The influence of suspended nanoparticles on the Frederiks threshold of the nematic host

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In recent years, several papers reported an enhanced dielectric anisotropy when ferroelectric particles were suspended in a liquid crystal. These results seem to be sensitive to the liquid crystal used and the preparation method of the ferroelectric particles. In this paper, we compare different preparation methods of suspended barium titanate in two different liquid crystal hosts. As a control experiment, we followed similar preparation steps with non-ferroelectric silica particles. In all cases, we found a broadening of the optical Frederiks transition but no change in the dielectric anisotropy. Raman spectroscopy has been used to investigate the loss of tetragonal structure in the barium titanate as a function of milling time and particle size. As reported in the earlier literature, barium titanate does not exhibit a well-defined tetragonal crystal structure below a certain particle size and loses its ferroelectric features. This provides a simple rationalization for the absence of any dielectric enhancement.

1. Introduction

The considerable experimental and theoretical interest in suspensions of ferroelectric particles in liquid crystal hosts has arisen from reports of an enhanced dielectric anisotropy [1] and a dramatic change in the Frederiks [2] transition relative to the pure nematic
host [3]. While these improved properties are of great interest for display manufacturing, they appear to be dependent on the nematic host used and on the particle preparation and dispersion methods [4,5]. In this paper, we have prepared and carefully characterized particle systems in various ways and assessed their behaviour in both the ubiquitous nematic liquid crystal 4-cyano-4’-n-pentylbiphenyl (5CB) and the commercially important ZLI2293—a Merck nematic blend.

2. Sample preparation

(a) Nanoparticles

Two nanoparticle systems were investigated: (i) potentially ferroelectric BaTiO3 and (ii) fumed silica. The non-ferroelectric fumed silica control was used to establish the impact of similarly sized nanoparticle fillers. The different grades of fumed silica were used as received, whereas the BaTiO3 was milled prior to being stabilized and dispersed in the different liquid crystals.

(i) Ferroelectric barium titanate

The barium titanate, BaTiO3, nanoparticles (as received from Sigma-Aldrich) were suspended in benzyl alcohol and their average radius was determined by dynamic light scattering using a Malvern Zetasizer Nano S equipped with a He–Ne laser emitting at 633 nm. For the data analysis, the viscosity was taken as that of the pure solvent and the general purpose option was chosen. The unmilled particles had an average hydrodynamic radius of approximately 60 nm. Milled BaTiO3 nanoparticles were prepared from a mixture of 30 wt% of BaTiO3 in benzyl alcohol by using a planetary bead mill (Fritsch Pulverisette 7 premium line), where milling was performed in two stages. During stage one, a mixture of BaTiO3/benzyl alcohol/0.3 mm yttria-stabilized zirconia (YTZ) beads at a ratio of 6.9 wt%/16.2 wt%/76.9 wt% was milled for 355 min at 900 r.p.m. after which a first size plateau was reached. To reduce the size further, the milling beads were exchanged for 0.1 mm YTZ beads. The exchange of the milling beads caused a loss of sample and the weight ratio of BaTiO3/benzyl alcohol/0.1 mm YTZ beads changed to 5.9 wt%/13.8 wt%/80.3 wt%. After 1045 min (the total time in the mill was 70 h excluding changeover time but including cooling cycles) the milling process was terminated to avoid damage to the seals. This protocol was developed following advice from the manufacturer and extensive trial and error. It optimized the milling efficiency and avoided contamination from degradation of the YTZ beads. The final hydrodynamic radius was determined as 22 ± 3 nm. Measurements of the same sample dried on a glass slide by atomic force microscopy (AFM) gave a radius of 16 ± 5 nm. Despite the extensive milling procedure, both size measurements of the milled BaTiO3 systems were larger than the 6 nm reported in Atkuri et al. [5] (figure 1).

The milled BaTiO3 was milled again at 500 r.p.m. for 60 min to attach the various carboxyl-terminated mesogenic stabilizers shown in table 1. This was typically done with a ratio of 10 g of BaTiO3 to 1 g of stabilizer which should provide complete coverage of the milled particles. We chose carboxyl terminations, adopting the protocol used in Atkuri et al. [5], where oleic acid was thought to attach well to BaTiO3. However, during our investigations we have found this assumption to be only partly correct.

The product was then washed off the beads with propan-2-ol followed by several further washes to remove any excess stabilizer. Finally, the sample was transferred into cyclohexane and then into the two liquid crystals at 0.5 wt%.

As a control experiment, we followed the protocol described as most successful in Atkuri et al. [5]. A composition of 4.5 wt% of BaTiO3, 4.5 wt% of oleic acid and 91 wt% of heptane was added to 3 mm YTZ milling beads and milled at 550 r.p.m. for 510 min. This speed was adapted to the different disc radius of the Pulverisette 7 and the 510 min is a pure milling time, excluding cooling cycles which are necessary to keep the temperature inside the pots below 50°C. The ratio of BaTiO3 to milling beads by weight was 1:10 as recommended in
Figure 1. Development of the hydrodynamic radius of BaTiO₃ as a function of milling time.

Table 1. Mesogenic stabilizers. All stabilizers were used as received and supplied by Synthon Chemicals with the exception of PXSA which was supplied by Sigma-Aldrich.

<table>
<thead>
<tr>
<th>code</th>
<th>chemical name</th>
<th>structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST 401</td>
<td>4-ethylbenzoic acid</td>
<td><img src="" alt="4-ethylbenzoic acid" /></td>
</tr>
<tr>
<td>ST 404</td>
<td>4-n-pentylbenzoic acid</td>
<td><img src="" alt="4-n-pentylbenzoic acid" /></td>
</tr>
<tr>
<td>ST 467</td>
<td>4-n-pentyloxybiphenyl-4′-carboxylic acid</td>
<td><img src="" alt="4-n-pentyloxybiphenyl-4′-carboxylic acid" /></td>
</tr>
<tr>
<td>ST 474</td>
<td>4-n-pentylbiphenyl-4′-carboxylic acid</td>
<td><img src="" alt="4-n-pentylbiphenyl-4′-carboxylic acid" /></td>
</tr>
<tr>
<td>ST2762</td>
<td>trans-4-(4-n-pentylcyclohexyl)benzoic acid</td>
<td><img src="" alt="trans-4-(4-n-pentylcyclohexyl)benzoic acid" /></td>
</tr>
<tr>
<td>PXSA</td>
<td>p-xylene-2-sulfonic acid hydrate</td>
<td><img src="" alt="p-xylene-2-sulfonic acid hydrate" /></td>
</tr>
</tbody>
</table>

Atkuri et al. [5]. The hydrodynamic radius of the sample in heptane was determined as 315 ± 9 nm by light scattering, indicating substantial aggregation. After washing and redispersing into benzyl alcohol, the radius dropped to 71 ± 2 nm. The radius of the washed sample, determined by AFM, was about 6 nm and would vary from sample to sample. We conclude, therefore, that
Table 2. Fumed silica particles were supplied by Evonik.

<table>
<thead>
<tr>
<th>commercial name</th>
<th>primary particle radius (nm)</th>
<th>compounds used in surface treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil R812</td>
<td>3.5</td>
<td>hexamethyldisilazane</td>
</tr>
</tbody>
</table>
|                 |                              | \[
|                 |                              | \text{\begin{tabular}{c}
| CH$_3$ & Si \end{tabular}} & \text{\begin{tabular}{c}
| H \end{tabular}} & N & Si & CH$_3$
| CH$_3$ & Si & H & N & Si & CH$_3$
| \end{tabular}}
|                 |                              |                                   |
| Aerosil R816    | 6                            | hexadecyltrichlorosilane          |
|                 |                              | \[
|                 |                              | \text{\begin{tabular}{c}
| CH$_3$(CH$_2$)$_{14}$CH$_2$ & Si & Cl
| Cl & Cl
| \end{tabular}}
|                 |                              |                                   |

the samples exhibit a substantial size distribution after milling and diluting as preparation for the AFM substrates. This may lead to a bias towards small particles because, in the process of stepwise dilution, bigger particles have a tendency to sink to the bottom of the container and not be transferred into the next dilution. An appropriate amount of the milled sample, washed in heptane, was transferred into the liquid crystals to yield the desired mass fractions.

(ii) Fumed silica

To avoid contamination of the liquid crystals by any surplus stabilizer, the pre-treated particles were washed several times in propan-2-ol and dried. The particles were dispersed into cyclohexane and transferred into the two liquid crystals following the same procedure adopted for the BaTiO$_3$. The primary particle radius of all the fumed silicas used here was given by the supplier as less than 10 nm (table 2).

(iii) Liquid crystals

We used two different nematic liquid crystals: 5CB and ZLI2293, whose properties are summarized in table 3. We chose 5CB as a well-known and well-characterized liquid crystal that was reported in recent studies [1,4] to show a shift in Frederiks transition when mixed with ferroelectric particles. The other liquid crystal used in Reznikov et al. [1], ZLI4801, a super fluorinated high holding ratio mixture for active matrix displays, was not available to us. Instead, we used ZLI2293 which is a broad range mixture for super twisted nematic displays. The choice was rationalized by the idea that if the observed shift in the Frederiks transition in Reznikov et al. [1] was caused by the ferroelectric particles only, it should be liquid crystal independent. For display applications the most interesting result would be a reproducible shift in any mixture already used in display applications.

(iv) Suspensions

The particles were transferred either from heptane or cyclohexane into the two different liquid crystal hosts (table 3). The suspensions were not dried to avoid the possibility of collapsing the stabilizing chains. The transfer solvents were selected with low boiling points to allow evaporation without decomposing the liquid crystal or the stabilizer. Prior to use, the suspensions were sonicated for 30 min.

The stability of the suspensions varied with the choice of stabilizer and particle size. Typically, the particles remained dispersed for between 5 h and five months before complete precipitation.
Figure 2. Suspension of BaTiO$_3$ in 5CB with different preparation methods and stabilizers. The arrows indicate the interface between liquid crystal and aggregated particles. The picture was taken four weeks after the suspensions were first made.

Table 3. Liquid crystals used in this study. 5CB is single component liquid crystal and was obtained from Synthon and ZLI2293 is a commercial mixture obtained from Merck.

<table>
<thead>
<tr>
<th>chemical name</th>
<th>components</th>
<th>transition temperature ($^\circ$C)</th>
<th>dielectric constants ($T = 20^\circ$C)</th>
<th>refractive indices ($T = 25^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB, 4-cyano-4$'$.n-pentylbiphenyl</td>
<td></td>
<td>35.3</td>
<td>$\varepsilon_{\parallel}$ 18.8, $\varepsilon_{\perp}$ 7.3</td>
<td>$n_{\parallel}$ 1.53, $n_{\perp}$ 1.50</td>
</tr>
<tr>
<td>ZLI2293 commercial mixture</td>
<td></td>
<td>85.0</td>
<td>$\varepsilon_{\parallel}$ 14.1, $\varepsilon_{\perp}$ 4.1</td>
<td>$n_{\parallel}$ 1.50, $n_{\perp}$ 1.63</td>
</tr>
</tbody>
</table>

The aggregation tended to be slower for stabilizers exhibiting a similar chemical functionality to the liquid crystal host and for the smaller the particles (figure 2). The samples prepared following the method in Atkuri et al. [5] tended to aggregate within minutes irrespective of the amount of washing. This meant that test cells could not be filled with a uniform suspension.

(v) Sizing

The particle size, measured with dynamic light scattering, was always greater than reported in recent studies [1,3,5]. Dynamic light scattering measures the hydrodynamic radius of the particles when in dilute suspension. The technique is, therefore, only useful for assessing primary particle size for well-dispersed (non-aggregated) suspensions. Atkuri et al. [5] determined the particle size by transmission electron microscopy (TEM). AFM was used here to attempt comparable measurements. The samples were drop cast as dilute suspensions onto clean glass substrates, dried and measured in tapping mode using a Dimension 3000 AFM by Digital Instruments. Using this technique, it was possible to measure the primary particle size even when...
Table 4. Comparison of hydrodynamic radius and AFM radius.

<table>
<thead>
<tr>
<th>sample</th>
<th>hydrodynamic radius (nm)</th>
<th>radius measured by AFM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$, as received, in ethylene glycol</td>
<td>405 ± 90</td>
<td>36 ± 7</td>
</tr>
<tr>
<td>BaTiO$_3$, as received, in 1-octanol</td>
<td>74 ± 1</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$, as received, in benzyl alcohol</td>
<td>60 ± 1</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$ milled for 1045 min at 1000 r.p.m. in benzyl alcohol</td>
<td>22 ± 3</td>
<td>16 ± 5</td>
</tr>
<tr>
<td>BaTiO$_3$ milled for 1045 min at 1000 r.p.m. in benzyl alcohol and treated with ( p )-xylene-2-sulfonic acid, suspended in benzyl alcohol</td>
<td>21 ± 0.5</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>BaTiO$_3$ milled for 1045 min at 1000 r.p.m. in benzyl alcohol and treated with ( p )-xylene-2-sulfonic acid, suspended in toluene</td>
<td>1122 ± 28</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$ milled following the procedure published in Atkuri et al. [5], suspended in benzyl alcohol and treated with ST404, suspended in benzyl alcohol</td>
<td>67 ± 3</td>
<td>4 ± 1.5</td>
</tr>
<tr>
<td>BaTiO$_3$ milled following the procedure published in Atkuri et al. [5], suspended in heptane</td>
<td>315 ± 9</td>
<td>6 ± 1 (after extensive washing and removal of all oleic acid)</td>
</tr>
<tr>
<td>BaTiO$_3$ milled using the ratios published in Reznikov et al. [1], suspended in heptane</td>
<td>71 ± 2</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$ milled using the ratios published in Reznikov et al. [1], suspended in benzyl alcohol</td>
<td>168 ± 2</td>
<td>4 ± 1 (after extensive washing and removal of all oleic acid)</td>
</tr>
<tr>
<td>BaTiO$_3$ milled using the ratios published in Reznikov et al. [1], suspended in benzyl alcohol</td>
<td>62 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

The particles were aggregated. In table 4, the measured hydrodynamic radius is compared with the radius measured with AFM. From these data it was concluded that the particles in suspension do not occur as isolated particles but as aggregates. The number of particles in those aggregates could vary between as few as two and as many as 100. The rapid separation of particles and liquid crystal host solvent by the sedimentation observed is likely to be indicative of the larger sized aggregates present in the unstable suspensions.

Even in highly dilute suspensions, the BaTiO$_3$ particles stabilized with oleic acid showed substantial amounts of free oleic acid that would crystallize when preparing AFM substrates (figure 3a). The size of particles could not be determined because of the needle-like crystals between them. After vigorous washing with propan-2-ol to remove the crystals, the particle radius was determined as approximately 5 nm (from the heights in figure 3b), confirming the results in Atkuri et al. [5].
Figure 3. AFM topological scans taken of BaTiO$_3$ (a) before rigorous washing and (b) after. The scales are height in metres.

Figure 4. Micrograph taken by AFM of unmilled BaTiO$_3$ stabilized with PXSA after washing. The scale is in metres.

In figure 3b, it is clearly apparent that the stabilizer has been removed by washing. This explains why it was not possible to suspend oleic acid stabilized particles after washing to remove surplus stabilizer and, therefore, avoid ionic contamination of the liquid crystal. Figure 4 shows an AFM scan of BaTiO$_3$ stabilized by PXSA. It can be seen that the particles are surrounded by a halo of stabilizer despite the sample undergoing the same rigorous washing procedure as the sample in figure 3b. The size was determined as approximately 10 nm, but this was a sample that had not been milled. As mentioned before, the process of diluting seems to favour small debris.

3. Ferroelectricity

To determine whether the BaTiO$_3$ particles were ferroelectric, we used Raman spectroscopy. BaTiO$_3$ is ferroelectric when its unit cell is tetragonal, rather than cubic [6,7]. The tetragonal phase (space group P4mm) should be Raman active so the optic phonon peaks are observable while, in principle, the cubic phase is Raman inactive. However, optic phonons may become observable
in the cubic phase [8]. We have measured Raman spectra from three different sizes of BaTiO$_3$ particles. They were specified by the manufacturer as 3–12 mm, less than 2 $\mu$m and a 30–50 nm nanopowder. However, TEM showed that the nanopowder had average diameter of 90 nm.

The micro-Raman measurements were performed using a PerkinElmer RamanFlex 300 system equipped with a fibre coupled 785 nm diode laser. The laser was focused on the sample using 50× microscope objective in a spot with diameter of about 40 $\mu$m. The total laser power on the sample was about 60 mW. Raman spectra were recorded in a backscattering geometry and no polarizers were used. The samples were placed in a Linkam TS600 temperature stage allowing control of the temperature with accuracy of about $\pm$0.1°C and spectra were recorded from 25°C to 200°C.

At room temperature optic phonon peaks $E(3TO)$ and $E(3LO)$ at 517 and 753 cm$^{-1}$, respectively [9,10], are clearly visible and they tend to reduce in amplitude as the temperature increases. There is also a sharp peak from a ‘silent’ mode at 308 cm$^{-1}$, which also decreases with increasing temperature (figure 5). It has been used as an indicator of the tetragonal phase [4]. It can be seen in figure 6 that for the large particles, there is a reasonably abrupt decrease at the Curie temperature of 120°C (see data for 3–12 mm in figure 7). For the smaller particles, the decrease is more gradual and the intensity remains to higher temperatures as shown in figure 6. Comparing the curves for the 2 $\mu$m and the nanopowder suggests that it is material near the particles’ surfaces that gives the observable phonon peaks even when the cores are in the cubic phase.

The effect of milling has been found to be quite dramatic. At room temperature, there are no visible Raman peaks in the milled sample (figure 7). This suggests that the crystalline structure is disrupted so that there are no significant regions of tetragonal structure. This is supported by powder diffraction measured on a Panalytical X-pert Pro diffractometer with copper radiation. The Scherrer broadening of the 110 Bragg peak at $Q = 2.22$ Å$^{-1}$ gives a crystal size of approximately 10 nm, very much less than for the unmilled powder. Guinier analysis [11] of the small angle X-ray scattering from many dilute suspensions gave radii of gyration in the range 10–20 nm indicating a particle size of at least 10 nm with some suggestion of aggregation. It therefore seems probable that the tetragonal structure was not present in these milled particles.

4. Frederiks transition

A reduction in the voltage required for a Frederiks transition has been extensively used as an indicator of enhanced dielectric anisotropy in nematic liquid crystals. To measure the transition voltage of the different samples, the suspensions were filled into transparent glass cells. For
each cell, one substrate consisted of a flat indium tin oxide (ITO) electrode covered with an insulating layer of SU8-2011 with rubbed Nissan 130 (both from Brewer Science) on top of it. The other substrate had a lollipop ITO electrode, again covered with SU3-2011 and rubbed polyimide Nissan 130. The cells were spaced by 5 µm spacer beads mixed in UV curable glue and applied to the outer edges of the substrates when the cell was assembled. Contact of the glue/spacer bead mixture with the liquid crystal was avoided to prevent any chemical contamination. The

Figure 6. Integrated Raman intensity of peak at 308 cm$^{-1}$ as a function of temperature. (Online version in colour.)

Figure 7. Raman intensity as a function of Raman shift for unmilled (dotted line) and milled (solid line) nanopowder at 22°C. (Online version in colour.)
Figure 8. 0.5 wt% of Aerosil R816 in ZLI2293.

Figure 9. Set-up for Frederiks threshold measurement. The sample was oriented at 45° between crossed polarizers.

dimensions of the lollipop were well defined such that the area and volume of the cell could be accurately determined. When inspected under the microscope, all suspensions showed particle aggregates as shown in figure 8.

The cell was connected to a power supply (Hewlett Packard 33120A waveform generator in combination with a Krohn Hite amplifier 7500) and put between crossed polarizers at 45° as shown schematically in figure 9. Transmission and capacitance were then recorded as a function of applied voltage after the cell had been aligned using a searching routine for maximal and minimal transmission. In order to minimize electrophoretic movement of the particles, the applied field was always a 1 kHz sine wave.
5. Results

To establish a base line for all experiments, pure ZLI2293 and 5CB were filled into the lollipop cells and the transmission, capacitance and resistance were measured simultaneously (figure 10). Capacitance and resistance measurements are not influenced by any scattering in the optical range and, therefore, were used to establish whether a shift of the Frederiks transition had indeed taken place.

Figure 10. (a) Transmission, (b) capacitance and (c) resistance for pure 5CB and pure ZLI2293.
The addition of particles, whether silica or BaTiO$_3$, leads to a reduction in optical transmission owing to scattering by the aggregates. After an electric field was applied beyond the threshold strength and a transition had taken place, none of our samples returned to their original optical state when the field was removed, indicating a memory effect. From the optical data, it was hard to determine whether a shift of the transition had occurred. In figure 11, the optical data suggest a shift towards a slightly higher threshold voltage but the capacitance measurement does not support this interpretation. For all stabilizers, we found the same result where apparent shifts in the Frederiks transitions for BaTiO$_3$ in 5CB were not confirmed by capacitance measurements.

ZLI2293 was more compatible with the added particles where, although aggregation took place it seemed to be less pronounced than in 5CB. Both optically and in capacitance, no shift of the Frederiks transition could be observed as shown in the examples of figure 12.

6. Conclusions

Even though the harvesting procedure described in Cook et al. [12] was not applied, some confirmation that milled BaTiO$_3$ retains the tetragonal phase was expected especially because a downwards shift of the Frederiks transition for BaTiO$_3$ suspensions was reported in Blach et al. [4] and Cook et al. [12] for milled particles. We tried to mill under equivalent conditions as described in Atkuri et al. [5], but failed to generate samples that showed any characteristic indicative of ferroelectricity. The particle suspensions tested showed no shift in the Frederiks transition whether BaTiO$_3$ or silica nanoparticles were used. This is not surprising because according to our Raman results both particles should behave like simple non-ferroelectric fillers. Comparing our results for milled BaTiO$_3$ in 5CB with those reported in Blach et al. [4], we conclude that the
precise details of the milling process are significant in preserving some ferroelectricity in particles that are small enough to suspend. Indeed, in Cook et al. [12], it was already noted that there was a large variability between batches milled in the same way.

In Blach et al. [4], the tetragonal peak is present in the Raman scattering from milled BaTiO$_3$ and a shift in the Frederiks transition was observed in 5CB suspension. In our results, the tetragonal peak has disappeared on milling and there is no shift. Cook et al. [12] have identified strain in the particles as an important factor for maintaining the ferroelectric phase, but it remains unclear why our, apparently very similar, procedure does not produce a significant amount of strained

Figure 12. (a) Optical transmission of particle suspensions in ZLI2293. (b) Capacitance data. Neither the optical data nor the capacitance data showed any shift of the Frederiks transition.
tetragonal particles. In following a strict protocol, we have endeavoured to minimize degradation and contamination of our milled product, but clearly the critical factor in producing ferroelectric particles remains to be identified. We suggest that Raman spectroscopy is a reliable tool in the future quest to find a means of production of ferroelectric BaTiO₃ nanoparticles in good yield.

Although oleic acid is a standard stabilizer in this area, we have found that materials with comparable structure to typical nematogenic molecules give much more stable suspensions. This line requires further development if useful materials for applications are to be achieved.

We would like to thank Jana Heuer and John Rudin for their help with experiments.

References