Dielectric Studies of Polystyrene-based, High-permittivity Composite Systems


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Abstract- In this paper, we report on a dielectric study of a series of composite systems based upon a polystyrene matrix ($\varepsilon_p' \approx 2.7$) containing dispersed particles of lead zirconate titanate (PZT) and barium titanate (BaTiO$_3$) (in both cases, $\varepsilon_m' \approx 1000$). These components were chosen to give a high dielectric contrast within the system and, because polystyrene is readily etched using permanganic reagents, the size and distribution of particles within the matrix could be readily determined by scanning electron microscopy. We report on the effect of composition on the effective permittivity of the composite; the precise composition of each system was determined by thermogravimetric analysis. The results obtained are compared with theoretical models. We show that, in systems with high dielectric contrast between the matrix and the particles, the variation in relative permittivity with filler loading is best described by the Lichtenecker Rother model.

I. INTRODUCTION

The addition of an inorganic filler to an organic polymer is a commonly used means of modifying material properties to suit particular requirements. Generally, the resulting composite will exhibit properties that are intermediate between those of the two components and, consequently, different mixing laws have been developed to deal with mechanical, thermal and electrical parameters.

In the case of dielectric materials, many theoretical approaches have been developed to evaluate the effective permittivity of a composite material. In the case of a two component system, the so-called Wiener bounds equate to series- or parallel-conformations and are represented by the following inequality:

$$\left(\frac{\phi_p (1-\phi_p)}{\varepsilon_p'} + \frac{\phi_m (1-\phi_m)}{\varepsilon_m'}\right)^{-1} \leq \varepsilon_p' \leq \phi_p \varepsilon_p' + (1-\phi_p)\varepsilon_m'$$

In this, $\phi_p$ indicates the volume fraction of one phase, $\varepsilon_p'$ and $\varepsilon_m'$ represent the real part of the permittivity of the constituents and $\varepsilon_p'$ the permittivity of the resulting composite. While the Wiener bounds are of value in that they equate to the limiting cases, they would not be expected to be representative of realistic systems (e.g. a particulate phase dispersed within a continuous matrix). Consequently, many other effective medium equations have been developed, such as those of Böttcher, Bruggeman, Looyenga, Polder-van Santen and Maxwell and Garnett [1, 2].

In this paper, we consider the applicability of various models to systems based upon high permittivity fillers within a low permittivity matrix. While such systems are of practical interest in connection with the generation of so called high $k$ dielectrics, our motivation here is, rather, to explore the ability of different effective medium approaches to describe such materials, where the high contrast in relative permittivity between the two phases will manifest itself in extreme forms of behaviour.

II. EXPERIMENTAL

A. Materials

All the composite systems used in this study were based upon atactic polystyrene (PS) (Sigma Aldrich) and a high permittivity inorganic filler. The lead zirconate titanate (PZT) was obtained from Meggitt (Denmark), while the barium titanate (BaTiO$_3$) was purchased from Sigma Aldrich. Both fillers were supplied in the form of micrometre-sized particles.

Composite samples were prepared from the above starting materials using a solution mixing procedure. Initially, the PS was added to dichloromethane (DCM) at a weight/volume concentration of ~10% and mixed using a magnetic stirrer until fully dissolved. The required mass of the filler was then added and dispersed with stirring and sonication before the mixture was added to methanol. Due to the insolubility of PS in methanol, the PS/filler rapidly formed a precipitate, which was then dried to remove residual solvent. The resulting product was melt pressed into the required form using a two-stage process. Initially, the composite was melt-pressed using a large press to eliminate trapped bubbles. The resulting films were cut up and repressed, using a Specac press fitted with a precision thin film making accessory, to give films of the required thickness (~200 μm).

B. Material Characterization

Samples produced as above were subjected to thermogravimetric analysis (TGA), in order to determine the absolute composition of each formulation. For this, each material was heated from room temperature to 750 °C under oxidizing conditions in order to remove the organic components, leaving the filler as a residue.

The structure of a representative range of systems was also examined by scanning electron microscopy (SEM). For this, the specimens were first etched using a permanganic reagent composed of a 1% solution of potassium permanganate in an acidic mixture of 5 parts concentrated sulphuric acid to 2 parts orthophosphoric acid to 2 parts water, following prescribed procedures [3].
Table 1: Composition data for all composites

<table>
<thead>
<tr>
<th>Nominal Filler Loading /% wt</th>
<th>Filler Type</th>
<th>TGA Filler Loading /% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (PZT batch)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>PZT</td>
<td>10.2</td>
</tr>
<tr>
<td>33</td>
<td>PZT</td>
<td>33.1</td>
</tr>
<tr>
<td>40</td>
<td>PZT</td>
<td>43.5</td>
</tr>
<tr>
<td>50</td>
<td>PZT</td>
<td>52.9</td>
</tr>
<tr>
<td>0 (BaTiO₃ batch)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>BaTiO₃</td>
<td>14.8</td>
</tr>
<tr>
<td>20</td>
<td>BaTiO₃</td>
<td>21.6</td>
</tr>
<tr>
<td>50</td>
<td>BaTiO₃</td>
<td>53.1</td>
</tr>
<tr>
<td>75</td>
<td>BaTiO₃</td>
<td>75.3</td>
</tr>
</tbody>
</table>

Dielectric spectra were obtained using a Solartron 1260A impedance analyser fitted with a Solartron 1296 dielectric interface. Gold electrodes were applied by sputter coating to all samples prior to the measurements.

III. RESULTS

A. Composition and Structure of the Composites

Table 1 shows a comparison of filler loading levels obtained from TGA with nominal values based upon the masses of PS and PZT or BaTiO₃ added to the solvent. Evidently, the chosen solvent-based sample preparation route does not result in any major loss of polymer or filler from the system.

The SEM images in Fig. 1 show the typical morphology of all the systems considered in this study, all of which were composed of a uniform dispersion of the inorganic phase within the polystyrene. The PZT, in this case, can be seen to take the form of agglomerates of irregularly shaped primary particles that are ~500 nm in size; the BaTiO₃ was composed of loose aggregates of particles of a similar size but, in this case, they exhibited an approximately cubic habit.

B. Permittivity and Composition of PZT-based Composites

Fig. 2 shows the frequency dependence of the real part of the relative permittivity for composites of various compositions. From this, it is evident that the frequency dependence is weak and that adding either PZT or BaTiO₃ results in a progressive increase in $\varepsilon'_c$. Liu et al. [4] reported that the permittivity of well-sintered PZT was 952 while Xu and Wang quoted a value of 4360 [5]. Evidently, there is some uncertainty in the appropriate value of the real part of the permittivity of PZT and therefore, here, we initially chose to evaluate this quantity by fitting the experimental data obtained at 1 kHz to an appropriate mixing law. For the sake of convenience, the Lichtenecker Rother equation was initially selected, namely:

$$\log \varepsilon'_c = \phi'_p \log \varepsilon'_p + \left(1 - \phi'_p\right) \log \varepsilon'_m$$  \hspace{1cm} (2)

where both $\varepsilon'_p$ and $\varepsilon'_m$ are freely fit-able parameters; the subscripts c, p and m respectively refer to the composite, particulate and matrix. This leads to a best-fit value of $\varepsilon'_p = 1777$ (PZT). While this value of $\varepsilon'_p$ is consistent with experimental data such as those cited above, as a consequence of the length of the extrapolation, the 95% confidence interval in $\varepsilon'_p$ was found to be of the order of ±100%. Comparing the permittivity value for the PS matrix derived using the above procedure ($\varepsilon'_m = 2.77 ± 0.35$) with published data (upper bound 2.7 [6]) indicates agreement within experimental uncertainties. Nevertheless, a number of additional unfilled PS samples were prepared using different methods and the measurement of real permittivity was repeated as above.
Average values of the real part of the permittivity of PS at 1000 Hz were found to be 2.86, 2.91 and 2.73 respectively for samples prepared by direct melt pressing of PS pellets, precipitation in methanol and simple evaporation of the DCM solution. These values suggest a small systematic offset relating to some stray capacitance in the system. In order to permit direct comparison between the PZT and BaTiO$_3$ systems, a fixed intermediate value of $\varepsilon_m'$ will subsequently be employed for the PS matrix in both systems. The fitting procedure described above was therefore repeated but with $\varepsilon_m'$ set at 2.75, which gives the real permittivity of the PZT particles as $\varepsilon_p' = 1900 \pm 800$. Clearly, permittivity values that are determined using any fitting procedure are dependent not only on the experimental data but also on the equation used for the extrapolation. From the above analysis, the Lichtenecker Rother equation has the following virtues:

(i) The best estimate of the PZT permittivity is consistent with experimental data, despite the length of the extrapolation.

(ii) The fit to the experimental data is, statistically, very good; $R^2 = 0.989$.

(iii) The residuals are randomly distributed.

Nevertheless, other effective medium equations exist and, arguably, are based on more fundamental concepts. Consequently, the above process was repeated but with the commonly-used Maxwell-Garnett and Bruggeman models, which can, respectively, be expressed in the form of the following equations:

$$\frac{\varepsilon_c' - \varepsilon_m'}{\varepsilon_c' + 2\varepsilon_m'} = \phi_p \frac{\varepsilon_p' - \varepsilon_m'}{\varepsilon_p' + 2\varepsilon_m'}$$  \hspace{1cm} (5)

$$\frac{\varepsilon_c' - \varepsilon_m'}{\varepsilon_m' + 2\varepsilon_c'} = \frac{\phi_p}{1 - \phi_p} \frac{\varepsilon_p' - \varepsilon_m'}{\varepsilon_p' + 2\varepsilon_c'}$$  \hspace{1cm} (6)

Fig. 3 shows (for PZT/PS composites) best fits to the Lichtenecker Rother, Maxwell-Garnett and Bruggeman models. In all cases $\varepsilon_m'$ is fixed as 2.75; it is evident that, while the Lichtenecker Rother model conforms well to the experimental data with physically reasonable parameters ($\varepsilon_p' \approx 1900$), neither of the other models can reproduce the relatively rapid rise in permittivity seen experimentally, irrespective of how high the value of $\varepsilon_p'$. Unsurprisingly, removing the $\varepsilon_m' = 2.75$ constraint does not improve matters (data not shown).

C. Permittivity and Composition of BaTiO$_3$-based Composites

In view of the widespread acceptance of both the Maxwell-Garnett and Bruggeman models, the above results were unexpected and, therefore, the analysis procedure was repeated using equivalent data obtained from systems based upon BaTiO$_3$ which, from published data, is generally characterised by a permittivity that falls within the range 3500-6000 [7]. Fig. 4 shows equivalent plots to those discussed above and, from this, it is again evident that neither the Maxwell-Garnett nor the Bruggeman models fit the data. Conversely, the Lichtenecker Rother equation again conforms well to the form of the experimental data set ($R^2 = 0.998$), albeit that, in this case, the derived permittivity value of BaTiO$_3$ is lower than anticipated, at 520 \pm 70. This result is, perhaps, less surprising than the very reasonable permittivity value determined for the PZT above, since it has been reported that, in general, effective medium theories do not conform to experiment across the complete composition range [8].
IV. DISCUSSION

Although the Lichtenecker Rother equation is commonly considered as being an empirical expedient, recent work has suggested that it does have a theoretical basis [9]. Considering the Maxwell Garnett equation in the form of the Rayleigh mixing formula, as shown in (5), provides a useful insight into why it cannot be applied to data that vary as seen experimentally here. If the permittivity of the matrix is known reliably, then the left hand side can be evaluated at different values of \( \phi_p \), whereupon, (5) reduces to a linear equation passing through the origin with gradient, \( m \), where:

\[
m = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}
\]

This equation only yields physically meaningful solutions for \( \varepsilon_p \) in the case that \( m < 1 \). In short, when the addition of low filler fractions results in a rapid increase in permittivity, as in Figs. 3 and 4 above, the Maxwell Garnett equation is inapplicable.

The Bruggeman equation can be considered in a similar manner to that described above for the Maxwell Garnett model; once again, provided the permittivity of the matrix is known reliably, then the left hand side can be evaluated at different values of \( \phi_p \) and plotted against \( \phi_p/(1 - \phi_p) \). Although, in this case, a straight line would not generally be anticipated, the following inequality must nevertheless hold:

\[
\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} < 1
\]

Thus, as \( \varepsilon_p \) tends to infinity, so the value of the left hand side of (8) tends to 1. That is, a plot of the left hand side of (6) against \( \phi_p/(1 - \phi_p) \) can never exhibit a gradient that is greater than 1. Using the experimental data generated here violates this requirement, thereby indicating that the Bruggeman model is inapplicable.

V. CONCLUSIONS

Although the above analysis concerns the conventional application of a number of commonly used effective medium theories to analyse the behaviour of systems than can reasonably be regarded as binary, our real interest in this topic relates to interfacial effects, which will become increasingly significant as phase sizes diminish. Under these circumstances, it can be argued that the incorporation of nanoscale inclusion into a matrix does not result in a binary system but, rather, a tertiary one: particles, matrix and interphase. Under these circumstances, in seeking to describe the mathematical form of the resulting data in which the effective permittivity is measured experimentally as a function of composition, different effective medium theories differ significantly in terms of their mathematical complexity. Consequently, is there any virtue in choosing a mathematically complex theory over simpler, more flexible formulae? Here, this has been exemplified by the Lichtenecker Rother equation, but other approaches, such as exponential mixing rules can also be considered. We conclude from the above results that the Lichtenecker Rother equation, which is easily modified to include a third component, is capable of providing an excellent mathematical description of even the extreme data sets presented here. In contrast, neither the Maxwell Garnett nor the Bruggeman equation can be made to fit the data, implying some deficiency in the underlying physics.

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