$ so that $C^* = \frac{G}{j\omega} + C = C - j\frac{G}{\omega}$. The complex capacitance is defined as $C^* = C' - jC''$ so that, in this simple example, $C' = C$ and $C'' = G/\omega$. Note that, if there is a true conductivity to be measured, this is seen at low frequencies as a slope of –1 on a plot of $\log(C'')$ versus $\log(\omega)$ and that *C′* is independent of frequency. This is a very good test to see if a true conductivity is actually being measured. The temperature required for DC conduction appears to be equal to the melting point of XLPE (380 K) shown by the square symbol in Figure 2. The conductivity at 373 K is approximately $7.7 \times 10^{-15}\ \Omega^{-1}\text{m}^{-1}$. The value of *n* did not drop below 0.5 at lower temperatures.

At lower temperatures, it is tempting to ascribe the power law behavior of *C″* ($C''(\omega) \propto \omega^{-n}$ (Equation 1) to a low-frequency dispersion (LFD), Quasi-DC (QDC) process [1,2]. However, it is important to note that, in such a case, the slopes of *C′* and *C″* on the Bode plot would be parallel giving a constant for tan δ. Clearly, this is not the case. The behavior seems to be percolation-like and described by Dissado and Hill [3] using a deterministic-fractal-circuit model. The behavior that they predict for percolation is shown in Figure 3.

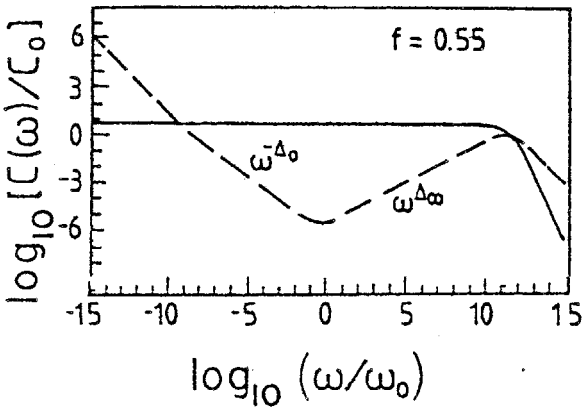

Figure 3: Computed AC response of a deterministic-fractal-circuit above the percolation threshold. Adapted from Fig. 3 of [3]; f=0.55 N=8, h=0.5, n=20

In this model, a fractal circuit of capacitors and resistors is constructed from *N* elements, a fraction, *f*, of these elements being resistors – i.e. capable of supporting current flow, the others being a parallel connection of two rows of sub-components. The sub-components are distributed such that there is a fraction *h* in one row and $(1-h)$ in the next. Reducing *f* towards the fixed value of *h* eventually eliminates the last percolation path when $f = h$. For $f > h$ the transport is percolative. Further evidence of this behavior is found by considering the broader dielectric spectrum. Unfortunately, the noise is rather significant in this low-loss material and so an averaging process has been used to give a representative spectrum of a slightly different XLPE in Figure 4.

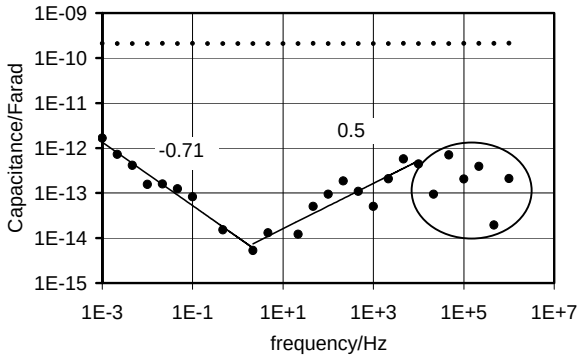

Figure 4: C′ (upper) and C″ (averaged results) for another power cable XLPE. The encircled points are unreliable.

This appears to lend further support to the Hill and Dissado percolative model being applicable to this situation. Comparing Figure 3 and Figure 4, the values of $\Delta_0 = 0.71$ and $\Delta_\infty = 0.5$ can be established, although these values should not be taken as being very accurate. An infinite number of solutions can be found for the values of *h*, *f* and *N*. Selecting $N = \{8,16,32\}$ and $h = \{0.45,0.50\}$, best fitting values of *f* can be computed, see Table 1. It can be seen that *f* is always bigger than *h*, indicating percolative behavior.

N	8	16	32	8	16	32
h	0.45	0.45	0.45	0.5	0.5	0.5
f	0.488	0.459	0.452	0.533	0.508	0.502

Table 1: Possible fractal circuit parameters

It seems therefore that, at least under the conditions studied, charge carriers percolate through XLPE. The conditions for percolation change with temperature – possibly through a variation in the fraction of sites that are able to support charge transport. As XLPE is heated, much of the crystalline lamella regions start to melt. This would suggest that conduction is primarily through the amorphous region (although possibly in the amorphous – crystalline interface) with true DC conduction not occurring until the onset of melting.

Finally on the subject of power cable XLPE, the low-frequency *C"* results can be used to estimate the conductivity as a function of temperature. An Arrhenius plot is shown in Figure 5. The squares are for two different aged cables and the circles for two different un-aged cables. Different manufacturers made the cables using similar materials for the XLPE. It is interesting that the cables can be so well differentiated using this technique. This may indicate permanent changes to the crystalline structure occurring during the ageing.

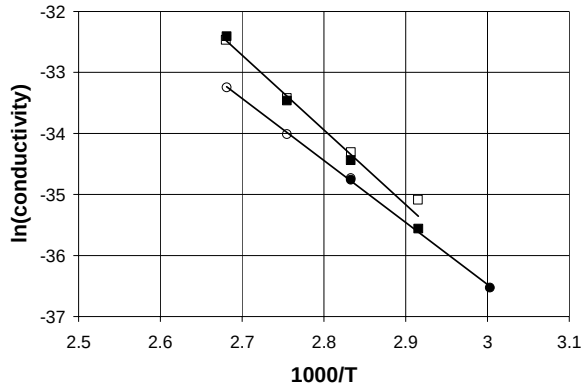

Figure 5: Arrhenius plot for two aged (squares) and two un-aged (circles) XLPE power cables.

Epoxy-Glass PCB Composite

Dielectric relaxation measurements on the printed-circuit board (PCB) epoxy-glass composite are shown in Figure 6. Measurements were made in 10˚C steps from 293 K (20˚C) to 363 K (90˚C). The relative displacement of the curves is shown by the index points in the graph – it can be seen that it was only necessary to shift the curves along the frequency axis to cause them to come into coincidence. It can be seen that the *C"* low-frequency dispersion has a slope of –0.8 and is therefore not that of a true DC conduction. Indeed, neither is *C'* independent of frequency. This is a Q-DC process [1]. The Arrhenius behavior of this Q-DC process, shown in Figure 7, is found by plotting the log {frequency shift} versus 1000/temperature. An activation energy of 1.1 eV was found.

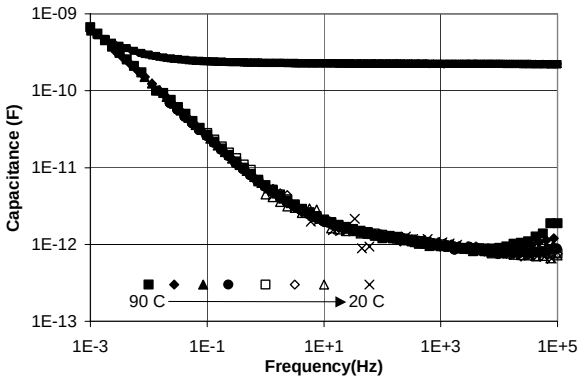

Figure 6: A master-curve formed from dielectric spectroscopy measurements on the epoxy – glass composite.

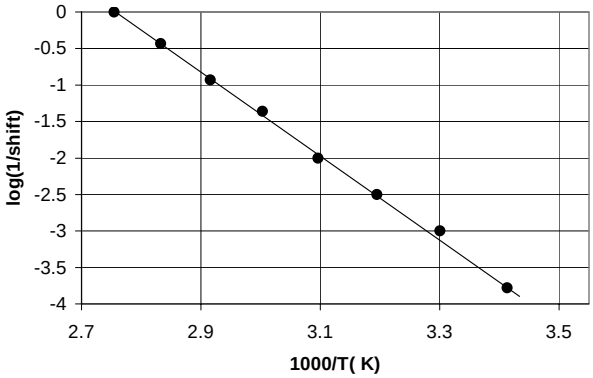

Figure 7: Arrhenius plot for low-frequency Q-DC process found in the epoxy-glass PCB composite.

Similar measurements were then made on specimens that had been aged to electrical failure under fields of 25 kV.mm^{-1} at 363K (90°C) and also on the glass mat. These all displayed Q-DC processes, whose temperature dependencies are summarized in Figure 8.

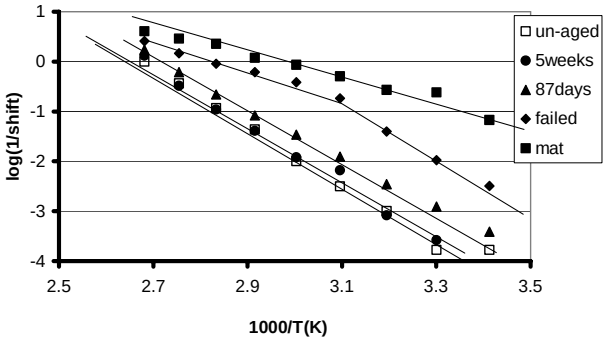

Figure 8: Arrhenius plots for un-aged, aged, failed epoxy PCB composites and the glass mat.

The glass mat had a much lower activation energy of only 0.67 eV since charge carriers can move over the glass surface; possibly through a hydration layer. It is clear that the ageing process is causing a displacement of the Q-DC process to higher frequencies – i.e. it is making the charges less constrained. It can be seen that

the specimen that broke down exhibited virtually the same activation energy as the mat. Further microscopic examination has shown that this was probably caused by gradual delamination of the epoxy from the glass mat.

This delamination is consistent with water absorption by the epoxy, which is known to occur [4]. This can lead to a weakening of the bonding between the glass and epoxy [5]. Electrolytes can form on the surface that may support charge movement and may contribute to breakdown (e.g. Janssen *et al* [6]). Certainly, the effect of humidity on epoxy-glass resins is very significant. Figure 9 shows some preliminary results for various hydrations: *dry* = 72 h in a vacuum oven at 50˚C, *room* = standard laboratory conditions, *x h* = specimen was left in water for *x* hours. Although the actual hydration levels were not measured, this shows a clear trend of increasing low-frequency loss with humidity. In these experiments, the real capacitance does not increase much at low frequencies except for the highest humidities, suggesting charge percolation along a hydrated interface between the glass mat and the epoxy.

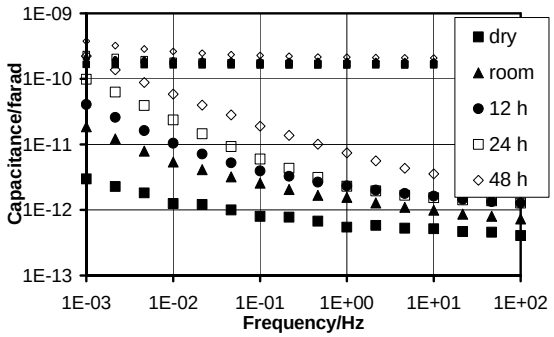

Figure 9: Effect of hydration on epoxy-glass PCB composite.

Comrie *et al* [7] have reported on the effects of exposure of thick film adhesive-bonded structures to moisture using broadband dielectric spectroscopy (10^{-2} Hz to 3 GHz). They note that changes in the low frequency dielectric response can be attributed, *inter alia*, to interfacial effects. Their data are complemented by mechanical failure analysis of the bond structure. The dielectric data parallels the changes in the mechanical data for these systems. Indeed, they state that their study, "demonstrates the usefulness of the dielectric approach for the assessment of ageing in adhesive-bonded structures and emphasized the importance of extending the dielectric measurements to lower frequencies."

Nano-Filled Epoxy Resin

It is also interesting to note that the sub-hertz dielectric spectroscopy of nano-filled epoxy resin exhibits a percolation (Q-DC) response evidenced by a constant tan δ, whereas that of the equivalent micro-filled material shows a classical Maxwell-Wagner behavior where charge transport is capacitively blocked [8], Figure 10. It may be speculated that this difference in charge transport is responsible for the lower charge densities observed in the nano-filled material

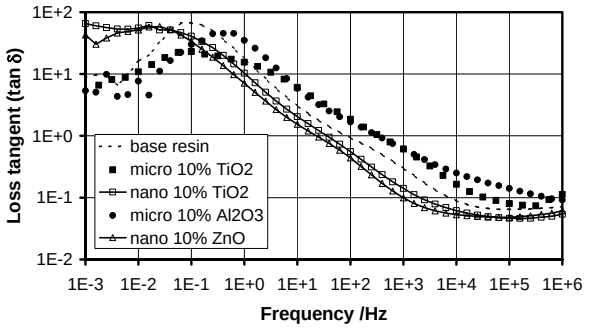

Figure 10: Loss tangent of unfilled and 10% micro- and nano-filled materials at 393 K

CONCLUSIONS

In this paper, we have attempted to emphasize the importance of low-frequency ("Sub-Hertz") dielectric spectroscopy. We note that such data can give insights into the way charge carriers move through such materials and how this might change with temperature. This has lead to new insights into such mechanisms in XLPE. We have also shown how such measurements may give insights into ageing, and electrical and mechanical failure mechanisms by using the example of an epoxy-composite and the effect on this of the variation of humidity. It is clear that this will also be important in considering the effects of water on the nano-composites being proposed for dielectrics.

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