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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1109/CEIDP.2004.1364251>

*Conference on Electrical Insulation and Dielectric Phenomena 2004 (CEIDP 04)
Annual Report, pp. 314-317, 2004-12-01*

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Role of the Interface in Determining the Dielectric Properties of Nanocomposites

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2004 IEEE Conference on Electrical Insulation and Dielectric Phenomena, Boulder, Colorado, USA,
October 17–20; 314 – 317 (2004).

Abstract: It has been demonstrated that the electrical breakdown properties of polymer composites can be substantially enhanced when the filler particles are of nanometric dimensions. These benefits are likely related to the mitigation and redistribution of internal charge. Using the example of an epoxy-TiO₂ nanodielectric (and a comparable conventional composite), this contribution seeks to examine this issue from the physical and chemical viewpoint. It is shown that a reduction in free volume cannot be used to explain the dielectric enhancements. The free volume of nanomaterials is actually higher than that of conventional samples. This conclusion is consistent with recent application of electron paramagnetic resonance methods, which have confirmed earlier speculation that the environment associated with the interface is radically changed when the in-filled particulates are reduced to nanometric dimensions and the associated interfacial area is greatly increased. Through examinations of infrared absorption & EPR, the paper provides some speculation on the part played by an interaction zone surrounding the particulate inclusions. The presence of a highly mobile interlayer is thought to be the key to the electrical property changes seen.

Introduction and Background

The incorporation of nanoparticles into a polymer matrix has been shown to permit improvements in both mechanical [1] and electrical [2] properties and, more recently, very significant enhancements in voltage endurance have been documented [3, 4] in comparison with conventional (microparticle) composites. The use of the pulsed electroacoustic method to examine the internal space charge in combination with dielectric spectroscopy would suggest that internal space charges present in the case of microcomposites are substantially mitigated in the case of nanomaterials. It would appear that the Maxwell-Wagner polarization, well known to be associated with composites, is diminished in the case of the nanocomposites despite the substantial increase in the interfacial areas involved with the finely divided particulates. Such behavior has also been confirmed by static and dynamic electroluminescence studies [5] that

support the view that the magnitude and distribution of the internal space charge is dramatically different in the two cases. The interpretation is clearly a major key to the engineering of useful nanodielectrics.

It has been postulated that fundamental to controlling the dielectric strength of insulating polymers is the cohesive energy density and the associated free volume [6] 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. In the simplest situation, the bonding of a polymer to filler may be expected to give a layer of “immobilized” polymer, and it has often been suggested [7] that the tethered entanglement associated with nanocomposites will result in a reduction in free volume and thus a concomitant improvement in electrical properties. However, there are other experimental observations that also have to be reconciled. A key feature can be extracted from dielectric spectroscopy and is encapsulated in Table 1 for a TiO₂ system with nano (23 nm) and micro (1.5 μ m) dispersed particles.

[23°C 1 kHz]	Rel. Perm. (ϵ_r)
Base Resin (measured)	5.68
10% micro-composite (measured)	6.01
10% micro-composite (calculated)	6.19
10% nano-composite (measured)	4.5

Table 1. Relative permittivity of TiO₂ composites at 1 kHz, and 23 °C

The permittivities in Table 1 were measured at 1 kHz, which is a high enough frequency that the results are uncomplicated by conduction and interfacial polarization effects. However, it is clear that although the permittivity of the base resin has been increased by the incorporation of the TiO₂ microparticles ($\epsilon_r \approx 100$), a reduction is indicated in the case of the nano-composite. The calculated value is the result of the application of the Lichtenecker-Rother law for chaotic mixing. This striking result has been replicated in independent experiments.

The second piece of evidence that is pertinent here is shown in Table 2, which shows the time constants of the decay for light emission [5] and for internal charge relaxation in the same TiO₂ nanocomposites.

	1.5 μm TiO ₂	23 nm TiO ₂
Charge decay (s)	1800	22
Light decay (s)	1200	<60

Table 2. Comparison of charge and electroluminescence decay in TiO₂ composites

While comparisons in the Table in the vertical direction are not legitimate as the electric field divergency is different, the horizontal comparison for the same fields configuration is striking and is difficult to explain on the basis of free volume. An internal conduction process is (WHAT???)

Sample Formulation

The material used in this investigation was a Bisphenol-A epoxy (Vantico CY1300 + HY956) with 23 nm and 1.5 μm TiO₂ particles incorporated in the host matrix (to form nano- and micro-composite materials, respectively). The formulation and processing have been described previously [2], except that now ultrasonic probe methods are also being used to lessen the agglomeration, which is prevalent when preparing nano-composites due to the inherent high surface energies involved. Particle size distribution for the nanomaterials have been derived by transmission electron microscopy and dispersion also checked microscopically. The mean particle diameter is 23 nm.

Free Volume Determinations

Careful measurements of free volume have been made by the PVT (Pressure-Volume-Temperature) method [8] at $T \cong 300$ to 500°K and $P = 1$ to 1900 Bar after drying under vacuum at 45°C for 24 hrs. For the epoxy an excellent reproducibility was achieved and only two runs were needed. Three tests were carried out for the composite specimens and only the reproducible data were used for the computation of the free volume parameter, as well as the characteristic pressure, volume and temperature reduced parameters, h , P^* , V^* , and T^* , respectively. The experimental data were fitted to the Simha-Somcynsky equation of state [9]:

$$\tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + 2yQ^2(1.011Q^2 - 1.2045)/\tilde{T} \\ 3\{[\eta(1/3)/(1-\eta) - yQ^2(3.033Q^2 - 2.409)/6\tilde{T}] + (1-s) - s\ell n[(1-y)/y]\} = 0$$

Here tilde (\sim) indicates the reduced variables, $y = 1 - h$ is the occupied volume fraction, $3c$ is the external degrees of freedom, s is number of statistical segments and functionals: $Q = 1/(y\tilde{V})$, and $\eta = 2^{-1/6}yQ^{1/3}$.

The procedure used to extract the reducing parameters and h is well described [8]. Statistical goodness-of-fit tests indicate that the data is reliable.

The resulting free volume data is depicted in Figure 1

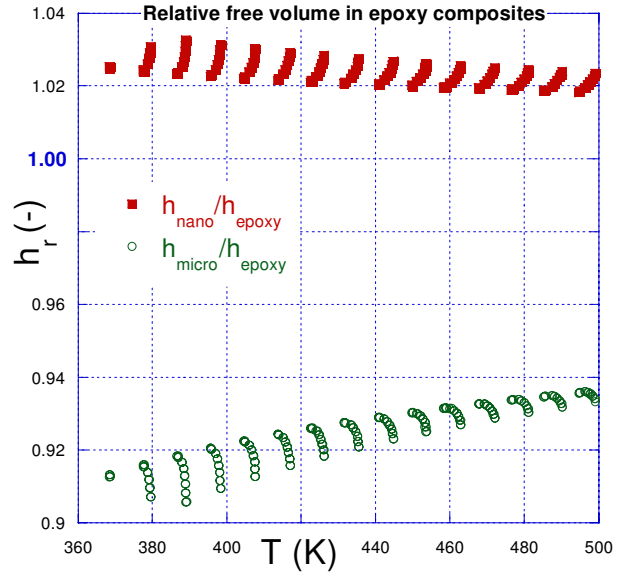


Figure 1. The relative free volume of micro- (bottom) and nano-composites (top) as a function of pressure and temperature.

as the ratio normalized to the free volume of the base resin. The relative magnitude of the free volume is decreased by the addition of micro-sized TiO₂, but increased by the incorporation of nano-sized TiO₂. The former effect is by -6 to -9%, whereas the latter by +2 to +3%. The relative free volume (originating exclusively in the polymeric matrix) must be equal to the relative specific volume, viz. $h_r \cong V_r$, but the calculations demonstrate that this is not the case. In micro-filled composite, the free volume is significantly more depressed than the volume exclusion by non-compressible solid would allow. This means that there is some adsorption of epoxy on the TiO₂ crystal, similar to that observed in organoclay filled polymers. Adsorption on high-energy solid surface must take place or the presence of other species that prevent contact between the solid and the matrix is indicated. This is precisely what is seen in the case of nano-TiO₂. Here the relative free volume, $h_r > 1$, which can only be explained by the presence of highly mobile interlayer

between the filler and the matrix. The PVT data show that there is no direct contact between the nano-TiO₂ particles and cured epoxy matrix and that the interphase has significantly higher molecular mobility than the epoxy. These contacts are present in micro-TiO₂ filled composites, where the expected reduction of free volume has indeed been observed.

Chemical Aspects

While many of the unique properties seen in TiO₂ nanocomposites have also been seen in other systems, the curing process used to crosslink the resin clearly has a role in establishing conditions at the interfaces. An extensive Fourier Transform Infra-Red (FTIR) study has been conducted in order to understand the surface bonding as it relates to the dielectric properties. Some of the results are shown in Figure 2, which depicts absorption spectra of both micro- and nano-composites. Normally, the epoxide group reacts with the amine group to generate a 3-D network with increased C-N bonding, identified by a peak at 1070 cm⁻¹ for the base

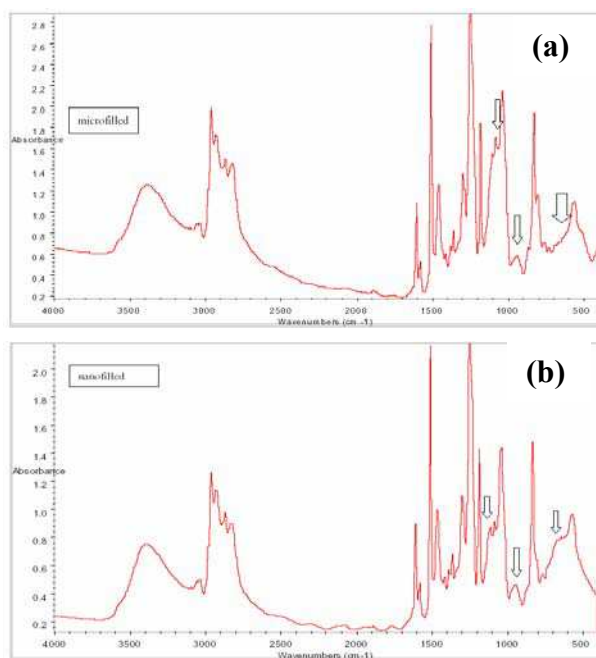


Figure 2. FTIR Absorption spectra for TiO₂ nanocomposites; (a) micro, (b) nano

resin. However, surface hydroxyl (-OH) groups on the TiO₂ particles will compete against such amine groups in reacting with the epoxide rings. As a result, ether groups are formed, as seen by changes in the C-N bands at 1070cm⁻¹. This process is much enhanced with

nanoparticles due to their large surface areas with significant coverage of -OH groups. The consumption of epoxide rings in this way will lower the crosslink density locally, forming a low density region at the interfaces. The shifts, or broadening of the peaks at 600-700 cm⁻¹ (in comparison with the base resin) are also attributable to the TiO₂ filler.

The EPR (electron paramagnetic resonance) spectra [10] of dried (at 400°C) nano-powder before, (a), and after, (b), incorporation into the epoxy composite are shown in Figure 3. These curves are the derivative microwave absorption at 9.77 GHz, plotted as a function of the applied magnetic field. EPR analysis is usually given in terms of g , defined by $g\beta H = h\nu$. For a free electron, the absorption is a maximum for $g = 2.0023$. The spectra (a) and (b) have been scaled such that the two features on the high field side of the large central peaks, at $g = 2.00$ are the same size and also displaced vertically for ease of comparison. It is well known that oxygen species (O₂⁻ say in a given environment) give rise to spectral features [11] on the low magnetic field side of $g = 2.00$ as well as a feature at $g \sim 2.0$. In contrast, Ti³⁺ species (Ti³⁺ ions say in a tetragonally distorted octahedron) are well known to give features on the high field side of $g = 2.00$, as well as features at $g \sim 2.00$. Qualitatively the spectrum (a) of the nano-powder indicates the presence of Ti³⁺ (described by the principle tensor components $g_1 = 1.925$, $g_2 = 1.995$ and $g_3 = 2.007$) as well as a comparable amount of oxygen radicals (described by the principle tensor components 2.2, 2.08, and 2.01, the first two being mean values of a wide distribution in principle values). After the nano-powder has been incorporated into the composite material, spectrum (b) indicates that the Ti³⁺ centers remain, that the oxygen radical species have decreased significantly (this assertion is based on there being less absorption from the previous wide line in (a), and, most significantly, shows the appearance of a new very large narrow line with g value of 2.007. This value of g is typical of an unpaired spin on an organic compound.

The as received micro-powder, as well as the resulting composite, show similar but much smaller spectra, about 1/200 the amplitude. Both particle sizes have a number of oxygen radical species, presumably on the surface, which react with appropriate components of the epoxy resin, and, in so doing, the oxygen radical spectrum is quenched. The Ti³⁺ species on the other hand are presumably internal to the particle, and being protected there, do not react with the resin components. The Electron Paramagnetic Resonance (EPR) spectra show evidence of alternative chemistry occurring at the particle interfaces when the composite is formed, related to oxygen free radicals present on the (dry)

micro- or nano-powder surfaces. The oxygen free radicals will also compete against amine groups in reacting with epoxide rings at the particle surface and it is expected that this reaction will be immediate and will take place freely, with minimum reaction energy involved, upon mixing and before curing of the epoxy takes place. As a consequence, when the composite is made, the EPR signal related to oxygen free radicals is significantly lowered and is replaced by a new, sharp signal, implying the unpaired spin of an organic group, feasibly that of the epoxide after reaction with the oxygen radical.

The Emerging Picture

It has become clear that the dielectric properties enjoyed by nanocomposites are intimately determined by the physics and chemistry of the individual internal interfaces and go beyond the interfacial polarization (Maxwell-Wagner effect) associated with such surfaces. Previous photoluminescence results in TiO_2 nanocomposites [5], have demonstrated that the local environment has been changed, which is here also

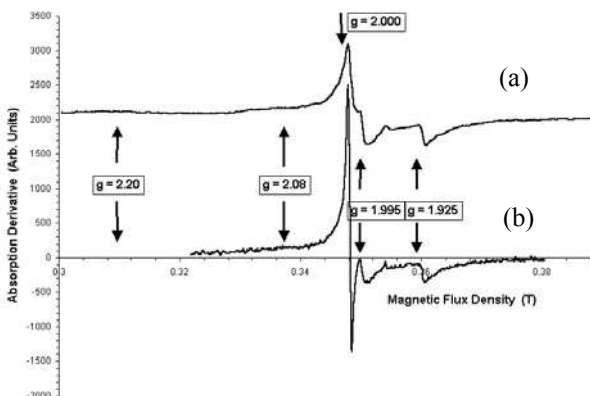


Figure 3. EPR Spectra of dried nanoparticles (a) and composite (b). [Traces vertically displaced for clarity]

indicated by the FTIR results. Furthermore, work carried out in functionalized SiO_2 nanocomposites [12] has indicated that, as the particle diameter increases, the proportion of hydrogen bonded groups at the interfaces increases. This is likely to promote O-H group polarization and might explain the results of Table 1. Furthermore, a surface layer of hydrogen-bonded molecular water on the particles causes an additional repulsive force which would explain the easier dispersion for the micromaterials. Such a picture is consistent with the concept of a Gouy-Chapman layer [13] at the surface which, in the case of nanocomposites, has a dominant effect because of the

very high surface areas involved. Since the surface functionality appears dominant in establishing the interface properties, EPR has proved a useful technique to detect the presence of radicals.

This concept has previously been advanced by Lewis [14], and a **local** conductivity is implied which would mitigate the charges residing at the interface without materially affecting the bulk conductivity, and would give rise to the dramatic time constant differences depicted in Table 2. Furthermore, such internal conductivity could be expected to reduce the substantial internal space charges which would lead to the demonstrated improvements in dielectric withstand and voltage endurance.

Acknowledgements

The authors are grateful to Ms. Yujie Hu who undertook some of the measurements reported.

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