Effect of water absorption on dielectric properties of nano-silica/polyethylene composites

I. L. Hosier, M. Praeger, A. F. Holt, A. S. Vaughan and S. G. Swingler

University of Southampton,
Electronic and Computer Science,
Southampton, SO17 1BJ, UK

Abstract- **The effect of moisture content on the dielectric properties of polymer/nano-silica blends was investigated. It was found that the DC breakdown strength, electrical conductivity and complex permittivity were all strongly influenced by absorbed water. However, a control sample without nano-silica was largely unaffected by changes in moisture content. This has important implications for researchers and cable designers.**

I. INTRODUCTION

Future development of electrical networks and the increasing use of renewable sources of energy such as solar, wave and wind requires that new high performance cable systems be implemented for the transmission of greater amounts of power over longer distances than previously. The insulation used in conventional high voltage cables is traditionally a polymer such as cross-linked polyethylene which has the advantages of low cost, high dielectric strength and low electrical losses.

The incorporation of a nano-filler into an existing polymeric insulation system seems an attractive way of improving the performance of the next generation of high voltage cables. Despite this, the majority of reports in the literature focus on the advantageous mechanical and thermal properties of nano-composites [1] and not on their dielectric properties. In terms of nano-silica/polymer composites, the situation regarding their dielectric properties is far from clear, since achieving good nano-particle dispersion and avoiding particle aggregation is very difficult [2-6]. Whilst this issue can be largely overcome by utilizing a pre-compounded master-batch (based on in situ nano-particle production or "sol-gel" processing) [1, 7], the measured dielectric properties are very sensitive to absorbed water [6, 8-10].

In this investigation we have undertaken a systematic study on the effects of water absorption on the dielectric properties of a nano-silica/polyethylene blend composite and have compared these data to a control sample treated identically but without nano-silica present. The implications for research methodologies and for practical nano-composite cable designs will be considered.

II. EXPERIMENTAL

A. Preparation of nano-silica

Nano-silica (Aldrich) with a quoted particle size of 10-20 nm was functionalised using trimethoxy(propyl)silane using an anhydrous route and the molar mass of functionaliser was identical to that employed previously [5]. In a flask. 15g of nano-silica was dispersed in 200 ml of dry tetrahydrofuran (THF) and 4.77 ml of functionalising agent was added. The mixture was sonicated for 10 min and then stirred within a sealed rotary evaporator (80 RPM for 48 h). The resulting mixture was centrifuged, the supernatant was decanted off and then fresh THF was added. This washing process was repeated twice with THF and twice with diethyl ether to remove any residues. The remaining solvent was then evaporated and the product was vacuum dried at room temperature for 24 h before being stored in a desiccator.

B. Polymer blending and sample preparation

Two blends comprised of 20 % HDPE (Rigidex HD5813, BP Chemicals) and 80% LDPE (LD100BW, ExxonMobil) were prepared [5, 6], namely, a control blend, not including nano-silica (referred to as CT1) and a second nano-filled blend incorporating 10 wt. % of treated nano-silica (referred to as NS1). First the required amount (1 g), of the treated nano-silica was placed into 200 ml of xylene and the resulting mixture was sonicated for 1 h to form a suspension. Then the polymer (9 g in total) was then added to the solution. The mixture was brought to the boil under vigorous stirring for around 20 minutes, precipitated by adding directly to 200 ml of methanol, filtered and finally vacuum dried at 60 ^{o}C for 24 h to remove the remaining solvent.

Samples were melt pressed at 160 ^{o}C into the required thickness and were then crystallized at 115 ^{o}C for 1 h in an oil bath [5, 6]. "Ambient" samples were then maintained under ambient conditions in an air conditioned environment (20 ^{o}C, 55 % RH) for at least 14 days prior to testing. "Dry" samples were vacuum dried for a period of 14 days whilst "wet" samples were immersed in water for the same time period, prior to testing. While changes in mass (water content) were below measureable limits (<0.02 %) in CT1, drying resulted in a water loss of ~0.5 % and wetting a weight gain of ~0.8 %. Such changes are consistent with earlier findings from comparable blends [6, 9].

C. Analysis

Melting and crystallization studies were performed using a Perkin Elmer DSC-7 calibrated with high purity indium. Melting scans were performed by heating at 10 K/min, whilst subsequent crystallization scans were performed by cooling at 5 K/min. Samples for scanning electron microscopy (SEM) were etched for 4 h in a permanganic reagent (1 % $KMnO_4$ in an acid mixture composed of 5:2:1 of sulphuric acid, phosphoric acid and water) [4-6]. These were mounted onto

SEM stubs, gold coated and examined at 15 kV in a Jeol JSM6500F FEG-SEM.

DC ramp breakdown testing (100 V/s) was carried out on 0.1 mm thickness samples placed between opposing 6.3 mm ball bearings immersed in silicone fluid. The results from 20 breakdowns were analyzed using Weibull statistics, the ball bearings being replaced after every 10 tests. Electrical conductivity measurements were undertaken at room temperature on 0.2 mm thickness samples. These were sputter coated with 20 mm diameter gold electrodes and placed into a test cell with opposing 20 mm diameter gold coated electrodes. A stepped voltage program (100 V increments, waiting for 10 s before recording the current) was applied. This was then followed by constant voltage testing up to 8 kV (40 kV/mm) where the conductivity was recorded over the next 3 h. Dielectric spectroscopy was performed on the same samples at room temperature from 0.1 Hz to 100 kHz, using a Solartron 1296 dielectric interface linked to a Schlumberger SI 1260 impedance-gain-phase analyzer.

III. RESULTS

A. Melting and crystallization behavior

Fig. 1 shows the melting and crystallization behavior. Two melting peaks are observed, the lower (~105 ^{o}C) being associated with the LDPE component and the upper (~124 ^{o}C) with the HDPE component. Whilst the melting behavior was largely unaffected by the presence of the nano-silica, crystallization of the HDPE phase occurs slightly earlier in NS1, indicating a nucleating effect of the nano-silica on the polymer [3, 6].

B. Morphology

The underlying morphology of CT1 is composed of banded spherulites (Fig. 2a) as reported elsewhere [5, 6]. In NS1, this underlying morphology is disrupted, perhaps nucleated by the nano-silica as suggested by the DSC data, and here particulates of up to 10 μm were observed (Fig. 2b). Whilst such micron-sized features were expected from this non-ideal
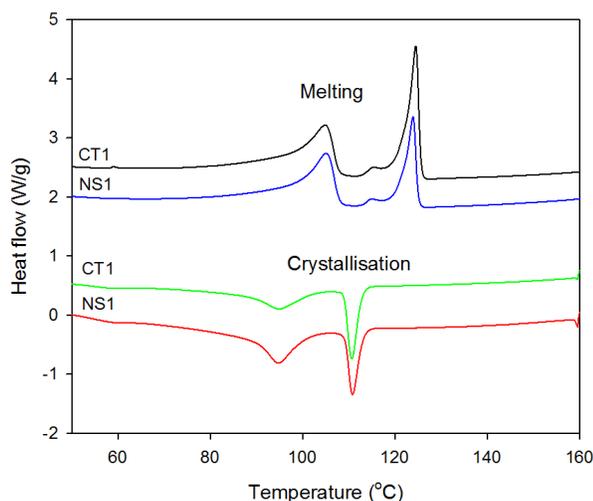
nano-silica incorporation route [2-6] and relatively high filler loading [1, 2, 6, 7], closer examination revealed that that these were composed of aggregates of much smaller particles having a dimensionality much closer to that expected (Fig. 2c). Clearly, particle aggregation is an issue in the current NS1 blend system.
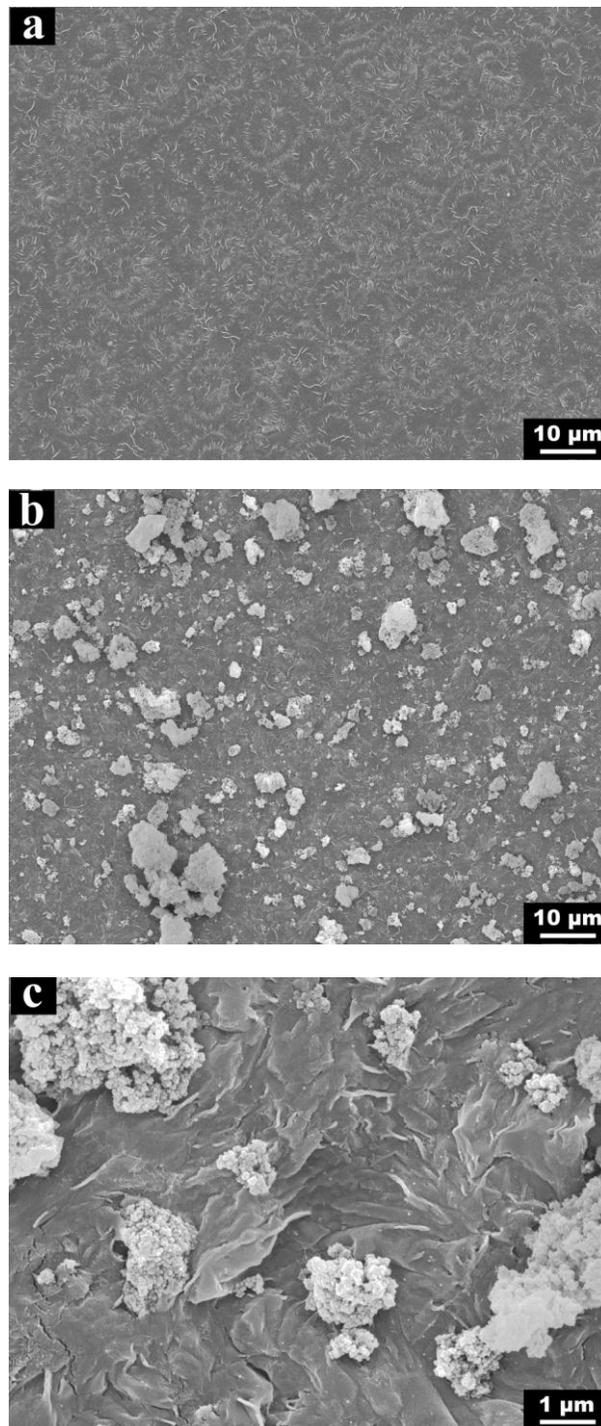
Fig. 2. SEM micrographs of (a) CT1, (b) NS1 and (c) detail of NS1
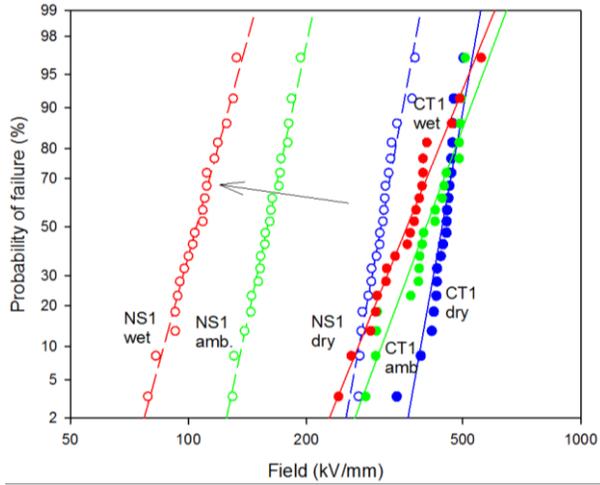
Fig. 1. DSC traces from melting and crystallization

Fig. 3. DC breakdown - Weibull plots for various conditions

C. DC breakdown

Weibull plots from DC breakdown testing are shown in Fig. 3 and associated numerical data is in Table 1. The inclusion of nano-silica lowers the DC breakdown strength as reported elsewhere [5]; this may be due to the permittivity mismatch between the polymer ($\varepsilon_r \sim 2.2$) and the silica ($\varepsilon_r \sim 3.9$). In CT1 (closed symbols in Fig. 3), the Weibull mean (E) decreases with increasing water exposure (uncertainty ± 20 kV/mm), which reflects a slight uptake of water by the polymer [9]. Of more significance, however, is the decrease in the shape parameter (β), indicating increasing scatter in the measured data. In NS1 (open symbols in Fig. 3) the Weibull mean decreases significantly (arrowed in Fig. 3) with increasing moisture content, while the β parameter is largely unchanged (Table 1). The uptake of moisture and the presence of nano-silica therefore cause a significant reduction in the measured breakdown strength, as reported elsewhere under ramped AC [9] and DC conditions [4, 5].

D. Electrical conductivity

The results from the initial (stepped voltage) electrical conductivity tests are shown in Fig. 4a. The conductivity of CT1 (closed symbols) is largely unchanged by exposure to water and is close to the minimum measurable conductivity ($\sim 10^{-17}$ S/cm), but increases somewhat with applied field to $\sim 10^{-16}$ S/cm at 40 kV/mm. Here NS1 has a significantly higher conductivity than CT1 as anticipated [2], although the opposite is possible in a better dispersed system [1]. More moist samples of NS1 exhibit stronger field dependence and hence a higher conductivity at any given applied field

TABLE I
Numerical values from DC breakdown testing

Blend	Conditions	E (kV/mm)	β
CT1	Dry	458	17.1
	Ambient	438	7.1
	Wet	399	5.0
NS1	Dry	325	10.4
	Ambient	167	10.4
	Wet	112	8.1

indicating that absorbed water is contributing to the measured conductivity. In order to restrict the conductivity to measurable values ($< 10^{-11}$ S/cm) and avoid any risk of electrical breakdown, the testing of NS1 was terminated at 40 kV/mm, 20 kV/mm and 10 kV/mm for dry, ambient and wet samples respectively, as shown in Fig. 4a.

Subsequent (constant voltage) tests were then performed at these applied fields (Fig. 4b). Considering only the time dependence here (since the values of conductivity depend on the applied field), the behavior of CT1 is independent of water exposure and falls slightly with time; remarkably similar behavior is also exhibited by NS1 exposed to ambient conditions. Dry samples of NS1 have a conductivity that falls and then increases as reported elsewhere [11] whilst wet samples show the opposite effect – a rise and then a fall in conductivity. No reason for the change in behavior in moving from ambient to dry conditions was given previously [11] but, since the conductivity is so strongly dependent on small changes in water content, we propose a gradual gain in water by the dry samples and a gradual loss of water from the wet samples is occurring during the testing. These changes in water content were, however, too small to measure here.
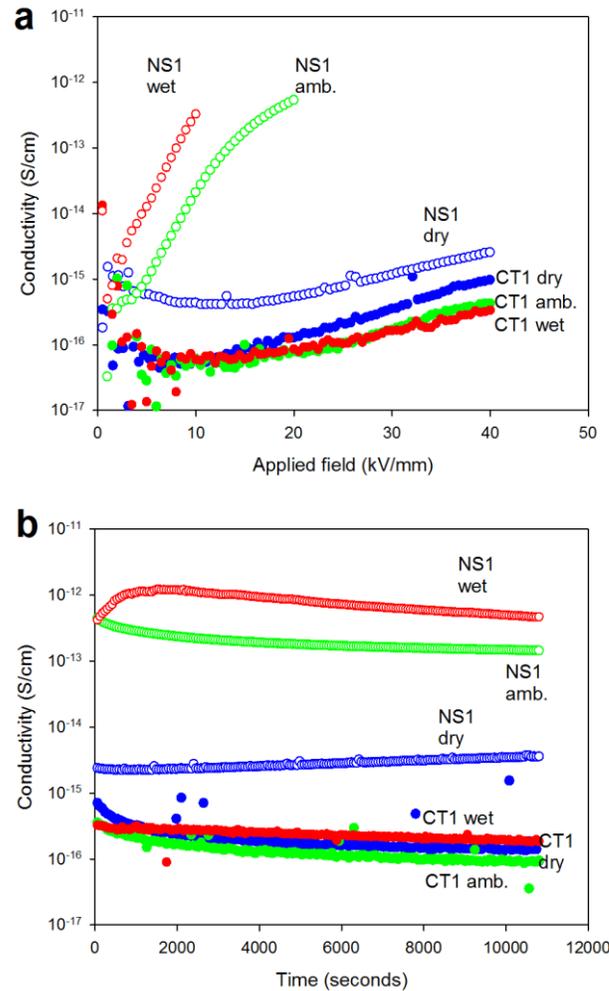

Fig. 4. DC conductivity results from (a) ramped tests, (b) constant voltage tests.

E. Dielectric spectroscopy

Dielectric spectroscopy results are shown in Fig. 5 as plots of imaginary and real permittivity. From these data, we see no changes occur in CT1, confirming that this sample is not affected significantly by exposure to water. In the imaginary permittivity of NS1 (Fig. 5a), a double relaxation feature is apparent, which moves to higher frequencies (arrowed in Fig. 5a) with increasing moisture content [6, 8 - 10]. The lower peak is usually ascribed to interfacial polarization, whereas the upper peak is ascribed to an accumulation of charges at the nano-silica/polymer interface [2, 3]. This is consistent with an increased mobility of charge carriers (water-related moieties) within the system.

Similarly, for the real permittivity (Fig. 5b), the observed increase at low frequencies with moisture content in NS1 (arrowed) is indicative of increased polarization due to the presence of an increasing amount of polarizable material (i.e. water) [6, 8, 9]. While the presence of nano-silica and water is deleterious here, one report [7] suggests that such increases in dielectric loss can be avoided in well dispersed systems.
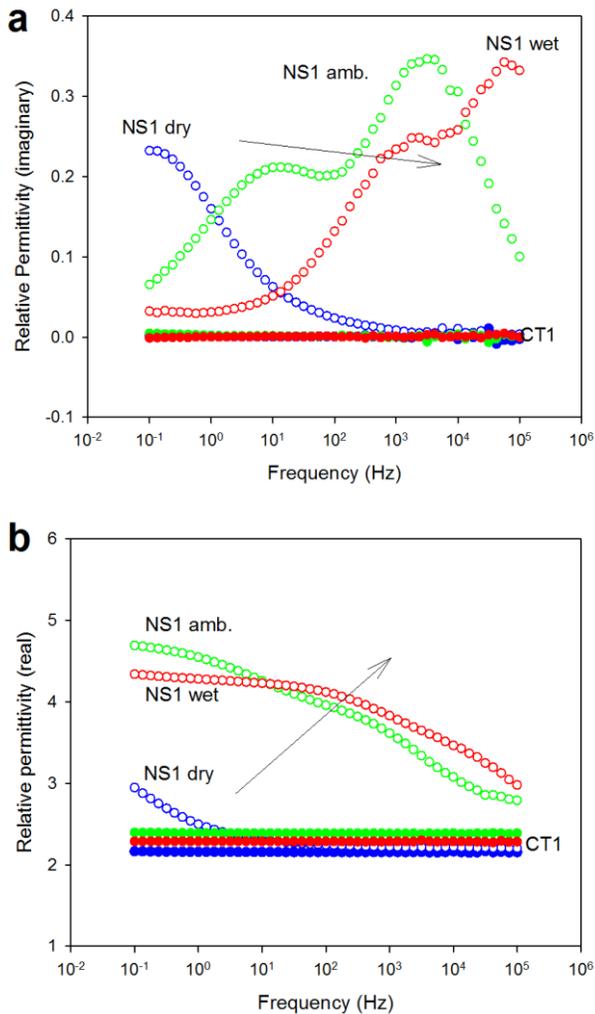
IV. CONCLUSIONS

Two polymer blends, one with and one without 10 wt. % of a functionalized nano-silica were investigated. Their DSC behavior and morphologies were compared to earlier work on the same blend systems and they were found to be typical. In particular, the aggregation problems reported previously were observed. The paper then focused on an investigation of the effects of water content on dielectric properties and the following conclusions can be drawn:

- A control sample (no nano-silica) was generally unaffected by water exposure.
- The nano-composite is capable of absorbing or losing a significant (measurable) quantity of water ~ 1 %.
- Moisture absorption leads to: (a) a reduction in the DC breakdown strength; (b) increased electrical conductivity; (c) increased dielectric loss at high frequencies and increased permittivity at low frequencies.

Care needs to be taken when working with these materials to avoid misleading conclusions being drawn and in, cable design, to exclude water during manufacturing and use.

REFERENCES

[1] M. G. Veena, N. M. Renukappa, J. M. Raj, C. Ranganathaiah,, K. N. Shivakumar, "Characterization of Nanosilica-Filled Epoxy Composites for Electrical and Insulation Applications", *J. Appl. Polym. Sci.*, Vol. 121, 2011, pp. 2752-2760.

[2] S. L. Abd-El Messieh, N. N. Rozik, "Dielectric and morphological studies on polyester/nanosilica fume composites", *J. Appl. Polym. Sci.*, Vol. 122, 2011, pp. 714-721.

[3] D. M. Panaitescu, Z. Vuluga, P. V. Notingher, C. Nicolae, "The effect of poly[styrene-b-(ethylene-co-butylene)-b-styrene] on dielectric, thermal and morphological characteristics of polypropylene/silica nanocomposites", *Polym. Eng. Sci.*, Vol. 53, 2013, pp. 2081-2092.

[4] M. Praeger, A. S. Vaughan, S. G. Swingler, "The breakdown strength and localized structure of polystyrene as a function of nanosilica fill fraction", *In Proc. 2013 Int. Conf. Sol. Diel*, IEEE, 2013, pp. 863-866.

[5] K. Y. Lau, A. S. Vaughan, G. Chen, I. L. Hosier, A. F. Holt, K. Y. Ching, "On the space charge and DC breakdown behavior of polyethylene/silica nanocomposites", *IEEE Trans. Diel. Electr. Insul.*, Vol. 21, 2014, pp 340-351.

[6] K. Y. Lau, A. S. Vaughan, G. Chen, I. L. Hosier, A. F. Holt, "On the dielectric response of silica-based polyethylene nanocomposites", *J. Phys. D: Appl. Phys.*, Vol. 46, 2013, Art. No. 095303.

[7] G. Iyer, R. S. Gorur, R. Richer, A. Krivda, L. E. Schmidt, "Dielectric Properties of Epoxy based Nanocomposites for High Voltage Insulation" *IEEE Trans. Diel. Electr. Insul.*, Vol. 18, 2011, pp. 659-666.

[8] A. Sami, M. F. Frechette, Eric David and S. Savoie, "Water as a Digression Relative to the Dielectric Response in the Frequency Domain for Polymer Composites", *In 2008 Ann Rep Conf Electr. Insul Diel Phen*, pp. 501-504.

[9] L. Hui, J. K. Nelson, L. S. Schadler, "The influence of moisture on the electrical performance of XLPE/silica nanocomposites", *In Proc. 2010 IEEE Int. Conf. Sol. Diel.*, pp. 305-308.

[10] M. Praeger, A. S. Vaughan, S. G. Swingler, "A dielectric spectroscopy study of the polystyrene/nanosilica model system", *In Proc. 2013 IEEE Int. Conf. Sol. Diel.*, pp. 859-862.

[11] K. Y. Lau, A. S. Vaughan, G. Chen, I. L. Hosier, A. F. Holt, A F, "Absorption Current Behaviour of Polyethylene/Silica Nanocomposites" *In Dielectrics 2013*, pp. 24-25.

Fig. 5. Complex permittivity plots from dielectric spectroscopy (a) imaginary, (b) real.