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Mechanically activated cholesteric polymer dispersed liquid crystals

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In this paper we deal with a cellulose derivative cholesteric dispersed liquid crystal (CCDLC) with mechanically tuneable optical properties. The composite is formed with a matrix of acetoxypropylcellulose with embedded micrometric and submicrometric droplets of a cholesteric mixture. Polarizing optical microscopy and atomic force microscopy (AFM) measurements performed on the system are reported and it is shown that the wavelength of the reflected light can be changed by a temperature variation and it is also changeable through a mechanical deformation. The pitch of the deformed droplets can be measured from AFM photographs and compared with the wavelength reflected by the CCDLC composite material.

1. Introduction

Main-chain cellulose liquid-crystalline thermotropic polymers have been synthesized and studied since 1981 (see [1]). Cellulose derivatives esters can be lyotropic and thermotropic cholesteric polymers and some aspects of their behaviour have been studied over the years [2, 3]. Bulk aliphatic esters exhibit cholesteric reflections in the visible range of the spectrum and their reflection properties have been measured in the function of side-chain length and molecular weight [4]. Acetoxypropylcellulose (APC), one of the most studied thermotropic esters of cellulose, is cholesteric from below room temperature up to 180°C (see [5, 6]).

More recently it was found that thin solid films prepared from lyotropic solutions of cellulose derivatives can be used as alignment layers for low molecular weight liquid crystals [7, 8]. Studies were also performed on the effects of the polymer orientation surrounding droplets of low molecular weight liquid crystal in a cellulose polymer surface [9] and a strong influence over the liquid-crystal orientation within the droplet was found [9, 10].

Liquid crystalline polymers may possess a high degree of molecular orientation induced by flows during polymer processing. Therefore, a liquid-crystalline polymer film having flow-induced molecular orientation can induce molecular alignment in low molecular weight liquid crystals. After the cessation of the shear stress a characteristic banded texture is developed perpendicular to the shear direction. The surface anisotropy of the mechanical and optical properties of the polymeric films [11] makes these systems very interesting from the applicative point of view for liquid-crystal displays. Films prepared from anisotropic solutions of cellulose derivatives used as alignment layers of liquid crystals have been described in the literature [12–14]. The surface topography and structure of these films could be finely tuned by modifying the experimental parameters [13]. Both the fundamental and technological interest in polymer dispersed liquid crystal (PDLC)-type materials arises primarily from their unique mesoscopic (i.e. micrometre- to nanometre-scale) properties.

There have also been many basic studies of liquid-crystal alignment in spherical and elliptical droplets in an elastomeric matrix [15]. It is also known that polymer chains align during the PDLC film stretching process and promote subtle changes in the low molecular weight liquid-crystal alignment [16]. Uniaxially stretched phase-separated polymer films can be used as non-absorbing polarizers, which efficiently reflect or backscatter light rather than absorbing [16].

Cholesteric liquid crystals have been used to produce liquid-crystal displays exhibiting attractive colour displays without the need for an auxiliary backlight.

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Normally, in this type of device, the cholesteric liquid crystal is confined in elliptical shaped droplets, dispersed in an isotropic matrix [17, 18]. In this system we use freestanding films and the displayed colours are obtained as a function of the temperature and the mechanical strain imposed with the advantage of using a cellulose liquid-crystalline matrix which can allow for different optical behaviours depending on the direction of stretching [19].

In this work we present a dispersion of cholesteric liquid crystal that is made on an anisotropic matrix having an elliptical shape. We show the morphology of PDLC-type free-standing films prepared from anisotropic solutions of APC with dispersed commercial cholesteric *TM1005* from Merck. Polarizing optical microscopy (POM) and atomic force microscopy (AFM) have been used as experimental techniques for investigation of the morphology resulting from phase separation of the LC droplets in the host anisotropic liquid crystalline APC matrix after the applied shear stress.

2. Experimental details

The synthesis of APC was performed according the procedure described in [20] (see also figure 1). For this work the acetylation of (hydroxypropyl)cellulose (HPC; Aldrich, nominal M_w=100,000; molar substitution equal to four determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy; 50 g) was performed by adding the HPC to acetic anhydride (160 g) to give a viscous solution on standing. Acetic acid (15 g) was added to initiate esterification and the mixture was allowed to stand for one week, with stirring. The polymer was washed with water and purified by solution in acetone and reprecipitation in water. The final product was dried in an oven at 60°C; the final yield was around 75%. The number of acetyl groups per residue was evaluated by ^{1}H NMR and was 2.0.

A 60 wt% nematic chiral solution was obtained by adding APC to dimethylacetamide (DMAc), at room temperature and the contents were allowed to mix for several weeks. Commercial cholesteric liquid crystal *TM1005* (15 wt%) from Merck was then added to the anisotropic host solution. After homogenization the phase-separated solutions were submitted to a shear flow mechanical field and cast onto a glass plate at room temperature with a calibrated Gardner knife moving at a controlled rate, v=5 mm s^{-1}. The composite film after solvent evaporation was then carefully peeled from the substrate. The films thicknesses were approximately 10 µm.

Small rectangular pieces of the cast films with dimensions 5×1 cm^2 were cut with the longest dimension of the sample perpendicular to the direction of casting. The rectangular samples were stretched uniaxially at a rate of 2 mm min^{-1} along their longest dimension (see figure 2).

The textures of the composite sheared anisotropic films were observed with a polarizing Olympus microscope. The POM observations were performed between cross polars. The wavelengths (λ_0) of the maximum selective reflection peaks were recorded with a Jobin Yvon monochromator mounted on the microscope stage, equipped with a photomultiplier and a chart recorder. The values of λ_0 are related to the cholesteric pitch (P) by the de Vries relationship, $\lambda_0=\bar{n}P$, where $\bar{n}$ is an average refractive index of the sample. A Dimension 3100 SPM with a Nanoscope IIIa controller from Digital Instruments was used for the AFM measurements performed in tapping mode under ambient conditions.

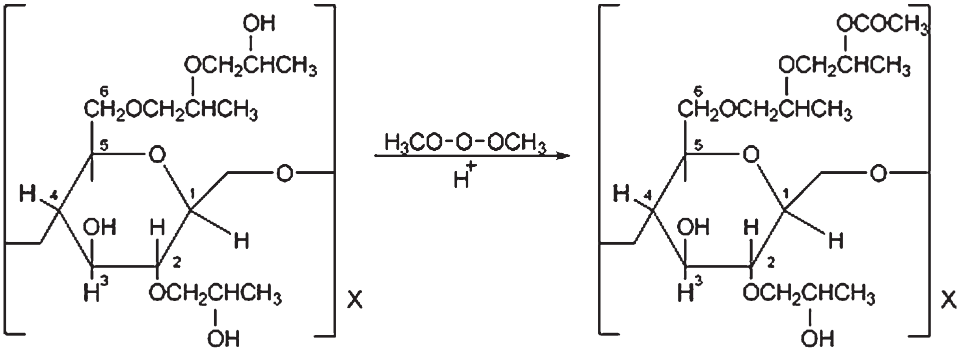

Figure 1. Chemical steps involved in the synthesis of the polymer matrix. Modification of hydroxypropylcellulose (HPC; $\overline{DS}$=2; $\overline{MS}$=3; $\overline{DP}$=236) to give the ester acetoxypropylcellulose (APC; $\overline{ME}$=2; $\overline{MS}$=3).

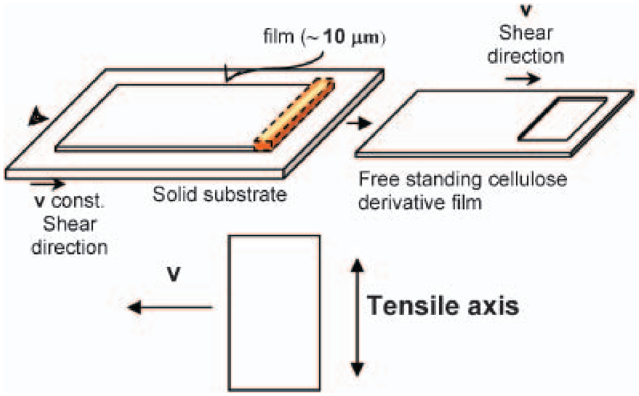

Figure 2. Preparation of the solid films giving an indication of the stretching direction transverse to the shear.

3. Results and discussion

As is well known, APC exhibits both lyotropic and thermotropic chiral nematic phases at room temperature. It is well established [21] for specific shear flow conditions that cholesteric liquid-crystalline cellulose derivatives exhibit an unwinding of the cholesteric helix and a cholesteric-to-nematic transition. The morphology of the sheared films prepared from lyotropic precursor solutions of APC in DMAc induces anisotropy of the mechanical properties [22]. They are different in parallel (brittle) and perpendicular (ductile) direction to the applied shear. By adding the liquid-crystalline component to the anisotropic APC matrix, the band size and the anisotropic mechanical properties are affected [22].

The composite thin film obtained from 60 wt% APC solution in DMAc and 15 wt% *TM1005* after shearing and casting develops a banded texture and stripes perpendicular and parallel to the shear, respectively, almost immediately after the cessation of shear, with dispersed cholesteric liquid-crystalline droplets.

Likewise for other cellulose derivative lyotropic solutions, the bands and stripes can be frozen in and their size controlled to some extent by varying the casting shearing conditions [7, 9, 10]. We have used a constant shear rate and the solvent was allowed to evaporate at room temperature. We relate our morphological observations with the surface alignment of the liquid crystal on the cellulosic matrix used in the method proposed in literature by Mori *et al.* [9]. Previously [19], for the composite material with nematic droplets, we investigated the effects of the mechanical stretching on the liquid-crystalline polymer orientation surrounding droplets of low molecular weight liquid crystal. Applying elongation along the shear direction produces an increased alignment on the polymeric matrix while a deep molecular reorientation is taking place in perpendicular direction. The effect of stretching, transverse to the shear, on the liquid-crystalline elliptical shaped droplets is also remarkable: the main axis of the elliptical shaped droplets almost aligns along the stretch direction. The anisotropic polymer matrix alignment influences in a dramatic way the droplet shape anisotropy and orientation.

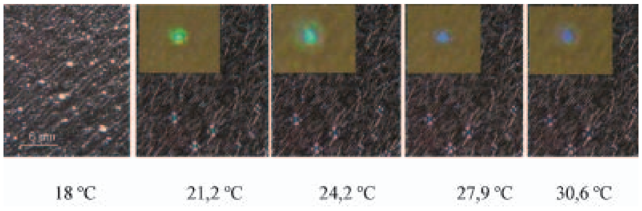

Figure 3. Photographs of the solid films for exposures to different temperatures. The reflecting colour changing inside the droplets from green to blue is presented in the inserts.

We have performed a temperature behaviour study of the films and the POM photographs are shown in figure 3; the inserts show reflection colours observed in the droplets as a function of temperature. We verify that due to the modification of the cholesteric helix and consequent variation of the pitch, as we increase the temperature, the reflected colour changes from green to blue. The wavelength dependence of the reflected light with temperature is shown in figure 4.

The cholesteric liquid crystal in contact with the APC matrix develops a planar anchoring, and therefore we are able to measure the cholesteric pitch in AFM photographs. In figure 5 we show AFM photographs of the deformed film (perpendicular to the shear direction) where we can see that the droplets have an oval shape after deformation and where we can see that inside each droplet there are periodic curves that correspond to the

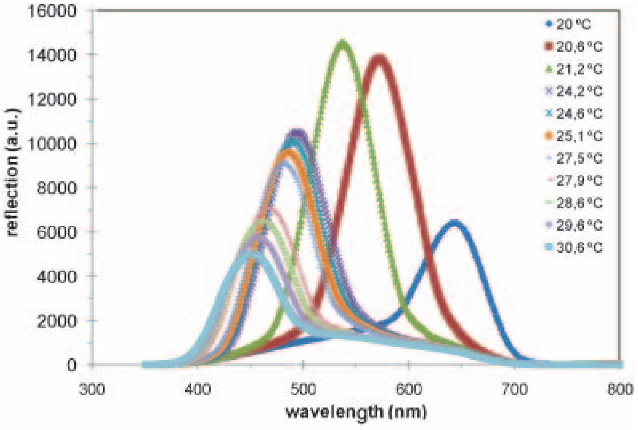

Figure 4. Dependence of the wavelength of reflected light on temperature for the composite material.

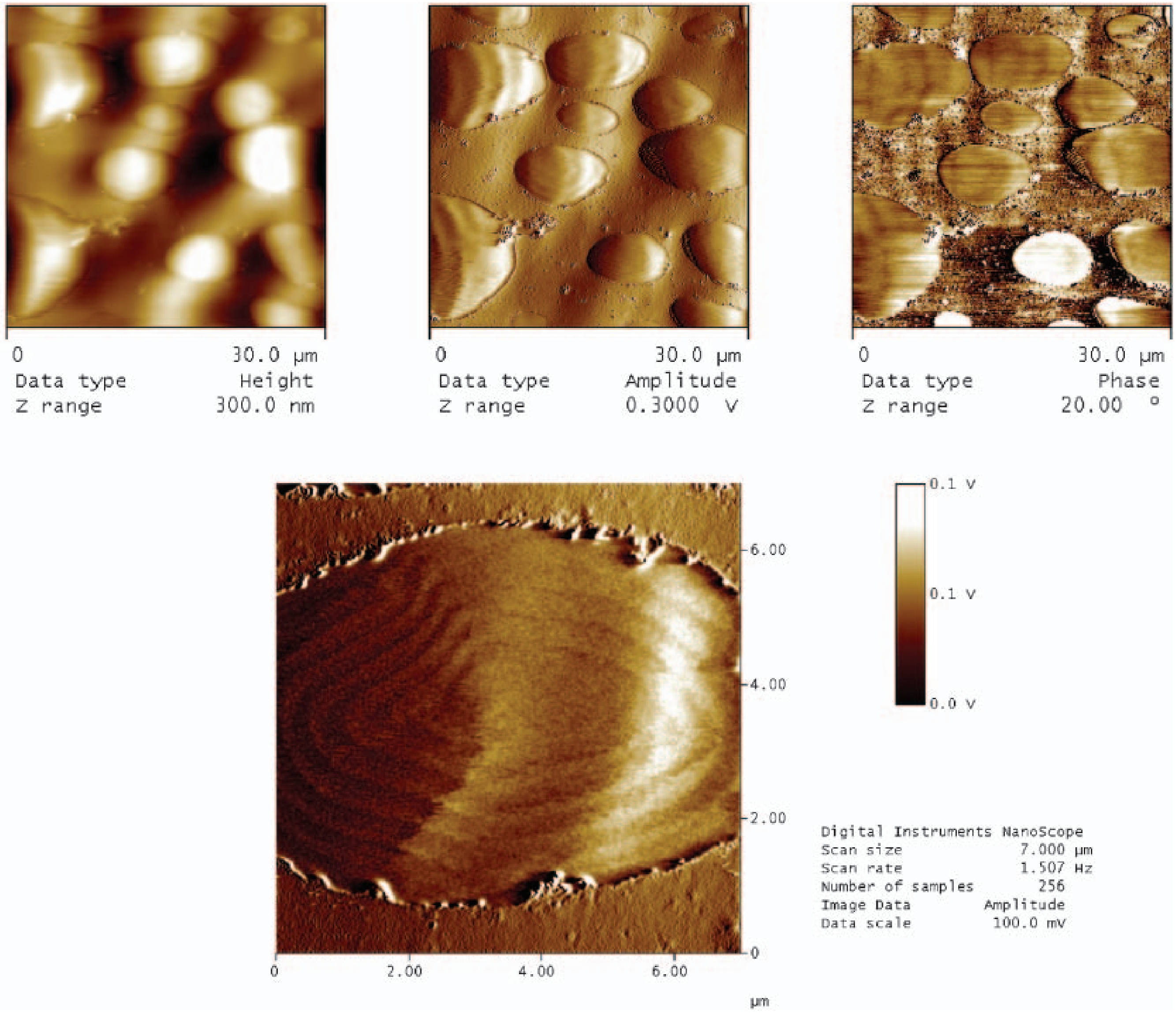

Figure 5. AFM photographs of the solid films revealing the oval shaped droplets and the pitch of the deformed droplet ($\varepsilon \approx 0.4$; $T = 22°C$).

rotation of the liquid crystal molecules and therefore to the cholesteric pitch.

Figure 6 shows POM photographs of an undeformed and a deformed ($\varepsilon \approx 0.4$) thin film where we can see the reflected colour variation with the imposed strain, and a measurement of the reflected wavelength for each case.

We verify that imposing a strain on the films has the same effect on the reflected colour as the temperature increasing. The modification of the reflected colour is due to the pitch modification and measuring the pitch (by measuring the distance between the visible curves inside a droplet) we verify that the deformation of the films and consequent deformation of the droplets changes the pitch to 490 nm. These values are in agreement with the measured wavelength of the reflected light for each case (deformed≈494 nm and undeformed≈523 nm).

4. Conclusions

We have presented new free-standing films of cellulose cholesteric dispersed liquid crystal material. The films can tune the optical properties by changing the temperature or by applying a uniaxial deformation. Detailed measurements of the pitch variation upon different imposed strains are under investigation.

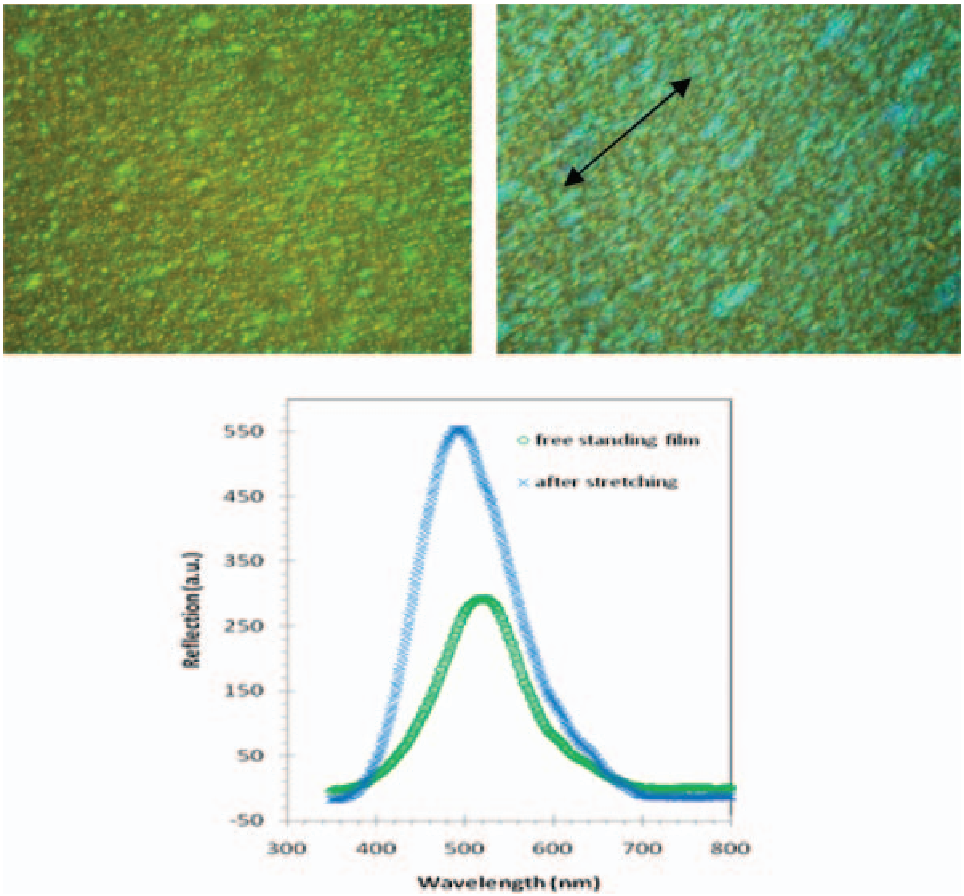

Figure 6. Top: POM photographs of the solid films where the reflected colour of the thin films is shown. Bottom: reflected wavelength for each case ($\varepsilon \approx 0.4$; $T = 22°C$).

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