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Dielectric Properties of Epoxy Nanocomposites containing TiO_2, Al_2O_3 and ZnO fillers

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Abstract: The paper presents results of dielectric spectroscopy and space charge (PEA) measurements on epoxy resin filled with 10% w/w micro- and nano- sized particles of TiO_2, Al_3O_2 and ZnO. The results appear to show that the material from which the nano-particle is made is not highly significant in influencing these results. The results support the proposition that the dielectric properties of such nano-filled composites are controlled by Stern-Gouy-Chapman layers ("interaction zones") around the particles.

Introduction

In an earlier paper [1], we reported on studies aimed at providing an understanding of the charge storage and transport of an epoxy resin containing TiO_2 nanoparticles. It was shown that nanometric fillers mitigate the interfacial polarization characteristic of conventional materials with a reduction in the internal field accumulations. In a more recent paper [2] we have shown that this has beneficial effects both for the dielectric withstand and voltage endurance.

In this paper, we present further, similar results for two other types of nanocomposites; these are based on the same base resin containing nano-particulates of alumina (Al_2O_3), and zinc oxide (ZnO), chosen to provide a range of permittivities and linearities. These results are compared with the earlier results obtained for TiO_2.

Specimen Preparation

The material used in this investigation was a Bisphenol-A epoxy (Vantico CY1300 + HY956) containing particles of TiO_2 (average diameter 23 nm and 1.5 μm), Al_2O_3 (17 nm and 1.5 μm), or ZnO (24 nm and 0.3 μm) to form nano- and micro-composite materials respectively. The resin was selected because it was benign (i.e. without other fillers or dilutents), had a low initial viscosity, and a glass transition below 100 ºC.

The formulation and processing of the planar specimens (having thicknesses between 500 and 750 μm) have been described previously [1]. These are cast under carefully controlled conditions to ensure good mixing, dispersion and the minimization of voids. Large shear forces were needed in the mixing process to obviate unwanted clustering of the particles. For some of the measurements, 100 nm aluminium electrodes were evaporated onto the cast films. In all cases, careful optical microscopic examination of the specimens was undertaken to reject those with agglomerations, cavities, and other defects.

Dielectric Spectroscopy

Insight into the way that the incorporation of materials of nanometric dimensions affected the dielectric properties was obtained by examining the variation of the real and imaginary components of relative permittivity as a function of temperature and frequency.

Figure 1: Real relative permittivity 10% TiO_2 nano-filled epoxy

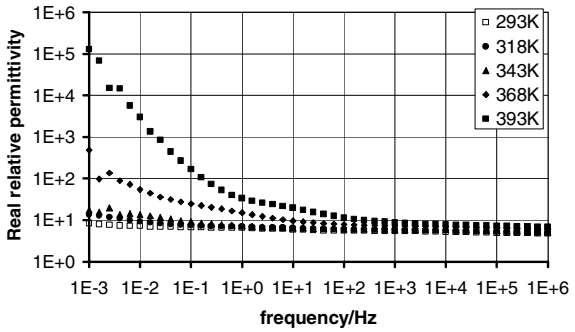
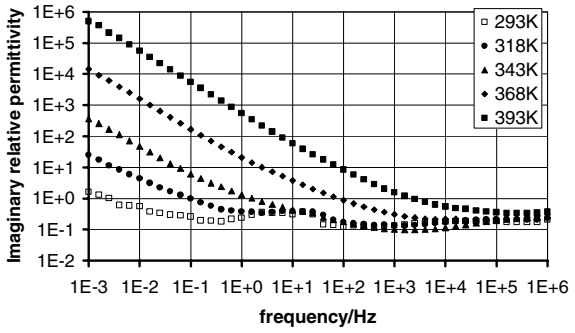


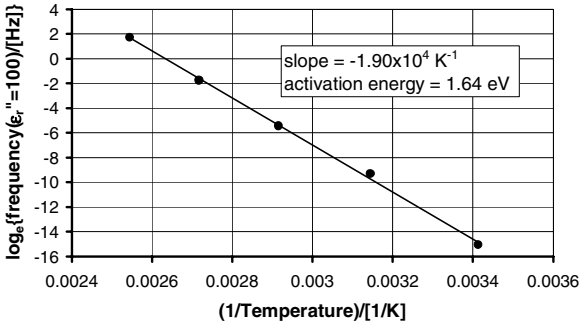
Figure 2: Imaginary relative permittivity 10% TiO_2 nano-filled epoxy



A Solartron H.F. frequency response analyser (type 1255) in combination with a Solatron Dielectric Interface, Type 1296 was used for this purpose with typically five temperatures spanning 100 K and a frequency range

of 10^{-3}-10^{6} Hz. An example of the relative permittivity Bode plots for the material filled with 10% w/w TiO_2 nano-particles is shown in Figure 1 and Figure 2. An Arrhenius plot, Figure 3, shows that the low frequency processes (judged by the frequency at which $\varepsilon_r"$=100) are temperature activated with an activation energy of 1.64 eV.

Figure 3: Arrhenius plot representing low frequency processes presented in Figure 1 and Figure 2



Dielectric spectroscopy measurements were also made on the base resin (i.e. without any filler) and with 10% w/w filled epoxy containing micro-particles of TiO_2 and Al_2O_3 and 10% nano-particles TiO_2 and ZnO. Representative results from measurements at 393 K are shown here in Figure 4 and Figure 5.

Figure 4: Real relative permittivity of unfilled and 10% micro- and nano- filled materials at 393 K

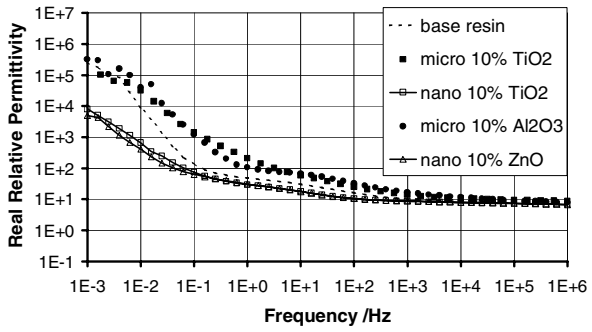


Figure 5: Imaginary relative permittivity of unfilled and 10% micro- and nano- filled materials at 393 K

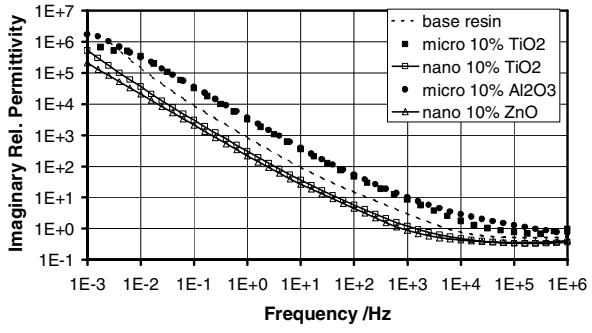
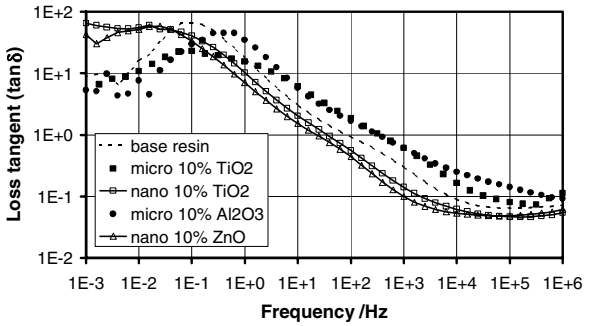


Figure 6 shows the loss tangent ($\varepsilon"/\varepsilon'$) calculated from this data. It can be seen that the dielectric properties of the systems are similar, irrespective of the chemical nature of the filler that was used.

Figure 6: Loss tangent of unfilled and 10% micro- and nano- filled materials at 393 K



At higher frequencies, the micron-filled material has a higher real relative permittivity due to the high relative permittivity of the filler, e.g. $\varepsilon_r(TiO_2)\approx 99$. Simple calculations show that the increase of permittivity from the base resin value of 9.99 to 13.8 when micro-filled is reasonable using the Lichtenecker-Rother logarithmic law of mixing [2]. However, the nanocomposite, under the same conditions, exhibits a measured value of 8.49, which is significantly **less** than that of the base resin matrix. This is true at all the temperatures measured. This surprising result, which has been confirmed using an independent second test utilizing a different spectrometer, appears to indicate that the interaction zone surrounding the nanoparticles has a profound effect on the dielectric behaviour of the nanocomposite; a conclusion that is consistent with the space-charge measurements described below.

The mid-range frequency behaviour has been discussed in detail elsewhere (e.g. [1,2]), where it is concluded that nanoparticles restrict chain movement.

The base resin exhibits classic Maxwell-Wagner interfacial polarisation below a frequency of 0.1 Hz with slopes of –2 and –1 on the real and imaginary permittivity Bode plots [3] and a peak in the loss tangent at 0.1 Hz (Figure 6). The micro-filled epoxies also display this peak in loss tangent, which is therefore also attributed to interfacial polarisation at the electrodes. At very low frequencies, the dielectric behaviour of the base resin and microcomposite become very similar as electrode effects dominate. The thickness of the samples (~750 μm) was approximately 500 times the inter-microparticle distance. It is interesting that the deviation between real permittivities of the microcomposite and the base-resin starts to occur at approximately 500 times the frequency of 0.1 Hz, giving some support for the theory that the microcomposite was

exhibiting Maxwell-Wagner polarisation due to the microparticle interfaces.

The nano-composites both show quite different behaviours from the base resin and micro-composites below 0.1 Hz. Instead of the real part of the relative permittivity having a slope of –2, it is parallel to the imaginary part with a slope of –1. This, together with the flattening out of the tan-δ response at lower frequencies (Figure 6), is indicative of "low-frequency dispersion (LFD)" [3] or "quasi-DC" (QDC) behaviour [4]. We consider that this is due to partially overlapping charge layers (Stern and Gouy-Chapman layers [5]), along the lines that Lewis has considered (e.g. [6, 7]), which form fractal-like quasi-conducting paths. This would allow a distribution of path lengths over which charges could move with greater or lesser ease of movement. This has been considered more quantitatively in [2] and is also discussed in [8].

Reduction of the particulate loading from 10% to 1% (by weight) did not have any very obvious fundamental changes, but the nano-filled material then does start to exhibit a low frequency response more typical of the base resin and micro-filled material, suggesting that loadings greater than a few percent are required to ensure sufficient overlap of the interaction zones.

Space Charge Measurement

Space charge measurements were made using a pulsed electro-acoustic (PEA) system. A voltage of 3 kV was applied to disks approximately 0.75 mm thick (i.e. an average field of 4 kV.mm^{-1}) for 10,800 s (3 hours) at room temperature (293±3 K). The sample was then short-circuited for at least 3600 s (1 hour). The space charge was measured periodically during the charging and discharging periods. We report selected representative results here for 10% w/w filled samples showing the charge accumulation at 3 hours and the subsequent decay. As the charge accumulates, the electric field is distorted and so we also report the observed electrical field after the 3-hour charging period. In each graph, the vertical dotted lines indicate the cathode (left) and anode (right), the grey line indicates the charge distribution at the end of the charging period (i.e. before short circuiting) and arrows show the charge decay with time.

Figure 7 and Figure 8 recap the comparison made in [1] between the epoxy composites micro- and nano- filled with TiO_2. In the nano-filled material, there is homo-charge near the electrodes whereas in the micro-filled there is hetero-charge. Since hetero-charge gives rise to increased, and homo-charge to decreased, electric fields at the electrodes, where breakdown is most likely to initiate, homo-charge is generally felt to be preferable to hetero-charge under DC conditions. The nano-filled material is therefore behaving preferentially under these conditions.

Figure 7: 10% TiO_2 micro-filled charge decay. Measurements made at 0 (volts on – grey curve), 30, 600, 1800, 3600, 7200 and 10,800 s.

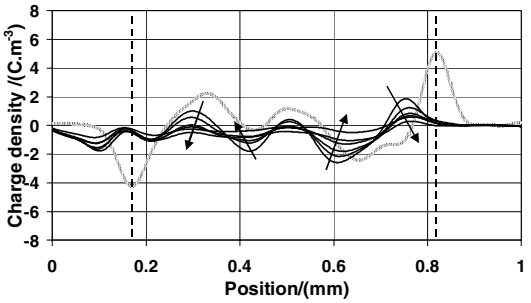


Figure 8: 10% TiO_2 nano-filled charge decay. Measurements made at 0 (volts on – grey curve), 10,30,60,120,300,600,900 and 1800 s.

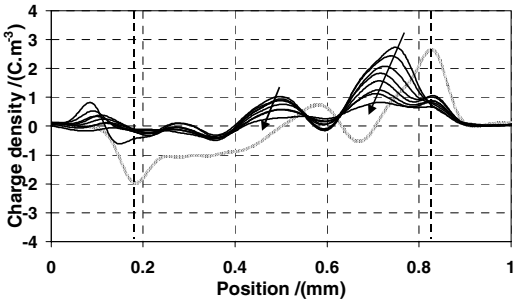


Figure 9: The maximum field intensity with the micro- and nano-filled TiO_2 systems as a function of time

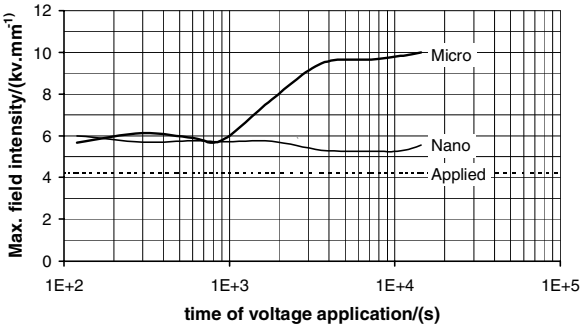


Figure 9 shows how the space charge distorts the field in the two systems and it is clear that the maximum field in the micro-filled system builds up to over twice the average ("applied") field whereas the nano-filled system stabilises at approximately 5.5 kV.mm^{-1}.

Similar results, shown in Figure 10 and Figure 11 are obtained for the ZnO micro- and nano- filled systems. Here the micro-filled system does show homo-charge accumulation but also a large change from positive to negative charge accumulation in the central part.

The nano-filled material shows a small negative charge in the centre after poling for three hours, but relatively little charge elsewhere.

Figure 10: 10% ZnO micro-filled charge decay. Measurements made at 0 (volts on – grey curve), 10, 30, 60, 300, 600, 900, and 1800 s.

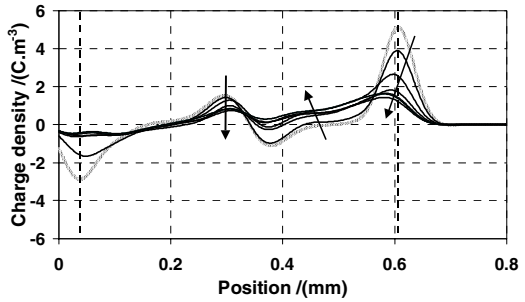
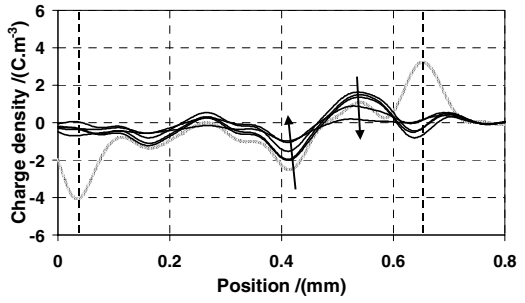


Figure 11: 10% ZnO nano-filled charge decay. Measurements made at 0 (volts on – grey curve), 30, 60, 300, 3600, and 7200 s.



The results on the Al_2O_3 nano-filled samples appear to show a large heterocharge accumulation near the anode, but we would like to repeat these results before we have sufficient confidence in them to present here.

A summary of the results after poling for three hours is shown in Figure 12 and a summary presented in Table 1.

Figure 12: Electric field throughout all samples. The very thick line is the base resin (unfilled). The grey lines are the micro-filled and the black lines are the nano-filled samples.

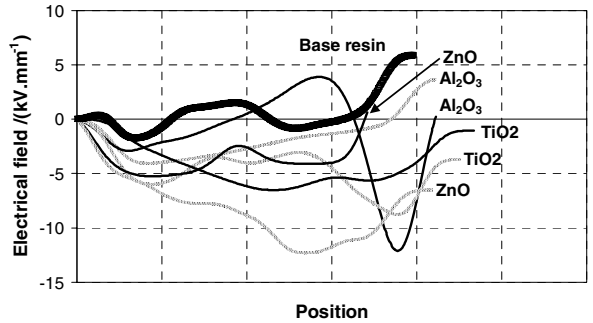


Table 1: Comparison of systems

Filler	Anode	Cathode	Central	Max Field (kV/mm)
None		Hetero	Negative	6, cathode
Al_2O_3 micro	Homo (small)			>4, cathode
Al_2O_3 nano	Hetero (big)	Hetero (small)		12, anode
ZnO micro	Homo	Homo	pos/neg	13, centre
ZnO nano			Small neg	5, cathode
TiO_2 micro	Hetero	Hetero		8, anode
TiO_2 nano	Homo	Homo	Positive	6, centre

Conclusions

The dielectric spectroscopy results show very little dependence upon the particle material; only the size appears to be important. The effect of space charge build up on the internal electric fields is similar for the TiO_2 and ZnO particles but there are some anomalies that require further work for the Al_3O_2 particles. The results appear to support our earlier conclusions regarding the formation of quasi-conductive regions around the particles that partially overlap in the case of the nano-particles. These allow charge dissipation and have been shown to greatly improve the dielectric withstand and voltage endurance characteristics (e.g. [2]).

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References

1 J.K. Nelson, J.C. Fothergill, L.A. Dissado and W. Peasgood, "Towards an understanding of nanometric dielectrics", IEEE Conf. Elec. Insulation & Dielectric Phenomena, Mexico, Oct. 2002, pp 295-298

2 Nelson, J.K. Fothergill, J.C.; "Internal charge behaviour of nanocomposites" Nanotechnology, volume 15, issue 5, (2004) p 586 – 595

3 Jonscher A.K, "Dielectric relaxation in solids", Chelsea Dielectric Press 1983, ISBN:0950871109

4 Dissado L.A. and R.M., "Anomalous low frequency dispersion. A near DC conductivity in disordered low dimensional materials", J. Chem. Soc. Faraday Trans. 2, 80, pp 291-319, 1984

5 Chapman D.L., "A contribution to the theory of electrocapillarity", Phil. Mag., Vol 25, 1913, pp 475-481

6 Lewis T.J., "Nanometric Dielectrics", IEEE Trans on Diel. And Elect. Ins., Vol.1, pp 812-25, 1994

7 Lewis T.J., "Interfaces and Nanodielectrics are Synonymous, Proc. IEEE 2004 International Conference on Solid Dielectrics, Toulouse, France, July 5-9, 2004, IEEE Pub. 04CH37539, Vol. 2, pp792-795

8 J. K. Nelson, L. A. Utracki, R.K. MacCrone and C. W. Reed, "Role of the Interface in Determining the Dielectric Properties of Nanocomposites", this conference