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The influence of physical and chemical linkage on the properties of nanocomposites

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Abstract: It has been shown by several groups that the mechanical and electrical behavior of composites changes quite substantially, and often beneficially, when the filler particle size is less than 100 nm in diameter. There is also good reason to believe that the interface between the embedded particulates and the polymer matrix holds the key to understanding the bulk phenomena observed. Materials based on an SiO_2-polyolefin system have been formulated with functionalized particulates so as to affect the physical and chemical linkages. The agents used to achieve this include amino-silane, hexamethyl-disilazane and triethoxyvinylsilane. The emerging picture of the interface is supported by detailed dielectric spectroscopy and internal space charge assessment. The nature of the internal structure has been related to the bulk properties observed such as the breakdown strength, voltage endurance, and the measurement of internal charges resulting from interfacial polarization.

Introduction and Background

In the last few years there has been a burgeoning interest in the use of nanocomposites to create composite materials with enhanced dielectric properties. This has been centered primarily on the augmentation of epoxy thermosetting resins and also polyolefins using either exfoliated clays [1] or a variety of mineral oxide materials of nanometric dimensions [2]. In searching for a mechanistic understanding of the physics and chemistry underlying nanodielectrics [3], it has become very clear that the interface between the enormously enhanced internal surface area and the host polymer is key to determining the properties of the composite material. Furthermore, it has become evident that, at least in some instances, the properties are dictated by the mitigation of internal space charge in the dielectrics [5]. This paper addresses the effect of the interface and space charge characteristics on the breakdown strength and voltage endurance behavior.

System Studied

The host matrix used in this study was a cable grade polyethylene (Borealis SuperTR^{TM}LE4212) into which was introduced 5% (by weight) fumed SiO_2 nanoparticulates having a mean diameter of 15 nm. However, these particles were functionalized using:

(a) aminosilane
(b) hexamethyldisilazane (HMDS)
(c) triethoxyvinylsilane

The detailed processing of these materials has been described elsewhere [3], but involves the drying of the nanoparticles, compounding using a high shear melt mixer, cross linking using dicumyl peroxide and hot pressing to form appropriate specimens. A final post cure cycle was also applied to remove cross-linking byproducts.

"Terminal" Properties

The dielectric strength of multiple recessed specimens (nominal thickness: 0.005 - 0.015 mm) was evaluated using ramp (500 Vs^{-1}) AC voltages. The characteristic values of the resulting Weibull distributions are shown in Table 1. It is clear that not only does the incorporation of nanoparticulates positively affect the dielectric strength, but there is a (lesser) secondary influence of the nature of the interface which is dependent on functional groups at the particle surface. It is seen that the most effective agent is the triethoxyvinylsilane which provides the largest increase

Table 1. The breakdown strength of functionalized polyethylene nanocomposites as a function of temperature

Temperature / Materials	25ºC	60ºC	70ºC	80ºC
XLPE	269	183	129	79
XLPE + untreated nanosilica	314	260	213	83
XLPE + aminosilane treated nanosilica	400	266	263	134
XLPE + HMDS-treated nanosilica	336	225	208	128
XLPE + vinylsilane-treated nanosilica	446	422	344	220

in strength. This material also shows much less reduction in strength as the temperature is increased, presumably because the covalent bonding with the host polymer stabilizes the matrix. The voltage endurance behavior seen in Fig. 1 shows an enormous improvement in the behavior due to the inclusion of nanoparticles, but only a marginal change due to type of coupling at the interface.

Dielectric spectroscopy can also provide considerable insight into the nature of the structure contributing to both polarization and loss. Such results for the functionalized materials under study are shown in Fig. 2 for a temperature of 23ºC. Several features are evident from these characteristics. First, the untreated nanocomposites exhibit a relative permittivity less that that of the base polymer. This is a feature that has been seen for other materials [5], and suggests the presence of an interfacial zone around the particles with lower dielectric constant than the bulk polymer. A marked dispersion seen in the XLPE at about 1 Hz for the base resin is eliminated for the cases of functionalized nanomaterials. It is also very significant that a quazi-DC conduction region is evident from the tan δ plots when nanoparticles are incorporated without the benefit of a coupling agent. This suggests that the untreated particles perhaps have a conductive interface.

Space Charge Study

It is known from previous work on nanodielectrics [5] that the internal space charge is both mitigated and exhibits different dynamics in comparison with conventional fillers.

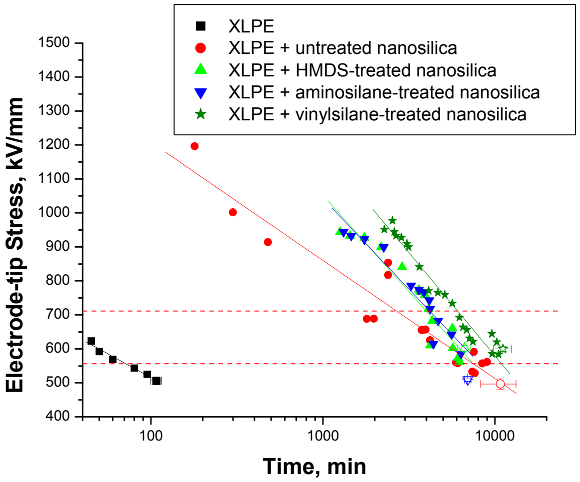

Figure 1. The voltage endurance of functionalized nanocomposites in comparison with the base polyethylene

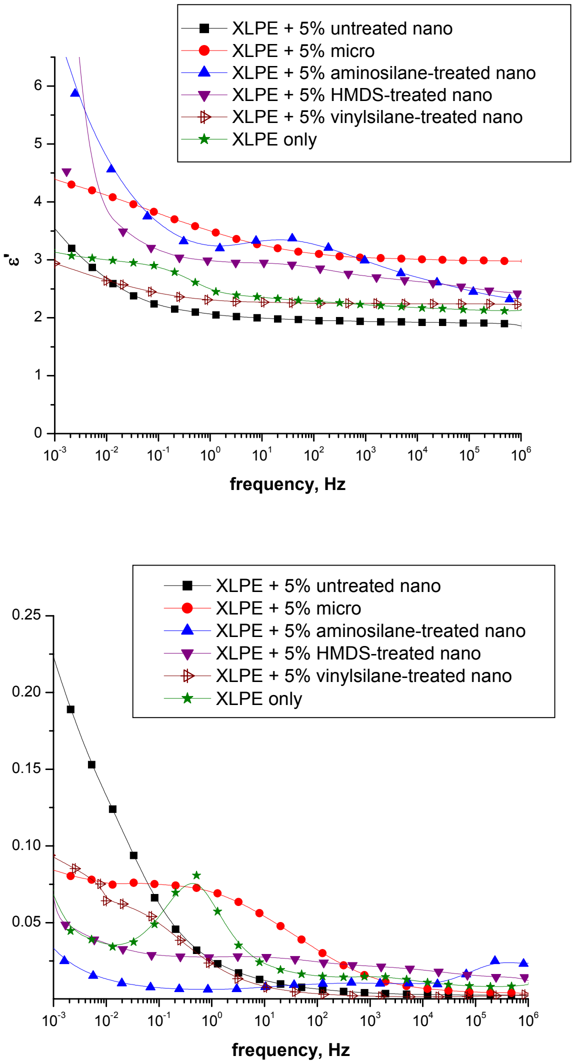

Figure 2. Dielectric spectroscopy of functionalized XLPE at 23 ºC

As a consequence, it is instructive to examine, using the pulsed electroacoustic method, the influence of the functionalization on the generation of internal charge. This has been done by examining the image charge magnitude on the electrodes as a function of applied voltage. As the voltage is increased (1 kV, 1 hour steps), a linear dependence of the image charge is expected as a result of the normal capacitive polarization of the dielectric. However, when significant internal charge is developed, a departure from linearity is expected.

This is depicted, for example, in Fig. 3 for the case of the untreated nanocomposite, and is consistent with injection into other polymers [7]. It may be seen that at about 12 kV mm^{-1} (-14 kV mm^{-1} negative) there is a departure from linearity depicting the onset of space charge development *(see arrows)*. This method has been utilized in Table 2 to compare onset of the generation of charge for all the materials tested (except the aminosilane treated material which did not reach its threshold before breakdown). When the experiments are analyzed in this way, it becomes clear that the onset of charge accumulation is changed little as a result of the incorporation of particulates. However, the change of the interface condition through functionalization has a substantial effect on the threshold field for both polarities.

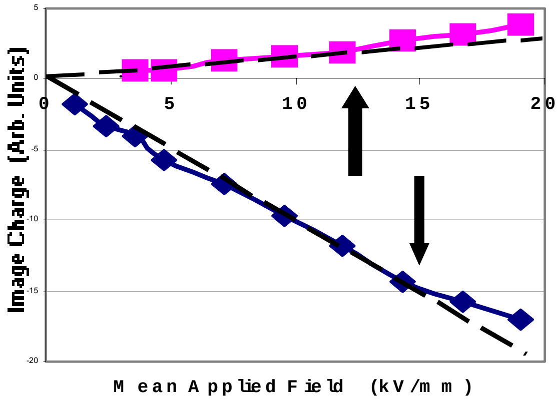

Figure 3. Illustration of the threshold field for the establishment of internal charge for untreated nanosilica in XLPE

Table 2. Space charge threshold field values for a range of SiO$_2$-XLPE samples at 20 °C

SAMPLE	**Threshold Field (positive)** (kV/mm)	**Threshold Field (negative)** (kV/mm)
XLPE (base)	13	-13
XLPE + micro SiO$_2$	15	-13
XLPE + untreated nano SiO$_2$	12	-14
XLPE + Amino treated nano SiO$_2$	*	*
XLPE + HMDS treated nano SiO$_2$	29	-29
XLPE + Vinyl treated nano SiO$_2$	25	-26

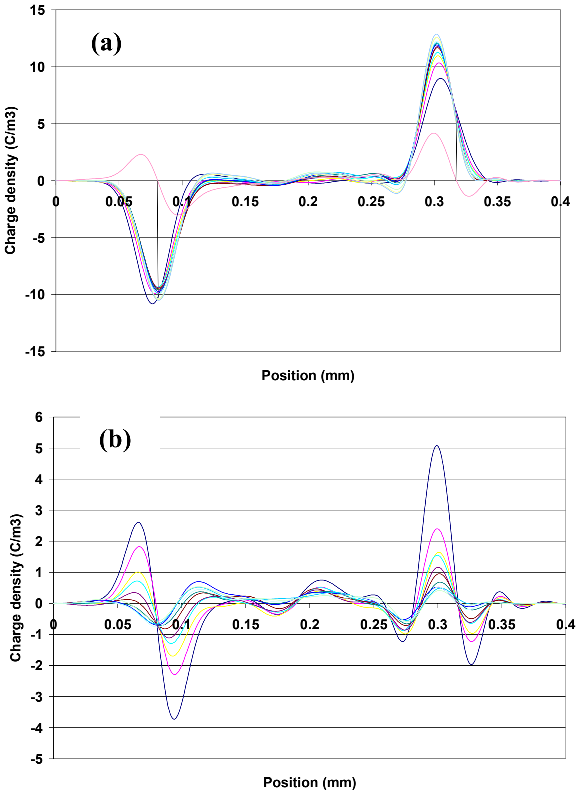

Figure 4. Charge accumulation (a) and decay (b) in vinylsilane functionalized composite each over a 2 hour period

This result is effectively measuring an average charge onset voltage. Since the image charge is being used, this says nothing about the exact position or distribution of the charge or even about the nature of the charge (homo or hetero) for which the individual PEA plots must be consulted such as that shown in Fig.4 for the case of a vinylsilane treated nanocomposite. A detailed study of plots such as Fig. 4 for all the materials leads to the following general conclusions:

(a) For the same nominal average Laplacian field, the functionalized nanocomposites generate less internal charge. This results in over 20% reduction in the peak internal field when, for example, the 5% vinylsilane-treated SiO$_2$ is compared with the base XLPE.

(b) All the materials exhibit the accumulation of homocharge in front of the electrodes, suggesting that carrier injection and trapping close to the electrodes is present.

(c) The functionalized composites exhibit a more uniform internal field.

(d) The aminosilane coupling agent results in anomalous charge behavior (internal charge decreases with time). This is likely to result from its polar nature.

(e) The greatest internal field distortion occurs for the microcomposite.

Appraisal

The results for breakdown strength and endurance clearly show that the biggest impact is the size of the filler. All the nanoscale fillers had significantly better breakdown strength and endurance than the base resin. One consistent measurement comparing the nanoscale filled composites with the micron sized particle filled composite is that the low frequency dispersion seen in Fig. 2 for the microcomposite is absent for all the nanocomposite materials. It is likely that this results from Maxwell-Wagner polarization, which is mitigated for the nanodielectrics. To test this hypothesis, time dependent conduction characteristics have been taken for both micro- and nano-composites which are shown in Fig. 5 at a constant nominal average stress level of 2 kV mm^{-1} (the voltage across the 100-150 μm samples was adjusted to achieve this). The departure from linearity shown for the micromaterial is a well-known characteristic of interfacial polarization [6]. In Fig. 5 the functionalized nanocomposites have the same slope as the untreated silica nanocomposites, but the absorption current is lower in magnitude. It is interesting to note that the absorption current for the nanomaterials is consistent with the tan δ behavior in the low frequency region (Fig. 2(b)). This strongly suggests that the conductivity thought to be associated with the interfacial region [4] through double-layer and/or hydration effects is altered by the enhanced coupling associated with the functionalized materials. Charge trapping also appears to be mitigated leading to the characteristics of Table 2. – *see comment (a) in previous section.* Although the crystallinity only has a second order effect on the breakdown characteristics since it changes little with the incorporation of nanoparticles [8], it remains to be established how particulates in semi-crystalline materials are incorporated into the morphological structure. In this context, study of polypropylene may be of significance.

Previous work in an epoxy-TiO$_2$ nanocomposite [5] system indicated that substantial differences in the internal charge accumulation may explain the improvements in breakdown strength**.** Although a small effect is demonstrated here, the effect is clearly dependent on the surface chemistry. However, the finding that the onset field for the charge injection is materially altered is important since it may provide some explanation of the breakdown and voltage endurance differences (Table 1 and Fig. 1) attendant on the use of coupling agents.

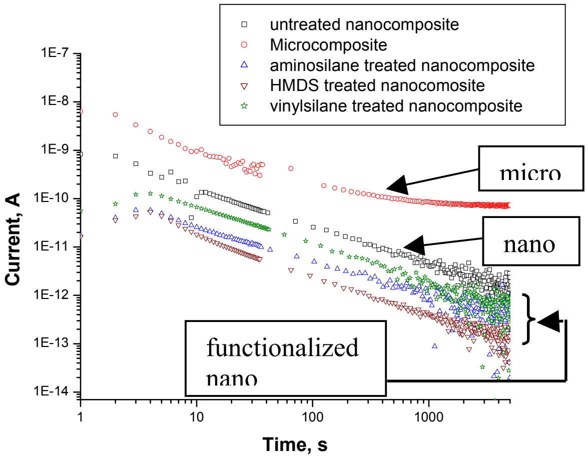

Figure 5. Time dependent conduction for XLPE-SiO$_2$ composites

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