Effect of nano-particulate additives on phase dispersion

Report for:

EP/I031707/1 - Transformation of the Top and Tail of Energy Networks
Work Package 1.3 Super-Scale HVDC; 1.3.1 The 1 MV, 5 kA Cable

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http://www.topandtail.org.uk/
Effect of nano-particulate additives on phase dispersion
Top and Tail Grand Challenge Work Package 1.3.1 Report

Preface – Work Package 1.3 ‘Super-Scale HVDC’

High-level studies indicate that new transmission links of the order of 20 GW are required. Across the North Sea and English Channel these will clearly need to be sub-sea cable links. Across Pyrenees, under-ground cable is presently being used. HVDC is clearly required as it offers increased efficiency for large scale transmission of power over long distances due to reduced dielectric losses. There are existing point-to-point overhead line HVDC links using line-commutated converters (LCC) at 6.4 GW. However, there is nothing close to this rating using cables or the (self-commutated) voltage source converter, VSCs needed for interconnected DC. A SuperGrid network is going to require an increase in cable capacity of around a factor of 10 and an increase of VSC converter power rating of around a factor of 20. Furthermore, the changed generating patterns are likely to result in the creation of networks where the power flows associated with HVDC transmission will dominate any local AC generating capacity and interplay between transient stability and modularity must influence the design at circuit level. The next steps require game-changing technology advances.

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Scope – Work Package 1.3.1 ‘The 1 MV, 5 kA Cable’

Addressing the challenge of increasing HVDC transmission capacity; work package 1.3.1 explores three possible technological avenues towards this goal. Efforts are spread across three institutions with the main focus of work at each institution being as follows:

- At the university of Cardiff – Gas Insulated Line technologies.
- At the University of Manchester – Breakdown at interfaces and laminar material systems.
- At the University of Southampton – Polymer nanocomposites; in particular, phase dispersion.

The scope of this report is limited to the work carried out at the University of Southampton.

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Format of this report

This report is composed of two “papers” which were written with journal dissemination in mind, as such each forms an integrated whole.

- The first paper looks at polymer/nano-silica composites utilising functionalised nano-silica where the chain length of the functionaliser was varied from 3 to 18 CH₃ units. Since water absorption is so important in nano-composites, we have examined the effect of chain length on phase dispersion and electrical properties as a function of conditioning (i.e. water content).
- The second paper considers un-functionalised silica based nano-composites but introduces silicon nitride as a mechanism of limiting the extent of water absorption. An improved blending method led to improved dispersion and again the phase dispersion and electrical properties were studied as a function of conditioning.

We have found that both optimising the phase dispersion and removing surface hydroxyl groups (to which water binds) are key to providing enhanced dielectric properties. The latter can be done in one of two ways; (a) functionalization to “use up” the available surface hydroxyl groups, or (b) elimination, i.e. by substituting silicon nitride for silica. Methods of chemically removing surface hydroxyl groups and studies of composites made therefrom will be considered in a later report.
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1 Effects of functionaliser chain length on the dielectric properties of nano-silica composites

1.1 Introduction

The science of nano-dielectrics is generally accepted to have begun in 1994 when John Lewis published a paper entitled “Nanometric dielectrics” [1] but it was some 6 years later that the first experimental data were published. Most of this early work focussed on epoxy resins filled with a suitable nano-filler and focussed on their advantageous mechanical properties. Concerning dielectric properties, which is of more relevance to the current project, Tanaka [2] provides an exhaustive review of the available data (up until circa 2005) and it is useful here to briefly summarise his findings. Several ways of incorporating filler are possible including, (a) direct mixing of nano-filler into the polymeric matrix, (b) the intercalation method (i.e. through mechanical shearing or sonication) and finally (c) the sol-gel method which focusses on chemical modification of the filler particles. Early theoretical models led to the development of the “multi-core model” [3] where the nano-particle is envisaged to be surrounded by a diffuse Guoy-Chapman layer of some 10 – 30 nm on a typical 50 nm spherical particle providing an interaction zone between particles with very different properties to either particle or matrix. In the case of silica nano-particles, surface hydroxyl groups are identified as being an important factor in determining the dielectric and electrical properties at this interface [2]. In properly prepared systems, the dielectric loss and electrical conductivity are reported to be reduced compared to an unfilled system, space charge accumulation is reduced due to the formation of a new, shallow trap band which reduces carrier mobility and improved electrical breakdown strength is reported in iPP and EVA based systems. Other potential benefits of nano-composites are improved treeing and PD resistance [2] and as such nano-composites provide, potentially a means of improving the dielectric and breakdown performance of existing polymeric insulation materials as used in both HVDC and HVAC transmission cables.

Another useful review of the state of the art in 2008 was provided by Smith et. al. [3], in the paper they discuss results from other authors indicating improved breakdown and PD resistance in well dispersed nano-composites compared to the host resin. Dielectric spectroscopy results are more mixed with some systems (i.e. HDMS treated nano-silica) showing reduced electrical losses whereas other systems (i.e. untreated nano-silica and certain micro-filled systems) give rise to an additional low frequency dispersion. The crucial role of the interfacial region in determining electrical properties is usefully summarised thus;

- The nanoparticle surface creates a change in polymer structure (free volume, mobility, etc.) and local charge distribution.
- As the size of the filler is reduced, the interfacial region becomes dominant.
- Due to the change in local structure, the density and perhaps the depth of trap sites are altered which reduce carrier mobility and energy.
- If the carriers are trapped more often, then they are accelerated over shorter distances and have reduced energy. This is the same for carriers that are scattered. This causes less damage in the material and increases the lifetime of the polymer.
- The homocharge resulting from carrier trapping mitigates the electric field at the electrodes and increases the voltage required for charge injection. This increases the voltage required for short
term breakdown. Because this charge takes time to build up, the breakdown strength is a function of the rate of measurement (ac, dc, or impulse).

- The large interfacial area also creates opportunities for increased scattering. During impulse test conditions, this may become the primary mechanism for the increase in the breakdown strength of nanocomposites, since significant shielding homocharge cannot be accumulated in such a short time.
- The diffuse layers of mobile charge create local conductivity, which can serve to reduce charge accumulation, providing that the percolation limit has not been exceeded so that the bulk conductivity is unaffected.
- Because the interfacial area is so large, while some of these mechanisms may operate in micro filled composites, they are then overshadowed by the large defects the micro scale fillers introduce and the field enhancements they create. Microcomposites exhibit Maxwell-Wagner interfacial polarization which is generally absent in nanomaterials.

Danikas et. al. [4] focussed on electrical treeing behaviour where nano-particles are envisaged as being barriers to electrical tree growth. Experimental evidence supporting this was presented and discussed. Tree growth was suppressed provided the nano-composite was free of agglomerations since these can serve as regions of locally high permittivity enhancing tree growth. Computer simulations based on a threshold field model appear to support these assertions.

Li et. al. [5] presented a useful review focussing on the dielectric breakdown of nano-composites. They identify proper filler dispersion as being a key pre-requisite for enhanced performance of nano-composites and the work of several authors on epoxy based nano-composites tested using various voltage waveforms was presented. Flashover voltage was improved at 50 Hz but was reduced in impulse tests and was unchanged under DC conditions. In another analysis the flashover properties of an ATH (Al(OH)₃) nano-composite were improved (maximum performance being reached above 5 % filler loading) but the properties of composites employing alumina and silica were unchanged from those of the base resin. Similar tests on composites employing micro-scale ATH fillers indicated a drop in flashover voltage up to 20 % filler loading; it was unclear why ATH and not silica or alumina should behave in this way. Presented AC and DC breakdown data on various nano-composites indicated an improvement in breakdown strength below 2 % filler loading but a detrimental effect for higher filler loadings (attributed to aggregation); in contrast micro-fillers had a detrimental effect at all filler loadings. Adding micro or nano-sized fillers can improve the ageing resistance with better performance (at 1 % filler loading) reported in epoxy nano-composites as opposed to polyethylene based nano-composites. The PD resistance was also reported to improve more when the matrix has a higher (epoxy) rather than a lower (polyethylene) permittivity.

In summary, nano-composites offer significant potential for improved performance insulation materials. However, some key issues still need to be addressed; two of these are (a) the problem of obtaining good dispersion of the filler (as poor dispersion is seen as detrimental to electrical properties) and (b) the role of water absorption on dielectric performance has not been adequately explored.

As a basis for this current work we have drawn on a pair of papers by Lau et. al. [6, 7] where polyethylene/silica nano-composites employing un-functionalised silica were compared to those containing silica functionalised with trimethoxy(propyl)silane; the role of water absorption is also
considered. Morphological studies [6] revealed good dispersion at low filler loadings but aggregation at high filler loadings and overall slightly improved dispersion was reported for composites utilising the functionalised silica. Starting from dried samples, water uptake measurements showed a maximum water uptake of 1.6 % and 0.7 % by mass in nano-composites containing un-functionalised and functionalised silica respectively (10 % filler loading). Dielectric properties were sensitive to water content with water uptake resulting in a higher permittivity and a shift in dielectric loss to higher frequencies. Whilst the effects of water were identical, the maximum permittivity and dielectric loss were reduced somewhat in composites containing the functionalised silica. In a second paper [7] the authors go on to examine the space charge and DC breakdown behaviour of the same nano-composites, however the effects of water content were not considered. Accumulated homocharge was exaggerated with nano-filler present, more so in composites containing un-functionalised silica. DC breakdown strength was reduced in the nano-composites compared to the reference material, an effect that was attributed to particle agglomeration.

In the current work we have considered similar systems, however we introduce two longer chain functionalisers; trimethoxyl(octyl)silane and trimethoxyl(octadecyl)silane in an attempt to improve the particle dispersion. We have also considered the effects of drying and wetting (i.e. sample conditioning) on the dielectric properties in much greater detail.

1.2 Experimental

1.2.1 Materials and functionalization

Three silane functionalising agents were employed with varying alkyl tail lengths ranging from 3 to 18 CH₂ units (Table 1). The nano-filler used throughout was silicon dioxide (SiO₂), with a quoted particle size range of 10 – 20 nm and all four materials were obtained from Sigma Aldrich.

The nano-silica as supplied was functionalised using an anhydrous route [8]; the advantages of anhydrous functionalization compared to the more common alcohol/water route are (a) reactions are largely confined to the hydroxyl groups located on the surfaces of the nano-silica particles and (b) silane-silane reactions are largely suppressed resulting in a higher overall level of surface functionalization [7]. To ensure roughly the same level of surface coverage, a constant molar concentration was used (Table 1). 15g of nano-silica was initially dispersed in 200 ml of dry tetrahydrofuran (THF) in a flask and the required amount of functionalising agent (Table 1) was added to the mixture. The mixture was sonicated for 10 min and then stirred within a sealed rotary evaporator (80 RPM for 48 h). The resulting mixture was divided into equal volumes for centrifuging at 3500 RPM for 10 min and then the supernatant was decanted off. Fresh THF was then added and was vigorously stirred until the nano-silica was again suspended in the solvent. This washing process was then repeated twice with THF and twice with diethyl ether to remove any unreacted functionalising agent. The solvent was finally removed using a rotary evaporator and the resulting white powder was vacuum dried at room temperature for 24 h before being stored in a desiccator.

Functionalization was verified by CHN analysis (Medac Ltd) by comparing to an un-functionalised nano-silica and it was found that the carbon (C) content of the functionalised materials was significantly higher confirming the existence of additional CH₂ groups in the functionalised materials.
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<table>
<thead>
<tr>
<th>Functionaliser</th>
<th>Physical structure</th>
<th>Molar mass (g/mol)</th>
<th>Density (g/ml)</th>
<th>Amount used (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethoxy(propyl)silane</td>
<td>Si-(OCH₃)₃-(CH₂)₂-CH₃</td>
<td>164.3</td>
<td>0.932</td>
<td>4.77</td>
</tr>
<tr>
<td>Trimethoxyl(octyl)silane</td>
<td>Si-(OCH₃)₃-(CH₂)₇-CH₃</td>
<td>234.4</td>
<td>0.907</td>
<td>7.00</td>
</tr>
<tr>
<td>Trimethoxyl(octadecyl)silane</td>
<td>Si-(OCH₃)₃-(CH₂)₁₇-CH₃</td>
<td>374.7</td>
<td>0.883</td>
<td>11.49</td>
</tr>
</tbody>
</table>

Table 1: Physical structure and data for the three functionalising agents

1.2.2 Blending

High density polyethylene (HDPE) was obtained from BP Chemicals under their trade name Rigidex HD5813EA whilst low density polyethylene (LDPE) was obtained from ExxonMobil Chemicals under their trade name LD100BW. Four solution blends (Table 2) were prepared in 10 g amounts using xylene as solvent and methanol as non-solvent [6]. First, the required amount (1 g), of the treated nano-silica was placed into 100 ml of xylene and the resulting mixture was sonicated for 1 h. The polymer was then added (9 g total; 1.8 g HDPE and 7.2 g LDPE). This mixture was brought to the boil whilst stirring vigorously for around 20 min. The mixture was then precipitated by pouring directly into 100 ml of methanol. The precipitate was separated from the remaining solvent by filtration. The resulting white solid was vacuum dried at 60 °C for 24 h and was then pressed at 160 °C into 1 mm thick sheets to remove any included air bubbles.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Base resin</th>
<th>Nano-filler used</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>20 % HDPE/80 % LDPE</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>18 % HDPE/72 % LDPE</td>
<td>10 % SiO₂ functionalised with trimethoxy(propyl)silane</td>
</tr>
<tr>
<td>C8</td>
<td>18 % HDPE/72 % LDPE</td>
<td>10 % SiO₂ functionalised with trimethoxyl(octyl)silane</td>
</tr>
<tr>
<td>C18</td>
<td>18 % HDPE/72 % LDPE</td>
<td>10 % SiO₂ functionalised with trimethoxyl(octadecyl)silane</td>
</tr>
</tbody>
</table>

Table 2: Blends used in these investigations

1.2.3 Sample preparation and conditioning

Samples for characterisation were prepared in the form of 0.2 mm and 0.1 mm thickness sheets using a hydraulic press and appropriate Melinex spacers (160 °C and 3 ton load). All samples were crystallised from the melt in oil baths maintained at 115 °C for 1 h prior to quenching in water [6]. Following sample preparation, specimens were then conditioned to vary their water content as follows: “ambient” samples were maintained under ambient conditions in an air conditioned environment (19 ± 2 °C, 55 - 80 % RH) for at least 14 d prior to testing; “dry” samples were vacuum dried at room temperature for periods of up to 14 d whilst “wet” samples were immersed in water for periods of up to 14 d.

1.2.4 Physical characterisation

In order to determine the extent of water gain or loss during conditioning, the mass of the samples was recorded at regular intervals to an accuracy of ±0.0001 g (i.e. ± 0.02 % on typical 0.5 g samples). Thermogravimetric analysis (TGA) was performed by heating 5 mg samples using a Perkin Elmer Pyris 1 TGA at a rate of 20 K/min in air. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC-7 which was calibrated using high purity indium. Melting scans were obtained by heating at 10 K/min whereas crystallisation behaviour was examined by cooling at 5 K/min from the melt. Optical microscopy was performed on 0.1 mm thickness samples using a Leitz Aristomet universal microscope between crossed polarisers. Samples for scanning electron microscopy were etched for 4 h in a solution of 1 % potassium permanganate in an acid mixture.
(5:2:1 of sulphuric, phosphoric acids and water respectively). After etching the mixture was quenched in a solution comprised of 1 part of hydrogen peroxide in 4 parts of an acid mixture composed of a 2:7 mixture of sulphuric acid in water. Samples were then rinsed twice with distilled water and once with acetone and left to dry overnight. Samples were then mounted onto aluminium SEM stubs, gold coated and were finally examined at 15 kV in a JEOL JSM6500F high resolution FEG-SEM.

1.2.5 Electrical characterisation

Dielectric spectroscopy was performed on 0.1 mm thickness samples incorporating gold coated electrodes using a parallel plate test cell with a guard ring (diameter of inner electrode 30 mm). Measurements of permittivity and dielectric loss were performed using a Solartron 1296 dielectric interface linked to a Schlumberger SI 1260 impedance-gain-phase analyzer. A 1 Vrms AC signal was applied over a frequency range from 0.1 Hz to 100 kHz and all measurements were performed at room temperature. Measurements of electrical conductivity were performed at room temperature on the same (coated) samples placed between opposing 20 mm diameter polished gold electrodes. For voltage ramp tests, a stepped voltage (100 V to 8 kV in steps of 100 V) was applied waiting 10 s after application of the voltage before measuring the current to allow any capacitive currents to dissipate. Constant field measurements were similarly performed at the indicated fields at a frequency of 1 reading per minute up to a maximum period of 3 h. DC breakdown testing was carried out on 0.1 mm thickness samples placed between opposing 6.3 mm ball bearings immersed in silicone fluid (Dow Corning 200/20CS). An increasing DC voltage (100 V/s) was applied to this arrangement until failure occurred. For each composite system, 20 such tests were carried out, each at a separate location, the ball bearings being replaced after every 10 tests. The resulting data were then analysed using Weibull statistics. Measurements of space charge behaviour were performed on 0.2 mm thickness uncoated samples using a 5-Lab “PEANUTS” pulsed electro-acoustic system utilising a semi-conducting anode and aluminium cathode. A constant field of either 25 or 40 kV/mm was applied and measurements of the resulting charging behaviour were subsequently made over an hour. The system uses a 600 V, 5 ns pulse and averages over 512 measurements.

1.3 Results

1.3.1 Thermogravimetric analysis (TGA)

Fig. 1a shows the TGA data. The unfilled reference starts to degrade at 300 °C, reaching 50 % of its original mass at 410 °C (T <sub>0.5</sub> in Table 3) and the sample then reaches zero mass at 570 °C. The composites all behave in a similar fashion; first the samples lose ~1 % mass above 100 °C (M <sub>init</sub> in Table 3) – this implies that the filler as supplied contains some 10 % water. Then 50 % of the original mass is reached at ~440 °C (thus the composites are somewhat more thermally stable than the unfilled reference material) and the samples then continue to lose mass up to 570 °C. Taking this to be the point at which the polymer is completely degraded (R _<sub>570</sub> in Table 3), the filler content of the composites is around 9 % which is consistent with an initial water content of some 10 %. Compared to C3 and C18, C8 degrades somewhat earlier.

1.3.2 Water absorption measurements

Fig. 1b shows the change of mass associated with wet and dry conditioning with asymptotic fitted lines. Without nano-silica present (i.e. C0), no significant water absorption or loss occurs as expected [6] (<0.02 %). In contrast, C3 is capable of losing (L <sub>max</sub> in Table 3) 0.5 % or gaining (G <sub>max</sub> in
Table 3) 0.8 % of water relative to ambient a variation of 1.3 %, which falls between the values for un-functionalised and functionalised composites reported previously [6]. Significantly less water is both gained and lost for the same conditioning time by C18 (i.e. through the use of a longer chain functionaliser). This behaviour clearly indicates that (a) in samples stored under ambient conditions a significant amount of water is held at the surfaces of the nano-particles and (b), utilising a longer chain functionaliser impedes the movement of water to or from the nano-particle surfaces.

1.3.3 Differential scanning calorimetry (DSC)

Fig. 2a shows the DSC melting behaviour. Each material displays two melting peaks ($T_m$ in Table 3) at 105 and 124 °C (LDPE and HDPE respectively); the total enthalpy is ~100 J/g ($\Delta H$ in Table 3) for C0, falling somewhat for the nano-composites to ~90 J/g as anticipated due to the proportion of included filler. On cooling at 5 K/min (Fig. 2b) C0 displays two crystallisation ($T_c$ in Table 3) peaks at 110 and 95 °C from HDPE and LDPE respectively. Whilst the lower (LDPE) peak is located at the same temperature in the nano-composites, crystallisation of the HDPE occurs somewhat earlier at ~112 °C, suggesting that the nano-silica is nucleating the more crystallisable HDPE component.
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<table>
<thead>
<tr>
<th>TGA data</th>
<th>Water absorption</th>
<th>DSC data</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(_{\text{init}}) (%)</td>
<td>(T_{0.5}) (°C)</td>
<td>R(_{570}) (%)</td>
</tr>
<tr>
<td>C0</td>
<td>-</td>
<td>411</td>
</tr>
<tr>
<td>C3</td>
<td>0.9</td>
<td>442</td>
</tr>
<tr>
<td>C8</td>
<td>1.1</td>
<td>431</td>
</tr>
<tr>
<td>C18</td>
<td>1.1</td>
<td>437</td>
</tr>
</tbody>
</table>

Table 3: Numerical data from TGA, water absorption measurements and DSC tests

1.3.4 Optical microscopy

Nucleation of the polymer by the nano-filler was confirmed by optical microscopy (Fig. 3); whilst C0 displays a coarse texture composed of ~20 μm diameter spherulites (Fig. 3a), in contrast each of the nano-composites exhibits a noticeably finer, more granular texture (Figs. 3b - 3d).

1.3.5 Scanning electron microscopy

SEM confirms the above findings. In C0, a texture of 10-20 μm diameter banded spherulites is evident (Fig. 4a) as anticipated [6, 7], whereas in each nano-composite, this texture is disrupted (Figs. 4b through 4d), resulting in a uniform background texture punctuated by obvious particulates. Whilst there are a large number of <1 μm particles present, there are also aggregates up to ~10 μm
in size, which are present in all three nano-composites. While overall the level of particle dispersion and aggregation state is consistent with the micrographs presented elsewhere [6], there is no evidence here that increasing the functionaliser chain length causes any obviously improvement to the level of particle dispersion or any significant reduction in the number density of observed aggregates.

**1.3.6 Dielectric spectroscopy**

*Comparison of the various composites.* Fig. 5 contains plots of the permittivity and dielectric loss obtained from samples which have undergone ambient conditioning. C0 has a permittivity of 2.3 and a dielectric loss of $\sim 10^{-3}$ (Table 4) which is close to the minimum measurable limit. In contrast the permittivity of the nano-composites increases from 2.4 to 4.2 with reducing frequency (Fig. 5a). At high frequencies the presence of the nano-filler ($\varepsilon_r \sim 4.0$) increases the permittivity of the composite, whereas, at sufficiently low frequencies, polarisable material (presumably absorbed water) is able to align in the applied field giving rise to an additional increase in permittivity. The associated dielectric loss plot (Fig. 5b) shows a corresponding loss feature with a maximum of 0.11 at 1.2 kHz which again is indicative of the effects of absorbed water. A subtle shoulder is also present at $\sim 5$ Hz which increases in intensity in the nano-composite employing the longest chain
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functionaliser. Being at a lower frequency this indicates the presence of more tightly bound water moieties; such a feature which is reported elsewhere [6], may therefore arise due to water which is more tightly trapped at the nano-particlefunctionaliser interface.

<table>
<thead>
<tr>
<th>Dielectric spectroscopy</th>
<th>Electrical conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of ε_r</td>
</tr>
<tr>
<td>C0</td>
<td>2.3</td>
</tr>
<tr>
<td>C3</td>
<td>2.4 - 4.1</td>
</tr>
<tr>
<td>C8</td>
<td>2.4 - 4.1</td>
</tr>
<tr>
<td>C18</td>
<td>2.3 - 4.2</td>
</tr>
</tbody>
</table>

Table 4: Numerical values from dielectric spectroscopy and electrical conductivity tests (ambient conditioning).

**Effect of conditioning.** The dielectric properties of C0 do not change with conditioning so no data are shown here. However, drying C3 (Fig. 6a) causes the permittivity to be lowered (at any given frequency) and the transition from low (2.4) to high (4.2) permittivity to occur at a progressively lower frequency. Drying extracts water from the composite (see Fig. 1b) and wetting increases the water content, therefore proportional changes in the relative permittivity are attributed to polarisation of the included water molecules. Fig. 6b shows the corresponding dielectric loss; evidently the same loss peak (with the same maximum value of 0.11) is shifted to higher frequencies with increasing amounts of water (or conversely shifted in the opposite sense in dried samples) due to changes in the mobility of included water moieties. Comparing these data to published results for functionalised nano-composites [6] indicates very good agreement. The remaining nano-composites reveal the same behaviour with conditioning (Figs. 6c through 6f), indicating that functionaliser chain length has only has a subtle effect and that absorbed water effects clearly dominate. In short, when excited at low frequencies (below some threshold frequency f_o) water molecules are able to align (polarise) in the applied field giving rise to an increase in the relative permittivity, this is paralleled by a peak in the dielectric loss which also occurs around f_o.
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1.3.7 Electrical conductivity

Comparison of the various composites. Fig. 7a shows conductivity measured as a function of applied field following ambient conditioning. In such measurements, the observed value of
conductivity is always a result of two factors; (a) polarisation, which tends to reduce the conductivity over time, and (b) the field dependence of conductivity; the various hopping models for charge transport predict that the conductivity increases with applied field. It is clear from the behaviour of C0 that polarisation effects are dominant at low fields (giving an initial decrease in conductivity) whilst at high fields steady state charge charge transport processes are dominant (giving rise to a subsequent increase in conductivity). In contrast, each nano-composite exhibits a conductivity that increases dramatically with applied field indicating that charge injection and other bulk conductivity processes are dominant even at very low applied fields. Here the experiments were terminated at 20 kV/mm to prevent risk of breakdown and possible damage to the equipment, however all of the nano-composites showed a conductivity several orders of magnitude higher than C0 (Table 4). In subsequent constant voltage measurements at the indicated fields (Fig. 7b), the behaviour of all four systems was identical – a gradual reduction in the measured conductivity over several hours. Curve fitting shows that the observed behaviour follows the expected Curie-von Schweidler law [9].

**Effect of conditioning.** The field dependence of conductivity is plotted as a function of conditioning for each composite in Fig. 8 both as field dependence and then subsequent time dependence plots. In C0, as stated above, (Fig. 8a) the conductivity shows a decrease and then an
increase with applied field. In terms of absolute values, the reproducibility is poor and effectively within these variations the conductivity of C0 is independent of conditioning - not exceeding $10^{-15}$ S/cm at the highest field of 40 kV/mm. Considering the subsequent time dependence traces recorded at 40 kV/mm (Fig. 8b), with the exception of “Wet 14 d”, which here shows a conductivity
that is apparently constant with time, the remaining traces fit well to the Curie-von Schweidler law. The three nano-composites provide, within the inherent uncertainties of the measurements, a common behaviour with applied field (Figs. 8c, 8e, 8g) indicating that functionaliser chain length is having a negligible effect on conductivity. On the role of water content we observe the following:

(a) Samples dried for 7 or 14 days have broadly the same conductivity which has a field dependence very similar to that of C0 (i.e. a fall followed by an increase). It ranges from $10^{-16}$ to $10^{-14}$ S/cm which is one order of magnitude higher than C0 (at 40 kV/mm).

(b) Wet conditioning for 7 or 14 days results in comparable conductivity values; the conductivity increases sharply with applied field from $10^{-16}$ to $10^{-12}$ S/cm. Measurements were restricted to a maximum of 10 kV/mm to avoid the risk of electrical breakdown.

(c) Samples with “Ambient” conditioning show an intermediate level of conductivity, ranging from $10^{-16}$ to $10^{-13}$ S/cm and consequently measurements were restricted to a maximum of 20 kV/mm.

Fig. 1b indicates that there is a negligible difference in absorbed water content between 7 and 14 days conditioning which explains the similarities in the associated conductivity data. It is clear from the data that an increase of only ~1 % of water content results in an increase in conductivity of around 4 orders of magnitude. In other words the electrical conductivity of nano-composites is very sensitive to small variations in water absorption.

Considering next the time dependence data (Figs. 8d, 8f, 8h), we again observed a common behaviour over all three nano-composites with conditioning;

(a) Dry conditioned samples (measured at 40 kV/mm) show a gradual increase in conductivity with time, such anomalous behaviour has been reported elsewhere [10] and does not conform to the Curie-von Schweidler law.

(b) Ambient conditioned samples (measured at 20 kV/mm) show a decrease in conductivity with time – a behaviour that fits the Curie-von Schweidler law.

(c) Wet conditioned samples (measured at 10 kV/mm) show an initial increase and then a fall in conductivity with time. These data do not fit the Curie-von Schweidler law.

Given such extreme sensitivity of conductivity to absorbed water content, we postulate that the dry samples are gaining water during the course of the experiments whilst, conversely, the wet samples are losing water to the environment. However it should be noted that the above measurements were performed over ~3 h whereas the measurements in Fig. 1b indicate that at least 24 h is required to obtain a measurable change in mass of ~0.1 %, which suggests a much longer timescale of ~days is required for changes in bulk water content. The fact that observable changes in conductivity do occur over much shorter timescales of ~hours suggests that it is only necessary for water to be adsorbed on the sample surfaces in order to have an effect on charge transport processes. This finding seems to agree with Lau et. Al. [7] who saw a switch from homo to heterocharge injection in initially dry samples during measurements undertaken over ~hours under ambient conditions where the sample presumably gradually gained water from the environment.

Each type of conductivity measurement clearly has its merits and drawbacks; (a) measurements undertaken at increasing field can be done relatively rapidly and hence should be independent of changes in ambient conditions albeit that the measured values will not reflect the true value of conductivity, being a combination of polarisation and charge transport effects (depending on the
residence time at any given applied field), (b) constant field measurements are more likely, after several hours, to provide a true measure of the conductivity but with the drawback that the measurements could be influenced by the sample’s environment.

1.3.8 DC breakdown

Fig. 9 shows Weibull plots for dry and wet samples and Table 5 contains derived numerical data. Within the uncertainties (± 20 kV/mm), C0 shows a slight decrease in breakdown strength when wet conditioned; average 430 kV/mm. Each nano-composite shows a lower breakdown strength than C0 even when dried for 14 days (Table 5 ~340 kV/mm) and progressively poorer breakdown performance when ambient (~160 kV/mm) and wet (~110 kV/mm) conditioned. Within the experimental uncertainties, there is no significant difference, for any given conditioning route due to functionaliser chain length. Finally the shape parameter β does not vary systematically with chain length, although it is somewhat lower overall in C8 especially after dry and ambient conditioning. Previous work [7] indicates a value of 480 kV/mm for an un-filled HDPE/LDPE blend (C0) and 194 kV/mm for a C3 treated composite with 10 % nano-filler. These findings seem to fit best with our data for ambient conditioning however it is not explicitly stated in this publication how the samples were conditioned prior to measurements being carried out.

Fig. 9a: Weibull plots, dry conditioning

![Fig. 9a: Weibull plots, dry conditioning](image)

Fig. 9b: Weibull plots, wet conditioning

![Fig. 9b: Weibull plots, wet conditioning](image)

<table>
<thead>
<tr>
<th></th>
<th>Dry (14 d) conditioned</th>
<th>Ambient conditioned</th>
<th>Wet (14 d) conditioned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₀</td>
<td>β</td>
<td>E₀</td>
</tr>
<tr>
<td>C0</td>
<td>458</td>
<td>17.1</td>
<td>438</td>
</tr>
<tr>
<td>C3</td>
<td>325</td>
<td>10.4</td>
<td>167</td>
</tr>
<tr>
<td>C8</td>
<td>359</td>
<td>4.9</td>
<td>163</td>
</tr>
<tr>
<td>C18</td>
<td>355</td>
<td>10.2</td>
<td>175</td>
</tr>
</tbody>
</table>

Table 5: Measured DC breakdown values and shape parameters

1.3.9 Space charge

**Control sample.** The space charge behaviour of C0 was independent of conditioning and is completely dominated by the response of bound surface charges at the electrode/polymer interface. Nevertheless decay measurements (with the poling voltage switched off and the sample short-circuited) indicate the presence of a very small amount of homocharge adjacent to the cathode (K) and anode (A). Consequently, only one example is shown in Fig. 10a. The stored charge largely
remains after 1 hour, showing that the charge, once injected, is confined to the vicinity of the electrodes and is not easily removed.

**Effect of conditioning.** The nano-composites all show a common behaviour with conditioning which is illustrated in the C3 system in Figs. 10b to 10d. After dry conditioning, homocharge is accumulated (Fig. 10b) and subsequent decay measurements confirm that negative charge is stored at the cathode and positive charge is stored at the anode, which shows negligible decay over the measurement period of 1 h. After wet conditioning heterocharge is dominant (Fig. 10c); here the positive heterocharge adjacent to the cathode is recombined more rapidly than the negative homocharge at the anode which, instead, builds up progressively during the poling process. However, on removal of the poling field the stored charge is dissipated rapidly in < 2 min. Finally, under ambient conditions (Fig. 10d) neither charge type appears to be dominant, leading to little or no net charge accumulation.

In [11] similar space charge profiles are explained as the interplay between two mechanisms of space charge generation, which occur simultaneously. Heterocharge production is attributed to auto-ionisation of water; in this process, water is ionised to produce OH\(^{-}\) and H\(_3\)O\(^{+}\) within the bulk of
The space charge response of the wet conditioned nano-composite samples is dominated by heterocharge production via ionisation of water. The neutralisation of charge that is observed at the cathode indicates that recombination of $\text{H}_3\text{O}^+$ ions with injected electrons (at the cathode) is more likely or occurs more quickly than the equivalent recombination of $\text{OH}^-$ with holes near the anode. The time delay between heterocharge accumulation and neutralisation may be due to the mobility of the $\text{H}_3\text{O}^+$ ions which is expected to be low because of their relatively high mass and low dipole moment. Additionally, the local electric field at the sample surface will be increased as heterocharge accumulates, this could cause the rate of charge injection to increase. The observed time dependence of charge accumulation will be determined by the net combination of these and other factors.

For samples that have been dried prior to space charge examination it seems that the same two mechanisms for space charge creation are present, but in the opposite ratio; i.e. homocharge creation by injection at the electrodes now dominates. As the sample charging time is increased, more and more homocharge is created; this progressively advances into the bulk of the material but does so slowly, because of the low electrical conductivity of the system. The dip in homocharge that develops near to the electrodes may indicate that the rate of homocharge injection is falling with time – this would explain the creation of homocharge packets that separate from the electrode charge. Alternatively, this effect could be due to the superposition of a small amount of heterocharge from ionisation of residual water over the injected homocharge and the electrode image charge – this requires that the two species of charge carrier can overlap spatially without immediately recombing.

Under ambient conditions, where samples carry an intermediate water content, presumably both effects are still operative but largely cancel out to reveal little or no net charge storage.

Finally, it is clear that the charge decay time on removal of the poling field is related to the electrical conductivity of the samples; although heterocharge (which increases the internal local electric field leading to electrical breakdown at a lower applied field) is injected into wet conditioned samples it is able to dissipate very rapidly, conversely homocharge which is injected into dry samples (which would lower the internal field leading to improved dielectric performance) is not able to leave the material under short circuit conditions. It is unclear which situation would be worse in terms of day to day HVDC cable operation and other factors such as the effects of polarity reversals and ageing would have to be considered.

**Effect of functionaliser chain length.** Functionaliser chain length has a negligible effect on the space charge behaviour when considered across all three nano-composites and the effects of water absorption dominate. Key data from C8 and C18 are reproduced in Fig. 11, here we have omitted the data from ambient conditioning since, as noted above the two charge types largely cancel out to
leave little or no net charge. In space charge measurements it is important to note that the absolute values of the charge density can vary somewhat due to contact pressure (i.e. better or worse transmission of the acoustic signal), the quality of the semiconductor/polymer interface and even the amount of oil used. Nevertheless dry conditioned samples always exhibit net homocharge (Figs. 11a and 11c) whilst wet conditioned samples always exhibit heterocharge (Figs. 11b and 11d). Thus a clear pattern emerges which is not unlike the experiments performed by Lau et al. [7]

![Fig. 11a: C8 space charge (dry 14 d, 40 kV/mm)](image1)

![Fig. 11b: C8 space charge (wet 14 d, 25 kV/mm)](image2)

![Fig. 11c: C18 space charge (dry 14 d, 40 kV/mm)](image3)

![Fig. 11d: C18 space charge (wet 14 d, 25 kV/mm)](image4)

### 1.4 Conclusions

Three polymer nano-composites containing 10 wt. % of nano-silica functionalised with silanes of varying chain lengths were compared to a reference sample containing no nano-filler.

- TGA was used to verify the correct filler loading in the blends, a small amount of water was lost from the nano-composites on heating and the nano-filler tended to improve the thermal stability of the composites (i.e. increase the degradation temperature).
- Mass change measurements showed that each nano-filler composite has a significant water content when kept under ambient conditions, composites were capable of losing 0.5 % or
gaining 0.8 % of water content. A longer chain functionaliser tends to disrupt the diffusion of water to and from the nano-particle surfaces.

- DSC measurements showed that the composites had identical melting behaviour but reduced enthalpy, whilst crystallisation of the polymer was nucleated by the nano-filler. Functionaliser chain length did not appear to influence the melting or crystallisation behaviour.

- The unfilled blend contained a texture of banded spherulites, which was disrupted by the presence of the nano-filler. Whilst there were a large number of sub-micron particles present, each blend also contained micron sized aggregates. The morphology of each blend appeared to be independent of functionaliser chain length.

- Dielectric spectroscopy measurements showed increased permittivity and dielectric loss in the nano-composites relative to the reference material. The permittivity was increased and the loss peak shifted to higher frequencies with increased water content, due to increasing mobility of trapped water moieties. Functionaliser chain length only has a minor effect.

- Electrical conductivity measurements showed increased conductivity in the nano-composites relative to the reference material. Even small increases in water content were found to dramatically change the conductivity behaviour of the nano-composites and functionaliser chain length has only a minor influence. Measurements over several hours indicate that wet or dry conditioned samples can lose or gain water from the atmosphere during the tests.

- Electrical breakdown measurements showed poorer performance from the nano-composites relative to the reference material and were independent of functionaliser chain length. Drying could improve the breakdown performance whilst wetting always has a detrimental effect.

- Space charge measurements showed increased charge storage in the nano-composites relative to the reference material. Homocharge was exhibited by dry conditioned samples, wet conditioned samples exhibited heterocharge whilst in ambient samples little or no net charge was stored.

In summary, absorbed water appears to dominate over functionaliser chain length effects in controlling the electrical properties of nano-composites. Functionaliser chain length might have more of an impact on mechanical properties (which have not been measured here) or alternatively a much longer alkyl chain is required to markedly influence the dielectric properties.

1.5 Acknowledgement

We would like to thank Dr Alex Holt for carrying out the anhydrous functionalization described in this report.

1.6 References


2 The effects of water content on the dielectric properties of silica nano-composites

2.1 Introduction

Nano-composites, where a nano-scale inorganic filler is incorporated into a polymeric host material, provide a novel way of enhancing existing polymeric materials. Potential improvements in mechanical properties, reduced dielectric loss and electrical conductivity, reduced space charge accumulation and enhanced electrical breakdown strength have been reported [1]. Other publications have cited improved PD resistance [2], improved treeing resistance [3] and improved flashover performance [4]. In the field of high voltage distribution cables, polyethylene has largely superseded paper/oil since it is of relatively low cost, offers good electrical breakdown strength and low electrical losses, is recyclable and offers favourable mechanical properties. Given that nano-silica is cheap and is chemically inert, it is no surprise that polymer/nano-silica composites have been studied extensively in the literature.

Many published papers focus on epoxy based systems and generally report improved dielectric and breakdown performance for low filler loadings, due to the relatively good dispersion within the polar host material, but detrimental performance at high filler loadings which is blamed on particle aggregation. Nevertheless the absorption of very small amounts of water (up to ~0.16 %) in epoxy/silica nano-composites [5] leads to significant increases in both relative permittivity and dielectric loss and is hence problematical. Additional studies undertaken by Veena et. al. [6] indicated improvements in both mechanical properties and increased volume resistivity up to 10 % filler loading; thereafter the composites showed reduced performance due to particle agglomeration. Iyer et. al. [7] focussed on the AC breakdown performance of such systems and it was noted that the breakdown strength was hardly influenced by the presence of either nano or micro silica. Analogous micro-composites showed increased permittivity and dielectric loss at low frequencies whereas the dielectric properties of the nano-composites reflected those of the host polymer (i.e. nano-silica was neither beneficial nor detrimental). Additional studies undertaken by Castellon et. al. [8] indicated an increase in electrical conductivity in both nano and micro-composites. Whilst the presence of micro or nano-silica reduced space charge accumulation compared to neat epoxy, the smallest amount of trapped charge was noted in composites with 62.5 wt % of micro-filler and 2.5 wt % of nano-filler. More recent investigations [9] reported improved tensile strength for low nano-silica loadings (<3 %) as well as improved AC breakdown strength; however, both parameters were observed to degrade above 3 % filler loading, an effect that is again attributed to agglomeration of filler particles. Finally Kochetov et al. [10] reported a slight improvement in DC breakdown strength was possible in a well dispersed epoxy nano-composite of a low filler loading.

Achieving optimal particle dispersion and avoiding aggregation in polyethylene, which is less polar than epoxy, is much more difficult and hence the literature presents a more mixed picture. A comparison of the effects of micron and nano-scale fillers is provided by Roy et. al. [11], vinylsilsane treatment of the filler was used to improve the bonding between the filler particles and the host polymer and to reduce the number of surface hydroxyl groups. With careful drying, excellent particle dispersion was reported and in the nano-composites the AC breakdown strength and voltage endurance time was improved, whereas the addition of micro-silica reduced the breakdown
strength. In space charge measurements, heterocharge was observed in the composites but at a lower level than in the unfilled material, micro-composites tending to increase positive (i.e. ionic) charge injection relative to the host. A low frequency dielectric loss peak was noted in the micro-composites which was suppressed in the nano-composites. In summary this paper demonstrated that significant improvements in dielectric properties are possible in composites utilising vinylsilane treated nano-silica. This comes about through improvements in (a), the chemical bonding between filler and host polymer and (b), improvements in the dielectric properties of the interfaces (i.e. through removal of surface hydroxyl groups combined with careful drying to remove adsorbed water). A later paper by the same authors [12] indicated that the type of surface treatment agent has only a minor role in determining the electrical and dielectric properties of the composite systems. It was hinted, however, that certain types of (polar) modifiers can introduce additional deep traps which can cause additional dielectric loss peaks to appear resulting in subtle changes in the electrical breakdown strength.

Nano-silica composites employing un-functionalised silica were compared to those containing silica functionalised with trimethoxy(propyl)silane by Lau et al. [13, 14] and the effect of water absorption was also considered. Morphological studies [13] revealed good dispersion at low filler loadings but aggregation at high filler loadings and, overall, slightly improved dispersion was reported for composites utilising the functionalised silica. Starting from dried samples, water uptake measurements showed a maximum water uptake of 1.6 % and 0.7 % in nano-composites containing un-functionalised and functionalised silica respectively (10 % filler loading). Dielectric properties were also found to be sensitive to water content, water uptake resulted in a higher permittivity and a shift in dielectric loss to higher frequencies. Accumulated homocharge was exaggerated with nano-filler present (more so in composites containing un-functionalised silica) [14] and the DC breakdown strength was reduced in the nano-composites compared to the reference material, an effect that was attributed to particle agglomeration. Hui et al. [15] also considered water absorption using XLPE as host, up to 1.5 % of absorbed water was reported regardless of the state of functionalization which contradicts some previous studies [13]. Whilst dry samples did not exhibit much increase in dielectric loss, wet samples showed a mid-frequency relaxation feature. Space charge behaviour switched from homocharge to heterocharge in moving from dried to wet samples and the AC breakdown strength was reduced, the results are dealt with in terms of a water shell model similar to the multi-core model presented by Tanaka [1]. Finally Zhang [16] presented improved DC breakdown strength in a series of nano-silica/XLPE nano-composites which showed good dispersion when functionalised.

A variety of other matrix polymers were also considered in the literature but these also provide a similarly mixed picture. Polyester based nano-composites were considered by Messiah et al. [17]; an increase in permittivity at low frequencies (<300 Hz) was observed in the nano-composites (which was attributed to an increase of ion mobility and the Maxwell-Wagner effect) along with an additional mid-frequency loss feature (~10^4 Hz) which was pronounced for filler loadings > 6 % where particle aggregation was observed. The effect of varying the polymer matrix has been studied by Grabowski et al. [18] and colloidal nano-silica was used to aid particle dispersion. It was noted that the permittivity and dielectric loss both increased in the nano-composites relative to the unfilled matrix polymer. Interestingly in PMMA and polyimide which have a high intrinsic breakdown strength, adding nano-silica resulted in a fall of breakdown strength. Conversely in materials with a low intrinsic breakdown strength (poly-4-vinylpyridine and
polystyrene) an increased breakdown strength was noted. Thus, well dispersed nano-silica can be used to enhance the performance of poorly performing polymers. Polypropylene systems with impact modifier (SEBS) and maleic anhydride grafted PP as compatibiliser were studied by Panaitescu et. al. [19]. In DSC measurements the crystallinity of the PP phase was reduced by SEBS and the nano-silica was found to have a nucleating effect. Whilst the presence of SEBS manifested a relaxation peak at ~1 Hz (attributed to α relaxation and interfacial polarisation), addition of the nano-silica led to a broad dispersion at 100 Hz, which was attributed to water absorbed at the nano-silica/polymer interfaces; this relaxation was shifted to higher frequencies at a higher temperature due to increased mobility. Results from polystyrene systems were considered by Praeger et. al. [20, 21] and tend to agree with Lau et. al. [13, 14], namely, that the introduction of nano-silica results in increased dielectric loss, especially in samples that had been exposed to water [20]. DC breakdown performance was also noted to fall in the nano-composites relative to the host [21].

Overall, whilst the situation in epoxy based systems is fairly clear and improvements in breakdown strength are possible provided the filler loading is not too high, contradictory results are reported for thermoplastic hosts. The authors propose that the origins of such variability are twofold. Firstly, there are variations in the level of particle dispersion and unwanted particle aggregation - where corroborating morphological data were provided, poor particle dispersion always resulted in reduced breakdown strength [14, 21, 22], particularly at high filler loadings [4, 9] whereas much better dispersion (obtained for example, from sol-gel or masterbatch compounding) resulted in improved breakdown performance [10, 11, 16] or no change [7]. Secondly, variations in water content - the few studies that do exist indicate that water absorption always leads to reduced breakdown strength [15, 22], increased dielectric loss [5, 13, 15, 22] and a switch in the space charge behaviour from homocharge to heterocharge [15]. The effect of vinylsilane functionalization is less clear with one study reporting a dramatic reduction in absorbed water with functionalization [13] and another study showing it has little or no effect [15]. However the majority of studies report an improvement in dielectric properties in functionalised nano-composites [11-13, 15]. Clearly, it is important to eliminate water absorption either through appropriate drying or through the reduction of surface hydroxyl groups that can bind water molecules [1, 2, 15].

In theory the use of silicon nitride in place of silica should provide a novel alternative method of reducing the susceptibility of nano-composites to absorbed water by reducing the number of surface hydroxyl groups [23]. Additionally silicon nitride provides composites with improved thermal conductivity [24] which could be advantageous in terms of heat removal from a cable system. Only one study of their breakdown behaviour exists to our knowledge [25] and this indicates that promising increases in breakdown strength are possible. Despite this, to our knowledge, no comparative study of the dielectric properties of silica and silicon nitride has been carried out - this is the purpose of the current study.

2.2 Experimental

2.2.1 Materials and blending

Nano-silica (quoted particle size 10-20 nm) and silicon nitride (spherical ~50 nm) were obtained from Sigma Aldrich and were used as supplied. High density polyethylene (HDPE) was obtained from BP Chemicals under their trade name Rigidex HD5813EA whilst low density polyethylene (LDPE) was obtained from ExxonMobil Chemicals under their trade name LD100BW. A
blend of 20 % HDPE and 80 % LDPE was prepared in advance by melt mixing at 160 °C using a Polylab twin screw mixer at a mixing speed of 40/min (measured torque 8-12 Nm) and mixing for 20 minutes. The blend was removed, cooled and pressed into 2 mm thickness sheets at 160 °C using a laboratory hydraulic press to remove included air bubbles. Differential scanning calorimetry (DSC) was then used to verify blend uniformity.

The traditional solvent blending method for nano-composites utilizes xylene as solvent and methanol as non-solvent [13, 22]. Due to the non-polar nature of xylene it is difficult to obtain a stable solution of nano-filler even after sonication and there are concerns that precipitation into methanol (a polar solvent) might introduce unwanted agglomeration of nano-filler prior to solidification of the polymer. To overcome these difficulties a modified solvent incorporation route was used here. 5 g of the pre-prepared polymer blend was dissolved in 50 ml of boiling xylene until a transparent solution was obtained. In the meantime either 0.25 or 0.5 g of the required nano-powder was dispersed in 10 ml of isopropyl alcohol (IPA). This solution was sonicated for 5 minutes using a Hielscher UP200S probe sonicator, stirred and was then sonicated for a further 5 minutes, resulting in a stable (>3 h) suspension. The xylene/polymer solution was removed from the heat, allowed to gel slightly and the nano-powder/IPA solution was immediately added; the small amount of IPA used here does not induce precipitation of the polymer. Vigorous stirring was maintained until the mixture had thickened to a waxy solid. This was then dried for 24 h in a fume cupboard, cut into ~5 mm cubes and then left a further 24 h to dry in the fume cupboard. It was then pressed into 2 mm thickness sheets at 160 °C, in order to remove any solvent residues and included air bubbles. A total of four blends, two using nano-silica and two using silicon nitride were prepared as in Table 6. These were designated along with a control sample (no nano-filler) according to their nominal filler content.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Base resin</th>
<th>Nano-filler used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>20 % HDPE/LDPE</td>
<td>-</td>
</tr>
<tr>
<td>SiN05</td>
<td>20 % HDPE/LDPE</td>
<td>5 % silicon nitride (Si₃N₄)</td>
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</tr>
<tr>
<td>SiO10</td>
<td>20 % HDPE/LDPE</td>
<td>10 % silica (SiO₂)</td>
</tr>
</tbody>
</table>

Table 6: Blends used in these investigations

2.2.2 Sample preparation and conditioning

Samples for characterisation were prepared in the form of 0.2 mm and 0.1 mm thickness sheets using a hydraulic press and appropriate Melinex spacers (160 °C and 3 ton load). All samples were crystallised from the melt in oil baths maintained at 115 °C for 1 h prior to quenching in water [13, 14]. Following sample preparation, specimens were then conditioned to vary their water content as follows: “ambient” samples were maintained under ambient conditions in an air conditioned environment (19 ± 2 °C, 55 - 80 % RH) for at least 14 d prior to testing; “dry” samples were vacuum dried at room temperature for periods of up to 14 d whilst “wet” samples were immersed in water for periods of up to 14 d.

2.2.3 Physical characterisation

Thermogravimetric analysis (TGA) was performed by heating 5 mg samples using a Perkin Elmer Pyris 1 TGA at a rate of 20 K/min in air. In order to determine the extent of water gain or loss during conditioning, the mass of the samples was recorded at regular intervals to an accuracy of
Effect of nano-particulate additives on phase dispersion
Top and Tail Grand Challenge Work Package 1.3.1 Report

±0.0001 g (i.e. ± 0.02 % on typical 0.5 g samples). Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC-7 which was calibrated using high purity indium. Melting scans were obtained by heating at 10 K/min whereas crystallisation behaviour was examined by cooling at 5 K/min from the melt.

Optical microscopy was performed on 0.1 mm thickness samples using a Leitz Aristomet universal microscope between crossed polarisers. Samples for scanning electron microscopy were etched for 4 h in a solution of 1 % potassium permanganate in an acid mixture (5:2:1 of sulphuric, phosphoric acids and water respectively) according to published procedures [26]. Samples were then rinsed twice with distilled water and once with acetone and left to dry overnight. Samples were then mounted onto aluminium SEM stubs, gold coated and were then examined at 15 kV in a JEOL JSM6500F high resolution FEG-SEM.

Filler samples for energy dispersive X-ray studies (EDX) were mounted using double sided carbon tape on carbon SEM stubs. They were then examined in a Philips XL30 ESEM operated at 10 kV. At least four spectra were recorded of each powder over a minimum 50 µm² area and averaged, taking care to ensure that they did not contain any areas where the carbon tape was exposed. The Kα peaks of Si (1.74 keV), O (0.52 keV), N (0.39 keV) and C (0.28 keV) were recorded and peak area analysis was used to determine the relative concentrations.

2.2.4 Electrical characterisation

Dielectric spectroscopy was performed on 0.2 mm thickness samples incorporating gold coated electrodes using a parallel plate test cell with a guard ring (diameter of inner electrode 30 mm). Measurements of permittivity and dielectric loss were performed using a Solartron 1296 dielectric interface linked to a Schlumberger SI 1260 impedance-gain-phase analyzer. A 1 Vrms AC signal was applied over a frequency range from 0.1 Hz to 1 MHz and all measurements were performed at room temperature.

Measurements of electrical conductivity were performed at room temperature on the same (coated) samples placed between opposing 20 mm diameter polished gold electrodes. A stepped voltage (100 V to 6 kV in steps of 100 V) was applied; waiting 10 s after application of the voltage before measuring the current to allow any capacitive currents to dissipate.

DC breakdown testing was carried out on 0.1 mm thickness samples placed between opposing 6.3 mm ball bearings immersed in silicone fluid (Dow Corning 200/20CS). An increasing DC voltage (100 V/s) was applied to this arrangement until failure occurred. For each composite system, 20 such tests were carried out, each at a separate location, the ball bearings being replaced after every 10 tests. The resulting data were then analysed using Weibull statistics.

2.3 Results

2.3.1 Thermogravimetric analysis (TGA)

Fig. 12a shows the TGA data. The unfilled control sample starts to degrade at 300 °C, reaching 50 % of its initial mass at 410 °C (T₀.5 in Table 7) and the sample then reaches zero mass at 570 °C. Whilst the silicon nitride samples do not show any initial loss of mass on heating to 250 °C, both silica samples show ~1 % of mass loss (arrowed, Fig. 12a, Minit in Table 7) above 100 °C, which suggests that the silicon nitride is dry when stored under ambient conditions but that the silica
includes a significant absorbed water content of ~10 % . Both SiN05 and SiO05 reach 50 % of their initial mass at ~420 °C whereas SiN10 and SiO10 reach the same point at ~440 °C, thus the addition of either nano-filler, particularly silicon nitride, improves the thermal stability of the composite. The final residue content at 570 °C (where the polymer is assumed to be completely degraded) ($R_{570}$ in Table 7) is close to the expected values.

<table>
<thead>
<tr>
<th>TGA data</th>
<th>Water absorption</th>
<th>DSC data</th>
</tr>
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<tbody>
<tr>
<td>$M_{int}$ (%)</td>
<td>$T_{0.5}$ (°C)</td>
<td>$R_{570}$ (%)</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>411</td>
</tr>
<tr>
<td>SiN05</td>
<td>-</td>
<td>420</td>
</tr>
<tr>
<td>SiN10</td>
<td>-</td>
<td>454</td>
</tr>
<tr>
<td>SiO05</td>
<td>0.8</td>
<td>424</td>
</tr>
<tr>
<td>SiO10</td>
<td>1.2</td>
<td>441</td>
</tr>
</tbody>
</table>

Table 7: Numerical data from TGA, water absorption measurements and DSC tests

### Water absorption measurements

Fig. 12b shows the measured water content relative to ambient with exponential fitted lines. The control sample is unaffected by conditioning whereas the various nano-composites approach constant mass after 7 days of conditioning time. As anticipated from Fig. 12a, the nitride based nano-composites do not lose much water when dried ~0.02 % (Table 7) but are capable of gaining significant water, up to 0.7 % when immersed. This confirms, in agreement with TGA data, that silicon nitride is dry when stored under ambient conditions but still has appreciable levels of surface hydroxyl groups which can bind available water molecules [23]. When wet conditioned, the silica based nano-composites are capable of losing or gaining about the same amount of water as the respective silicon nitride based nano-composites, ~0.3 and ~0.6 % for SiO05 and SiO10 respectively, confirming that they have some intermediate water content when stored under ambient conditions. The total change in water content from dry to wet for 10 % silica loading is ~1.1 % which is comparable to other published data [13, 15, 22]. No comparable data exist for the nitride nano-composites.
2.3.3 EDX measurements

Results of EDX characterisation of the silica and silicon nitride powders are shown in Table 8; four measurements were made from different areas of the same sample and average values and uncertainties were calculated. In all cases, the background carbon contribution was < 0.1 % so can be considered negligible. Silica (SiO$_2$) contains close to the expected 1:2 ratio of silicon to oxygen and negligible nitrogen content. Silicon nitride (Si$_3$N$_4$) contains, within the experimental uncertainties, a 1:1 ratio of silicon to nitrogen and not the expected 3:4 ratio. Instead the powder contains ~10 % oxygen in place of nitrogen which confirms the presence of a significant amount of surface hydroxyl groups [23].

<table>
<thead>
<tr>
<th>Powder</th>
<th>Silicon (%)</th>
<th>Oxygen (%)</th>
<th>Nitrogen (%)</th>
<th>Carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>39 ± 2</td>
<td>61 ± 2</td>
<td>0.3 ± 0.2</td>
<td>&lt; 0.1 %</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>46 ± 2</td>
<td>11 ± 2</td>
<td>43 ± 3</td>
<td>&lt; 0.1 %</td>
</tr>
</tbody>
</table>

Table 8: Results from EDX analysis of the nano-fillers

2.3.4 Differential scanning calorimetry (DSC)

Fig. 13a shows the DSC melting behaviour, each material displays two melting peaks as expected [22] (T$_m$ in Table 7) at 105 and 124 °C (LDPE and HDPE respectively), the total enthalpy is ~110 J/g (ΔH in Table 7) for the control sample falling somewhat for the nano-composites to ~100 J/g as anticipated due to the proportion of included filler. On cooling at 5 K/min (Fig. 13b) the control sample displays two crystallisation (T$_c$ in Table 7) peaks at 110 and 95 °C (HDPE and LDPE respectively). Whilst the lower (LDPE) peak is located at the same temperature in the nano-composites, crystallisation of the HDPE occurs somewhat earlier at ~112 °C, thus both nano-fillers are nucleating the more crystallisable HDPE component of the blends [19, 22, 27].

![Fig. 13a: DSC melting behaviour](image1.png)
![Fig. 13b: DSC crystallisation behaviour](image2.png)

2.3.5 Optical microscopy

Fig. 14 shows a series of optical micrographs. The control sample shows a morphology composed of ~10 µm diameter spherulites (Fig. 14a), whereas SiN05 and SiN10 (Figs. 14b and 14c) both show much finer, granular textures indicative of enhanced nucleation. Contrasting SiO05 and SiO10 (Figs. 14d and 14e) it is obvious that SiO10 has a slightly more granular texture than SiO05, both however are more granular than the control sample. The optical microscopy therefore supports the DSC findings, that the nano-filler is nucleating the polymer.

![Fig. 14: Optical microscopy](image3.png)
2.3.6 Scanning electron microscopy (SEM)

SEM micrographs are shown in Fig. 15. The control sample (Fig. 15a) shows a morphology of 10-20 μm diameter banded spherulites, as expected for crystallisation under these conditions [13, 14, 22]. In contrast, each silicon nitride composite (Figs. 15b and 15c) shows a disrupted polymeric
texture containing a uniform distribution of particles the majority of which are composed of small clusters of the expected 50 nm diameter particles. Not surprisingly SiN10 (Fig. 15c) shows a higher particle density. Whilst both silica composites (Figs 15d and 15e) show a uniform distribution of nano-filler within the polymeric matrix, and a large number of the required sub-micron sized particles, aggregates of up to 10 µm nevertheless persist in these materials. Other studies where nano-silica is used, indicate similar aggregations even at low filler loadings so such aggregations are not entirely unexpected [13, 14, 22]. Comparison with a functionalised analogue [22] reveals very little difference in the observed level of particle aggregation and an examination of the nano-silica powder directly by SEM by the authors revealed that such aggregations are present; they are not therefore introduced during blending or completely removed through sonication. In contrast similar SEM studies on the silicon nitride powder indicate a uniform dispersion of ~1 µm clusters so in this case sonication is quite effective at breaking these up.

### 2.3.7 Dielectric spectroscopy

*Ambient conditions:* Fig. 16 provides a comparison of the relative permittivity and dielectric loss of ambient conditioned samples. The control sample has a permittivity of 2.5 and a maximum dielectric loss of $5 \times 10^{-3}$ (Table 9) and therefore it can be considered as a low loss material. In
contrast, both silicon nitride nano-composites show an uplift of relative permittivity and dielectric loss at low frequencies and therefore such effects can be directly attributed to the presence of the nano-particles. Although comparative dielectric loss data for very low frequencies is not provided, the behaviour exhibited here seems to be consistent with published work [23]. Low frequency relaxation processes are usually attributed to interfacial polarisation and the Maxwell-Wagner effect [15, 17] – i.e. dipoles due to tightly bound water clusters at the nano-particle interfaces are only free to rotate at relatively low applied frequencies [1, 2, 15]. In contrast, the two silica nano-composites display a much broader relaxation feature, with two distinct peaks, one at ~10 Hz and a stronger relaxation at ~2 kHz. Such broad relaxation features have been widely reported in silica nano-composites [5, 8, 11-13, 15, 17-20, 22] and are typically attributed to water absorbed at the nano-particle interfaces in loosely bound clusters – these create dipoles that are then able to rotate at much higher applied frequencies. The maximum dielectric loss (0.09) and centre frequency (2.5 kHz) are consistent with other work on silica nano-composites [22] (see also Fig. 5).
to a maximum value of ~4.3 (Fig. 17a) and the dielectric loss peak (maximum 0.07) shifts to higher frequencies with increasing conditioning time (Fig. 17b). This shift in relaxation peak to higher frequencies with increasing water content has been widely reported [13, 15, 22] and indicates an increasing mobility of water moieties, the dipoles of which are capable of rotating with the field at a progressively higher frequency as the composite becomes more saturated with water.

Figs. 18a and 18b show the data for SiN10 plotted on the same scales; drying for > 3 days removes much of the contribution towards permittivity (Fig. 18a), however significant dielectric loss remains after drying for 7 d and is identical after 14 d (Fig. 18b) which indicates either that the hydration layer cannot be completely removed by vacuum drying [15] or that such features arise solely as a result of the nano-particle addition (i.e. Maxwell Wagner interfacial polarisation). Log-log plots are provided in Figs. 18c and 18d and illustrate the effects of wetting where the relative permittivity can increase to very high values (Fig. 18c) as can the dielectric loss (Fig. 18d). Compared to ambient conditioned samples which display a low frequency relaxation peak (labelled “a”), the addition of water introduces a low frequency region of gradient -1 (labelled “b”) indicative of electrical conductivity which may be indicative of the formation of a percolating network [15].
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Fig. 18c: Permittivity of SiN10 (Log-log)  Fig. 18d: Dielectric loss of SiN10 (Log-log)

Numerical model: The volume filler fraction of SiN10 is 3% (assuming a filler density of 3.44 g/cm³ and a polymer density of 0.95 g/cm³) which is well below the threshold for percolation for conducting spheres in a non-conducting matrix [28]. However numerical modelling calculations by other authors [15] have shown that it is possible to obtain the required percolating network in a system composed of 50 nm diameter particles by introducing water shells of ~60 nm thickness. To confirm that water shells are responsible for the percolation behaviour observed in SiN10 and to verify that no percolation is observed in SiN05, a similar numerical model was implemented in MATLAB by the authors. A random distribution of the required number of 50 nm diameter nanoparticles (calculated from the filler fraction) were assumed which were not permitted to overlap. These were then each surrounded by a water shell which was permitted to overlap with adjacent water shells. Assuming 2% free volume [29] and a total water content of 0.4 and 0.7 mass % (see Table 7) for SiN05 and SiN10 respectively, the model was run and the results are shown in Figure 19 for a simulation within a cube of side 0.75 µm. In the model of SiN05 (Fig. 19a) percolation was never achieved whilst in SiN10 (Fig. 19b) percolation was always achieved. In both cases the required water shells were 50 nm thick which is consistent with other authors [15].

Fig. 19a: Modelling results for SiN05, particles in red, water shells in blue; no percolation.  Fig. 19b: Modelling results for SiN10, the percolating pathway is shown in green.
Effects of conditioning II: Fig. 20 shows permittivity and dielectric loss plots for SiO05 and SiO10 as a function of conditioning. The behaviour with increasing water content is consistent with analogous published data for silica nano-composites [13, 15, 22] and indicates an increasing mobility of included water moieties, the dipoles of which are capable of rotating with the field at a progressively higher frequency as the nano-composite becomes more saturated with water. In this case a percolating network is not formed, due most likely, to extensive particle aggregation (see Fig. 15e); aggregation allows water shells to overlap hence reducing the volume fraction occupied by the interphase region to below the limit required for percolation [15, 28]. Unlike the nitrides, where it is possible to largely remove the low frequency relaxation through drying, here, it is not possible to completely remove this relaxation and hence there remains a significant hydration layer in such samples which is not possible to remove by vacuum drying.

2.3.8 Electrical conductivity

Fig. 21a shows electrical conductivity values measured as a function of field after ambient conditioning, all of the nano-composites show increased conductivity relative to the control sample (Table 9) as observed in other studies [17, 22]. The oxides and nitrides show very different field
dependencies, the conductivity of the nitrides is largely independent of applied field whereas the conductivity of the oxides strongly increases with the applied field. A strong field dependence of conductivity in silicon oxide/epoxy composites has been reported elsewhere and is consistent with a field assisted Schottky injection process [8] and we would therefore suggest that a similar process is operative here, perhaps mediated by included water ions which provide an additional ionic contribution to the steady state conduction current. The situation in the silicon nitride systems is less clear although it is suggested that due to the scarcity of available water (see Table 7) that the conduction current is mainly electronic in nature and hence may be space charge rather than field limited [8]; to our knowledge no corroborating data for silicon nitride systems exists in the literature so this assertion remains largely speculative at this point. Nevertheless, the data suggest that very different conduction mechanisms are operative in the oxide and nitride based nano-composites. A comparison of the current data to those obtained from functionalised analogues [22] (see Fig. 8a) indicates a significantly reduced conductivity in the current systems, which suggests that the presence of the functionaliser may be having a detrimental effect on the electrical conductivity. Again no other corroborating data are available in the literature.

Dry conditioning reduces the conductivity (Fig. 21b) to values approaching those of the control sample, with only SiO10 showing any measurable increase. It is suggested that this increase is either due to the hydration layer [15], or is due to the addition of the nano-filler (i.e. Maxwell Wagner interfacial polarisation).

Wet conditioning increases the electrical conductivity (Fig. 21c); the conductivity of the oxide based nano-composites at any given field and the same filler loading is always higher than the nitride based nano-composites which is in accordance with a greater degree of absorbed water (Table 7); the increased conductivity presumably comes about through an ionic (i.e. water) contribution. As noted above the oxide based nano-composites show a stronger field dependence than the nitride based nano-composites suggesting very different conduction processes are operative despite the additional contribution due to absorbed water. SiN10 has a conductivity which is close to the maximum measurable value and the lack of any obvious field dependence indicates that the conduction current is entirely carried by free water ions, this assertion is consistent with the notion of a percolating network of water shells discussed previously.

2.3.9 DC breakdown

Fig. 22 shows Weibull plots for ambient, dry and wet conditioning and Table 10 contains numerical data. The breakdown strength of the control sample is consistent with other studies given the uncertainties (± 20 kV/mm) associated with the measurements at ~420 kV/mm. The nitride based nano-composites continue to give excellent performance (>390 kV/mm) even when exposed to ambient conditions, whilst the silica based systems give reduced performance ~200 kV/mm (Fig. 22a). It is proposed that this difference is due to the ~0.5 % of included water in the latter nano-composites which is largely eliminated in the former nano-composites (Table 7). Compared to the functionalised systems studied previously [14, 22], the breakdown strength of the current silica based nano-composites is significantly higher. Since the water contents are broadly comparable, we propose this is due to better particle dispersion and reduced particle aggregation associated with the modified blending route utilised in the current work.
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Fig. 21a: Conductivity, ambient conditioning
Fig. 21b: Conductivity, dry (14 d) conditioning
Fig. 21c: Conductivity, wet (14 d) conditions

Fig. 22a: Weibull plot, ambient conditioning
Fig. 22b: Weibull plot, dry (14 d) conditioning
Fig. 22c: Weibull plot, wet (14 d) conditioning

Drying the samples provides breakdown strengths comparable to the control sample (Fig. 22b) in three of the four nano-composites and a slight increase in SiN10 to ~450 kV/mm; although
not as high as the reported increase in other better dispersed systems [24] the result is still very promising.

Wetting as expected (Fig. 22c) reduces the breakdown strength of all four nano-composites in line with expectations [15, 22], in this case even the nitride based nano-composites are able to absorb water (Table 7), nevertheless even under such extreme conditions the nitride nano-composites still provide greater breakdown strengths than the silica nano-composites (Table 10).

<table>
<thead>
<tr>
<th></th>
<th>Dry (14 d) conditioned</th>
<th>Ambient conditioned</th>
<th>Wet (14 d) conditioned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E₀</td>
<td>β</td>
<td>E₀</td>
</tr>
<tr>
<td>Control</td>
<td>425</td>
<td>8.0</td>
<td>416</td>
</tr>
<tr>
<td>SiN05</td>
<td>431</td>
<td>6.7</td>
<td>409</td>
</tr>
<tr>
<td>SiN10</td>
<td>450</td>
<td>8.5</td>
<td>389</td>
</tr>
<tr>
<td>SiO05</td>
<td>431</td>
<td>6.7</td>
<td>228</td>
</tr>
<tr>
<td>SiO10</td>
<td>414</td>
<td>7.3</td>
<td>194</td>
</tr>
</tbody>
</table>

Table 10: Measured DC breakdown values and shape parameters

2.4 Conclusions

Four nano-composites, two containing silica and two containing silicon nitride were compared to a control sample containing no nano-filler. The effects of conditioning (dry, ambient or wet) were also explored.

- TGA data showed filler contents in line with expectations and an initial loss of some 1 % of water in the silica nano-composites.
- Direct measurements of water uptake and loss indicated that the silicon nitride nano-composites were dry under ambient conditions (but are capable of absorbing water when wetted) and that the silica nano-composites have some intermediate water content.
- DSC measurements show identical melting behaviour, but a slight nucleating effect of the nano-filler which was confirmed by microscopy.
- In SEM observations, silicon nitride provided a well dispersed system free of obvious aggregations, whereas the silica nano-composites contained some large aggregates.
- Dielectric spectroscopy showed a low frequency dispersion in the silicon nitride composites and a broad mid-frequency relaxation in the silica nano-composites. The relaxation shifted to higher frequencies with water uptake, indicating increased mobility of included water moieties. It was possible largely to suppress the (unwanted) relaxation by drying the silicon nitride composites but some loss always remained in the silica composites. A nano-composite containing 10 wt % of silicon nitride was observed to contain a percolating network which is consistent with the various theoretical water shell models.
- Electrical conductivity was always higher in the nano-composites relative to the unfilled polymer. Silicon nitride samples showed a higher conductivity at low fields whilst silica showed a higher conductivity at high fields. Wetting the samples increased the conductivity whereas drying the samples reduced the conductivity.
- Under ambient conditions, silicon nitride composites offered a DC breakdown strength comparable to the unfilled host, whereas both silica systems showed reduced performance. Drying increased the breakdown strengths of all four composites to values approaching or exceeding those of the unfilled host material, whereas wetting always had a detrimental effect.
In summary, the use of a nitride in place of an oxide nano-filler significantly improves the dielectric performance of the nano-composite and reduces the sensitivity of the various dielectric parameters to absorbed water from the environment. The improved performance presumably comes about through a reduced water content in the nitrides as opposed to the oxides when stored under ambient conditions. Nano-composites based on nitride rather than oxide fillers therefore have significant potential in HVDC cable systems. It is also recommended that the thermal conductivity of the various nano-composites used here be measured in order to fully appreciate the benefits of using a silicon nitride filler.

2.5 References

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