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New cellulose derivatives composites for electro-optical sensors

I. Costa [a,b], D. Filip [a,c], J.L. Figueirinhas [b,d], M.H. Godinho [a,*]

[a] *Department de Materiais, FCT/UNL and CENIMAT, Quinta da Torre, 2829-516 Caparica, Portugal*
[b] *CFMC-UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal*
[c] *"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, 700487, Iasi, Romania*
[d] *Department de Física, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

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Abstract

In this work we used hydroxypropylcellulose (HPC) and acetoxypropylcellulose (APC) to produce free standing solid films (~60 μm) for electro-optical devices. Cellulose derivatives films were prepared from crosslinked both HPC and APC isotropic and liquid crystalline solutions without and with a low molecular weight nematic liquid crystal mixture (LC) E7.

Films prepared from anisotropic solutions presented a band texture and E7 droplets of micron and submicron size were found to coexist with the band texture in the films prepared with E7.

The optical cells were composed by the cellulose derivatives films covered on both free surfaces by a layer of the LC E7 and placed between two transparent conducting substrates. All the electro-optical cells prepared showed switching times in the range of some milliseconds to hundreds of milliseconds. The on-voltage (V_{on}) is lowered for cells prepared with the ester derivative film obtained from isotropic solutions. The maximum transmission values show a clearly tendency to decrease for the cellulosic matrix prepared from anisotropic solutions with and without nematic liquid crystal droplets.

Keywords: Ester and ether cellulose derivatives; Liquid crystals; Electro-optical cells; Electro-optical properties

1. Introduction

Hydroxypropylcellulose (HPC) and HPC esters can generate lyotropic and thermotropic mesophases (Bianchi, Marsano, Picasso, Matassini, & Costa, 2003; Gray, 1994). Due to the ability of their molecules to spontaneous self-assemble in helicoidal arrangements light can be reflected selectively (Giasson, Revol, Gray, & Stpierr, 1991; Hou, Reuning, Wendorff, & Greiner, 2000; Sato, Nakamura, Teramoto, & Green, 1998; Tseng, Valente, & Gray, 1981).

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 (Bhadani & Gray, 1983) and on the temperature (Rusig et al., 1994). The pitch of the cholesteric helix can also be locked by using different procedures among them by photoinitiated crosslinking of pendant acrylate groups (Muller & Zentel, 2000). One of the most studied thermotropic cellulose esters is Acetoxypropylcellulose (APC), it is cholesteric from below room temperature up to 180 °C (Tseng et al., 1981) and can originate lyotropic phases in some common solvents (Laivins & Gray, 1985a; Laivins & Gray, 1985b). Rheo-optical and rheological studies (Riti, Cidade, Godinho, Martins, & Navard, 1997) 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 (Godinho, Martins, & Figueirinhas, 1996; Graighead, Cheng, & Hackwood, 1982). Electro-optical cells were produced by enclosing a cellulose derivative film, obtained

* Corresponding author. Tel.: +351 21 294 85 84; fax: +351 21 295 78 10.
E-mail address: mhg@fct.unl.pt (M.H. Godinho).

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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 (Figueirinhas, Almeida, & Godinho, 2004).

It was found that a fine tuning of the surface properties of the solid cellulosic matrix can be achieved by varying their preparation conditions (Godinho, Fonseca, Ribeiro, Melo, & Brogueira, 2002). The influence of different matrix parameters upon the electro-optical behaviour of the cells was studied (Almeida et al., 2002; Sebastião et al., 2002). 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 (Fonseca, Godinho, & Ribeiro, 2005).

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 (Zhou & Huang, 2002). 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.

There have also been several basic studies of liquid crystal alignment in spherical and elliptical droplets in elastomeric matrices (Aphonin, Panina, Pradin, & Yakolev, 1993). 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 (Amimori, Priezjev, Pelvovits, & Crawford, 2003). Uniaxially stretched anisotropic phase separated polymer films were recently obtained from APC and their optical (Filip, Costa, Figueirinhas, & Godinho, 2006a) and mechanical properties (Filip, Costa, Figueirinhas, & Godinho, 2006b) have been studied.

In this work we have studied the electro-optical behaviour of several cells assembled with APC and HPC films crosslinked with a diisocyanate obtained from isotropic and anisotropic solutions with and without dispersed liquid crystal droplets/LC composite systems. The influence upon the electro-optical properties of the acetylated cellulose matrix was studied and compared with the results obtained for the ether derivative. A qualitative relationship between the structure of the matrix and the electro-optical behaviour of the cells was also established.

2. Experimental

2.1. Materials

Hydroxypropylcellulose (HPC) ($M_w = 100{,}000$ g mol^{-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 1,6-Hexamethylenediisocyanate (HDI) (Aldrich) were used without further purification. N,N-dimethylacetamide (DMAC) (Merck) was used as received.

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 (Tseng et al., 1981). For this work the acetylation of (hydroxypropyl)cellulose (Aldrich, nominal $M_w = 100{,}000$) (molar substitution equal to 4 determined by NMR^{1}H) (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 NMR^{1}H and is 2.0.

Isotropic (30% by weight) and nematic chiral (60% by weight) solutions were obtained, in 5 ml glass containers, by adding APC and HPC to dimethylacetamide (DMAc), at room temperature, the contents were allowed to mix for several weeks.

The HPC and APC were lightly cross linked with HDI, under nitrogen atmosphere, and to the anisotropic solutions the commercial low molecular liquid crystal E7 (12% wt) was also added. The polymers idealised structures along the chemical steps involved are shown in Fig. 1.

2.3. Preparation of solid films

After homogenization the solutions were cast onto a Teflon plate at room temperature with a calibrated Gardner knife moving with a controlled rate, $v = 5$ mm/s. The films were cured at room temperature and then carefully peeled from the substrate. The film average thickness was approximately 60 μm.

2.4. Preparation of electro-optical cells and measurements

The cells, with the four kinds of 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.

Five distinct cells were prepared, APC films were used in three of them and HPC films in the other two. Two of the three APC film samples used in the cells were prepared from anisotropic solutions with (APCaniE7) and without (APCani) added E7, respectively. The third APC film sample was prepared from an isotropic solution (APCiso). The