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Towards an understanding of nanometric dielectrics

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Abstract: Dielectric studies are described aimed at providing an understanding of the charge storage and transport of an epoxy resin containing TiO₂ nanoparticles. Comparative results for conventionally filled composites are given, and the results discussed in terms of the underlying physics. It is shown that nanometric fillers mitigate the interfacial polarization characteristic of conventional materials with a reduction in the internal field accumulations.

Background and Vision

Nanoparticles are the fundamental building blocks in the design and creation of assembled nano-grained larger scale structures with excellent compositional and interfacial flexibility. However, rather surprisingly, the current push to develop nanomaterials based on nanotechnology has not focused much on the opportunities for dielectric materials, but rather centred on optical and mechanical applications. Nonetheless, the few examples in the literature provide encouragement that this is likely to be fertile ground. Furthermore there are good theoretical reasons why the pursuit of nanomaterials for dielectric applications may have particular promise. Some of these have been reviewed by Lewis[1] and by Frechette[2]. While the technology is in its infancy, one may speculate that it may be possible to self-assemble nanodielectrics by providing chemical structures with “hooks” which provide preferential attachment points for the nanostructured materials allowing automatic and predictable self assembly.

Fundamental Issues and Rationale

The use of conventional fillers for polymer materials is well known and is usually employed to reduce the cost of a material or to modify one of the material properties for a particular application. Examples of that would be discharge resistance, thermal expansion, etc. Often the use of such fillers will affect dielectric strength and loss in a negative way. In this context, it is thought that fundamental to controlling the dielectric strength of insulating polymers is the cohesive energy[3] density and the associated free volume[4] of a polymer structure. This may be gauged by examining the

changes in electric strength (up to a factor of 10) exhibited by most polymers as they are taken through their glass transition temperature[5]. In the simplest situation, the bonding of a polymer to a filler can be expected to give a layer of “immobilized” polymer. The size of this layer is critical to the global properties (electrical, mechanical and thermal) of the composite.

Such a picture is not, however, complete since the in-filled material will give rise to space-charge accumulation and the associated Maxwell-Wagner polarization due to the implanted interfaces. Furthermore, the macroscopic theories of interfacial polarization do not incorporate a molecular approach since the response is given by relaxation equations if the wavelength is large in comparison with molecular dimensions. In considering pre-breakdown high-field conduction in pure materials, the existence of localized states within the energy band gap (close to the conduction or valence bands) is usually invoked, so giving rise to a mobility edge for electron (or hole) transport[6]. These states are essentially localized on individual molecules. This is because, unlike the strong covalent bonds of elemental crystalline solids, the intermolecular binding arises from weak van der Waals’ forces that do not allow inter-molecular electronic exchange

System Characterization

In order to provide the basis for engineering nanodielectrics, this study has provided a characterization of micro- and nano-particulates of Titanium Dioxide (TiO₂) when embedded in a resin matrix. A Bisphenol-A epoxy (Vantico CY1300 + HY956) was chosen because it was benign (i.e. without other fillers or dilutents), with a low initial viscosity,

Material + Filler	Size (nm)	Loading (%)	T_g (°C)
CY1300 Resin	N/A	N/A	63.8
CY1300 + TiO ₂	Micro (1500)	1	76.1
CY1300 + TiO ₂	Micro (1500)	10	73.9
CY1300 + TiO ₂	Micro (1500)	50	79.9
CY1300 + TiO ₂	Nano (38)	1	62.9
CY1300 + TiO ₂	Nano (38)	10	52.4
CY1300 + TiO ₂	Nano (38)	50	62.1

Table 1 Glass transition of nano- and micro-filled TiO₂

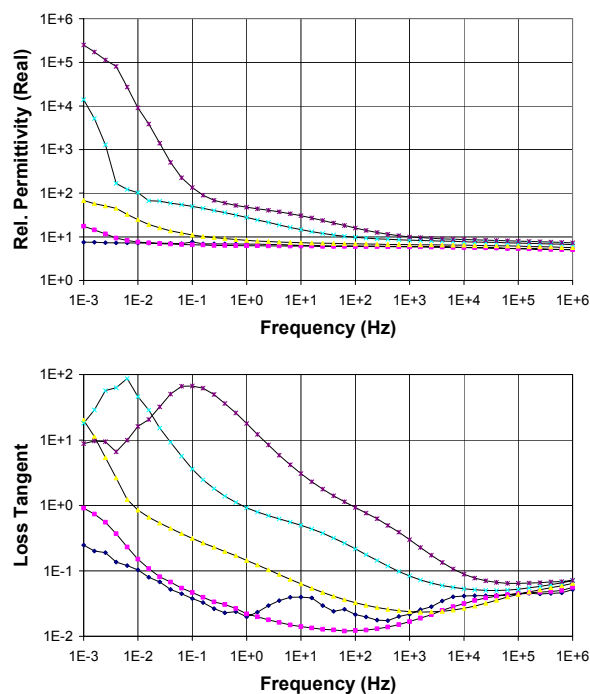


Figure 1. Permittivity and loss tangent for micro-filled epoxy. Temp: (bottom to top) 293, 318, 343, 368, 393 K

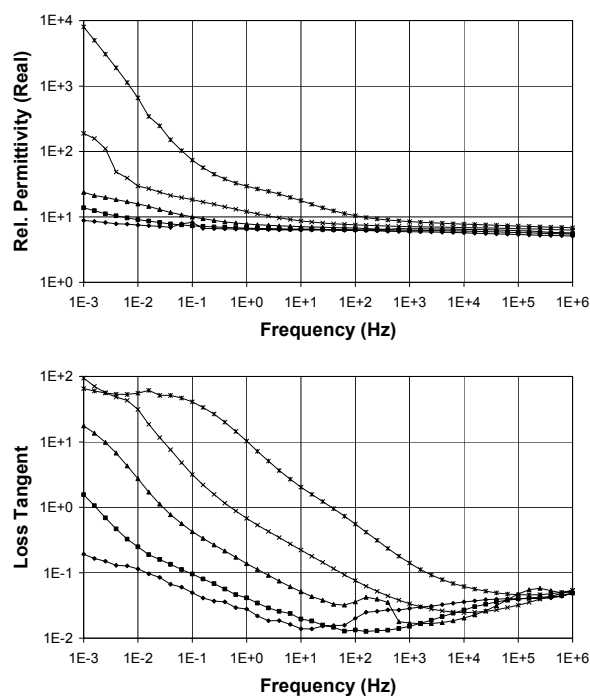


Figure 2. As Figure 1, but for nano-filled material

and with a glass transition below 100 °C. Test samples were formed by molding between polished surfaces held apart by spacers in the manner previously described[7]. The molded films ranged in thickness between 500 and

750 μm . The weighed resin and hardener were degassed at 35 °C and the relevant dried particulate fill was incorporated into the resin by mechanical stirring. Due to their small size, surface interactions for nanoparticles, such as hydrogen bonding, become magnified. This means that the particles tend to agglomerate and dispersion in resins is quite difficult, even in polymers that should be relatively compatible. Hence, in the case of nano-particles, large shear forces are needed in the mixing process to obviate unwanted clustering of the particles. For most electrical characterization, the cast film was provided with evaporated 100 nm aluminium electrodes.

Differential Scanning Calorimetry (DSC)

A Stanton Redcroft DSC 1500 calorimeter was used to thermally characterize the materials. Results on the determination of glass transition temperatures are provided in Table 1 for post-cured samples from which it is evident that the nano-material reduces T_g in contrast to the larger size particles that have the opposite effect. This suggests that particles of nanometric dimensions behave in a similar way to infiltrated plasticizers[8], rather than as “foreign” materials creating a macroscopic interface.

Dielectric Spectroscopy

Some insight into the way that the incorporation of materials on nanometric dimensions affect the dielectric properties may be obtained by examining the variation of the real and imaginary components of relative permittivity as a function of temperature and frequency. This has been done for the TiO_2 material using a Solartron H.F. frequency response analyzer (Type 1255) in combination with a Solartron Dielectric Interface, Type 1296. Examples for the micro- and nano-filled materials are shown in Figs. 1 and 2 respectively. At a nominal 10% (weight percent) particulate loading, the spectra of the resin when filled with particles of micron size (1.5 μm) are virtually indistinguishable from the base resin. This suggests that the low frequency process is probably associated with charges at the electrodes and not due to particulates in the bulk. With the filler replaced with 10% of nanometric size TiO_2 (38 nm average diameter measured by TEM), the main differences seen relate to a marked modification of the process seen in the base resin at low frequencies and high temperatures. For the nanometric material the process exhibits a flat $\tan \delta$ response at low frequencies in marked contrast to the micron-sized filler. This suggests that a percolation conduction process is operative. In the presence of the nano-filler, the mid frequency dispersion is noticeably reduced. The nano

materials are clearly inhibiting motion (see PEA results below). The mid-frequency process shows a small change in estimated activation energy from 1.7 eV to 1.4 eV. The magnitude of this process is reduced in the case of nanoparticles since the side chains responsible for the mid-frequency dispersion bind to the particle surface.

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 changes engineered by the nanomaterials do require loadings greater than a few percent.

Space charge assessment

In order to determine whether nanomaterials function cooperatively as opposed to providing sites for interfacial polarization, a Pulse ElectroAcoustic (PEA) study has also been conducted to assess the field distortions in the bulk. The method has been described elsewhere[9]. The initial distribution of stress shows

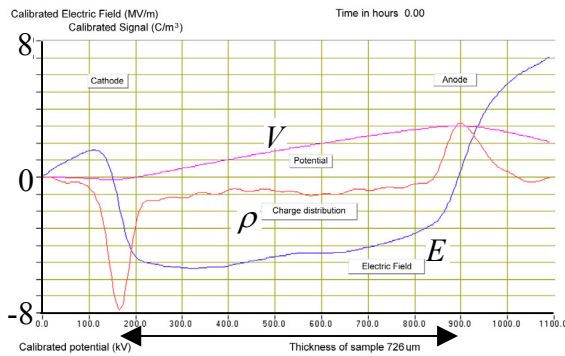


Figure 3 Initial distribution of electric field . Electroacoustic study of nano-filled material. Voltage, V (kV); charge, ρ (C.m⁻³), and electric field, E (kV.mm⁻¹). The double headed arrow indicates the 726 μm thickness of the sample (cathode on left).

little deviation from the nominal 4.3 kVmm⁻¹ uniform level across the bulk (see Figure 3). However, characteristic results are shown in Figs. 4 and 5 for the micro- and nano-materials (10% loading) respectively after several hours of stressing. These plots show the charge, potential and field distributions, for a 3 kV steady DC field applied. The 1.5μm filler generates substantial internal charge, in marked contrast to the nano-material which behaves in a similar way to the base resin. Fig 4 shows several distinctive features:

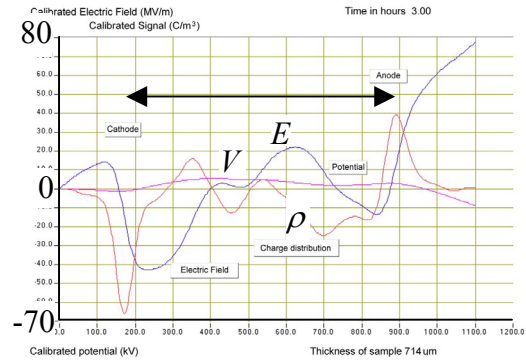


Figure 4. Pulsed electroacoustic study of micron-sized filler.

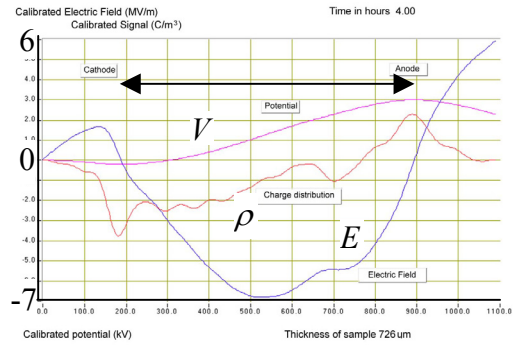


Figure 5. Pulsed electroacoustic study of nano-sized filler

- heterocharge accumulation of both signs leading to steep internal charge gradients
- a cathode field augmented to over 40 kVmm⁻¹ (10x the nominal value)
- field reversal yielding a point of zero stress which will greatly complicate charge transport.

Transient studies (*not shown here*) indicate that subsequent increase of applied voltage increases the size of the charge peaks with little change to the complex internal distribution. The stable stationary positioning of these peaks may be due the interaction of space charge with local polarization to create a self-compensating situation.

Appraisal

Very marked differences in charge accumulation are seen in filled materials depending on whether the filler has micron or nanometric dimensions. Furthermore, the characteristics suggest that, for the micron-sized filler, carriers are blocked at the anode yielding a heterocharge

situation, and giving rise to the large anomalous field distortions seen in Figure 4. This behavior clearly has substantial implications for the subsequent migration of charges and probably accounts for the fact that temporal studies (not given here) show that the image charge in the cathode at first decreases and then recovers. Again in contrast to the micro-filled material, the decay of charge in the nano-filled TiO_2 is very rapid; with insignificant homocharge remaining after just 2 minutes. Although there is some injection of negative charge at the cathode, the nano-filled material is characterized by much less transport perhaps brought about by the larger density of shallower traps.

The PEA results taken in conjunction with the Dielectric Spectroscopy and DSC studies suggest that significant interfacial polarization is implied for conventional fillers which is mitigated in the case of particulates of nanometric size, where a short-range highly immobilized layer develops near the surface of the nanofiller (1-2 nm). This bound layer, however, influences a much larger region surrounding the particle in which conformational behavior and chain kinetics are significantly altered. This *interaction zone* is responsible for the material property modifications especially as the curvature of the particles approaches the chain conformation length of the polymer. Evidence suggests that the local chain conformation and configuration play major roles in determining the interactions of a polymer with nanofillers[10], as is evidenced here by the DSC results of Table 1. The polymer binding to the nanoparticles replaces some of the cross-linking and thus loosens the structure. In contrast, the micron scale case produces significant Maxwell-Wagner polarization giving rise to the characteristics of Fig.4.

In the case of nanofillers, there is evidence that a grafted layer is formed by the absorption of end-functionalised polymers onto the surface especially when the functional groups are distributed uniformly along the polymer backbone. Hence the local chain conformation is critical to determining the way in which bonding takes place (and thus the cohesive energy density). The defective nature of nanoscale particles can be expected to enhance the bonding if chemical coupling agents (CVD coatings on nanoparticles or triblock copolymers) are employed.

The large interaction zone in nanofilled polymers with reduced mobility (free volume) should be accompanied by a significant change in electrical properties. Studies of electrical behavior thus provide an opportunity both for a fundamental study of this interaction zone, and also an opportunity for optimizing performance for specific and critical applications.

The finding that conventional fillers are accompanied by substantial bulk charge accumulation is clearly a factor in the common experience of the lower electric strengths exhibited for filled materials. The mitigating effects of nanoparticles provides encouragement that nanocomposites can be engineered with strengths that are commensurate with the base polymer. Such studies are ongoing.

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