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Ageing, Space Charge and Nanodielectrics: Ten Things We Don't Know About Dielectrics

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Abstract: Three areas of considerable progress are identified in the area of polymeric insulation since the mid 1990s (i.e. since the inception of the Eric O. Forster Memorial Lectures): the understanding of ageing, the measurement of space charge, and the development of nanodielectrics. The paper proposes a typology to distinguish and define electrical ageing, degradation and breakdown. With reference to the principal theories of thermo-ageing, it is concluded that there is little direct evidence for ageing even though it is likely to exist, at least above a critical field. The capability to measure space charge has improved considerably and this shows considerable potential as a diagnostic tool. Space charge behaviour is extremely difficult to analyse and general predictions may be impossible in practice. It is, however, necessary to control space charge accumulation in HVDC systems. Nanodielectrics continue to offer promise and understanding is improving in this area, particularly in the development of models of interaction zones around nanoparticles.

ERIC O. FORSTER

Eric Forster was internationally recognized as a father figure in the IEEE Dielectrics and Electrical Insulation Society. He was Secretary from 1974 – 1978 and Treasurer from 1974 – 1986 [1]. Amongst the conferences that he initiated was this series, the ICSD, the first of which was held in Toulouse in 1983. It was difficult to imagine a conference without Eric proudly presenting new data or his new ideas. He greatly encouraged young people too. He had the knack of bringing newcomers into a conversation and, in this way, had a strong positive influence on many students and individuals, including me. After the 1992 ICSD, he asked me to chair the 1995 meeting at Leicester. Unfortunately he passed away before that (in December 1993) and so, in his honour, I was pleased to arrange the first "Eric O. Forster Memorial Lecture" for that conference. It was presented by John Densley on *Ageing and Diagnostics in Extruded Insulations for Power Cables*. I feel honoured to present it in 2007.

INTRODUCTION

In preparing this lecture, it was suggested by my colleague, Len Dissado, that I discuss "ten things we don't know about dielectrics". There are two problems with this suggestion. Firstly, just because I don't know something about dielectrics, doesn't mean that you, the reader, doesn't know about it. Secondly, where do I start: there are so many things we (or at least I) don't know about dielectrics? I have therefore taken a slightly different tack. I thought it would be interesting to ask, "What have been the main developments in my area of dielectrics – i.e. polymeric insulation – since the start of the Eric O. Forster Memorial Lectures – i.e. over the last 15 years or so?" I can then point to 10 things we ought to try to understand better.

There seem to be three main developments that I would like to highlight:

1. *Ageing*. Although there had been a lot of discussion of ageing before 1995, the term was loosely used. I would like to try to define what I mean by ageing (as opposed to degradation for example) and to consider the evidence and theories surrounding it.

2. *Space Charge Measurement.* Sophisticated methods of space charge measurement started to be used widely in the mid-1990s. Some unexpected and many unexplained results have been published since then.

3. *Nano-dielectrics.* Whilst Lewis predicted unusual properties for these materials in 1994 [2], this field has only really burgeoned in the last five years.

No doubt others would include other areas, or even discount some of these; I appreciate this is something of a personal choice.

AGEING

In 1992, Dissado and I published a book [3] on *Electrical Degradation and Breakdown in Polymers*; we did not include *ageing* in the title. Mechanisms ranging from "intrinsic" electrical breakdown to water trees, covering time scales from 10^{-9} to 10^{9} s, were considered; Figure 1 is adapted from Figure 3.8 in the book.

At the time, we discussed whether other mechanisms (here indicated as "???" in Figure 1) would be operative at long(er) times and lower fields. I believe this is what we now refer to as ageing. We also alluded to the lack of a clear distinction between *breakdown* and *degrada-*

tion (not really knowing what to do with partial discharges). In Table 1, I have tried to rectify this situation and suggest a typology for the three processes of breakdown, degradation and ageing.
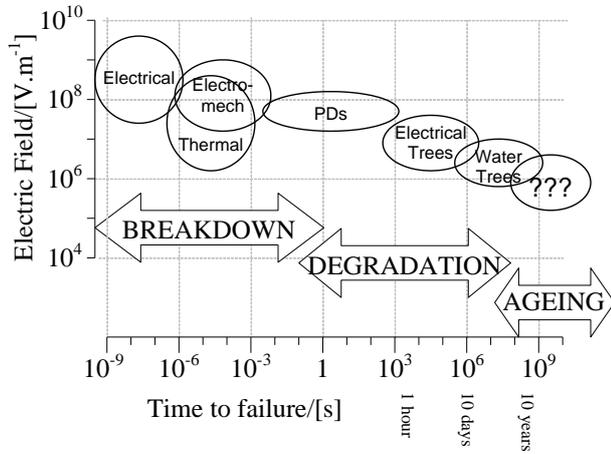
Figure 1: Indicative times and electric fields over which various electrical breakdown and degradation mechanisms are operative (adapted from [3])

Table 1: Characteristics of Breakdown, Degradation and Ageing Processes

	Breakdown	*Degradation*	*Ageing*
Effect	**Catastrophic:** insulation cannot be used afterwards	**Leads to breakdown:** reduces b/down voltage	**May lead to degradation:** may not reduce b/down voltage
Speed	**Fast:** occurs in << 1s	**Less than required service life:** ~hours – years	**Continuous process:** whole service life
Evidence	**Direct observation:** normally by eye - hole through insulation	**Observable directly:** may require microscopic or chemical techniques	**Difficult to observe:** may even be difficult to prove existence
Place	**Continuous filament:** bridges electrodes	**Occurs in weak parts:** may form fractal structures	**Assumed to occur throughout insulation**
Size	**>mm:** dependent on energy of event.	**>μm:** may form larger structures	**>nm:** molecular scale
Examples	Thermal Electromechanical Mixed mode Avalanche Intrinsic	Electrical Trees Water Trees Partial Discharges	Bond scission Nano-voids Trap formation Non-electrical changes (oxidation etc)

The key difference between breakdown and degradation is that breakdown is an event that is sudden and catastrophic - the insulation cannot withstand the service voltage following breakdown – whereas degradation is a process that takes places over a period of time. It both increases the probability of breakdown and decreases the breakdown strength. Figure 2 [5, 6] shows that water treeing leads to a reduction in

breakdown strength (as well as changes in the dielectric and viscoelastic response [4]). Degradation due to water trees typically leads, after a period of months to years, to electrical treeing. This degradation process, after a period of hours to weeks, leads to a breakdown. This may be a discharge arc through the electrical tree or/and thermal breakdown if the tree is sufficiently conductive.
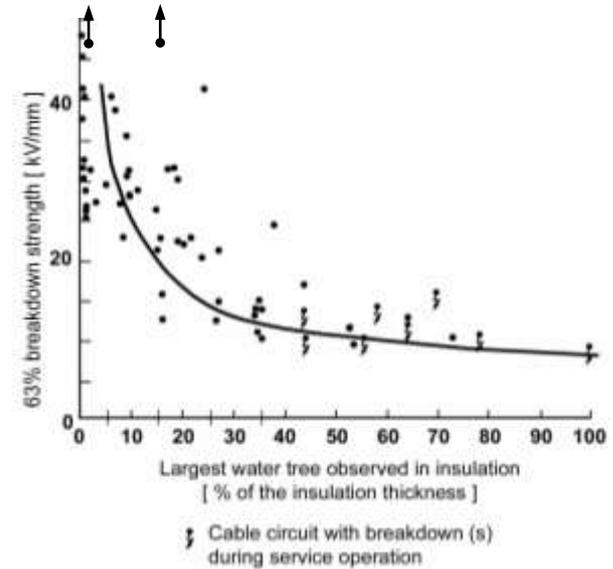
Figure 2: Breakdown strength for cables as a function of maximum water tree length (% of insulation thickness) From [5], data from [6]

Well-designed insulation systems, operated within the scope of the design parameters (including the design life), should not breakdown or degrade. Both these processes are irreversible and directly observable. If degradation is diagnosed then the prognosis is poor and the system is liable to breakdown.

Ageing, however, is less clear. Indeed there are questions as to whether ageing solely due to an electrical field actually exists at all (see, for example, [7]). It is widely accepted, however, that the time-to-breakdown does decrease as the electric field increases (at least above a critical field), even in the apparent absence of any degradation mechanisms such as water treeing. So something seems to be going on! Crine and Vijh [8], in 1985, proposed "an approach to physico-chemical factors in the electrical breakdown of polymers" in which they took forward some of the classic ideas of Artbauer [9] and, importantly, considered processes at a molecular and morphological level. However, since 1995, there has been considerably more interest in this area, possibly because much of the expensive plant of many transmission and system operators is coming to the end of its design life and also because of the work of the IEEE DEIS multifactor aging committee. Current interest has focussed on the theories of (i) Dissado, Montanari and Mazzanti [10, 11, 12, 13, 14, 15], (ii) the Bangor group including Lewis, Llewellyn, Griffiths, Sayers and Betteridge [16, 17, 18, 19,

20, 21, 22, 23, 24, 25], and (iii) Crine and Parpal [26, 27, 28]. All the mechanisms assume the characteristics given in Table 1 and generally predict the formation of regions of reduced density or free volume throughout the insulation. The ageing rate is assumed to increase in regions of high space charge concentration (model (i)), high electro-mechanical stress (ii), or in regions of free volume that allow high local currents (iii). In all cases, such ageing may result in sub-micro-cavities (here referred to as nano-cavities) and a greater prevalence of charge traps. Models (i) and (iii) arrive at different expressions relating the time-to-failure with field and temperature, but the argument that persists as to which is "correct" suggests that more data is required, the expressions are not sufficiently different to distinguish between the models, or/and there is more than one mechanism of thermo-electric ageing. A principle difference is that model (i) assumes that space charge is the cause whereas model (iii) assumes it is the effect of ageing [29]. In model (i), space charge accumulates at centres giving rise to enhanced electric fields and, electro-mechanically, to the formation of centres of ageing (e.g. local chain scission). In model (iii), electrically induced mechanical deformation of intermolecular (van der Waals) bonds is first step (following a Griffith's criterion approach) and is a rate-controlled process; at sufficiently high fields, electrons injected into nano-voids can acquire enough KE to be hot and generate further damage. Model (ii) considers that the morphology is changed at points throughout the material, principally through electromechanical forces which unravel crystallites; it appears to have been specifically developed with polyethylene in mind. More recently, Rowe [7] and Raine [30], have suggested an ageing mechanism appropriate to filled materials, in which ageing preferentially occurs at interfaces between the host material and the filler particles. These aged damage surfaces start to link and eventually cause sufficient damage to lead to breakdown through a percolation type process. Certainly we have had our attention drawn to the criticality of dielectric interfaces (whether at electrodes, with fillers or between phases within a given material), by Lewis for many years (e.g.31). Tanaka [32] has also reviewed ageing and has included outdoor insulation as well as the effects of manufacturing defects, and mechanical, environmental, thermal and electrical effects.

So why should we care which theory or theories are correct? The most obvious reason, at least from an engineering standpoint, is that it would be useful to know to what extent an insulation system is "aged" and whether it would make economic sense to replace it. Whilst the ageing models are shown to fit the test data well (e.g. Figure 3), and much better than an inverse power law, the data points for the longest ageing times are extremely expensive to get and therefore quite rare; and it can be argued that extrapolation gives optimistic life times [26]. (Even in Figure 3, the longest time corresponds to "only" about 6 years.) Prediction is

further complicated by the stochastic nature of break-down (e.g. [3,33]) giving rise to a wide distribution of times to failure amongst a set of identically stressed insulation systems.
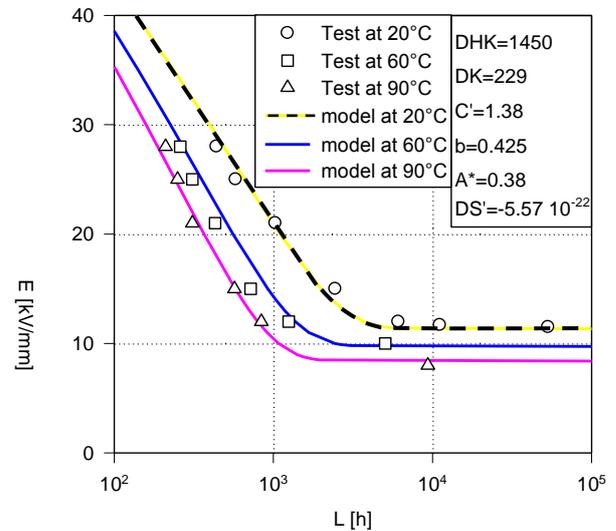
Figure 3: 50Hz life tests on XLPE mini-cables [34] compared with model calculations (from [13])

The objectives of the European ARTEMIS project [35,36] were to develop techniques to assess the state of ageing of cable materials under combined thermo-electrical stresses, and to develop a diagnosis system to predict their remaining life time. It comprised eleven partners, including one material supplier, two cable manufacturers, three utilities and five universities. Two 90 kV XLPE cables were produced by the cable manufacturers, which were aged in dry conditions for various times extending to 10,000 hours, voltages corresponding to 14.1, 21.8 and 31.2 kV/mm at the inner semicon and temperatures (20 and 90°C). A mathematical construction was developed to apply ageing models to cables as well as plaques [37]. A very wide battery of experimental techniques, described in [38] were used to analyse the aged materials. Included in these were some laborious experiments, akin, but possibly more difficult to, finding a needle in a hay-stack, to find and characterise nano-voids (mostly < 100 nm) in unaged cable and a cable aged for 9000 hours in a cyclic voltage stress experiment at 30 kVmm^{-1}. The results are summarised in Table 2.

The results indicate that the concentration and internal surface area of voids is much higher close to the inner cable screen than away from it (consistent with the idea that voids originate from voltage stress, which is higher closer to the screen). It is possible, however, that this could arise from the manufacturing process. A weak effect of ageing may be seen close to the screen: there is a slight decrease of the total void concentration and an increase in the total void internal surface area. This would be expected if voids grow upon ageing (internal surface increase) but also coalesce (slight decrease in concentration). The cables were thermally aged as well

as electrically aged and it is not known whether this would have been found under solely electrical ageing. However, this is the only *direct* measurement that I know of, of the development of nano-voids during polymeric ageing.

Table 2: Total void concentration and total void internal surface area calculated for each sample both close to, and 4 mm from, the inner semicon.

Distance from inner semicon/[mm]	Cable condition	Total void concentration/[m^{-3}]	Total void internal surface area/[
0	Unaged	5.30×10^{16}	5.39
0	Aged	4.34×10^{16}	6.70
4	Unaged	2.67×10^{16}	3.85
4	Aged	2.13×10^{16}	3.99

Various *in*direct measurements also resulted in observed changes. In particular, the threshold for the onset of space charge was found to be useful; this is described in the next section. Because of the expected changes to trapping centres, one would also expect the conductivity to change (although one could argue that almost anything would change the conductivity!). This was measured accurately using low-frequency dielectric spectroscopy [39] as a function of temperature for both cables, before and after ageing. An Arrhenius plot is shown in Figure 4. The squares are for two different aged cables and the circles for two different un-aged cables. 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. Again, however, it is unclear whether this is predominantly due to the thermal or electrical contributions to the process.
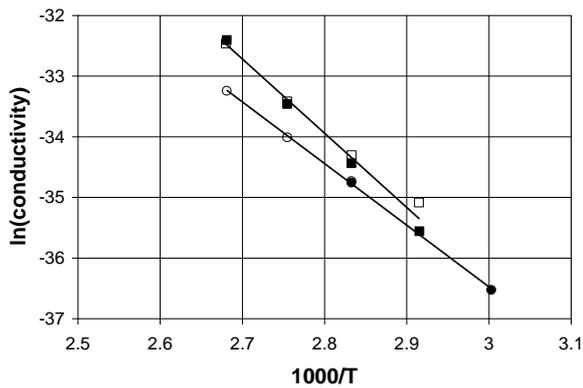
Figure 4: Arrhenius plot for two aged (squares) and two un-aged (circles) XLPE power cables. From [39]

Laurent *et al* have advocated the use of electroluminescence (EL). Electrical ageing of insulating polymers would involve dissipation to the lattice of the energy of mobile or trapped space charges. EL has been used to characterise such energy releases. Provided sufficient light is available, it could be used to define the onset

and rate of electrical aging and to investigate the dissipation mechanisms [40].

SPACE CHARGE MEASUREMENT

Currently used techniques for space charge (or, more exactly, field gradient) measurement have their origins in the 1980s: including the laser induced pressure pulse (LIPP) [41], the pulsed electro-acoustic (PEA) [42], and the pressure wave pulse (PWP) [43] techniques - all of which provide similar information [44]. It was with the easy availability of powerful digital instrumentation that these started to be widely used from the mid 1990s. A book was produced following the 1997 meeting of the UK Dielectrics Society on "Charges in Solid Dielectrics" [45]. Various notable advances have been made in techniques including: the observation of space charge in cable geometry (e.g.[46]), techniques for simultaneously measuring the external current so as to distinguish polarisation and conduction current density profiles [47, 48], improvements in speed of acquisition (e.g. [49, 50, 51]) and portability [52], measurements on multilayer dielectrics (e.g. [53]), suggestions that it should be possible to improve the spatial resolution to better than 60 nm or less in certain materials [54], and systems with spatial resolution in more than one dimension (e.g. [55]) (to name but a few!).

Despite the significant improvements in instrumentation, the theory to explain, or certainly to predict, the observations is largely lacking. In part, this is not surprising. For example, Wintle, who states, "our basic knowledge is not in good shape", has pointed out that moving from a very simple system to even a slightly more complicated one causes huge problems in the analysis of an apparently simple space charge decay observation [56]. The simplest system might contain no permanent dipoles, only one carrier species, in which the carriers are all excess carriers. The current (due to conduction, diffusion and polarisation) may then be given by equation 1:

$$ j = pq\mu E - qD\frac{\partial p}{\partial x} + \varepsilon_0 \varepsilon_\infty \frac{\partial E}{\partial t} \qquad 1 $$

Wintle then points out that this would be easy to integrate (equation 2) to check the model (the only adjustable parameter is the mobility, μ.

$$ jl = \frac{\mu \varepsilon_0 \varepsilon_\infty}{2}\left[E^2\right]_0^l - qD\left[p\right]_0^l + \varepsilon_0 \varepsilon_\infty \left[\frac{\partial V}{\partial t}\right]_0^l \qquad 2 $$

However, even a very slight increase in complexity in the model, that of moving to a second carrier, makes the problem intractable analytically. Equation 1 develops into equation 3 and the integration can no longer be done as it is impossible to distinguish p and n in the data.

$$j = pq\mu_p E + nq\mu_n E - qD_p \frac{\partial p}{\partial x} + qD_n \frac{\partial n}{\partial x} + \varepsilon_0 \varepsilon_\infty \frac{\partial E}{\partial t} \qquad 3$$

At the risk of being accused of plagiarising Wintle [57] (who is renowned for pointing out what we don't know about dielectrics), he subsequently notes that even in a simple bipolar model one could have up to 20 parameters to consider, Figure 5.
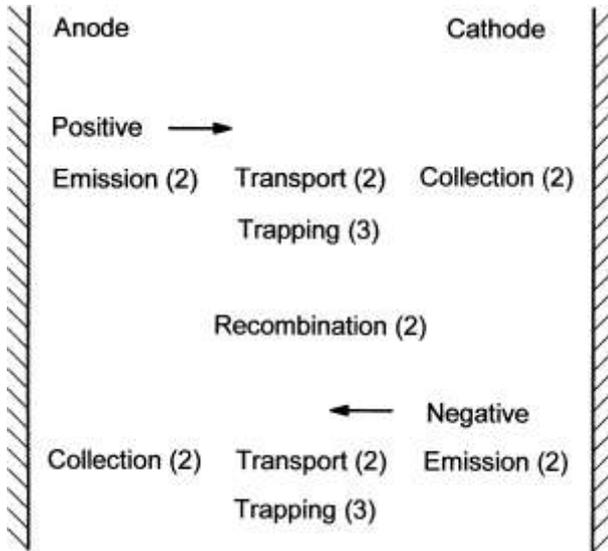
Figure 5: Schematic showing the mechanisms involved in a model of bipolar transport. The number of parameters associated with each process is shown in brackets. From [57]

There are, of course, many attempts at modelling the behaviour, e.g. [58] and strenuous attempts to extract the last drop of information from data (e.g. [59]) by looking a charge dynamics and dependencies on both the poling stress and that used to produce the electro-acoustic pulse. Using such analysis it has been possible to gain reasonably detailed information: in the last example it was shown that space charge decay was governed by de-trapping from traps in range 0.94 – 1.15 eV over an essentially uniform distribution – however, one could still argue that we have no idea what the traps are.

Sophisticated numerical computer models have been developed more recently using high-power computing, for example by the Toulouse group of Le Roy, Teyssedre, and Laurent working with Dissado and others in the European HVDC project [60], which have resulted in useful tools for analysis [61]. An example of the output from such a programme is shown in Figure 6 [62]. For well-controlled systems, such as power cables, there is a place for such tools, as well as those based on macroscopic physics (e.g. [53]) for predicting space charge. In DC power cables, for example, this could be used to optimise their operation whilst minimising their ageing.

The use of space charge measurements for the diagnosis of ageing, in particular cable ageing, - i.e. the estab-

lishment of "markers" to determine cable ageing using space charge, has been suggested by various authors [25,38,63,64] and has been pursued particularly vigorously by Montanari *et al* (e.g. [29,65,66,67]).These techniques generally consider where the accumulation of space charge becomes non-linear with field. Fu [68] has suggested the use of plotting the induced charge on an electrode (or the PEA signal that is proportional to this charge) as a function of applied voltage. Ideally the charge on a capacitor's electrode should be proportional to the applied voltage and so this should be a straight line. However, above a threshold field a deviation is found, the direction being dependent on whether the inducing charge near the electrode is homo-charge or hetero-charge. The Southampton group suggested the use of a simple method they termed "X-plots" for this purpose under AC conditions [63]. In this technique, which uses high speed LIPP, plots of peak space charge magnitudes at both electrodes are plotted against peak voltage during the AC cycle. At sufficient voltage, the resulting "X" shape of the plot becomes distorted and this is taken as being indicative of charge injection into the specimen under test.
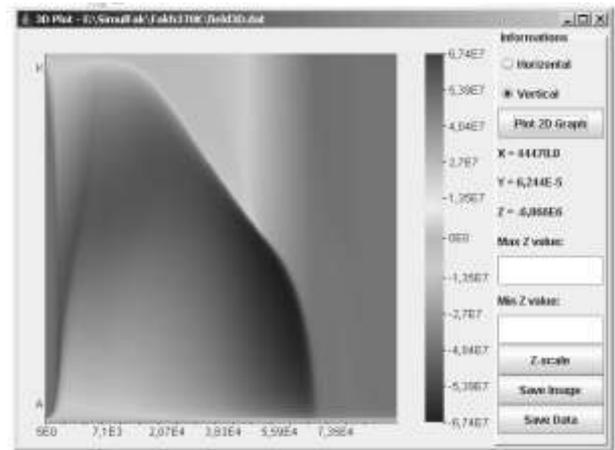
Figure 6: Example of 3D plot of field vs. time and depth
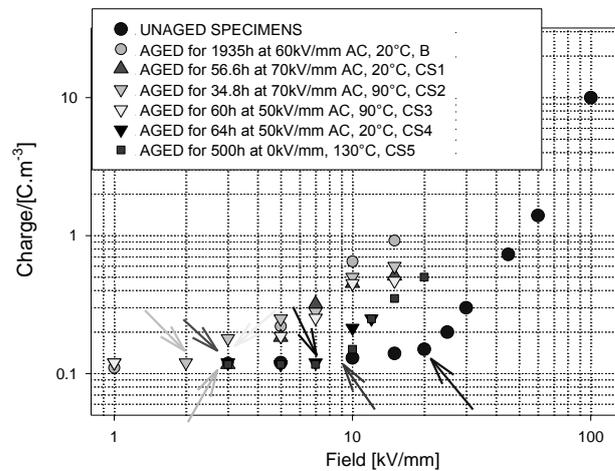
Figure 7: Determination of space charge threshold as part of the ARTEMIS project (measurements by Montanari *et al*)

The technique pioneered by Montanari has been to plot the average absolute value of space charge measured over the thickness of the specimen. Figure 7 shows typical results made on plaques of XLPE as part of the ARTEMIS project in which the threshold voltage decreases from about 20 kV/mm for unaged specimens to around 2 kV/mm for heavily aged materials. Thermal ageing alone (black squares) does decrease the threshold voltage, but not as much as combined thermo-electric ageing. Threshold voltages measured in this way appear to correlate well with those measured by conduction current vs. field experiments and EL vs. field experiments. [67].

In crosslinked polyethylene the situation is somewhat complicated by the crosslinking by-products. It is very clear that these give rise to significantly increased charge accumulation and there may be a case for not using PE containing such products for HVDC applications. Hirai et al [69] soaked an additive-free low-density polyethylene sheet in various liquid chemicals corresponding to crosslinking by-products and the space charge distribution inside the sheet was measured under DC voltage application. They concluded that the hydroxyl group in the cumyl alcohol was responsible for carrier trapping. Since this is such a volatile chemical, it could be interesting to see whether this molecule, when ionised, i.e. when it has trapped a charge, would drift through the XLPE slowly under the influence of a high applied field rather than relinquish its charge. Chong et al [70] tested the hypothesis that the annealing resulting from degassing of these chemicals would also change the morphology of the XLPE, which may be responsible for the observed change in charge accumulation characteristics. However, they also concluded that the presence and amount of by-products takes precedence over the morphology of the material as far as space charge evolution is concerned. Similar results were noted by Fu et al [68] using the space threshold technique.

Another interesting observation using space charge measuring systems was that of charge packets. These were not entirely unexpected, since they occur in solid state semiconductors. They have given rise to some interesting "movies" being shown at conferences. Hozumi et al [46] had spotted them in cables and again the mechanisms may be different in XLPE from other materials. Charge packets appear as diffuse clusters of charge that slowly drift across the insulation under sufficiently high applied fields, usually >70kV/mm. There are various proposed mechanisms, for example, we had ascribed them to fronts of ionisation [71]. They clearly require a dependence on a non-linear function of field (in the case of ionisation, this would be the carrier concentration). In an unpublished Dielectrics Society meeting [72], I had suggested that these may have a 3-D rather than a planar character (i.e. akin to the globules of wax floating up through the hot oil in a lava lamp), since these were found to occur in poorly made avalanche diodes. This indeed has been found, using a PEA capable of 2D spatial resolution [73]. Since the divergence of the field at the front of such "charge globules" will be much higher than that assuming they are planar fronts of charge (as one might from conventional PEA measurements), it is difficult to estimate the fields involved. However, local conditions at the electrodes seem to control their initiation, and it may be necessary to reconsider their initiation and propagation mechanisms. I must admit that charge packets are probably more an academic curiosity than of practical application. At the fields required for their existence, they are probably a sign that the insulation is being stressed beyond its healthy limits.

NANODIELECTICS

(Following another Dielectrics Society meeting) Lewis considered the future of dielectrics in a paper entitled "Nanometric Dielectrics" in 1994 [2] in which he suggested "that a major field of study in the future development of dielectrics will concern their properties when relatively few molecules are involved. Such smallness arises naturally at interfaces of nanometric thickness and will occur also when dielectrics are employed in the nano-technical devices of the future." Fréchette picked up on this theme in 2001 [74] and later remarked, "The preliminary studies, still in their infancy, tend to show that the polymer nanocomposites exhibit improved dielectric performance as compared to their coarse-grained ancestors." [75] The latter article contains useful definitions and descriptions of nano-dielectrics including a review of the history of the subject to that point. In the Spring of 2002, I was fortunate that Keith Nelson joined me as a visiting professor for six months and after some assiduous experimental work gained the first experimental evidence that nanodielectrics were likely to offer enhanced properties [76]. The work was conducted on epoxy resin specimens incorporating ceramic nano-particles as well as unfilled specimens and those containing "boulders" 10's of microns in diameter.

It was clear that these nanodielectrics behaved in a completely different way to the micro-filled composites. It was speculated that the "interaction zone" around the particles was having a dominant effect in the case of nano-particles. Clearly an interaction zone of a given thickness (e.g. 10 nm) would be much more significant for nano-particles than micro-particles. This was in agreement with Lewis' proposal that interfacial effects, similar to the Stern and Gouy-Chapman layers found in electrolytes surrounding solids, may also occur in solid dielectrics. See [25,77] for fuller discussions of this.

In a composite in which the particles are well dispersed, unless they are arranged to be "self-repelling" the distance between the particles will be distributed according to a Poisson distribution. The probability, P, that one interaction zone will overlap with one of its

neighbour's (for low concentrations) is then given by equation 4 for spherical particles and shown in Figure 8 where t is the zone thickness and d the average particle separation. So for a 50% probability of overlap, t/d would be 0.347 and a 50 nm particle would require a interaction zone thickness of 17.3 nm.

$$P = 1 - \exp\left\{ -\frac{2t}{d} \right\} \qquad 4$$
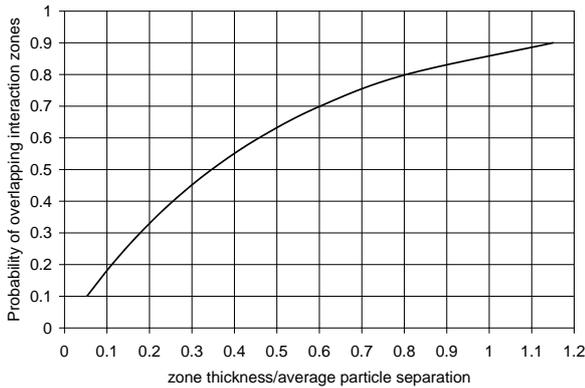
Figure 8: Probability of interacting particle zones
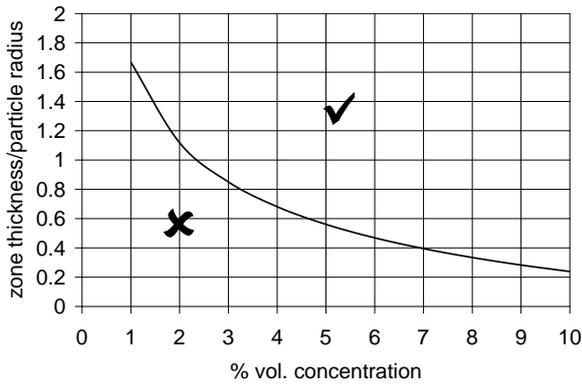
Figure 9: Percolation occurs on the "✓" side of the line

For complete percolation through interaction zones, the volumetric concentration of (zone+spherical particle) must exceed 19%. Figure 9 shows the required ratio of zone thickness to particle radius as a function of % volumetric concentration for such percolation to occur. So for example, a 5% volume concentration of 50 nm particles would require a 28 nm interaction zone thickness for full percolation. Clearly these calculations should be treated with some caution: the particles are not likely to be spherical, the nature of the interaction zone will change through its thickness, local morphology will influence interactions, the particle dispersion may not be different to the assumption here, etc.

If the particles are charged or have dangling bonds on their surface, then a layer of counter-charge will form around the surface. Depending on how tightly bound this is, this layer could be reasonably conductive at low

frequencies. The "order" resulting from such charge – i.e. in the form of a net local electric field - may hinder polarisation of dipoles surrounding the Stern layer in the Gouy-Chapman layer. Tanaka has considered these ideas further in a "multi-core" model [78]. For quasi-DC conduction or low frequencies dispersion to occur there must be some overlap between interaction zones – although it could well occur at a sub-percolation level. Such effects were found for 10% w/w (approx 5% vol.) TiO_2 particles in epoxy resin [79]. Figure 10 shows dielectric results for the micro-composite whilst Figure 11 shows similar results for the nano-composite. At low frequencies the micro-composites exhibit Maxwell-Wagner dispersion (as one might expect) whereas the nano-composites exhibit parallel C' and C'' slopes characteristic of LFD with percolative pathways. If higher frequencies are considered (e.g. 1 kHz – i.e. well above this LFD), the addition of micro-particles increases the permittivity from 9.99 to 13.8 in approximate agreement to the Lichtenecker-Rother law whereas the nano-particles, despite their high permittivity ($\varepsilon \approx 99$), actually cause the permittivity to decrease slightly to 8.49 [79] presumably due to the restriction motions of dipoles in the interaction zone.
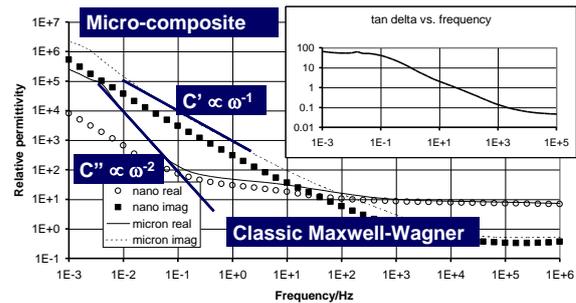
Figure 10: Dielectric spectrum: epoxy – TiO_2 MICRO-composite [39]
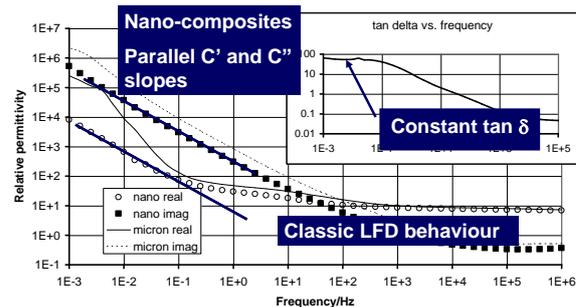
Figure 11: Dielectric spectrum: epoxy – TiO_2 NANO-composite [39]

Following the publication of these results in 2002, a workshop on nanodielectrics was organised at the 2003 CEIDP and a special issue of the IEEE DEI Trans on nanotechnology was produced in October 2004. An analysis of the manufacturing technologies, characteristics and possible future applications of polymer nanodielectrics is included in this issue [80]. More recent work [81] gives further support to Fréchette's

remarks in which it is reported that the incorporation of silica nanoparticles into polyethylene increased the breakdown strength and voltage endurance significantly compared to the incorporation of micron scale fillers. Like the epoxy composites, dielectric spectroscopy showed a decrease in dielectric permittivity for the nanocomposite over the base polymer. In this work, because the interaction zone is likely to be pivotal in controlling properties, the bonding between the silica and polyethylene was characterized and controlled using particle surface functionalisation techniques to good effect.

It is well-known that epoxy resins absorb water, typically up to several % depending on the temperature. It is also known that the interface between epoxy and silica is weakened by humidity as it is thermodynamically more favourable for water to be bonded to the silica than epoxy. On the surface of silica there are many dangling bonds which tend to attract the H^+ ions in the water. These concepts have led to new ideas for ageing in silica-epoxy nano-composite materials which are being presented at this conference by Zou *et al* [82].

It would be impossible to try to give a comprehensive review of nanodielectrics here both because of lack of space but also because the subject is changing so fast. I look forward to seeing many other papers on this subject at this conference.

CONCLUSIONS AND THE 10 THINGS WE DON'T KNOW

So what would I choose as 10 things we don't know about dielectrics – and should strive to find out? Some important questions based on the above seem to include:

1. The effects of ageing do seem to be felt but what direct evidence is there for thermo-electric ageing? The changes in nano-void number and sizes cited here was the result of difficult experimental work but was still not very conclusive, particularly as the specimens were thermally aged as well as electrically aged.

2. There may be different mechanisms of ageing, just as there are different mechanisms of degradation and breakdown. Is there a critical field or voltage for ageing to occur in these mechanisms?

3. If such a critical field exists, then is this the same as the threshold field (measured fairly easily) at which the space charge starts to increase non-linearly?

4. What would be appropriate techniques for checking the state of ageing of systems *in service*? (Space charge, EL, dielectric spectroscopy?)

5. To explain observed space charge behaviour and (even better) to predict it for a new system should be a goal. But is this possible given the number of variables? We haven't been able to do this for conduction in polymeric insulation despite efforts over the last century.

6. If this is not possible, what techniques could we use to control it? "Techniques" here include the manufacturing, maintenance *and operation* of the insulating system.

7. What is the dielectric nature of the interaction zone around nano-particles – accepting this may be material dependent?

8. What is the thickness of the interaction zones and the layers that they comprise?

9. Are charge packets just an academic curiosity?

10. Why do the mechanical properties of polymers seem to be better understood that the electrical properties?

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