A dielectric spectroscopy study of the polystyrene/nanosilica model system

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Abstract— **In this study a simple solvent blending technique is used to produce silica/polystyrene nanocomposites. Dielectric spectroscopy is then used to measure both the real and imaginary permittivity of the samples. The nanosilica/polystyrene system is characterized over a range of different filler loadings, and additionally, as a function of temperature. To supplement this, absorbed water is used as a dielectric probe to explore molecular relaxation processes at the nanoparticle interfaces.**

Keywords—nano; silica; composite; polystyrene; dielectric; spectroscopy; permittivity

I. INTRODUCTION

Nanoscale fillers are emerging as an attractive tool for customization of the mechanical, thermal and electrical properties of polymers. Nano fillers offer greatly increased surface area, relative to their micro-scale equivalents, and this has the potential to dramatically enhance their effectiveness. This report focuses on modification of the dielectric response.

In this study, polystyrene is chosen as the polymer matrix. Its relatively simple polymer structure and the amorphous nature of its matrix help to reduce the morphological and stoichiometric effects which would be present in more commonly used polymer dielectrics and might otherwise mask the effect of the nanoparticles. The use of this simplified, model system allows the investigation to discern the effect of the nanosilica fillers more clearly, bringing new insight into their method of action.

A. Sample Preparation

Throughout this work polystyrene with an average molecular mass of 192000 g.mol^{-1} was used (430102 Aldrich).

TABLE I.   NANOSILICA FILLER TYPES

Filler type	Supplier Data		
	Description	*Supplier #*	*Particle size*
M	Silicon Dioxide, nanopowder (spherical, porous)	637246	5-15 nm
Q	Silicon Dioxide, nanopowder.	637238	10-20 nm
S1	Fumed silica powder (aggregate) Avg. part. Size 100-200 nm.	S5130	7 nm
S2	Fumed silica powder (aggregate) Avg. part. Size 200-300 nm.	S5505	14 nm

The website for the Top & Tail Transformation project can be found at: http://www.topandtail.org.uk/

Four types of nanofiller were used; details of these are given in Table I. Polystyrene nanocomposites were prepared using the simple protocol outlined 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 min.

The glove box is used (along with procedures such as triple bagging of nano-contaminated waste and a filtered external ventilation 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. Samples were left uncoated to allow water absorption; however, the test cell electrodes were polished to ensure good electrical contact.

B. Dielectric Spectroscopy Measurements

Dielectric spectroscopy [1] 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.

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 Fig. 1 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 Fig. 1). The dissipation factor $tan(\delta)$ is the ratio of Z' to Z'' and so by assuming a value for $tan(\delta)$ it is also possible to estimate the magnitude of Z'. For $tan(\delta) = 1\times10^{-4}$ (dashed lines in Fig. 1) 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 $tan(\delta)$.
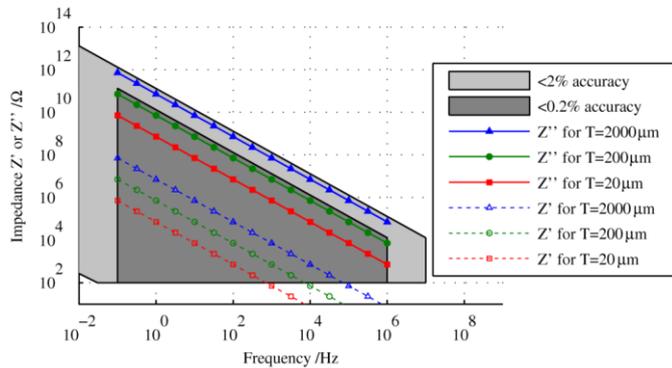

Fig. 1. Diagram showing the expected magnitudes of Z'' (solid lines) and Z' (dashed lines) as a function of frequency and sample thickness. Calculation assumes 40 mm diameter electrodes and polystyrene as the dielectric. The shaded regions illustrate the operating range of the solartron and are taken from a similar diagrams in the 1296 operators manual and in [1].

C. Temperature Dependent Measurements

For temperature dependent measurements, the Solartron system described in Section I B 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. In order 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.

II. RESULTS

A. Dielectric Spectroscopy vs Filler Type

Nanocomposite samples were produced using the procedure described in Section I A 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 I B and the results are compared in Fig. 2. The solid lines in Figs. 2, 3 and 5 result from simultaneous fitting of ε' and ε'' to the Havriliak-Negami equation (1):

$$\varepsilon^*(\omega) = \varepsilon_\infty + [\ \triangle\varepsilon\ /\ (1 + (i\omega\tau)^\alpha)^\beta\ ] \qquad (1)$$

Where ε^* is the complex permittivity which is a function of the angular frequency ω, $\triangle\varepsilon$ corresponds to the change in permittivity, τ is related to the relaxation rate and α and β are shape parameters. Only frequencies up to 1.5×10^4 Hz were included in the fit because at higher frequencies the measurement of ε'' is noise limited as described in Section I B.
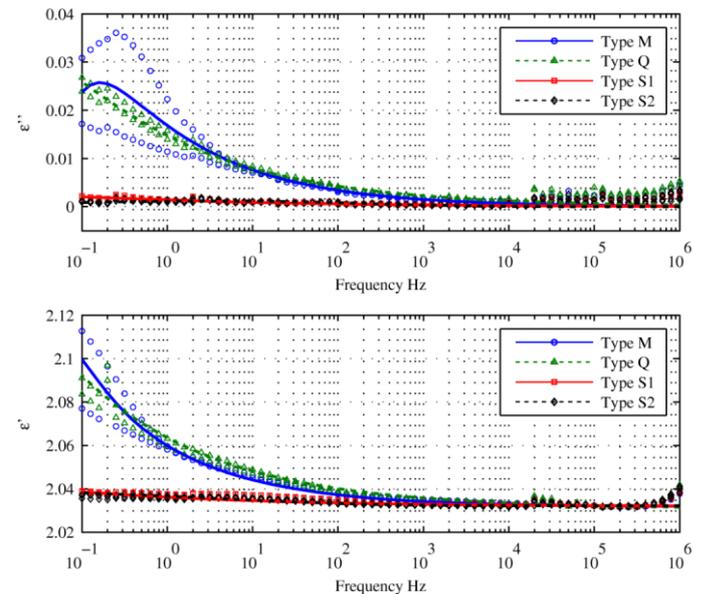

Fig. 2. ε'' and ε' for polystyrene nanocomposites of four different filler types (all at 2.5 % loading). The ε' data were normalized at 100 kHz to eliminate a variable offset caused by thickness measurement errors. Markers are measured data (2 samples per filler type); curves are Havriliak-Negami fits.

For the imaginary permittivity, ε'', 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 ε'' for samples S1 and S2 appears noisy. This is because the real impedance Z' (from which ε'' 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 $tan(\delta)$ value of ~6x10⁻⁴. In reality the real component Z' could be even smaller but for small $tan(\delta)$ this measurement is impaired by even very small errors in the phase angle.

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

In Fig. 2 the real permittivity ε' 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 ε' as large as ±0.1; however, multiple measurements of the same sample showed that the errors resulting from the Solartron system itself are lower than ±0.002. This means that the increase towards low frequencies is certainly statistically significant. The increase both for ε' and ε'' is far higher for nanofillers of type M and Q than for fillers S1 and S2.

B. 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 Fig. 3.
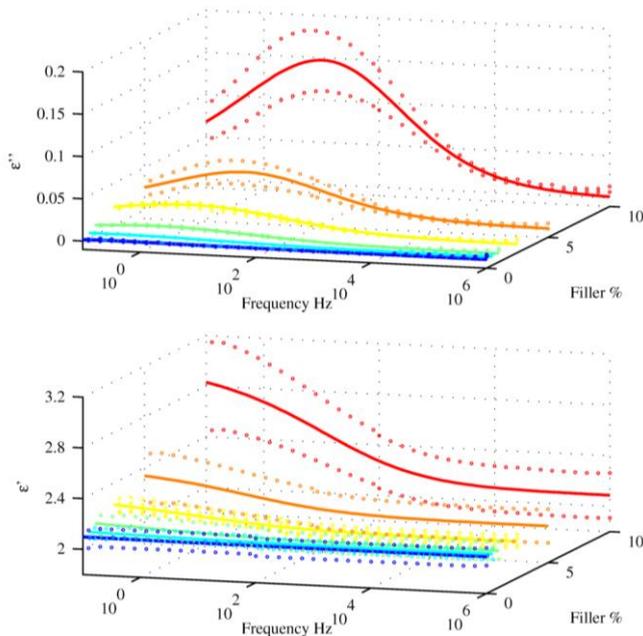

Fig. 3. Imaginary (upper) and real (lower) permittivitty for polystyrene nanosilica composites at several filler loadings between 0 and 10 %. The solid lines show Havriliak-Negami fits to the measured data. Measured data are shown for at least two samples at each composition. The plots for ε' are normalized so that at 1 MHz the Havriliak-Negami fits agree with the mean.

The most striking feature in Fig. 3 is the peak in imaginary permittivity ε'' which dramatically increases with filler loading. The peaks in ε'' correspond to a step decrease in real permittivity ε' confirming that this feature is a dielectric relaxation.

As filler loading is increased, sample-to-sample variations in the magnitude of permittivity (both ε'' and ε') also increase. Furthermore, the peak in ε'' shifts towards higher frequencies, moving from <1 Hz up to about 10 Hz.

C. 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 is shown in Fig. 4.

Clearly the 10 % nanofiller samples show the largest effect of water absorption. In the imaginary permittivity ε'' 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 ε'' that means the data points no longer fit a single Havriliak-Negami curve. Very little change is observable for ε'' 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 ε', the effects are more complex. As described in Section II A, 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 ε' above ~1 kHz. The fact that there is no additional upward step in ε' at low frequencies (to correlate with the upward shift in ε'') indicates that this effect may be caused by an increase in DC conduction rather than the presence of an addition relaxation process.
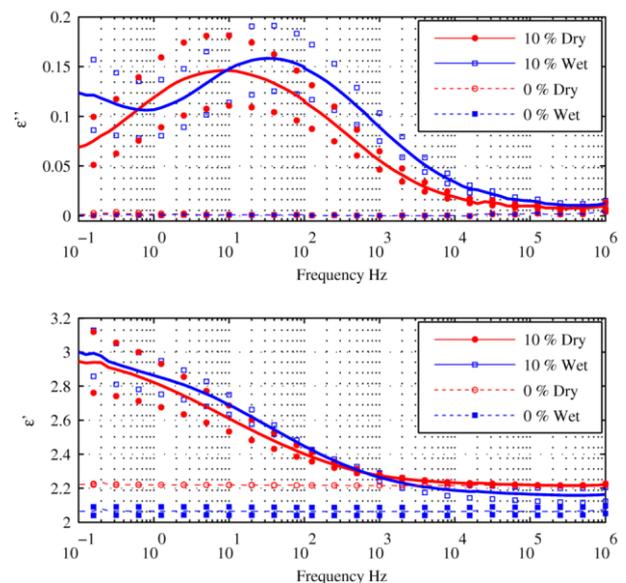

Fig. 4. Imaginary permittivity ε'' (upper) and real permittivity ε' (lower) showing a comparison between "as produced" and water soaked samples for both 0 and 10 % filler loadings. The markers show the measured data (two samples for each condition) the curves show the mean response.

D. Dielectric Spectroscopy vs Temperature

Using the cryostat and the procedure described in Section I C, the temperature dependent dielectric spectra of type M nanocomposites was measured. Both unfilled and samples with 10 % of filler type M were tested (see Fig. 5).

The imaginary permittivity ε'' for the unfilled samples is at the lower limit of the measurement system. For the real permittivity ε' 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 ε' differs significantly to 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 ε'' is clearly evident and this correlates with a step change in ε'. 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 ε'' 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 ε'.
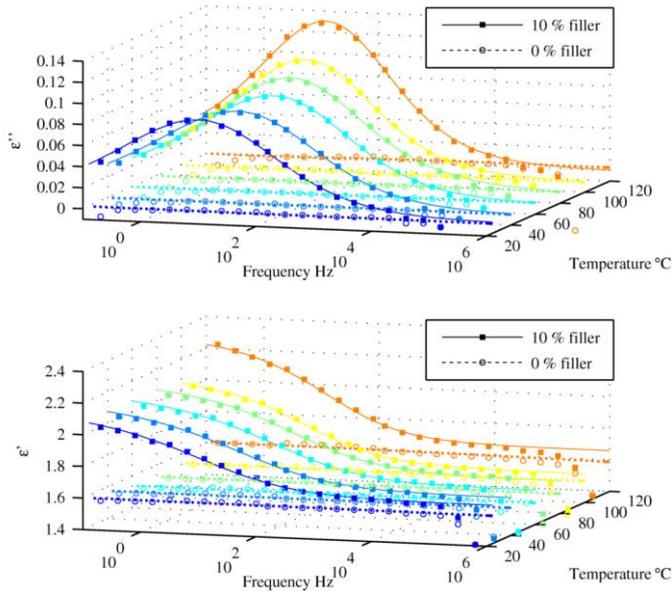

Fig. 5. Temperature dependant dielectric spectra for unfilled polystyrene (circle markers) and 10 %, type M nanofilled samples (filled square markers). The dashed and solid lines show Havriliak-Negami fits to the data for unfilled and filled samples respectively.

III. Conclusion

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 1×10^5 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 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.

In Section II A significant differences were observed between conventional and fumed silica type fillers. The fumed silica fillers (in which the sub-particles are fused into clusters of a few hundred nanometers) exhibited behavior that was similar to the unfilled samples. 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. The more dispersed nanofillers of type M and Q produced a significant response in both ε' and ε'' at low frequencies. This variation with particle size indicates that the relaxation processes may be focused at the interface between the filler and the matrix.

In Section II B 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.

During the water absorption experiments in Section II C the dielectric loss peak for the nanocomposite shifted to higher frequencies. The additional moisture seems to have increased the relaxation rate; probably by increasing conductivity 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.

In Section II D 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 [2] where the response is attributed to α-relaxation of polystyrene molecules. The addition of nanofiller in our work seems to increase the amplitude of dielectric response (as in Fig. 3). One possible mechanism for this is that the filler introduces more space charge into the system which increases the charge on polystyrene molecules in the interface region. This agrees with the observation in [3] for microfiller (TiO2 in epoxy) but not for nanofiller for which mitigation of space charge was reported. This discrepancy could arise either from particle agglomeration or the filler type.

References

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