Nanocomposites of ferroelectric liquid crystals and FeCo nanoparticles: towards a magnetic response via the application of a small electric field


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ABSTRACT
We study a nanocomposite consisting of a ferroelectric liquid crystal and a magnetic nanoparticle in order to explore the possibility of using it as a magnetic resonant imaging contrast agent which will measure a field of 20 V/m. To achieve this we use the ferroic properties exhibited by the nanocomposite. We used the ferroelectric liquid crystal 2-((4-((2-fluorooctyl)oxy)phenyl)-5-(octyloxy)pyrimidine mixed with FeCo nanoparticles nominally 2–3 nm in diameter in concentrations of 0.56, 4.3 and 10.8 wt%. The 10.8 wt% sample was chosen for our study because the nanoparticles acted as a lubricant for the ferroelectric liquid crystal. This concentration yields nanoparticle clusters in about 5–10 μm diameter spherulites. An electric field as low as 5V/cm is enough to turn and realign the spherulites where the particles are contained. We estimate the value of the magnetic in a spherulite and associate it to the number of spherulites aligned as a function of electric field. We find thus that we can achieve low electric fields.

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1. Introduction
Nanocomposites that consist of liquid crystals and nanoparticles have been used for a variety of applications that include those that respond to small applied magnetic fields [1–6], in addition to bioengineering applications [7–11], membrane fabrication and drug delivery [12,13], photonics [14–16], photovoltaics...
Nanoparticles will tend to concentrate along the liquid crystal disclination lines, and along the layer separations, if the liquid crystal is in the smectic phase [23–26]. Magnetic nanoparticles in particular tend to align in lines, with their magnetisation vectors aligned with each other with the application of a magnetic field (see for example [26–28]), similarly to what is observed in nematics doped with micron size particles (see for example [29,30]). When they assemble thus, a magnetic field results that reduces the intensity of the applied external field needed to re-align the liquid crystal sample, by up to five orders of magnitude [31].

A nanocomposite that consists of a ferroelectric liquid crystal and magnetic nanoparticles will result in a multiferroic system, where a magnetic field can be generated by the application of an electric field and vice versa [32–35]. The effects of magnetic nanoparticles on the SmA-SmC* transitions have been studied extensively [25,36,37]. These nanocomposites have been explored for the possibility of using the resulting nanocomposites as soft indirect magnetoelectrics [32–35]. The magnetic nanoparticles are always magnetised to a single domain [34]. In the presence of an applied electric field, the presence of the magnetic nanoparticles results in a reduction of all critical fields [34].

We note that the nanoparticle concentration can vary between 0.1 and 20 wt % [38–41], depending on the properties that one seeks to enhance [42,43]. The magnetic nanoparticles cluster for higher concentrations. This phenomenon has been observed for other phases of the liquid crystal [31,44,45] in addition to the nematic phase (see for example [14,46]), and for different nanoparticles. The nanoparticles form visible aggregates as observed with polarised optical microscopy. These aggregates tend to exist inside small spherules, commonly formed by cooling from the isotropic phase of the liquid crystals. They do not re-aggregate when cycled through in temperature. This formation is observed in nematic liquid crystals [14,47] and in the isotropic-nematic-smectic A transition regions for 8CB [48], as mentioned before.

We are interested in generating a magnetic field with an electric field of 20V/m, and to have a magnetic field that will be detected by an MRI instrument. We report on a study performed on a nanocomposite of the ferroelectric 2-(4-((2-fluoroctyl)oxy)phenyl)-5-(octyloxy) pyrimidine, mixed with FeCo magnetic nanoparticles. The nanoparticles have an average size of 2.5–3.5 nm, and are functionalised with polyethylene glycol (PEG) [31]. Three concentrations of FeCo are examined: 0.56, 4.35 and 10.8 wt %. We begin to observe the realignment of the clusters at fields as low as 5V/cm. The re-alignment seems to saturate at 10³V/cm for a concentration of 10.8 wt % of the FeCo in the ferroelectric liquid crystal. We find it takes a small applied electric field to begin to align the nanoparticles. The magnetic response to an applied electric field can be applied to an MRI contrast agent. This can been done by encapsulating the nanocomposite, such that it can be easily introduced and removed from the body [48]. Our purpose is: 1. to reduce the applied electric field that produces the required magnetic field down to the electric fields produced by biological systems, 2. while keeping the concentration of nanoparticles relatively low.

2. Experimental

The ferroelectric liquid crystal 2-(4-((2-fluoroctyl)oxy)phenyl)-5-(octyloxy)pyrimidine was available in our laboratory. The chemical formula is shown in Figure 1. The phase sequence is I – 94.15°C – smA – 78.49°C – SmC* – 44.94°C – C. The second order SmA-SmC* transition is not easily detected by using a differential scanning calorimeter (Mettler FP90A), with an accuracy of ±1°C, as observed in Figure 2. However, this transition can easily be distinguished by the study of the spontaneous polarisation, $\mathbf{P}_s$ (Figure 3).

The mixtures were prepared using a method similar to that used to prepare FeCo in 8CB [31,49] and ZnO in 8CB [19,20]. We add the magnetic nanoparticles until they comprise approximately the desired weight per cent of the mixture with the ferroelectric liquid crystal. The samples were weighed again after a 24-hour period. There was a consistent loss of weight in the sample that we attribute to some of the glycol evaporated, since that is the most volatile of the materials in the mix. This loss in weight has been observed before with different samples and different balances used. The weight percentage was then calculated. A magnetic rod was added, and the mixture was placed in a magnetic stirrer for about three hours in the isotropic phase at about 150°C so that a homogeneous mixture is obtained. This part of the preparation is repeated several times so as to obtain a homogenous mixture every time it is probed. We ended with weight percentages of 10.08, 4.3 and 0.56 wt%.

The ferroelectric properties were measured by placing the sample into a commercial LC-4–6.8 INSTEC...
sandwich cell with a thickness of 6.8 μm with a polyimide anti-parallel planar alignment. These cells were placed in a thermal oven (INSTEC HCS-302), with a temperature control between 0.1 and 20 μCmin (STC-200). The process of heating or cooling was monitored using WINTEP software. The textures in the liquid crystal sample were viewed using a Leica DLPM polarising microscope equipped with a Nikon DXM-1200 CCD camera. The spontaneous polarisation was obtained using the triangular wave method \[50,51\] with a function generator (TTI TG1010A, 10 MHz), connected to an amplifier (FLC 400D). A voltage of 200Vpp and 70 Hz was applied to the sample cell and monitored using an oscilloscope (HP5460B). The time switching was obtained by applying a square wave to the samples and reading the time scale from the data stored in the computer.

We deposited a droplet on an open ITO substrate with interdigitated electrodes and applied an electric field perpendicular to the grooves of the substrate to observe its effect in the motion of the droplets. These droplets had a thickness of approximately 100μm. They were measured at 75°C, which is in the smC* phase, and close to 100°C, which is in the smA phase for the 10.8%wt sample, and in the isotropic for the pure and the 0.53%wt sample. In addition to monitoring them on the Leica polarising microscope, we observed their size using an Olympus B50 polarising microscope equipped with an INFINITY 2 CCD camera.

We used the following equipment to obtain information on the FeCo nanoparticles. Studies using X-ray scattering were performed in a Rigaku 18kW source, with a Cu 1.54Å source and a bent graphite monochromator with a resolution of Δq = 0.015qo operating a 50kV and 100mA. The dynamic light scattering (DLS) experiment was performed on a Malverne Zetaziser Nano S90. The polarising microscope studies were performed in both a Leika microscope and an Olympus B50 microscope, as mentioned above.

3. Results

The nanoparticles of FeCo were prepared by polyol processing \[52\] and functionalised with PEG. The

![Figure 2](Colour online) Differential scanning calorimeter measurements of the different mixtures. Note that the SmA-SmC* transition is not evident in these measurements.

![Figure 3](Colour online) Spontaneous polarisation as a function of temperature for different concentrations of FeCo in the ferroelectric liquid crystal.
polyol method is a low-temperature method of growing the nanoparticles. The nanoparticles were analyzed by X-ray scattering and DLS. The X-ray scattering shows the [110] peak of the disordered BCC structure of FeCo, several peaks that correspond to the PEG [53] (not shown for clarity) that cover the [200] peak and a very disordered peak close to the aforementioned [110] peak. The very disordered peak corresponds to the [110] peak of the B2 structure (CsCl) that occurs in the region where the quantity of Fe is almost equal to the quantity of Co in the alloy, between the values of 48 and 52, and at lower temperatures [54]. Analysis of the peaks showed that the lower is centred around 2.94Å⁻¹, and the slightly higher peak is centred around 3.1Å⁻¹. The peak at 2.94Å⁻¹ gives a size of 2.6 ± 0.4 nm by analyzing the width of the peak. There is a wider peak centred at q = 3.1Å⁻¹. This peak has a width of 0.5 ± 0.2 nm. The two peaks blend into each other, as seen in Figure 4a. The size of the particles comes mostly from the disordered BCC structure. The size of the particles is 4.0 ± 1.5 nm determined by Dynamic Light Scattering (Figure 4b). The smaller size shown in the X-ray analysis does not appear in the Dynamic Light Scattering because it is at the lower limit of what the machine can measure.

The FeCo nanoparticle is superparamagnetic at smaller sizes as the ones determined above. The magnetisation is close to 10⁻²⁰ J/T or 10⁻¹⁷ emu [31]. The application of the magnetic field realigns the magnetisation vector and orients it along the magnetic field direction. This same reference [31] looks at the effect of the size of the nanoparticles with respect to the layer separation of the smectic liquid crystal. The smaller size interacts more because of the similarity in size with the liquid crystal, and while it can act to disorder it, under a field it can act to order it.

Figure 2 shows the results obtained for the spontaneous polarisation $P_s$ [51] for the different concentrations, in the entire range of the smC* phase. The smA-smC* transition temperature does not vary for the small concentration (0.53% wt) sample from where it is at 0% wt sample, and decreases close to three degrees in the high concentrations (4.35% wt and 10.8% wt). The values of the $P_s$ tend toward the same value in the deep smC* phase for all concentrations.

Figure 5 shows the switching time as a function of

![Figure 4](image-url) (Colour online) (a) X-ray scattering measurements showing the two peaked structure due to the BCC and the B2 (CsCl) structure of the FeCo nanoparticles. Analysis of the peaks show that the particles are 2.6 ± 0.4 nm for the disordered BCC structure. (b) Dynamic light scattering, showing a size that is about 4 ± 1.5 nm.
temperature. The behaviour of the switching time between 0% and 10.8% wt shows a variation that goes from being almost constant as a function of temperature at 0% wt to having a large variation as a function of temperature for 4.35% wt to being constant as a function of temperature for 10.8% wt. The 0% wt sample shows a decrease close to the crystalline phase transition at 66°C, and exhibits an increase of about 0.06%. The 0.53% wt concentration has an increase in switching time of approximately 17%. The 4.35% wt concentration has an increase in switching time of approximately 51% in the same temperature range. The 10.8% wt exhibits a switching time that remains constant all through the smC* phase within the resolution of the measurement and is constant even in the smA-smC* transition.

The nanoparticles form visible aggregates as observed with polarised optical microscopy for the highest concentration, Figure 6. These aggregates tend to exist inside small spherulites, commonly formed by cooling the isotropic phase of the liquid crystals. They do not re-aggregate when cycled through in temperature. This is observed in nematic liquid crystals [14,47] and in the isotropic-nematic-smectic A transition regions for 8CB, shown in Figure 6a–c. The spherulites tend to disappear in the isotropic phase, allowing the aggregates to move freely, as observed in Figure 6a. We note that not all of the spherulites contain aggregates of the nanoparticles as seen for our system in Figure 6a. These nanoparticles can interact, line up their magnetisation vector through the effect of an applied external field, and produce an ordered magnetic field from their collective lining up as shown up in Figure 6f. This interaction will depend on the concentration of the nanoparticles in the liquid crystal [28,34,55].

We observe the motion of the spherulites on the substrate to monitor the alignment of the magnetic nanoparticles with polarised optical microscopy. These spherulites were on average about 5–10 μm in diameter. Their sizes vary, as can be seen from Figures 6 and 7, depending on where in the sample they are located. For example, Figure 6d,e were taken at the border of the sample, to better compare them with Figure 6a–d which were taken at the border of the sample. Figures 6f and 7 were taken in the bulk where the measurements were taken. An applied electric field will move these spherulites in the substrate such that they form lines at the higher electric fields, as

**Figure 5.** (Colour online) Switching time as a function of temperature for different concentrations of FeCo in the ferroelectric liquid crystal. As the concentration increases the switching time becomes more constant.

**Figure 6.** (Colour online) Polarised optical micrographs of FeCo nanoclusters in the (a) isotropic; (b) nematic; (c) smA phase of the liquid crystal 8CB showing how the isotropic spherulites surround them in the nematic (b) and the smA phase (c). Compare the smA phase to the FeCo nanoclusters in the smC* phase of ferroelectric liquid crystal (d) and (e). Note that not all of the spherulites contain a nanocluster. The amount depends on the concentration of the particles. All pictures are taken near the border of the film to facilitate the viewing.
shown in Figure 6f. The quantity of spherulites that move is calculated from the pictures shown in Figure 7 and plotted in Figure 8 as a function of applied electric field. We observe from that the spherulites increase in number as the electric field is brought from 0V/cm to 500V/cm. We observe that there is an increase of spherulites at a field as low as 5V/cm. We note that an electric field of 5V/cm is comparable to the voltages observed in many biological states, for example the local field potential in the brain.

4. Discussion

The variation of the switching time $\tau$ as seen in Figure 5 influences the strength of the electric field needed to move the spherulites. The rise time for the pure FLC is given by [50,51,56],

$$\frac{\eta}{P_s E} = \tau_m$$  \hspace{1cm} (1)

The rise time can be determined by observing the modified square signal applied to the sample [51]. The rise time increases from its value in the smA phase for the smallest concentration measured (0.53%) as well as for the intermediate concentration (4.35%), and it becomes almost constant for the larger concentration (10.8%). One can compare the rotational viscosities if we compare $\eta$ and $\tau$ to obtain an idea of how the viscosity varies by using the plot of $\tau$ in Figure 5. Using this comparison the rotational viscosity gives $\eta_{0.53\%} > \eta_{10.8\%} > \eta_{4.35\%}$ is initially...
smaller but comparable to $\eta_{10.8\%}$ but increases at or below 72°C. This is almost the opposite as observed in systems of nematic liquid crystals and bismuth ferrite nanoparticles [57]. The lower switching time may be due to the widespread interaction of the magnetic nanoparticles with the ferroelectric liquid crystals that order the liquid crystal such that it responds faster to a lower applied electric field. It is much faster than the behaviour exhibited at 0% wt concentration. The anomalous behaviour shown in Figure 5 between the 4.35% and the 10.8% wt samples may be due to the fact that the sample is crossing to concentrations that have a larger number of nanoparticles and where many of the nanoparticles congregate in the aggregates shown in Figure 6.

We have noted that the nanoparticle concentration can vary between 0.1 and 20 wt % [38–41], depending on the properties that one seeks to enhance [42,43]. We are interested in decreasing the electric field at which a magnetic field can be generated. At 10.8 wt % concentration, a relatively high concentration of the magnetic nanoparticles has apparently a lower viscosity than the other concentrations. The viscosity makes it easier to move the nanoparticles with a smaller applied electric field. $E_{\text{applied}}$ refers to the electric field required to start reorienting the sample. In other words, this concentration acts like a lubricant to the sample. The higher the value of the component of $P_s$ along the direction of the applied field, the lower value of the applied field. Thus, the expression for $E_{\text{applied}}$ becomes,

$$E_{\text{applied}} \sim \eta \frac{f(1/P_s)E}{\eta f(1/P_s e_{\text{applied}}) / \epsilon} \quad (2)$$

where $e_{\text{applied}}$ is the unit vector along the direction of $E_{\text{applied}}$. $\eta$ depends on the concentrations $c_{\text{nano}}$ where the switching time will exhibit a smaller increase over the smC* phase. In addition, this behaviour will depend on the size of the nanoparticles, and how they are functionalised [31,49,58], which is not studied in this paper.

Our previous experience performing the same experiment in 8CB mixed with 30%wt of FeCo [31] nanoparticles coated with PEG shows that the field strength to produce nanoparticle displacement in the smA phase is quite large compared to the values observed in this ferroelectric liquid crystal mixed with the same nanoparticles [48]. We note that in order to observe any change in this case, we need at least 30% wt of the nanoparticles [31], which can be toxic from our application’s point of view.

The magnetic field depends on the $P_s$ of the sm-C* phase at a particular temperature. The electric field couples to the $P_s$, which determines how low this electric field can be to produce a magnetic field. Thus, the magnetic field will depend on the concentration [34], and also the spontaneous polarisation,

$$H \sim c_{\text{nano}}(P_s) \quad (3)$$

The magnetisation in one spherulite can influence the magnetisation in the other spherulites and can align them in order to produce a larger magnetic field. The size of both the sample and the sample holder kept us from making direct measurements of the magnetic field. However, from the pictures in Figure 7, we can determine indirectly how the magnetic field increases as the electric field is increased, by monitoring the motion of the spherulites as a function of electric field. The motion is determined as movement of spherulites/surface area as a function of applied electric field, shown in Figure 8. The spherulites move at a rate almost six times larger in the first 50V/cm than in the next 450 V/cm, where it seems to saturate. The motion of spherulites increases again between 5000V/cm and 10000V/cm. These are not shown because the results were taken at a different time than the results between 0 and 500V/cm, and may introduce a counting error.

A spherulite 7μm in diameter can hold a maximum number of nanoparticles of $2 \times 10^{10}$ nanoparticles, assuming we have 2.6 nm size particles. In general for the range of nanoparticles estimated in Figure 7, we get a number of nanoparticles in the order of $10^{10}$. If the magnetisation aligns, then each spherulite that contains the nanoparticles will contribute $4\pi M = 4\pi 10^{-17}(2\times10^{10})/(4\pi/3(3.5\times10^{-5})^3) \text{ Gauss} = 7 \times 10^3 \text{ Gauss}$ or 0.7T. We note that this is an upper estimate, where the nanoparticles occupy most of the spherulites and the magnetisation tends to align in the same direction. The total number of spherulites is multiplied by the concentration to obtain the magnetic field which in this case is $0.108 \times 0.7 \text{ T}$ (total number of particles), which brings the total magnetic field to the O(0.1 T). The field in the MRI is about 0.8T. The number of spherulites will determine the magnetisation field. Figure 8 shows that even at low electric fields, less than 50V/m and even at 20V/m there is enough magnetic field generated for this nanocomposite to be able to serve as an agent.

4. Conclusions

We have found that a ferroelectric liquid crystal doped with magnetic nanoparticles will respond to a very small applied electric field due to its polarisation and due to a reduction of the rotational viscosity as a function of the concentration. We observed the magnetic field indirectly through the motion of the spherulites and estimated it to be in the order of 0.1 T. We found also that the
concentration of nanoparticles is not as large as required for an smA sample. A more detailed study is needed to figure the exact relation between the polarisation and the electric and magnetic field in the system and to determine which concentrations will enhance the effect of applying the electric field, reducing it to electrical fields observed in many biological states.

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Disclosure statement

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