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Research articles

Novel colloidal system: Magnetite-polymer particles/lyotropic liquid crystal under magnetic field

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ABSTRACT

We obtained a new highly ordered colloidal composite using specially manufactured magnetite-polymer nanoparticles and lyotropic liquid crystal. A good compatibility between the components was ensured by the functionalization of the particles during their synthesis. We studied the laser light transmission for the mixtures filled in sandwich-glass cells with homeotropic and planar treatment of the surfaces under external magnetic field. The Fréedericksz transition critical field was estimated, and its' behavior was compared to our new theoretical model based on the Brochard-de Gennes one.
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1. Introduction

Liquid crystals (LC) have been in the center of attention for the last four decades, when their application in displays attracted the interest of companies, scientists and engineers. Liquid crystals are characterized by the presence of orientational order and total or partial absence of positional order [1]. Due to their properties, they have proven themselves extremely useful in a variety of application fields, from optics, electronics, to medicine and biology. For medicine and biology, lyotropic liquid crystals are favored to thermotropic ones. In lyotropic LCs, the known phase transitions (smectic, nematic, isotropic) [2] are induced by a variation in the concentration of chemical compounds in a dissolving liquid, such as water. When used in conjunction with magnetite particles, new composite materials known as ferronematics are obtained [3,4]. These composites exhibit distinct characteristics (biocompatibility, non-immunogenic, non-toxic) and can be successfully used in industrial and biomedical applications, including magnetic drug targeting, hyperthermia and magnetic separation of cells. By incorporating a certain metal in the liquid crystal molecule, unique properties are obtained regarding the colour, polarizability, electric and magnetic properties [5,6]. In order to maintain their characteristics, homogeneity throughout the composite must be preserved. This is generally achieved by introducing a surfactant [7,8], chosen in such a way that it anchors itself to the surface of the particle, forming a 'hairy' particle [9,10]. A better compatibility is obtained when the particles are especially synthesized to be compatible with a specific liquid crystal [11]. We present a new colloidal composite formed by combining a specially designed nano-structured magnetite-polymer and a lyotropic nematic liquid crystal. The magnetite-polymer composite was dispersed in a lyotropic liquid crystal based on sodium dodecyl sulfate (SDS), decanol (DeOH) and water. The mixture exhibited long term stability (month-order). The structural units of these lyotropic liquid criystalline materials are anisotropic micelles. Mixtures with two different amphiphiles show three nematic phases (calamitic, discotic and biaxial), where micelles have orthorhombic symmetry or flattened prolated ellipsoid shape [12,13]. Our samples were created using glass slabs, with planar and homeotropic alignments on the anchoring surface. The critical field for magnetic Fréedericksz transition B_C was estimated using the optical method presented in [14,15]. A laser beam was sent through the LC sample placed under crossed polarizers, while the magnetic field was gradually increased. When the field reaches a critical value B_C, the LC's molecular director exhibits a change in orientation, leading to a variation of the refractive index [16]. This, in turn, leads to a change in the intensity of the emerging laser beam, indicating the start of the transition [17].

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2. Experimental methods

2.1. Composite particles

To obtain a good chemical compatibility between the colloidal particles and the liquid crystal we used a novel polystyrene latex containing magnetite (Fe_3O_4) with covalent bonds to the polymeric chains, functionalized with alkoxysilanes containing double bonds, synthesized as in [18]. The high-resolution TEM (HRTEM) images for the hybrid-type latex magnetite-polymer show magnetite crystals of 5–15 nm anchored within polymeric chains of tens of nanometers. A full characterization has previously been performed on the resulting magnetite-polymer particles in [18].

2.2. Sample preparation

The magnetite-polymer particles were mixed with a lyotropic liquid crystal, in two concentration versions, 0.1% and 0.2% b.w. Homogenization of the mixture was performed by ultrasound techniques. The concentrations of the components of the lyotropic LC are: 28.2% sodium dodecyl sulfate, 5.7% decanol and 66.1% water. From a structural point of view, the liquid crystal forms discotic nematic domains [19,20]. The samples containing the mixtures were manufactured using glass plates, with a spacing of 100 μm. To produce surface alignments, the following steps were executed: for a homeotropic alignment, a solution of DMOAP-metaxibenzen-butyl-anylin (N-dimethyl-N-octyl-3-aminopropyl-trimetoxyl-xylil) was used. The ratio of the components is 899 parts isopropanol, 100 parts distilled water, and 1 part DMOAP. Deposition of the solution was performed by spin coating, and polymerized for 10 min at 100 °C in an oven. For the planar alignment, a solution of polyvinyl alcohol (1% volume fraction). The solution was deposed by spin coating, and heated at 120 °C for one hour, slowly cooled to room temperature, and rubbed with a smooth cloth in the desired direction of alignment. In Fig. 1, we illustrate the observation of the nematic phase of the SDS/DeOH/water system and its' planar alignment by Polarizing Optical Microscopy. For the homeotropic alignment, a dark image was obtained [20].

The nominal parameters of the samples are given in Table 1.

2.3. Experimental apparatus

The experimental setup used consists of the following: a linearly polarized, 632.8 nm, continuous wave He-Ne laser having an output power of 2.5 mW with superior spatial and spectral resolution, two crossed polarizers having a transmission ratio of 99.3% and an cross-polarization extinction ratio of 99.7%, a Silicon p-i-n photodiode for the visible range, equipped with a controllable amplification of up to 70 dB and 5% distortion level at maximum amplification, and a high precision multimeter for recording the voltage offered by the photodiode. The magnetic field generator is an electromagnet ranging from 0.1 to 1 Tesla, with poles having a diameter of 35 cm, an iron core of 10 cm, and a pole-to-pole distance of 10 cm. For the homeotropic alignment, in which the laser beam has to be parallel to the magnetic field, the iron core has been drilled in its' center, forming a 5-mm diameter hole, which does not affect the field homogeneity. The scheme of the setup is presented in Fig. 2. The sample was placed under crossed polarizers, at the center of the pole-to-pole distance of the electromagnet and the optical intensity of the laser field was observed for different values of the applied magnetic field [21].

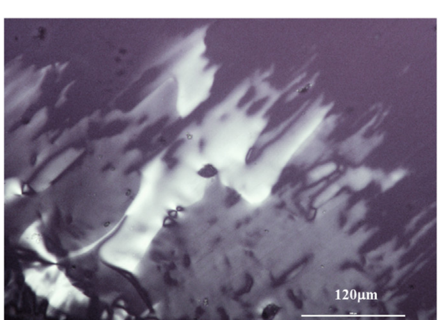
Table 1
Nominal construction parameters for the samples used in testing.

Sample Code	Composite	Concentration [%]	Alignment
H2	LLC/PM-171	0.1	Homeotropic
H3	LLC/PM-171	0.2	Homeotropic
P2	LLC/PM-171	0.1	Planar
P3	LLC/PM-171	0.2	Planar

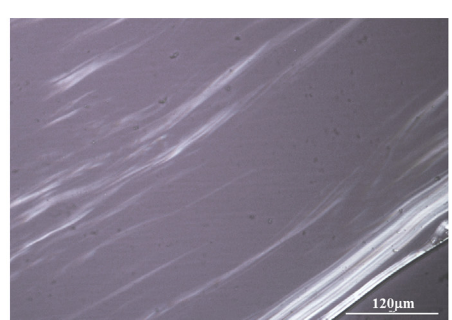
3. Results and discussions

The magnetic Fréedericksz transition experiment was conducted for samples containing magnetite-polymer in liquid crystal, in the circumstances of planar and homeotropic alignments. The experimental data for the planar alignment of the LC samples is shown in Fig. 3, while the data for the homeotropic alignment of the samples is shown in Fig. 4.

It is known that in the discotic nematic phase, the natural orientation of the micelles leads to a homeotropic alignment, with the director normal to the anchoring surface [20]. In order to reorient the liquid crystal director using a magnetic field, when rotating from a homeotropic to planar orientation, the field must also compensate for this natural tendency, and therefore $B_{CH} > B_{CP}$. Studies conducted on pure discotic liquid crystals have established the critical magnetic field of the Fréedericksz transition $B_C \simeq 1T$, and exhibits a decrease when the liquid crystal is mixed with magnetive responsive materials, regardless of the surface orientation of the liquid crystal [12]. Experimental plots of the emergent beam intensity vs. magnetic field were recorded for each sample, and the critical field was estimated. In our estimations, we have considered the critical field as the value of the magnetic field for which we begin to observe an increase in the intensity of the emerging beam. Within the transition zone, the estimated critical field values were determined as follows: For the planar



a)



b)

Fig. 1. Polarization Optical Microscopy images: observation of obtained nematic phase for SDS/DeOH/water system a) and planar alignemnt of LLC sample b).

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