Supporting Information

Dielectric Properties for Nanocomposites Comparing Commercial and Synthetic Ni and Fe$_3$O$_4$ Loaded Polystyrene

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Contents

1. Supporting Figures. S3
1.1 Figure S1: pXRD patterns of nanoparticles S3
1.2 Figure S2: Magnetic (SQUID) measurements of nanoparticles and nanocomposites S4
1.3 Figure S3: TGA of nanoparticles and polystyrene S5
1.4 Figure S4: DSC thermographs for polystyrene and highest volume fraction nanocomposite samples S6
1.5 Figure S5: TGA of nanocomposite samples S7
1.6 Figure S6: pXRD patterns of nanocomposite samples S8
1.7 Figure S7A: SAXS Analysis of Syn-Fe₃O₄ (Form Factor Contribution) S9
1.8 Figure S7B: SAXS Analysis of Com-Fe₃O₄ (Form Factor Contribution) S11
1.9 Figure S8: Back-scattered electron data for cross section of sample discs S12
1.10 Figure S9: Back-scattered electron and energy-dispersive x-ray mapping of cast films S13
1.11 Figure S10: Imaginary permittivity (ε″) as a function of volume fraction for nanocomposites S14
1.12 Figure S11: Fitting of imaginary permittivity values at 1 MHz S15

2. SUPPORTING TABLES S16
2.1 Table S1: Equations for dielectric models used to fit permittivity data S16
2.2 Table S2: Calculated real permittivity values at 1 MHz from fitting experimental data of nanocomposites with various models S17

References S18
1. Supporting Figures

1.1 Supporting Figure S1. Powder X-Ray diffraction (pXRD) characterization of the nanoparticles. (A) $\text{Fe}_3\text{O}_4$ nature of iron oxide (syn and com). (B) Face-centered cubic (fcc) and hexagonal close-packed (hcp) nature of com-Ni and syn-Ni nanoparticles respectively.
1.2 Supporting Figure S2. Superconducting quantum interference device (SQUID) magnetic measurement data for the saturation magnetization of the nanoparticles (a) and saturation magnetization ($M_s$) of the polystyrene nanocomposites as a function of nanoparticle volume fraction (b). Synthesized nickel particles were of the HCP crystalline variant, which accounted for the ~1 emu/g value.
1.3 Supporting Figure S3. TGA analysis of surface ligand functionalization on filler nanoparticles used in study sans matrix showing 28, 7.6, 7.4, and 3.7 w/w% ligand mass for synthesized iron oxide, commercial iron oxide, synthesized nickel, and commercial nickel respectively.
1.4 Supporting Figure S4. DSC thermographs for (a) com-Fe$_3$O$_4$, (b) syn-Fe$_3$O$_4$, (c) com-Ni and (d) syn-Ni nanocomposites at the highest loading level, and (e) pure polystyrene. The data indicated that there was a minimal change ($\pm 2^\circ$C) in glass transition temperature (Tg) of the system upon nanoparticle incorporation.
1.5 Supporting Figure S5. Thermogravimetric analysis (TGA) of the composite samples in comparison to pure polystyrene for (a) com-Fe$_3$O$_4$, (b) syn-Fe$_3$O$_4$, (c) com-Ni and (d) syn-Ni nanocomposites. TGA of the samples suggests that the decomposition temperature of the polystyrene is increased to a small extent as the loading level of particles in the composite increases.
1.6 Supporting Figure S6. pXRD patterns for (a) com-Fe$_3$O$_4$, (b) syn-Fe$_3$O$_4$ (c) com-Ni and (d) syn-Ni nanocomposites. The peak at 20 degrees corresponds to the polystyrene matrix which decreases as the volume percentage of nanoparticles increases.
1.7 Supporting Information Figure S7A. Scaled intensity as a function of \( q \) for different samples as shown. The green curve is experimental \( I \) vs \( q \) for the synthetic iron oxide (0.69 vol % - Figure 2a in paper) – results have been scaled by a factor of 1000. The black curve is the experimental data divided by the form factor after polydispersity has been taken into account. The orange line is a guide to the eye to show that the peak position has not changed after taking into account the effect of form factor.

SAXS Analysis (form factor contributions)

The peak in Intensity (\( I \)) vs \( q \) is also taken to be the first peak in the structure factor – this will be made clear in the text. This is in agreement with a number of studies in literature which have made this assumption.\(^1\)\(^2\) We can also prove in our case that the first peak in \( I \) vs \( q \) is the same as the position of the first peak in structure factor – confirming the approach taken by investigators in literature.
The intensity $I(q)$ from a suspension of particles of volume fraction $\phi$ is given by

$$I(q) \sim \phi P(q) S(q) \quad (1)$$

where $P(q)$ is the particle form factor and $S(q)$ is the structure factor which is a relative measure of how the particles are spaced with respect to each other. $P(q)$ is given by

$$P(q) = \left[ 3 \frac{\sin \left( \frac{qd_i}{2} \right) - \frac{qd_i}{2} \cos \left( \frac{qd_i}{2} \right)}{\left( \frac{qd_i}{2} \right)^3} \right]^2 \quad (2)$$

where $d_i$ is the particle diameter.

One can account for modest Polydispersity in particle size by calculating $P(q)$ for a size distribution but assume $S(q)$ remains that for monodisperse particles. This can be done by employing a Gaussian diameter distribution to calculate an average form factor for a population of particles with mean diameter $d_i$ and standard deviation $\sigma_i$. The integration variable $x$ is the variable diameter of the particle.

$$\overline{P}(q) = \frac{\int \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp \left[ -\frac{(x-d_i)^2}{2\sigma_i^2} \right] x^6 P(q) dx}{\int \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp \left[ -\frac{(x-d_i)^2}{2\sigma_i^2} \right] x^6 dx} \quad (3)$$

For the synthetic Iron oxide particles – as reported in Table 1 (main text) – the average diameter is 11 nm with $\pm 0.9$ nm. From equation (1), the experimental $I(q)$ can be divided by the polydisperse form factor to yield the structure factor $S(q)$. Results are shown in figure S7 below.

Thus it can be seen in the figure that even after taking into account the effect of the form factor – the position of the first peak does not change. The conclusions in the paper are based on the position of the first peak and in agreement with other studies in literature. This can be shown to be true for the higher concentration iron oxide sample as well.

The effect of polydispersity on form factor is also shown for the commercial iron oxide samples $16.8 \pm 5.6$ nm in Figure S7B. As can be seen from the figure – polydispersity wipes out features in the form factor.
1.8 Supporting Information Figure S7B. Intensity as a function of q for commercial iron oxide sample with and without taking into account Polydispersity.

The commercial and synthetic nickel samples are almost double the size than synthetic iron oxide. If we do assume hard sphere behavior then the peak that we see in Figure 2 (main text) at 0.25 nm\(^{-1}\) would occur at 0.125 nm\(^{-1}\) – which is very close to the beam stop and hence we feel it is masked in our experimental measurements. Even in these samples, the peak in intensity vs q would be unaffected by the form factor as shown above.
1.10 Supporting Figure S8. BSE data for cross section of pressed sample discs for com-Ni (A i-iv), syn-Ni (B i-iv), com-Fe$_3$O$_4$ (C i and ii) and syn-Fe$_3$O$_4$ (C iii and iv). Dashed white lines indicate boundaries of sample.
1.11 Supporting Figure S9. BSE and corresponding EDS data for cross-section of cast films for lowest (i and ii) and highest (iii and iv) volume fraction of com-Fe₃O₄ (A), syn-Fe₃O₄ (B), com-Ni (C) and syn-Ni (D). White lines indicate boundaries of film.
1.12 Supporting Information Figure S10. Frequency dependent (0.1 Hz – 1 MHz) measurements of the imaginary permittivity ($\varepsilon''$) of (a) com-$\text{Fe}_3\text{O}_4$, (b) syn-$\text{Fe}_3\text{O}_4$, (c) com-$\text{Ni}$, and (d) syn-$\text{Ni}$ nanocomposites.
1.15 Supporting Figure S11. Imaginary permittivity ($\varepsilon''$) at 1MHz as a function of volume fraction for (a) com-$\text{Fe}_3\text{O}_4$, (b) syn-$\text{Fe}_3\text{O}_4$, (c) com-Ni and (d) syn-Ni nanocomposites with fitting using a linear (syn- samples) or power law (n=2, for com- samples).
2. SUPPORTING TABLES

| Model (Group) | Equation |
|---------------|----------|
| EMT (1)       | \( \varepsilon' = \varepsilon'_m (1 - v_f) + \varepsilon'_f v_f \) |
| Maxwell-Garnett (1) | \( \varepsilon' = \varepsilon'_m + 3\varepsilon'_m v_f \left( \frac{\varepsilon'_f - \varepsilon'_m}{\varepsilon'_f + 2\varepsilon'_m - v_f (\varepsilon'_f - \varepsilon'_m)} \right) \) |
| Lichtenecker (1) | \( \varepsilon' = \varepsilon' \left( 1 - v_f \right) \ln(\varepsilon'_m) + (v_f) \ln(\varepsilon'_m) \) |
| Sillars (1)    | \( \varepsilon' = \varepsilon'_m \left( 1 + \frac{3v_f (\varepsilon'_f - \varepsilon'_m)}{\varepsilon'_f + 2\varepsilon'_m} \right) \) |
| Maxwell-Garnett (with interactions) (2) | \( \varepsilon' = \varepsilon'_m \left( 1 + \frac{3v_f}{1 - v_f} \frac{\gamma (\varepsilon'_f - \varepsilon'_m)}{(1 - v_f) (\varepsilon'_f - \varepsilon'_m) + \gamma} \right) ; \quad \gamma = \frac{\varepsilon'_f - \varepsilon'_m}{\varepsilon'_f + 2\varepsilon'_m} \) |
| Looyenga (2)   | \( \varepsilon' = ((\varepsilon'_m)^{1/3} (1 - v_f) + (\varepsilon'_f)^{1/3} v_f)^3 \) |
| Yamada (3)     | \( \varepsilon' = \varepsilon'_m \left( 1 + v_f n' (\varepsilon'_f - \varepsilon'_m) \right) \left( n' \varepsilon'_m + (1 - v_f) (\varepsilon'_f - \varepsilon'_m) \right) \) |
| Van Beek (3)   | \( \varepsilon' = \varepsilon'_m \left( \varepsilon'_m + n(1 - v_f) + \varepsilon'_f (\varepsilon'_f - \varepsilon'_m) \right) \left( \varepsilon'_m + n(1 - v_f) (\varepsilon'_f - \varepsilon'_m) \right) \) |
| Bergman (3)    | \( \varepsilon' = \varepsilon'_m + \varepsilon'_f v_f \left( \frac{(\varepsilon'_m - \varepsilon'_f)}{\varepsilon'_f + n (\varepsilon'_m - \varepsilon'_f)} \right) \) |
| Tinga (3)      | \[
\begin{align*}
\varepsilon' &= \varepsilon'_m \\
&+ \varepsilon'_m v_f \left( \frac{(\varepsilon'_f - \varepsilon'_m)}{\varepsilon'_f + n (\varepsilon'_f - \varepsilon'_m) - n_m v_f (\varepsilon'_f - \varepsilon'_m)} \right)
\end{align*}
\] |

\( \varepsilon', \varepsilon_m, \varepsilon_f \) and \( v_f \) are the effective real dielectric of nanocomposite, real permittivity of matrix, real permittivity of filler and volume fraction of filler respectively.

\( n \) is a depolarization factor and \( n' \) is a shape parameter for models in Group 3 (group denoted in parentheses).

\( n_m \) and \( n_f \) are factors corresponding to matrix and filler in the Tinga model.

2.1 Supporting Information Table S1. Equations of various models used to fit dielectric real permittivity data. 

S16
### 1MHz Dielectric Data Fitting

| Model                                      | Syn Ni | Com Ni | Syn Fe$_3$O$_4$ | Com Fe$_3$O$_4$ |
|--------------------------------------------|--------|--------|----------------|----------------|
|                                            | $\varepsilon'_f$ | Chi squared | $\varepsilon'_f$ | Chi squared | $\varepsilon'_f$ | Chi squared | $\varepsilon'_f$ | Chi squared |
| 1 Effective Medium Theory                   | 6.79 ± 0.58 | 9.72E-03 | 5.93 ± 0.42 | 7.27E-03 | 3.88 ± 0.12 | 6.65E-04 | 4.95 ± 0.42 | 6.09E-03 |
| 1 Maxwell-Garnett                          | 11.70 ± 2.56 | 8.99E-03 | 8.38 ± 1.19 | 6.77E-03 | 4.16 ± 0.17 | 6.33E-04 | 5.95 ± 0.80 | 5.76E-03 |
| 1 Lichteneker                              | 12.68 ± 2.47 | 8.68E-03 | 9.10 ± 1.3 | 6.57E-03 | 4.28 ± 0.19 | 6.18E-04 | 6.33 ± 0.91 | 5.61E-03 |
| 1 Sillars                                  | 12.54 ± 3.19 | 9.72E-03 | 8.81 ± 1.44 | 7.27E-03 | 4.19 ± 0.18 | 6.65E-04 | 6.14 ± 0.92 | 6.09E-03 |
| 2 Looyenga                                 | 9.34 ± 1.25 | 9.02E-03 | 7.46 ± 0.78 | 6.79E-03 | 4.12 ± 0.16 | 6.33E-04 | 5.69 ± 0.65 | 5.77E-03 |
| 2 Maxwell-Garnett (with interactions)      | 11.60 ± 2.47 | 8.89E-03 | 8.34 ± 1.17 | 6.72E-03 | 4.15 ± 0.17 | 6.31E-04 | 5.93 ± 0.79 | 5.73E-03 |

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| Model                                      | Syn Ni | Com Ni | Syn Fe$_3$O$_4$ | Com Fe$_3$O$_4$ |
|--------------------------------------------|--------|--------|----------------|----------------|
|                                            | $\varepsilon'_f$ | $n$ or $n'$ | Chi squared | $\varepsilon'_f$ | $n$ or $n'$ | Chi squared | $\varepsilon'_f$ | $n$ or $n'$ | Chi squared |
| 3 Yamada                                   | -      | -      | -             | 243.8 ± 1.05e+05 | 1.2641 ± 8.03 | 6.18E-03 | -             | -             | -             |
| 3 van Beek                                 | 2.3391e+05 ± 0.62741 ± 0.178 | 8.38E-03 | -             | 3.7385e+05 ± 0.268 | 0.79478 ± 8.03 | 6.18E-03 | -             | -             | -             |
| 3 Bergman                                  | -1462.4 ± 5.86e+04 | 9.72E-03 | -             | 3390.3 ± 4.21e+04 | 989.21 ± 1.22e+04 | 7.27E-03 | -             | -             | -             |

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| Model                                      | Syn Ni | Com Ni | Syn Fe$_3$O$_4$ | Com Fe$_3$O$_4$ |
|--------------------------------------------|--------|--------|----------------|----------------|
|                                            | $\varepsilon'_f$ | $n_r$ | $n_m$ | Chi squared | $\varepsilon'_f$ | $n_r$ | $n_m$ | Chi squared | $\varepsilon'_f$ | $n_r$ | $n_m$ | Chi squared |
| 3 Tinga                                    | 8.1617 ± 2.25e+05 | 1.018 | 1.018 | 11.08 ± 11.7 | 11.08 | 13.8E-03 | 6.5539 ± 1.6e+05 | 0.67115 ± 2.43e+04 | 5.7493 ± 14.2 | 3.92E-03 | 4.1055 ± 7.76e+03 | 5.7493 ± 14.2 | 2.14E-04 | 3.0417 ± Inf | 3.5246 ± Inf | 55.752 ± Inf | 1.06E-03 |

- Does Not Fit

### 2.2 Supporting Information Table S2

Table showing dielectric data model fitting to real component of permittivity values obtained at 1 MHz using experimental volume fractions, real effective permittivity values of nanocomposites and the real permittivity of polystyrene.
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