# Tunable topographical cellulose matrices for electro-optical liquid crystal cells

I. COSTA[3,5], P.L. ALMEIDA[1,3], D. FILIP[3], J.L. FIGUEIRINHAS[4,5], and M.H. GODINHO[*2,3]

[1]Dept. Eng. Mecânica, EST/IPS, Campus do IPS, Estefanilha, 2910-761 Setúbal, Portugal
[2]Dept. de Materiais, FCT/UNL, Quinta da Torre, 2829-516 Caparica, Portugal
[3]CENIMAT, Quinta da Torre, 2829-516 Caparica, Portugal
[4]Dept. de Física, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[5]CFMC-UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal

*In this work we have used acetoxypropylcellulose (APC) to produce free standing solid films (~60 μm) that were used for assembling electro-optical devices. Thin films were obtained from concentrated lyotropic solutions of cellulose derivatives. Induced by the cast and shearing preparation conditions wrinkles and band textures can be observed in their free-surface plane. In order to eliminate and control these textures we used a process similar to that introduced in literature [1] which consists of storing the films in the same solvent-vapour atmosphere as the solution system. Lyotropic APC liquid crystalline solutions in dymethylacetamide (DMA) with crosslinker were prepared, thin films were obtained by using a shear/casting technique and stored in the solvent-vapour atmosphere until a planar structure was achieved. The dried crosslinked films were analyzed by optical polarised microscopy (POM) and scanning electron microscopy (SEM). The films with different topographies were used to produce optical cells composed by the cellulose derivative film covered on both free surfaces by a layer of the nematic liquid crystal E7 and placed between two transparent conducting substrates. The electro-optical properties of these cells were obtained.*

**Keywords:** acetoxypropylcellulose, liquid crystals, PDLC, electro-optical properties.

## 1. Introduction

Hydroxypropylcellulose (HPC) and HPC esters can generate lyotropic and thermotropic mesophases [2,3]. Due to the ability of their molecules to spontaneous self-assemble in helicoidal arrangements light can be reflected selectively [4–7].

Bulk aliphatic esters can exhibit cholesteric reflections in the visible range of the spectrum. The selective reflection depends on several parameters including the degree of esterification [8] and on the temperature [9]. The pitch of the cholesteric helix can also be locked by using different procedures among them by photoinitiated crosslinking of pendant acrylate groups [10]. One of the most studied thermotropic cellulose esters is acetoxypropylcellulose (APC), it is cholesteric from below room temperature up to 180°C [6] and can originate lyotropic phases in some common solvents [11,12]. Rheo-optical and rheological studies [13] were also performed in APC in order to better understand the relationship between the textures observed in optical microscopy and the light scattering patterns.

The study of composite materials making use of cellulose layers and liquid crystals for electro-optical applications opened new horizons for using cellulose derivatives [14,15]. Electro-optical cells were produced by enclosing a cellulose derivative film, obtained from an isotropic solution, with two E7 nematic liquid crystal layers and the set placed between two transparent conducting substrates. These cells show electro-optical properties similar to those reported for polymer dispersed liquid crystals (PDLCs) but the polymer matrix and the liquid crystal component are arranged in a diverse fashion that enables the modification of the polymer surface in order to optimize the optical properties of the cell [16].

It was found that a fine tuning of the surface properties of the solid cellulosic matrix can be achieved by varying their preparation conditions [17]. The influence of different matrix parameters upon the electro-optical behaviour of the cells was studied [18,19]. In order to optimize and understand the electro-optical characteristics presented by these kinds of cells, the study of the anchoring properties of the LC on the solid cellulosic films was also performed [20].

Some cellulose derivatives were used as matrix materials for preparation of PDLC films. The influence of the curing temperature on the morphology of the films prepared from ethyl cyanoethyl cellulose/poly(acrylic acid)/4'-n-pentyl-4-cyanobiphenyl was analysed [21]. It was reported that the size of the dispersed droplets and the uniformity of their diameter depends on the curing temperature of the composite material.

[*]e-mail: mhg@fct.unl.pt

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There have also been several basic studies of liquid crystal alignment in spherical and elliptical droplets in elastomeric matrices [22]. It is also known that polymer chains align during the PDLC film stretching process and this promotes subtle changes in the liquid crystal alignment in the droplets as a result of the polymer alignment induced by the tensile strain [23]. Uniaxially stretched anisotropic phase separated polymer films were recently obtained from APC and their optical [24] and mechanical properties [25] have been studied.

In this work we have studied the electro-optical behaviour of several cells assembled with APC solid films obtained from anisotropic solutions and a nematic liquid crystal (E7) placed in layers above and below the polymeric film. A qualitative relationship between the structure of the matrix and the electro-optical behaviour of the cells was established.

## 2. Experimental

### 2.1. Materials

Hydroxypropylcellulose (HPC) (Mw = 100 000 gmol$^{-1}$) was purchased from Aldrich and dried in vacuum at 50°C for about 48 h before use. Acetic anhydride (Merck), acetic acid (Merck), and dimethyl acetamide (DMA) (Merck) was used as received. Glutaraldehyde (GA) (Aldrich) was used

without further purification. The nematic liquid crystal mixture used was the commercially available mixture E7 (Merck Ltd., UK).

### 2.2. Synthesis of acetylated polymer and cross linked reactions

The synthesis of acetoxypropylcellulose was performed according to the procedure described in literature [6]. For this work, the acetylation of (hydroxypropyl)cellulose (Aldrich, nominal Mw = 100 000) (molar substitution equal to 4 determined by NMR1H) (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 NMR1H and is 2.0.

A nematic chiral (60% by weight) solution was obtained, in 5 ml glass containers, by adding APC to dimethylacetamide (DMA), at room temperature, the contents were allowed to mix for several weeks. The APC was lightly cross linked with glutaraldehyde. The polymer idealised structure along the chemical steps involved are shown in Fig. 1.
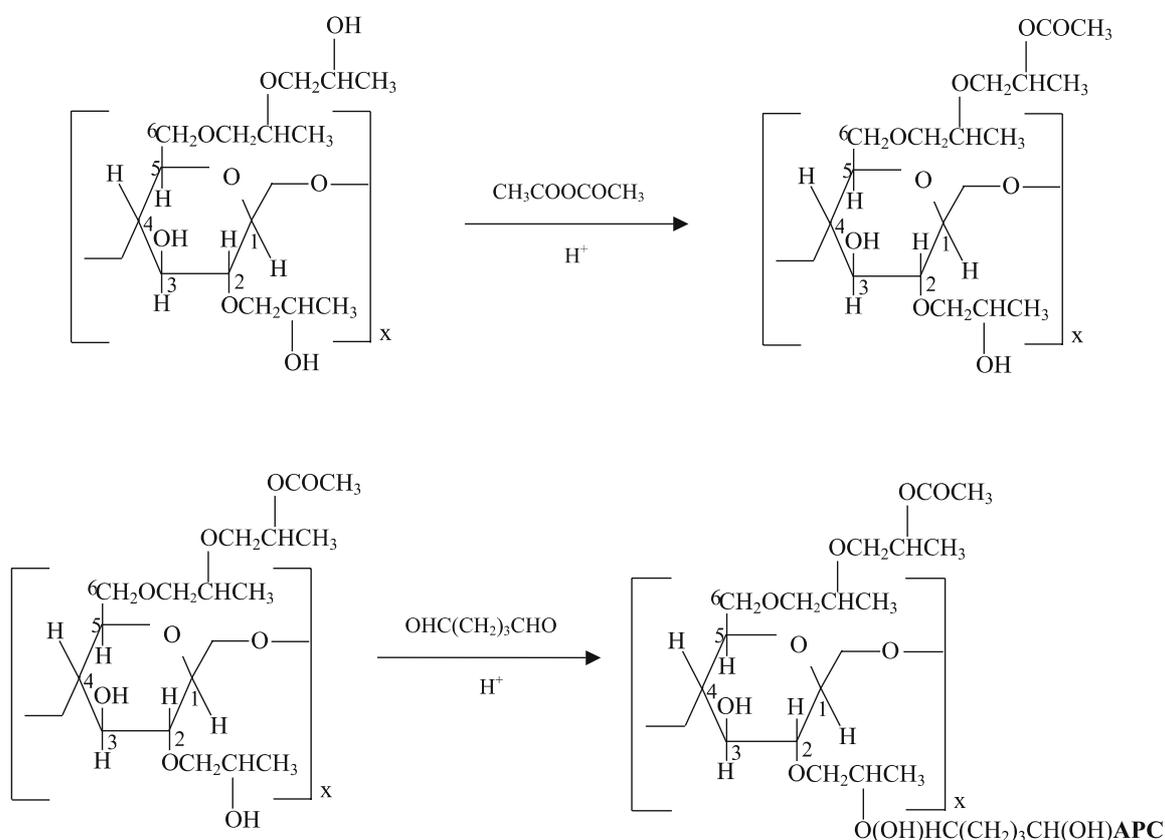


Fig. 1. Chemical steps involved in the synthesis of the polymer matrix. Step I – modification of hydroxypropylcellulose (HPC) (DS = 2, MS = 3, DP = 236) to give the ester acetoxypropylcellulose (APC) (ME = 2, MS = 3). Step II – crosslink reaction between the free unreacted hydroxyl groups from APC and the diisocyanate to give urethane links.

## 2.3. Preparation of solid films

After homogenization, the solution was cast onto a Teflon plate at room temperature with a calibrated Gardner knife moving with the controlled rate $v = 5$ mms$^{-1}$. After the film's casting, six samples were prepared one was allow to stay exposed to the normal atmosphere immediately after casting, while the other five were stored in a solvent-vapour atmosphere and removed after different periods of time. The films were cured at room temperature and then carefully peeled from the substrate. The film average thickness was approximately 60 µm. Table 1 shows the time of exposure to the solvent-vapour atmosphere as well as the average thickness of different samples.

Table 1. Time of exposure to the solvent-vapour atmosphere and average thickness of the samples.

| Film sample | Time of exposure to the solvent-vapour atmosphere (min) | Average thickness (µm) |
|---|---|---|
| #1 | 0 | 12 |
| #2 | 30 | 50 |
| #3 | 60 | 64 |
| #4 | 90 | 67 |
| #5 | 120 | 70 |
| #6 | 210 | 65 |

## 2.4. Preparation of electro-optical cells and measurements

The cells, with different cellulosic matrices obtained, were prepared from the cellulose derivative film surrounded by two nematic liquid crystal layers, placed in between two transparent conducting glasses substrates. In Fig. 2, we illustrate the cell preparation. Six distinct cells were prepared, using the six solid films described in Table 1.

The electro-optical characterization of the cells was carried out using a helium-neon laser-equipped optical bench in association with a function generator, a voltage amplifier and a diode detector. The optical cells were excited with a 1 kHz AC voltage with controlled amplitude. The voltage amplitude was made to cycle between 0 and the maximum voltage and back to zero at least twice for each cell to detect any hysteresis. All the electro-optical results were obtained for normal sample incidence, at room temperature $T \sim 25°C$.

## 2.5. Optical microscopy

Optical microphotographs were taken using a polarising Olympus microscope (POM) equipped with a camera. All observations were performed at room temperature (20°C) and between crossed polars.

## 2.6. Scanning electron microscopy

The free surfaces of the films were characterised by scanning electron microscopy (SEM) using a SEM DSM 962 model from Zeiss Company.

## 3. Results and discussion

Figure 3 shows the polarized microphotographs and SEM pictures of free-surface acetoxypropylcellulose dried films, crosslinked with glutaraldehyde, as a function of the storing time to solvent-vapour atmosphere. Microscopy observations show that a band structure appears in sample 1 obtained after casting, at room temperature, with no exposure to solvent-vapour atmosphere. The band texture, which develops after shearing for liquid crystalline cellulose solutions is very well described in literature [1] and was frozen in the solid film. The band spacing which represents the distance between two adjacent patterns' dark lines is of the order of 0.5–0.6 µm. Detailed microscopy observations, using a 530-nm retardation plate inserted diagonally between crossed polars, enable a better characterization of the bands growth process. In sample 1, the bands were frozen in a direction roughly perpendicular to the flow direction and then in sample 2, 30 min of exposure time, increase their width 0.6–0.8 µm in the flow direction. The bands vanished very slowly with time and in sample 6, 210 min exposure time, the typical liquid crystalline mosaic-like texture of cellulose derivatives [1] seems to be produced. The distinct non-monotonous processes, clearly visible, have an important repercussion upon the electro-optical properties of the cells studied.
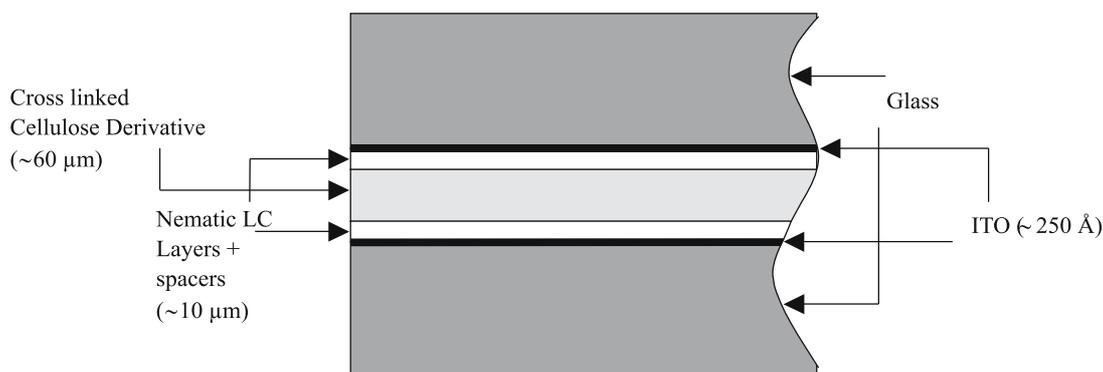


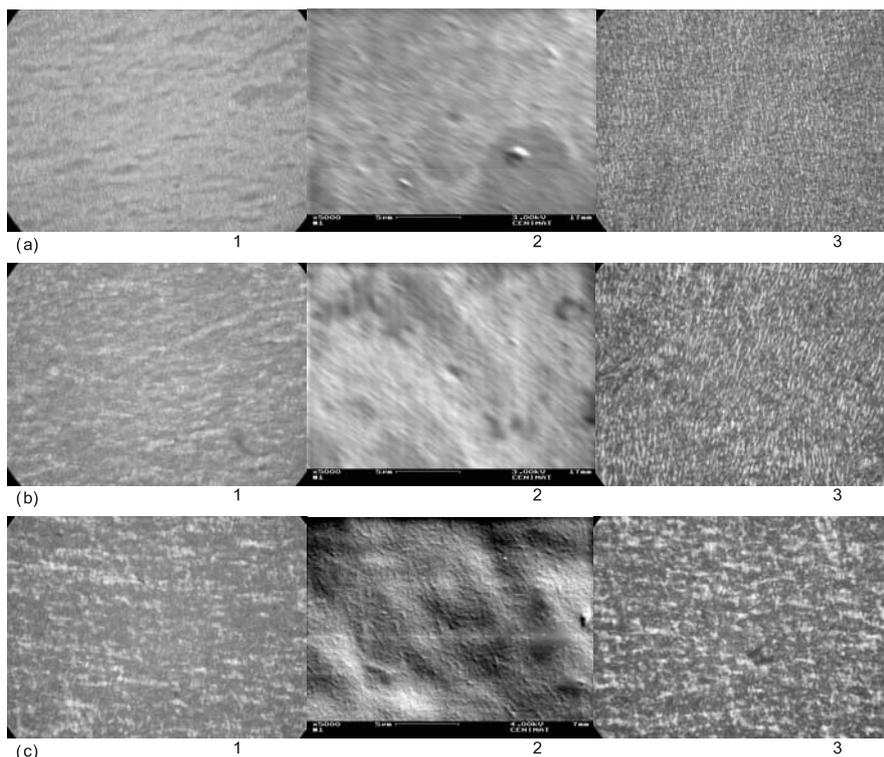Fig. 2. Schematic representation of the cellulosic/liquid crystal electro-optical cell.

Fig. 3. POM (1 and 3) and SEM (2) pictures of free-surface for the APC crosslinked films; storing time (a) sample #1, 0 min, (b) sample #2, 30 min, and (c) sample #6, 210 min.

Table 2. Summary of the electro-optical results obtained for the four different cells analysed. The contrast of the cells was obtained from the ratio (maximum transmission)/(minimum transmission). $V_{on}$ was calculated from the voltage dependence of the transmission coefficient and represents the applied rms voltage necessary to reach 95% of the maximum transmission of the sample.

| Cell sample | Maximum transmission (%) | Maximum contrast | $V_{on}/V_{rms}$ |
|---|---|---|---|
| #1 | 40.0 | 25.35 | 206 |
| #3 | 29.8 | 37.13 | 199 |
| #5 | 42.1 | 21.33 | 213 |
| #6 | 25.0 | 13.01 | 191 |

The voltage dependence of the light transmission coefficient obtained in the four cells analysed is shown in Fig. 4 and the main results are summarized in Table 2. It is observed that all the samples show maximum transmissions below 50% in sharp contrast to similar cells assembled with HPC solid films prepared from isotropic solutions [16]. The low maximum transmission observed is probably a combination of two factors, one arising from the mismatch between the ordinary refraction index of the nematic liquid crystal and the average index of the polymer film, and the other has its origin in the periodic structures present in the polymer film that scatter light. The exposure of the films to the solvent- vapour atmosphere produces some

relaxation of these structures, induced by the shearing cast process, and indeed a variation of the maximum transmission is found but its non-monotonous variation with the solvent-vapour exposition time is an indication of the complex evolution process observed for these structures has seen in both the POM and SEM images shown in Fig. 3. This account of the maximum transmission behaviour that elects the solid polymer film as causing the relevant changes between the samples and in comparison with related systems [16] is in agreement with the $V_{on}$ voltage which is similar for samples 3, 5, and 6 indicating the liquid crystal response does not change significantly among these 3 samples. It is in agreement with the voltage $V_{on}$ which is similar for samples 3, 5, and 6 that were subjected to solvent vapour treatment, indicating that the liquid crys-
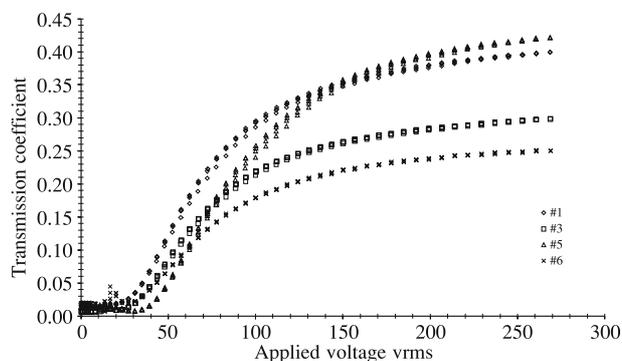


Fig. 4. Voltage dependence of the light transmission coefficient measure in cells numbers 1, 3, 5, and 6.

tal response does not change significantly among these 3 samples. Sample 1, assembled with a much thinner film, requires a switching field significantly higher than the treated samples suggesting that the solvent-vapour treatment alters the films surface anchoring properties lowering the anchoring energies involved.

## 4. Conclusions

In this study, it is shown that the composite system of APC polymeric solid films prepared from anisotropic solutions and the nematic liquid crystal E7 exhibit electro-optic behaviour similar to other cellulose based optical cells [16] but with a significant decrease of the maximum transmission. The evolution of the optical properties detected with the solvent-vapour exposition time are a consequence of the development of different textures arising in the polymeric films studied and may help to monitor these subtle solvent-vapour changes induced in the polymeric film.

## Acknowledgements

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