Phase dispersion of filler and its influence on dielectric properties

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/
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. 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.

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.
Phase Dispersion of Filler and its Effect/Influence on Properties
Top and Tail Grand Challenge Work Package 1.3.1 Report

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1 Introduction

1.1 Nanotechnology in HVDC applications
Nanotechnology has already provided significant gains in the mechanical performance of materials and has found widespread acceptance in industry[1]. In particular, nanofillers enable the production of higher modulus materials with comparatively lower filler loading than is possible for fibre reinforced systems[2]. The potential exists for similar development in the field of electrical properties, but as yet, this potential has not been realised.

The introduction of nanoscale fillers into polymers adds considerably to the complexity of the system[3]. Additional molecular interactions are possible and conformational constraint and/or alignment of polymer chains near to the nanoparticles have been theorised to produce an interface layer (the interphase) with properties that differ significantly from those of the matrix and filler materials[4]. The nature of the interactions occurring in the interphase and the relationships between these interactions and the externally measured electrical properties of the nanocomposite are, however, currently poorly understood. Our lack of knowledge about the fundamental processes at play leads to inadequately controlled production of nanocomposites and experimental results that can be highly variable or even contradictory.

The aim of the work presented here is to study the relationship between the externally measured electrical properties and the state of the nanoparticles within the nanocomposite. It is hoped that this study will lead to further insight into the underlying physics that occurs at the interface between the nanofillers and the polymer matrix, thereby allowing optimised materials to be designed and produced reliably.

1.2 Material considerations for HVDC
Historically, high voltage cable links have predominantly been operated with alternating current. The desire to develop international energy markets and power generation in remote locations (i.e. offshore wind farms) produces a continual demand for higher power capacity and lower loss over long distance cable links[5, 6]. Emerging technologies such as Voltage Source Converters[7] allow these demands to be met by the use of HVDC cables, where losses associated with capacitive charging of the cable upon each AC cycle are eliminated.

In AC systems the continual reversal of polarity effectively prevents the accumulation of space charge within the insulating material. The situation is very different in HVDC applications where changes in the applied voltage cause accumulation and/or redistributions of space charge that take place over timescales of several hours[8]. The presence of space charge will modify the electric field within the insulating material and can cause a reduction in the apparent breakdown strength of the material which, in turn, mandates the use of more conservative cable ratings.

Space charge accumulation is therefore largely neglected in HVAC applications but may be an important consideration in HVDC cable technology. As a result, material systems that are tried and tested in AC cables may be inappropriate for HVDC use. A prime example of this is XLPE, which offers excellent properties under AC but can accumulate significant heterocharge under DC poling[9]. The accumulation of heterocharge increases the electric stress near to the electrodes
during continuous operation and can produce a large spike in electric stress in the event of cable polarity reversal.

In general the intrinsic breakdown strength of insulating materials is maximised by the use of high purity polymers. The addition of micro or nanoparticle fillers typically introduces defects which lower the breakdown strength (for example, TiO$_2$ and Al$_2$O$_3$ in epoxy$^{[10, 11]}$). For certain filler types (boron nitride in epoxy$^{[12]}$) and particularly when the particles are used with a coupling agent (BaTiO$_3$ in epoxy$^{[13]}$, SiO$_2$ in XLPE$^{[14, 15]}$) enhancement to breakdown strength can be observed.

For some DC applications the advantage of having high intrinsic breakdown strength may be outweighed by a requirement either to mitigate space charge accumulation or to improve thermal conductivity. Under these circumstances a cable produced from a material with relatively high charge mobility (for example by using conducting nanofillers) could potentially be operated at higher voltages than one made from unfilled polymer (albeit with increased conduction losses). Similarly, a cable with high thermal conductivity may be able to operate at higher current and overall power levels, despite having a lower voltage rating$^{[16]}$.

The above examples serve to illustrate that new materials may be required in order to get the maximum benefit from HVDC cable systems and that nanotechnology provides a possible means of tailoring material properties to this new regime of HVDC.

1.3 Nanocomposite fundamentals.

One of the most fundamental and interesting concepts of nanocomposites is that their properties cannot be accounted for as a simple linear combination of the properties of the matrix and the nanoparticles. This fact is typically explained by the postulated existence of a layer of interphase material surrounding the nanoparticles in which the properties of the matrix are modified by proximity to the nanoparticle$^{[17]}$. This is a powerful concept because it provides an explanation for the observed variation in material properties as a function of filler particle size. For the same quantity of filler material; as filler particle size is reduced the surface area (and hence the interphase volume) is dramatically increased (see Figure 1).

![Interphase Volume vs Filler Particle Size](image)

**Figure 1:** Interphase volume as a function of nanoparticle size; calculated for a filler loading of 10 % and for three different assumed interphase thickness values.
Additional complexity in the behaviour of nanocomposites is expected to arise from the fact that (depending upon the effective thickness of the interphase zone) it may be possible to saturate the volume of interphase material at relatively low filler loadings. For illustration Figure 2 shows some simulated distributions of 20 nm particles at a 5% (by weight) loading with shaded interphase zones of differing thickness.

Figure 2: Simulated nanoparticle distributions (5% by weight, silica in polystyrene) with interphase volume shown for three different values of the interphase layer thickness.

Figure 3 shows the results of a simple 2D Monte Carlo simulation which demonstrates the saturation of interphase volume effect. While the details of the simulation are outside of the scope of this report, it is nevertheless clear that the amount of interphase material rapidly increases with filler loading until very little unmodified matrix remains. Further addition of nanoparticles (increase in filler loading) tends to decrease the amount of interphase material.

Figure 3: Results from a 2D Monte Carlo simulation of a nanocomposite. The image plots (above) show the condition of the nanocomposite schematically at the three filler loadings indicated by markers on the line plot (left). In this case the interphase saturates at approximately 25% loading by volume.
2 General methods

2.1 Material selection

The aim of this study is to correlate externally measured properties of a nanocomposite with the configuration of its filler particles; in particular, their agglomeration state. It was decided that direct measurements of the particle dispersal within the nanocomposite would be made by Scanning Electron Microscope (SEM) analysis. The sub-surface structure of the nanocomposite samples would be revealed using the permanganic etching technique described in Section 5.1.

In order to get the clearest possible information from the SEM analysis, an amorphous matrix material was required. This eliminates the possibility that lamellae, spherulites or other crystalline structures would add unwanted complexity to the SEM images and reduce the visibility of the filler particles. Simultaneously, the use of a relatively simple, amorphous matrix material removes possible sources of variability in the measured properties that might, for example, occur if different quenching rates were used.

Cross-linked polyethylene (XLPE) is one of the most widely used forms of cable insulation; however, this and other forms of PE were discounted from this study because of their propensity to crystallise. Similarly epoxies, which are frequently used for “potting”, could not be used in this study because they are incompatible with the permanganic etching technique and they add unwanted complexity due to the curing reaction.

Despite being an unlikely candidate for cable insulation, polystyrene is both amorphous and amenable to permanganic etching; for these reasons it was chosen as the matrix material for this study. Silica nanoparticles were chosen because of their ready availability and widespread use. Polystyrene/silica nanocomposites therefore provide a simple model system which should allow investigation of the underlying action of the nanoparticles with minimal extraneous complexity. Throughout this work, polystyrene with an average molecular mass of 192000 g.mol\(^{-1}\) was used (430102 Aldrich).

Nanocomposite samples were produced (according to the procedure described in Section 2.2) using four different types of nanosilica filler (all supplied by Sigma Aldrich). Details of the nanofillers used are provided below in Table I. The primary particles of all systems are comparable in size but, while M and Q are claimed to exist as nanoparticles, S1 and S2 are aggregated, albeit, still on a scale comparable with nanoscopic dimensions (i.e. ~100 nm).

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Supplier Data</th>
</tr>
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<tbody>
<tr>
<td><strong>M</strong></td>
<td>Supplier #: 637246</td>
</tr>
<tr>
<td><strong>Q</strong></td>
<td>Supplier #: 637238</td>
</tr>
<tr>
<td><strong>S1</strong></td>
<td>Supplier #: 55130</td>
</tr>
<tr>
<td><strong>S2</strong></td>
<td>Supplier #: 55505</td>
</tr>
</tbody>
</table>
2.2 Sample preparation
In line with the philosophy for material selection; the sample preparation procedure was kept as simple as possible. Not only does this reduce sample to sample variability, but it also ensures that the scheme is appropriate for industrial scale production. In these experiments the fillers were used without surface functionalization; the effects of such additives are scheduled for study in the subsequent work package 1.3.1 B and 1.3.1 C. The basic steps of the sample preparation protocol are listed below:

- Weigh out nanosilica (NS) inside a glove box and add to dichloromethane (DCM).
- Sonicate the NS-DCM solution for 1 hour.
- Weigh out polystyrene (PS) and dissolve in DCM.
- Combine the sonicated NS-DCM and the PS-DCM solution by shaking for 1 hour.
- Allow the DCM solvent to evaporate at room temperature for 3 days.
- Produce sample discs by pressing at 175 °C with 5 tons of pressure for 4 minutes.

The glove box is used (along with procedures such as triple bagging of nano-contaminated waste and a filtered external venting system) in order to prevent inhalation of the nanoparticles. A water bath sonicator is used to disperse the nanosilica within the DCM solution; to prevent overheating of the DCM the sonicator bath water is replaced at 15 minute intervals. If required, multiple pressings were used to remove residual solvent and gas bubbles from the samples.

This simplistic protocol is not expected to yield optimally dispersed nanoparticles; however, partially agglomerated samples are required in order to observe the effects of particle dispersal.
3 DC breakdown strength

3.1 Method
DC breakdown measurements are made using a purpose built apparatus (see Figure 4) which is operated within an interlocked metal cage. The disc shaped samples are held between two spring-loaded, 6.35 mm diameter, chrome-plated, steel ball-bearings. The entire assembly is then immersed in silicone oil and a steadily increasing voltage (100 V/s) is applied between the ball-bearings. The silicone oil ensures that the path taken by the breakdown is through, rather than around, the test sample\[18\]. A digital multimeter records the voltage applied between the ball-bearings immediately prior to DC breakdown of the test sample.

Figure 4: (Left) Photograph and (right) schematic of the DC breakdown test cell. There is an integrated handle to lift the entire assembly out of the plastic tank of silicone oil and one of the rods is spring loaded to allow easy sample changes.

For each composition, 8 discs of approximately 75 μm thickness and 30 mm diameter were pressed. It was usually possible to obtain 4 breakdown measurements per disc. This DC breakdown data were processed using Weibull analysis\[19\].

3.2 Results: DC breakdown strength vs filler type
Nanocomposite samples were produced using the four different types of nanosilica filler described in Table I. In each case the samples were given a nanofiller loading of 2.5 % by weight. Nanofillers and their resulting nanocomposites will be referred to by the “Nano-filler type” labels as denoted in Table I.

The DC breakdown results (see Figure 5) appear to fall into two categories: The two nanocomposites produced from fumed silica powders (filler types S1 & S2) display very similar performance. These nanocomposites had breakdown strengths of 390 and 395 ±10 kV:mm\(^{-1}\) respectively. These two results are equivalent within experimental errors; furthermore, they show essentially the same breakdown strength as unfilled polystyrene samples (see Section 3.3). The nanocomposites made from filler types M and Q exhibit lower breakdown strength (349 and 360 ±10 kV:mm\(^{-1}\) respectively) but the steeper gradient of the Weibull fit and the larger β parameters indicate that the measured breakdown values were slightly more consistent (the 95 % confidence bounds for β are ±4).
These results are surprising since the SEM analysis (which is described in Section 5.2) indicates that the fillers of type M and Q are more homogeneously dispersed than the type S1 and S2 fillers. This result and possible explanations are discussed in more depth in Section 6.1.2.

3.3 Results: DC Breakdown Strength vs Filler Fraction

Nanocomposite samples were produced using filler type M and with filler fractions in the range 0 - 10 %; the DC breakdown results are shown in Figure 6. In the Weibull analysis, the fit lines run almost parallel; this indicates that the spread of DC breakdown values is very similar for each composition. The average β value for the Weibull fits is 10.7 with 95 % confidence bounds of ±3; this is lower than was achieved in the “filler type” measurements shown in Figure 5. These two data sets are derived from different batches of samples and so this discrepancy may be attributed to production variability.

Figure 5: Weibull plots showing DC breakdown measurements for polystyrene/silica nanocomposites produced with four different types of nanosilica; each at 2.5 % loading.

Figure 6: Weibull analysis of DC breakdown measurements for polystyrene nanosilica composites with different nanofiller loadings. The inset in the upper right shows the DC breakdown strength as a function of filler fraction.
4 Dielectric spectroscopy

4.1 Method

Dielectric spectroscopy[20] was carried out using a Solartron 1260 frequency response analyzer in combination with a 1296 dielectric interface. Aside from the temperature dependent data, all measurements were made using a Solartron 12962 test cell which was shielded from electrical interference within a grounded metal box. For frequencies >100 Hz a Solartron 12961 calibration device was used to provide an external reference of 100 pF; this was also placed inside the shielding box. The 12962 test cell incorporates a guard ring to eliminate fringing effects and was fitted with 40 mm diameter electrodes (the largest that were available to us).

The use of large electrodes allows high capacitance values to be achieved without requiring extremely thin samples. Thin samples are undesirable for several reasons; they are more susceptible to inhomogeneity in the test material; measurement of their thickness is more critical and introduces proportionally larger errors to the derived permittivity values; pressing of thin samples could result in filler alignment that would not be representative of the bulk material.

4.1.1 Sample thickness

In this series of tests a sample thickness of ~200 μm was typically chosen based on an estimate of the resulting sample capacitance. (~140 pF if a value of ~2.5 is assumed for the dielectric constant of polystyrene). For polymer dielectrics the dominant component of the complex impedance (Z*) is the capacitive reactance. The estimated sample capacitance can therefore be used to calculate the expected magnitude of the imaginary component of impedance (Z’’) to check that this falls within the measurement range of the Solartron system (see Figure 7 solid lines). A sample thickness of 200 μm is just sufficient to bring Z’’ down into the range in which the Solartron is most accurate (dark shaded region in Figure 7). The dissipation factor tan(δ) is the ratio of Z’ to Z’’ and so by assuming a value for tan(δ) it is also possible to estimate the magnitude of Z’. For tan(δ) = 1x10^-4 (dashed lines in Figure 7) this means that the real impedance Z’ will fall below the optimal measurement range of the Solartron for frequencies exceeding ~10 kHz. This highlights the difficulty in making measurements of materials that have small values of tan(δ).

![Figure 7: Diagram showing the expected magnitudes of Z’’ (solid lines) and Z’ (dashed lines) as a function of frequency and sample thickness. Calculation assumes 40 mm diameter electrodes and polystyrene as the dielectric. The shaded regions illustrate the operating range of the solartron and are taken from a similar diagram in the 1296 operators manual and in[20].](image)
4.1.2 Havriliak-Negami fitting

In the following sections analysis of the dielectric response is conducted by simultaneously fitting the real and imaginary parts of the measured data to the Havriliak-Negami equation (1). This equation produces a dielectric relaxation response; such as would be seen for an idealised glass transition (α-relaxation).

\[
\epsilon^*(\omega) = \epsilon_\infty + [\Delta \epsilon / (1 + (i\omega\tau)^\alpha)]^\beta
\]  

Where \( \epsilon^* \) is the complex permittivity which is a function of the angular frequency \( \omega \), \( \Delta \epsilon \) corresponds to the change in permittivity, \( \tau \) is related to the relaxation rate and \( \alpha \) and \( \beta \) are shape parameters. Only frequencies up to 1.5x10^4 Hz are included in the fits because at higher frequencies the measurement of \( \epsilon'' \) is noise limited, as described in Section 4.1.1.

In Figure 8 there are multiple frequency sweeps for each composition under test yielding both real and imaginary values for permittivity. The Havriliak-Negami fits are made using a nonlinear least squares routine which simultaneously fits all the measured data points (real and imaginary from all sweeps relating to that composition) in the range 10^-1 – 10^5 Hz. Where multiple samples are tested this fitting procedure effectively determines the average response.

4.2 Results: Dielectric Spectroscopy vs Filler Type

Nanocomposite samples were produced using the procedure described in Section 2.2 for the four different nanosilica filler types defined in Table I. In each case, a nanofiller loading of 2.5 % by weight was used. Dielectric spectroscopy measurements were conducted as outlined in Section 4.1 and the results are compared in Figure 8.

For the imaginary permittivity, \( \epsilon'' \), samples of type M and Q show a clear increase in dielectric loss towards low frequencies. This differs significantly from the response of the type S1 and S2 nanocomposites, which is much flatter across the measured frequency range. In fact, when viewed on a suitable scale the imaginary permittivity \( \epsilon'' \) for samples S1 and S2 appears noisy. This is because the real impedance \( Z' \) (from which \( \epsilon'' \) is calculated) is at the lower limit of the measurement system. At 1 Hz, for example, the imaginary impedance \( Z'' \) is ~1.4 GΩ whilst the reported measurement for the real component \( Z' \) is ~0.9 MΩ; this gives a tan(δ) value of ~6x10^-4. In reality the real component \( Z' \) could be even smaller but for small tan(δ) this measurement is impaired by even very small errors in the phase angle.

For the real permittivity \( \epsilon' \) the type M and Q samples again show a tendency to increase towards low frequencies. The fact that both \( \epsilon' \) and \( \epsilon'' \) show this increase suggests that the cause is a low frequency relaxation process rather than DC conductivity.

In Figure 8 the real permittivity \( \epsilon' \) is normalized so that at 100 kHz all traces conform to the mean value of 2.03. This is necessary to eliminate sample-to-sample variations for which the most likely cause is measurement errors in the sample thickness. Thickness measurements were carried out using the digital micrometer that is incorporated into the Solartron 12962 test cell; however, this gives only a single point measurement and cannot account for differences in thickness across the sample. Sample-to-sample variation was found to introduce offsets in \( \epsilon' \) as large as ±0.1; however, multiple measurements of the same sample showed that the errors resulting from the Solartron
The system itself are lower than ±0.002. This means that the increase towards low frequencies is certainly statistically significant. The increase both for $\varepsilon'$ and $\varepsilon''$ is far higher for nanofillers of type M and Q than for fillers S1 and S2.

**Figure 8:** $\varepsilon''$ and $\varepsilon'$ for polystyrene nanocomposites of four different filler types (all at 2.5 % loading). The $\varepsilon'$ data were normalized at 100 kHz to eliminate a variable offset caused by thickness measurement errors. Markers are measured data (2 samples per filler type); curves are Havriliak-Negami fits.

### 4.3 Results: Dielectric Spectroscopy vs Filler Fraction

The effect of filler loading on the dielectric response was studied in the case of filler type M. Nanocomposite samples with filler loadings between 0 and 10 % (by weight) were produced and tested. The real and imaginary components of permittivity are shown in Figure 9.

The most striking feature in Figure 9 is the peak in imaginary permittivity $\varepsilon''$ which dramatically increases with filler loading. The peaks in $\varepsilon''$ correspond to a step decrease in real permittivity $\varepsilon'$ confirming that this feature is a dielectric relaxation.

As filler loading is increased, sample-to-sample variations in the magnitude of permittivity (both $\varepsilon''$ and $\varepsilon'$) also increase. Furthermore, the peak in $\varepsilon''$ shifts towards higher frequencies, moving from <1 Hz up to about 10 Hz.
Figure 9: Imaginary (upper) and real (lower) permittivity for polystyrene nanosilica composites at several filler loadings between 0 and 10%. The solid lines show Havriliak-Negami fits to the measured data. Measured data are shown for at least two samples at each composition. The plots for $\varepsilon'$ are normalized so that at 1 MHz the Havriliak-Negami fits agree with the mean.

Figure 10: The real permittivity at 1 Hz and 10 kHz plotted as a function of filler loading.

Part of the dataset shown in Figure 9 is re-plotted in 2D in Figure 10; this plots the variation in real permittivity (at 1 Hz and 10 kHz) as a function of filler loading. When plotted in this way it is clear
that the real permittivity does not simply increase monotonically with filler loading. The data point at 5% loading seems to deviate from the trend which otherwise displays a minima at approximately 0.5% and increases towards both low and high frequencies.

4.4 Results: Dielectric Spectroscopy vs Temperature

For temperature dependent measurements, the Solartron system described in Section 4.1 was used in conjunction with a model 129610 cryostat manufactured by Janis Research. This necessitated the use of smaller samples as the active electrode diameter is just 10 mm. To prevent the capacitance from decreasing too much (which would push the imaginary impedance $Z''$ above the measurement range) the sample thickness was reduced to ~100 μm; yielding a capacitance of ~20 pF.

In this study, the temperature was varied from room temperature up to 120 °C and so cryogenic cooling was not required. The Lake Shore temperature controller and the electric heaters inside the cryostat are capable of maintaining the sample temperature to within ±0.05 °C of the setpoint.

![Image](image1)

![Image](image2)

Figure 11: A Temperature dependant dielectric spectra for unfilled polystyrene (circle markers) and 10%, type M nanofilled samples (filled square markers). The dashed and solid lines show Havriliak-Negami fits to the data for unfilled and filled samples respectively.

The cryostat was used to measure the temperature dependent dielectric spectra of type M nanocomposites. Both unfilled samples and samples with 10% of filler type M were tested (see Figure 11).
The imaginary permittivity \( \varepsilon'' \) for the unfilled samples is at the lower limit of the measurement system. For the real permittivity \( \varepsilon' \) the unfilled samples produce a flat response but with a pronounced “roll off” at high frequencies which is a measurement artifact. The magnitude of the real permittivity \( \varepsilon' \) differs significantly from that measured using the Solartron 12962 test cell; changes in the test cell geometry, electrode contact and sample thickness measurement errors are the likely cause.

For the samples with 10 % nanofiller the peak in the imaginary permittivity \( \varepsilon'' \) is clearly evident and this correlates with a step change in \( \varepsilon' \). The Havriliak-Negami fit lines are able to follow the data closely confirming that a relaxation process is the likely cause of this response. As the temperature is increased the peak in \( \varepsilon'' \) shifts from ~4 Hz at room temperature to ~30 Hz at 60 °C and increases slightly in magnitude. Above 60 °C the magnitude of the peak increases still further and shifts back to ~10 Hz. At 120 °C there is also an increase in the magnitude of the real permittivity \( \varepsilon' \).

4.5 Results: Dielectric Spectroscopy vs Water Absorption

Nanocomposite samples with 0 and 10 % loading of filler type M were analyzed in their as produced “dry” condition and after immersion in distilled water for 24 hours. The dielectric spectroscopy data are shown in Figure 12.

Clearly the 10 % nanofiller samples show the largest effect of water absorption. In the imaginary permittivity \( \varepsilon'' \) there is an increase in the magnitude of the peak and a shift towards higher frequencies. At low frequencies there is also a sharp increase in \( \varepsilon'' \) that means the data points no longer fit a single Havriliak-Negami curve. Very little change is observable for \( \varepsilon'' \) in the unfilled samples which appear to be at the lower limit of the measurement range in any case.

For the real part of permittivity \( \varepsilon' \), the effects are more complex. As described in Section 4.2, the real permittivity data were normalized to mitigate sample-to-sample variation. In this case only the “dry” data sets were constrained to the same mean value at 1 MHz. This means that any offset introduced by the addition of nanofiller will still be displayed. After water absorption, the unfilled samples show a decrease in real permittivity for all frequencies; in contrast, the 10 % nanofiller samples only show a decrease in \( \varepsilon' \) above ~1 kHz. The fact that there is no additional upward step in \( \varepsilon' \) at low frequencies (to correlate with the upward shift in \( \varepsilon'' \)) indicates that this effect may be caused by an increase in DC conduction rather than the presence of an additional relaxation process.
Figure 12: Imaginary permittivity $\varepsilon''$ (upper) and real permittivity $\varepsilon'$ (lower) showing a comparison between “as produced” and water soaked samples for both 0 and 10% filler loadings. The markers show the measured data (two samples for each condition) the curves show the mean response.
5 Analysis of filler dispersal

5.1 Permanganic etching
Permanganic etching has been demonstrated to be a highly effective means of studying the structure of polymer materials[21, 22]. The technique relies on amorphous and crystalline regions of a material experiencing differing etching rates. It is thought that the etching solution penetrates the amorphous regions more readily and that this results in accelerated etching. In this way permanganic etching is capable of revealing crystalline structures, such as lamellae or spherulites, within semi crystalline materials (Bassett, 1985 #176). Crystalline structures that were previously concealed are given increased relief; this makes SEM imaging possible and/or offers dramatically improved contrast.

In this work permanganic etching is used to remove a thin layer of the amorphous polystyrene matrix; the etchant is expected to have little effect on the silica nano fillers. The etching process therefore reveals the condition of the nanofillers in-situ within the nanocomposite material.

The permanganic etching procedure consists of the following key steps:

- The etchant mixture is produced; 5:2:1 of sulphuric acid, phosphoric acid and water.
- 1 % by weight of potassium permanganate is gradually added to the etchant mixture.
- The mixture is continuously stirred with no additional heating for 10-20 minutes. The mixture should turn dark green in colour.
- The samples are submerged in the etchant mixture and shaken throughout the desired etching duration.
- After etching the mixture is “quenched” by a 2:7 mixture of sulphuric acid and water to which 20% by volume of hydrogen peroxide is added.
- The samples are rinsed in distilled water and then in methanol.

Care must be taken when producing the etch and quench mixtures because significant heat is generated. Particular caution is required when adding the potassium permanganate as inadequate stirring could result in production of manganese heptoxide, which is explosive.

5.2 Results: Permanganic Etching and SEM vs Filler Type
The permanganic etching procedure described in Section 5.1 was followed. Etch durations of 1, 2 and 4 hours were used in order to observe the etch progress as a function of time. After etching, the samples were mounted on pin stubs and gold coated to prevent surface charge accumulation during SEM imaging; the resulting images are shown in Figure 13.

All of the samples contain particles that are larger than the dimensions given in Table I. At high magnification the granular structure of the particles is visible, confirming that these particles are agglomerations of primary units.

Just as with the DC breakdown data the SEM images also fall into two categories: For the M and Q type samples the agglomerated filler formed particles with typical diameters of approximately 500 nm. The distribution of particles throughout the M and Q type samples was fairly homogenous. In
contrast, the particle distribution in the type S1 and S2 samples was patchy. Large regions of very high particle density were observed, whilst other areas were almost devoid of filler (see Figure 13, S1). In regions where the particle density was similar to that observed for the M and Q type samples, the typical particle size was slightly lower at ~350 nm, (see Figure 13, S2). For the M and Q type fillers the typical particle sizes were observed to increase as a function of etch duration; the same effect was not evident for the type S1 and S2 samples.

![Figure 13: SEM images comparing polystyrene nano composites with 2.5 % loading of four different filler types. The labels denote the filler type as shown in Table I. The 1 hour etched samples are shown except for the case of S1 where the 4 hour etched image is used. This particular image was chosen because it clearly illustrates the non-uniformity of the particle distribution that was observed both for S1 and S2 type fillers. The image shows a region of highly agglomerated material adjacent to a region of low filler density. Other parts of the S1 sample displayed better filler dispersal and appeared similar to that shown for S2.](image)

### 5.3 Results: Permanganic Etching and SEM vs Filler Fraction

Once again the etching procedure described in Section 5.1 was followed. Samples were prepared using different loadings of filler type M; SEM images of these samples are shown in Figure 14. For obvious reasons there is a clear correlation between the filler loading and the spatial density of the particles. More interestingly, the typical particle size seems to be almost independent of the filler concentration. As noted in Section 5.2; the typical particle size for type M samples varies considerably more as a function of the etch duration. The samples shown in Figure 14 were all etched for 2 hours except for the 2.5 % sample in Figure 14C. This sample was processed in a
different batch and appears to have experienced a higher etch rate; the 1 hour etched sample is therefore more comparable.

Figure 14: SEM images of type M nano composites after permanganic etching. Images A to D show filler fractions of 0, 1, 2.5 and 10 % respectively.

5.4 Results: Particle size analysis
In an attempt to verify the supplier’s data for the nanoparticle filler size; dynamic light scattering (DLS) was used to measure the particle size distribution. These measurements were made with a Malvern Instruments Zetasizer. Prior to measurement the particles were dispersed in water at three different concentrations. The mixtures were thoroughly shaken and sonicated in order to break up any agglomerations of particles that may be present. The stability of particle dispersal was assessed by leaving the mixtures undisturbed for 48 hours. Figure 15 shows that some settling took place but that many of the nanoparticles remained in suspension. In all cases silica filler type Q was used (as described in Table I).
Phase Dispersion of Filler and its Effect/Influence on Properties
Top and Tail Grand Challenge Work Package 1.3.1 Report

Figure 15: Photographs of nanoparticle dispersions at 0.01 %, 0.1 % and 1 % concentration by weight. (Upper) dispersions immediately after sonication, (lower) after 48 hours of settling.

The 0.1 % concentration proved to be optimal for the DLS measurements. The results of this analysis are shown in Figure 16. There is a very clear double peak in the particle distribution indicating that there are two groups of particles. The majority of the particles have diameters between 100 nm and 300 nm. The second group of particles has diameters that are centred at approximately 1 μm. Despite being fewer in number these larger particles produce most of the scattered light intensity.

The manufacturers quoted particle size for this type of filler (type Q) is 10 - 20 nm. No particles were observed in this size range even after a syringe filter was used to remove the larger particles. (Removing the larger particles potentially increases the measurement sensitivity for scattered light from the smaller particles).

Figure 16: Particle size distribution produced for 0.1 % concentration of nanosilica (type Q) dispersed by shaking and sonication in water.
6 Conclusions

Permanganic etching and SEM imaging have been demonstrated as an effective technique for studying the condition of nanofillers “in-situ” within an amorphous polymer nanocomposite. This information helps us to understand what happens to the nanofillers during sample preparation and informs new protocols. In the following sections the results are discussed in order to correlate the observed filler condition with measured properties of the nanocomposite (such as breakdown strength and dielectric spectroscopy measurements). Sections 6.1 and 6.2 describe the variations observed as a function of filler type and filler loading respectively. In the future it is hoped that this type of technique will reveal which aspects of the filler distribution are critical for control over the measured material properties. This information is vital if the aim of customizing nanodielectrics to specific applications is to be achieved.

6.1 Filler type

The main aim of this work is to correlate the nanofiller dispersal state with the externally measured electrical properties. SEM analysis has shown that the quality of filler dispersal varies significantly with filler type. Comparison of the measured DC breakdown strength and dielectric spectra for different filler types is therefore key.

The type S1 and S2 fillers used are produced using the fumed silica (pyrogenic) process. The base particle sizes for type S1 and S2 fillers are 7 nm and 14 nm respectively. However, the process involves high temperatures and this allows the particles to fuse together into chains several hundred nanometers in length. Additionally the high processing temperatures will modify the surface chemistry of the particles, removing hydroxyl groups and potentially modifying the hydrophobicity.

In contrast the type M and Q fillers are claimed to exist as particles between 5 and 20 nm in size that are not expected to be permanently fused together into larger groups. The main difference between the two is that the type M fillers are porous which may permit more intimate contact with the matrix to be achieved but is also expected to increase the capacity for water absorption.

6.1.1 SEM analysis

The main observations relating filler type to dispersal/agglomeration state are summarised below:

- For all filler types the observed particles were considerably larger than quoted by the supplier. The base particles appear to have agglomerated to form clusters of approximately 500 nm in size.
- Dispersion of the fumed silica derived nanofillers was more “patchy”. Batch-to-batch variability was problematic; indicating that critical parameters are not easily controlled.

For the M and Q type samples, the observed increase in particle size after 4 hours of etching may indicate that some of the filler has been released from the matrix and has begun to aggregate on the surface despite the shaking and rinsing procedures used. Consequently the 1 and 2 hour etched SEM images are most representative of the condition of the nanofiller “in-situ” within the nanocomposite. The fused particle chains in the type S1 and S2 samples may also hinder release of the filler particles from the matrix; this could explain why particle size did not increase with etch duration for these samples. Furthermore, the larger, fused particle chains in the S1 and S2 filler
types may have reduced the effectiveness of sonication during sample preparation; this could therefore be responsible for the patchy dispersal of filler in these samples.

6.1.2 DC breakdown
The highest breakdown values were observed for the fumed silica derived nanoparticles in the type S1 and S2 samples (see Figure 5). The breakdown strength of these samples was in line with that of unfilled polystyrene (see 0% filler in Figure 6). Samples with type M and Q fillers seem to degrade the breakdown strength relative to the unfilled case.

Although they exhibit high breakdown strength the type S1 and S2 samples also show increased variability. This fact is displayed in the lower gradient of the Weibull fit and in the correspondingly lower β parameter values.

The SEM analysis (Figure 13) showed that the dispersal of the type M and Q fillers was better than that seen in the S1 and S2 samples where the dispersion was “patchy”. Conventional wisdom is that regions of agglomerated filler act as defects and will decrease the DC breakdown strength. This was not borne out by our measurements. A possible explanation is that since the clusters in the S1 and S2 samples were large enough to be visible (hundreds of microns in size but spaced several mm apart) they were therefore subject to negative selection bias. Large clusters take up large quantities of the available nanofiller and result in an apparent reduction in filler density elsewhere in the sample. This would mean that for the patchy S1 and S2 samples breakdown measurements are made most frequently in regions of low filler density; in accordance with the inset of Figure 6 their reduction in breakdown strength (relative to the unfilled case) will be proportionally lower.

6.1.3 Dielectric Spectroscopy
Dielectric spectroscopy measurements of unfilled polystyrene were difficult because of the low values of tan(δ), which challenged the dynamic range of the detector. For nanocomposites with higher filler loadings useful measurements were made between 0.1 Hz and 1x10^5 Hz. In all cases the measurement of sample thickness was a significant source of errors. This resulted in a (sometimes quite large) variable offset, primarily visible in ε′. This means that the magnitude of ε′, which is rather lower than the expected literature values[23], is probably inaccurate. Despite this, the variations in ε′ and ε″ with frequency are expected to be accurate and much useful information can be extracted.

As noted in Section 6.1.1; the sub-particles in the fumed silica fillers are fused into clusters of a few hundred nanometers. In the type M and Q nanocomposites there were some agglomerations of comparable size (observed with SEM) but the dispersion was in general more homogeneous. In Section 4.2 the dielectric response of fumed silica type and conventional fillers differed significantly. The fumed silica fillers exhibited dielectric behaviour that was similar to the unfilled samples with little measurable loss and a flat response for ε′. The more dispersed nanofillers of type M and Q produced a significant relaxation response at low frequencies in both ε″ and ε′. The fact that the magnitude of response apparently varies with filler dispersal (and hence with particle size) may indicate (as described in Section 1.3) that the relaxation process is occurring (or is enhanced) at the interface between the filler and the matrix (which is larger for well dispersed fillers).

In Section 4.5, Figure 12, water absorption is also shown to change the low frequency dielectric response. For the samples containing 10% type M filler; ε″ and ε′ both increase by “0.05 after
soaking. This is comparable to the difference between the type S1 and S2 samples and the type M and Q samples at 2.5 % loading; as shown in Section 4.2, Figure 8. In this case ε’’ and ε’ at 0.1 Hz were 0.025 and 0.05 higher respectively for the non-fumed silica fillers. This indicates that part of the reason for the observed difference between type S1 and S2 fillers and type M and Q fillers may be the increased presence of surface adsorbed water and/or surface hydroxyl groups for type M and Q fillers.

The two effects described above (dielectric response of the interface and the presence of adsorbed water) may both occur to some degree in order to produce the larger variation with frequency than is observed for the type M and Q fillers. Simultaneously, the negative selection bias proposed in section 6.1.2 would make the response of the type S1 and S2 samples tend towards that of the unfilled samples.

6.2 Filler Loading

6.2.1 DC breakdown

The DC breakdown data in Figure 6 clearly show that as the concentration of nanofiller is increased the breakdown strength of the resulting nanocomposite is reduced. These data were obtained for the type M filler, for which the particles, although agglomerated, were homogeneously distributed. The SEM images in Figure 14 show that the agglomeration size is approximately independent of the filler concentration. Although the sample preparation procedure undoubtedly has an effect (through the duration and effectiveness of sonication) the observed agglomeration size may represent the most energetically stable configuration of filler particles for electrochemical reasons (i.e. Zeta potential). The approximately constant agglomerate size means that the chief effect of varying filler concentration is to change the spatial density of the agglomerated particles. This in turn must be the effect that is driving the observed decrease in breakdown strength.

6.2.2 Dielectric Spectroscopy

In Section 4.3, Figure 9 the amplitude of the dielectric response clearly increases with filler fraction. The relaxation process is either introduced or drastically enhanced with the addition of nanofiller. At 10 % nanofiller loading the real permittivity is increased by >11 % at 50 Hz and >30 % at 0.1 Hz.

As discussed in section 6.1.3 the increase at 0.1 Hz is probably related, in part, to moisture that is adsorbed onto the nanofiller. During the water absorption experiments in Section 4.5 the dielectric loss peak for the nanocomposite shifted to higher frequencies. The additional moisture seems to have increased the relaxation rate; probably by increasing the mobility of the polystyrene chains near to the nanofiller-matrix interface. This hypothesis is supported by the fact that there is no frequency dependent change when moisture is added to the unfilled samples.

On the other hand; in Figure 9, the peak in ε’’ and the step increase in ε’ observed at ~10 Hz seems to correspond to the α-relaxation of polystyrene molecules. This is confirmed by the temperature dependent measurements made in Section 4.4, where the dielectric response for 10 % nanosilica exhibits an increase in amplitude for temperatures above the glass transition temperature of polystyrene (Tg ≈ 100 °C). The profile of the trace for ε’’ at 100 °C is similar to that observed for unfilled polystyrene in[24] where the response is attributed to the α-relaxation of polystyrene.
molecules. The fact that the amplitude of this relaxation response increases with filler loading suggests that the signal is being enhanced by the presence of the nanofiller. Possible mechanisms for this are enhancement of the electric field near the nanofillers (due to their geometry) and perhaps increased space-charge in the interface region (due to the presence of surface adsorbed moisture). Space charge has previously been observed to increase for micro-scale fillers \cite{10} (TiO$_2$ in epoxy) but was reportedly mitigated for nanofillers. Since the typical agglomeration size in this study is ~500 nm an increased space charge at the interface would be in agreement with \cite{10}.

6.3 Executive summary

- The technique of dispersal in a polystyrene matrix, followed by permanganic etching and SEM imaging proved to be an extremely effective tool for analysis of nanofiller dispersion.
- Fumed silica type fillers were found to exhibit a “patchy” dispersal whereas non-fumed silica fillers were homogeneously dispersed.
- For all filler types, the particles agglomerated to approximately ~500nm in size; this is considerably larger than the base particle sizes quoted by the manufacturer.

6.3.1 Summary for DC breakdown measurements

- With the simple sample preparation protocol tested; silica nanoparticles (of the non-fumed type) were found to degrade the DC breakdown strength of polystyrene.
- Breakdown strength was found to reduce as loading of non-fumed type filler increased.
- Dielectric strength was only reduced slightly for the fumed silica derived nanofillers; however, the measurements were significantly more variable and negative selection bias may have meant that regions of lower filler density were preferentially tested.

6.3.2 Summary for dielectric spectroscopy measurements

- Changing nanosilica filler type can have a large impact on the dielectric response. Fumed silica derived particles may behave differently due to their different surface chemistry.
- The $\alpha$-relaxation response of the polystyrene molecules was observed. This response was well described by the Havriliak-Negami equation.
- The magnitude of $\varepsilon'$ decreases for low filler fractions and then shows a marked increase for higher filler loadings. This effect is most pronounced at low frequencies.
- The dielectric response changes significantly near to the $T_g$ of polystyrene; therefore the response is probably generated in the matrix or the interphase.
- The presence of the nanofiller makes it possible to observe the effects of absorbed water which accumulates at the interface.
- Addition of nanosilica fillers appears to increases the amplitude of dielectric response. This could be due to field enhancement in the interphase regions and/or because additional space charge is provided to the interphase by water adsorbed on the surface of the filler.
7 References


