Candidate Mechanisms Responsible for Property Changes in Dielectric Nanocomposites

J.K. Nelson* and Y. Hu
Department of Electrical, Computer & Systems Engineering
Rensselaer Polytechnic Institute, 110 8th Street,
Troy, NY 12180-3590, USA
* E-mail : k.nelson@ieee.org

Abstract: This contribution seeks to provide some insight for the documented changes in the electrical properties of filled polymers when the filler size is reduced to nanometric dimensions. After examining the possible underlying mechanisms, experiments are described in which composites based on a benign biphenol epoxy resin formulation are subjected to photo- and electro-luminescence studies in which the spectrum of the emitted light can be resolved as a function of formulation. It is shown that there is a red shift in the spectral peak at 600 nm as a result of the reduction of particulate size. The electroluminescence measurements are complemented by a detailed study of the internal space charge distribution in these materials, using the pulsed electroacoustic method. By examining both the internal charge distribution and dynamics, some linkage between the field-dependent electroluminescence and the changes of the internal charge in nanodielectrics can be established.

BACKGROUND

There has been a burgeoning interest in the last 5 years in dielectrics formed by the incorporation of nano-particulates into polymeric insulators. The resulting composites have been shown to have unique, properties which manifest themselves when the fillers have dimensions of the same order as the polymer chain lengths. In particular, the dielectric strength and the voltage endurance of these materials appear substantially enhanced when compared with conventional fillers at the same loading, and, sometimes, when compared with the base polymer [1]. Improvements in thermal and mechanical properties can also be demonstrated. It is now recognized that the underlying reason relates to the very large interface to volume ratio which is inherent in nanocomposites. Indeed, when the particle size is of the order of 15 nm, particle loading of just 10% implies that the internal interfaces represent about 50% of the bulk volume. As a result, the material properties become essentially controlled by the physics and chemistry of the internal interfaces.

For this reason, chemical or physical processes at the interface (brought about, for example, by functionalization) can be used both to offer some self-assembly of these materials as well as an opportunity to exercise some control over the properties. In order to facilitate this, a much better

understanding of the interface is needed. It is clear that the proliferation of internal surfaces may affect the dielectric properties through the generation of surface states and the provision of copious scattering sites. However, there is also some evidence that the interaction zones formed at the internal interfaces resemble the electrochemical double layer familiar in liquid/solid interfaces [2]. Such layers may be expected to modify the internal space charge behavior as has been documented previously in nanodielectrics [3]. This contribution seeks to combine the techniques of electroluminescence (EL) and pulsed electroacoustic analysis (PEA) to examine the relationship between charge carrier activity and the internal charge storage and dynamics in a nanocomposite thermoset.

FORMULATION

The fabrication of these TiO₂/epoxy composites has been described previously in detail [4]. In brief, the 23 nm diameter nanoparticles (or 1.5 μ m microparticles for comparison), were vacuum treated at 195°C for 12 hr, and compounded with the Diglycidyl Ether-Bisphenol A resin (Vantico CT1300) using a SpeedMixer™ from FlexTek Inc. utilizing a dual asymmetric centrifuge mixing method. Particles and base resin were mixed using a protocol involving a variety of speeds up to 3500 RPM to achieve even dispersion of particles. This non-invasive mixing method not only avoids the possibilities of contamination but also reduces air entrapment during the mixing process. After degassing, molding was conducted to form either divergent field (using electrolytically etched needles having a tip radius $\sim$ 5 μ m) or planar samples. A cross linking sequence using an amine-based agent (Vantico NY956EN) was undertaken at 25°C for 48 hours followed by 60°C for 3 hours. Cure was monitored by differential scanning calorimetry and dispersion checked by electron microscopy. Plane surfaces were metallized to form intimate electrodes.

EXPERIMENTAL RESULTS

Electroluminescence

EL measurements were conducted in a special cell coupled to an Oriel Model 77348 9-dynode gated photomultiplier tube (PMT) having a multi-alkali photocathode response which was approximately flat

between 400 – 700 nm. Scintillation counting mode was used over a period of 60 s using a Tracor Northern Model 710 analyzer. The collimated light transmission path included a section in which calibrated 50 nm bandwidth interference filters (Andover Corp.) could be inserted, so as to establish a piecemeal EL spectrum which was corrected for the quantum efficiency of the PMT at different wavelengths. Direct voltages, of either polarity, were applied to the point/plane specimens. Nominal negative tip fields for EL onset were:

Base resin: 203 kVmm⁻¹,
Microcomposite: 189 kVmm⁻¹, and
Nanocomposite: 378 kVmm⁻¹.

Figure 1. Frequency resolved electroluminescence spectra for 10 % TiO₂/epoxy composites [nano (a), and micro (b)] in comparison with the cured base resin (c).

Fig.1 shows comparative EL results for nano- and micro-composites with a 10% (by weight) loading in comparison with the base resin at tip field stresses of 500 kVmm⁻¹. Although the EL counts are in arbitrary units, the conditions for each test were the same so that the relative values have some meaning. Several aspects are clear from this result. All variants are characterized by two spectral peaks within this

Figure 2. Frequency resolved electroluminescence spectra for 10 % TiO₂/epoxy nanocomposites in comparison with the cured base resin. (solid line: -ve polarity; broken line: +ve polarity).

wavelength range – a common peak at a wavelength of about 450 nm (*see later note*) and peaks at higher wavelengths which depend on the formulation. In particular, the base resin and the microcomposite share a common peak at about 600 nm, whereas this peak is shifted to lower frequencies for the nanodielectric. This “red” shift amounts to an energy of about 1.3 eV. Experiments undertaken with different loadings would indicate that, although these features are affected by the particulate size, they are not strongly influenced by loading in the range 5 – 20% (by weight). This result is reproducible and is also mirrored in Fig.2 which illustrates the effects of polarity. Point cathode conditions are seen to generate significantly more emission than the opposite polarity. This might be expected for stresses above the field emission threshold due to electron injection at the point electrode.

Photoluminescence

Table 1 depicts photoluminescence (PL) data on these materials (*courtesy Dr. G. Teyssèdre*) as a function of excitation wavelength (from a xenon lamp coupled through a monochromator used to select the excitation frequency), and Fig.3 provides the PL spectrum when

Table 1. Photoluminescence data of the TiO₂ composites

Excit. w/l (nm)	BASE RESIN		10% MICRO		10% NANO	
	Pk λ	Pk Mag	Pk λ	Pk Mag	Pk λ	Pk Mag
280	413	7.0	411	25.5	418	29.6
320	409	21.5	414	35.8	420	44.6
340	407	65.4	405	128.1	412	35.2
360	408	85.8	406	151.2	423	14.1

excited at a wavelength of 340 nm. All variants have a strong emission peak in the range 405-425 nm which is in agreement with Griseri [5] at room temperature. Given the lack of resolution in establishing the high

Figure 3. Photoluminescence spectra for 10 % TiO₂/epoxy composites [nano (a), and micro (b) in comparison with the cured base resin (c)]. Excitation wavelength 340 nm

frequency peak in Fig.1, it is likely that these processes are synonymous particularly as the peak is known to be asymmetrical.

Internal charge distribution and dynamics

The use of the PEA technique has permitted an assessment of the internal charge behavior for the same materials for which EL results have been taken. A TechImp™ cell has been used together with a Tektronix Model TDS3032B oscilloscope. Calibrated charge densities and internal fields have been estimated through the use of deconvolution methods. Disc specimens were used having a diameter of 25 mm and a thickness of about 0.5 mm.

Typical charge profiles are shown in Fig.4 which depicts, for both nano- and micro-composites, the

Figure 4. Charge distribution profiles for 10 % TiO₂/epoxy composites at an average stress of 20 kVmm⁻¹ both after 1 hr of stressing (indicated) and with the voltage removed. [Top: nano and bottom: micro; cathode on left]

internal charge after 1 hr of stressing at 20 kVmm⁻¹ and at various times (10 s to 30 min) after voltage removal (to highlight the trapped charge). Several statements can be made from these, and other, characteristics:

- The nanomaterial exhibits an accumulation of negative (homo) charge in front of the cathode and a small amount of anode heterocharge.
- The microcomposite is characterized by much larger internal charges, and the accumulation of heterocharge in front of the cathode (and little charge elsewhere).
- The maximum internal field in the nanomaterial falls with stressing time for nanocomposites (-9% in 200 s) whereas the opposite is seen (+11% in 200 s) for the micromaterial. This is illustrated in Fig.5 and confirms the trends documented by Fothergill *et al.* [6] for the same material.
- The charge decay is characterized by 2

time constants (24/2210 s, 40/4800 s and 90/6300 s respectively for nano, base resin & micro materials respectively), presumably as the result of the relaxation of polarization and space charges.

Figure 5. The temporal development of the maximum internal field for 10 % TiO₂/epoxy nano- and micro-composites at an average stress of 15 kVmm⁻¹

DISCUSSION, IMPLICATIONS & APPRAISAL

Despite the poor resolution, two EL spectral peaks are clear in all the materials from Fig.1. The higher frequency emission peak ($\lambda \sim 450$ nm) is probably not actually at the same wavelength for both the composites. Table 1 indicates that the luminescence peak changes somewhat with excitation frequency suggesting that the luminescence center (probably the phenyl group associated with the base resin [5]) is affected. Indeed, it is reasonable to assume that the environment will be changed in the presence of nanoparticles having oxygen ions at the interfaces which become more dominant as the particle size is reduced. It is speculated that minor conformational changes would be sufficient to bind the excimer units more tightly. The microcomposite, in contrast, forms a two-phase system; with the particles and polymer acting as independent phases.

Perhaps of more importance is the large change in EL wavelength shown at about 600 nm (cured base resin and microcomposite) in Fig.1. The increase in wavelength for the nanomaterial is reproducible and substantial. Although the species responsible for this emission is unknown, the reduction in energy associated with the introduction of nanoparticles invites the speculation that again the luminescence center has been modified or that the predominance of interfacial regions is creating substantial scattering in the material. The absence of a 600nm peak in the PL spectrum of cured resin, and its presence for EL in different stressed epoxy resin systems suggests the peak is probably associated with degradation. In particular, earlier work shows that positive repetitive surges created the 600 nm EL peak [10], and also more easily initiated trees in epoxy resin compared to

negative surges [11]. This points to a correlation between the peak at 600nm and the aging of the material [5].

While EL has been measured under essentially steady-state conditions, it is dependent on the Poisson and not the Laplacian field. The PEA measurements of Fig.5 confirm earlier work [3] which showed that nanofillers mitigate the internal space charge. However, the PEA measurement is for a planar sample which does not have the highly divergent field associated with the EL experiment. The voltage-off characteristics of Fig.5 indicate that homo charge accumulates in front of the cathode for nanocomposites which is in striking contrast to the heterocharge which develops for the micromaterial. This is consistent with the finding that a Laplacian tip field of $\sim 200 \text{ kVmm}^{-1}$ is necessary for onset when it is known that the onset field can be as low as $\sim 20 \text{ kVmm}^{-1}$ in uniform fields [5]. In the case of the nanofiller, the preponderance of interfacial $-\text{OH}$ groups will decrease the network's crosslink density by competing with the amine group to react with the epoxide ring. The remaining $-\text{OH}$ groups at the interface could be expected to affect the particle's electrostatic potential [7] and thus contribute to a charge zone adjacent to the interface as has been suggested [2]. These processes at the interface are the likely cause both of the different time constant associated with charge relaxation in nanodielectrics, and the characteristics of Fig.5 which show the reduction of the internal field now well documented in nanocomposites. Indeed the, dramatic 2:1 change in EL onset voltage is likely the result of the modifications in internal field.

The finding that negative charge is formed in front of the cathode for nanocomposites suggests that charges injected are slowed by scattering and trapped as seen previously by Hibma [8]. The accumulation of space charge is intimately tied to the trap distribution in the polymer. Charges are injected and trapped during field application. The fast charge decay seen both in uniform field and divergent field [3] could be linked to relatively shallow traps existing in nano- compared to micro-composite. It is known that both the trap depth [9] and separation are substantially affected through the use of nanometric fillers in other materials [12]. In contrast, the lack of scattering in the microcomposite allows impact ionization in the divergent field tip region with the resultant accumulation of positive charge in front of the cathode as seen in Fig.4.

SALIENT CONCLUSIONS

The combination of luminescence and space charge studies in thermoset composites reinforces the view that the electrical properties of nanodielectrics result from the substantial enhancement of the interaction zone volume, scattering and the attendant effects on

space charge and changing charge transport.

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