Phase-segregated liquid crystalline cellulose derivative elastomers

D. Filip\textsuperscript{a,b}, I. Costa\textsuperscript{a,c}, J.L. Figueirinhas\textsuperscript{c,d}, and M.H. Godinho\textsuperscript{a}\textsuperscript{a}

\textsuperscript{a}Dept. de Materiais, FCT/UNL and CENIMAT, Quinta da Torre, 2829-516 Caparica, Portugal. \textsuperscript{b}“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41 A, 700487, Iasi, Romania. \textsuperscript{c}Centro de Física da Matéria Condensada, Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal. \textsuperscript{d}Departamento de Física, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

Recibido el 7 de diciembre de 2005; aceptado el 25 de marzo de 2006

New free-standing elastomeric thin films of liquid crystalline cellulose derivative and with embedded nematic liquid crystal E7 were prepared by a shear casting technique. Film samples were prepared from anisotropic and isotropic precursor solutions and were analyzed by mechanical testing, polarizing optical microscopy and small angle light scattering. For the free-standing anisotropic thin films (10 ± 2 µm thick) prepared from lyotropic precursor solutions, the added low molecular weight LC proved to be a tuning factor for the mechanical anisotropy. The polymer chain alignment induced by mechanical stretching produces changes in the LC droplet orientation, in their shape anisotropy and in the E7 nematic director field inside them.

Keywords: Cellulose derivative; elastomer; liquid crystal; band texture; interfacial.

Nueva capas suspendidas elastoméricas líquido cristalinas derivadas de celulosa con cristales líquidos nemáticos embebidos, fueron preparadas por medio una técnica de sometimiento a esfuerzos de corte. La muestras fueron sintetizadas a partir de soluciones precursoras anisotrópicas e isotrópicas y han sido analizadas por medio de pruebas mecánicas, microscopía óptica de polarización y dispersión de luz para ángulos pequeños. Para las capas suspendidas anisotrópicas (10 ± 2 µm) preparadas a partir de soluciones precursoras liotrópicas, probamos que el cristal líquido de bajo peso molecular agregado es un factor crucial para generar anisotropía mecánica. El alineamiento de la cadena del polímero inducido al estirar las capas produce cambios en la orientación y forma de las gotas de cristal líquido, y en la orientación del director del nemático dentro de éstas.

Descriptors: Derivados de celulosa; elastómero; cristal líquido; textura de banda; alineamiento interfacial.

PACS: 47.50.+d; 61.30.-v; 61.41.+e; 62.20.Dc

1. Introduction

Various types of phase-segregated structures on different scales could be achieved by means of the self-assembly of interacting molecular components. Phase segregation with liquid crystals on a micrometer or submicrometer scale typical of polymer-dispersed liquid crystals (PDLCs) is a key factor in producing PDLC-type electro-optical display materials [1-3].

LC-cellulose derivative composites have also been used to create electro-optical devices [4]. The cellulose derivative based PDLC-like optical cell (CPDLC) [5-7] consists of a thin rugged polymeric film covered on both surfaces with a liquid crystal layer and placed between two transparent conductive substrates. However, a nematic LC have also been phase separated as droplets dispersed in the cellulose polymer [8].

The performance of the PDLCs is influenced by the geometry and the orientation of the LC droplets embedded in an elastomer film and can be modified by applying mechanical stress. Therefore the investigation of the mechanical properties [9] of the structurally phase-separated PDLCs consisting of fluid LC droplets embedded in an elastomer polymeric matrix is of particular importance. The role of the polymeric matrix in these composites is very important with respect to the stabilization and orientation of the dispersed LC droplets. Depending on the anisotropy of precursor solutions, the material properties can be tuned.

For materials of this type an external factor might change their self-assembled structure through dissociation and association of physical interactions promoting or destroying order and, because of this, they can be useful in sensor applications [10]. Controlling of the network material permits the control of the coupling between the mechanical stress and molecular alignment constituting, as is well-known, the origin of the “soft elasticity” in nematic elastomers [11]. The anisotropically oriented phase-separated structures define the light-scattering electro-optical properties.

In this work we address new results on free standing thin films of polymer dispersed-liquid crystals based on (acetoxypropyl)cellulose. These systems were prepared by a shearing casting technique from anisotropic and isotropic precursor solutions of the thermotropic (acetoxypropyl)cellulose (APC) in N,N-dimethylacetamide (DMAC) with different amounts of nematic E 7. The low molecular weight liquid crystal droplets of micron and sub-micron size are dispersed in the polymeric matrix. Mechanical properties like stress-strain curves and Young’s modulus...
were determined along and perpendicular to the shear direction. The morphology of the film samples, the evolution of the nematic droplets’ shape and anisotropy, disclination lines inside the LC droplets and light-scattering patterns were followed while stretching the composite films parallel and perpendicular to the initial direction of the shear flow.

2. Experimental part

(Acetoxypropyl) cellulose was synthesized as described in Ref. 12 through acetylation of (hydroxypropyl)cellulose (HPC) (Aldrich, nominal M_w 100 000, molar substitution equal to 4 as determined by ^1H NMR). The number of acetyl groups per residue evaluated by ^1H NMR was 2. The commercial liquid crystal mixture E7 was purchased from Merck, UK. The anisotropic (60 wt%) and isotropic (30 wt%) solutions were obtained by mixing APC with DMAC at room temperature. To these solutions were added amounts up to 15% wt of low molecular weight liquid crystal E7. The solutions were left for a few weeks to be well mixed. Films were cast and sheared simultaneously at room temperature on a Teflon plate by moving a Gardner casting knife at a controlled speed of 5 mm/s. The films were stored at room temperature for about 2 weeks. The thickness of the dried films was 10 ± 2 µm.

The morphology of the films was observed with an Olympus polarizing optical microscope (POM). The mechanical properties of the samples were registered at room temperature with a home-made extensiometer using a XFTC 300 force sensor from GS sensors coupled to an optical bench (HeNe laser λ = 545.5 nm) allowing simultaneous light-scattering measurements. The films were cut into 10 mm by 5 mm rectangular pieces, with the longest dimension of the sample along the direction of the casting shear and perpendicular to it. The films were stretched uniaxially at a rate of 2 mm/min, along the longest sample dimension. The diagrams of the chemical reaction for obtaining APC and the film preparation are outlined in Fig. 1.

3. Results and discussion

Cellulose derivative esters can exhibit lyotropic and thermotropic cholesteric mesophases, and several studies on their behavior have been done over the years [13,14]. Aliphatic esters of cellulose in bulk exhibit cholesteric reflections in the visible range of the spectrum and their reflection properties were measured as a function of side-chain length and molecular weight [15]. Of the thermotropic esters of cellulose acetoxypropylcellulose (APC) received wide research interest. It presents a cholesteric mesophase from below room temperature up to 180°C [16] and can form lyotropic phases in some common organic solvents such as acetone and dibutyl phthalate [17,18]. This behaviour is favoured by the cellulose backbone that provides enough stiffness for near-parallel arrangements of the chains, while the macroscopic helicoidal structure is a consequence of the chirality of the anhydroglucose units, and the flexible side chains inhibit crystallization and allow the molecules sufficient mobility to achieve their preferred orientation. Rheo-optical and rheological studies [19] were also performed in APC in order to better understand the relationship between the textures observed by optical microscopy and the light-scattering patterns.

Figure 2 presents an optical microphotograph that was obtained between cross polars of anisotropic composite film.

This picture shows the LC droplets dispersed in the matrix of micron and submicron size as well as the characteristic band texture perpendicular to the shear direction. The band texture formation has constituted a challenging subject for study over many years [20,21]. Under certain shear flow conditions, after the cessation of the shear stress the thermotropic and lyotropic liquid crystalline polymers can develop, a periodic oscillation of the molecular director which is at the origin of the band texture running perpendicular to the shear flow. It is also well established [22,23], for specific shear flow conditions, that cholesteric liquid crystalline cellulose derivatives exhibit an unwinding of the cholesteric helix and a

---

**Figure 1.** Diagram of the chemical reaction for obtaining of APC and film preparation. Shearing (→) and stretching directions (↔) are also indicated.

**Figure 2.** Optical microphotograph of an anisotropic composite film. The arrow indicates the shearing direction.
cholesteric-to-nematic transition. The liquid crystalline elastomers prepared from hydroxypropyl cellulose [24,25] have global orientation effects when stretched, but with a less dramatic response when compared with side-chain liquid crystal elastomers [24]. The swelling behavior and the optical properties were investigated for crosslinked films of hydroxypropyl cellulose [24,25] have global orientation effects when stretched, but with a less dramatic response when compared with side-chain liquid crystal elastomers [24]. The swelling behavior and the optical properties were investigated for crosslinked films of hydroxypropyl cellulose [25]. When stretching these anisotropic films, a brittle behaviour along the shear direction and a ductile one in a transverse direction were found [26]. The films based on APC studied herein also show these two characteristics of mechanical anisotropy.

These film samples, namely anisotropic (type I) and isotropic (type II), exhibit archetypical stress-strain curves represented in Figs. 3a, 3b, respectively. Young’s modulus, stress and strain at break evaluated from the tensile results are given in Table I. The stress-strain curves were registered for several film samples originating from different precursor solutions. Young’s modulus was determined from the slope of the first linear part of the stress-strain curve, where the nominal stress (σ) is given by the force divided by the cross-sectional area in the initial undeformed state, and the strain (ε) is given by (L-L₀)/L₀, where L is the final length and L₀ is the initial length, respectively.

As expected, the values of Young’s modulus estimated are lower for our (acetoxypropyl)cellulose material than those found in the literature for (hydroxypropyl)cellulose [26,27], due to the thermotropic liquid crystalline phase state of APC at room temperature. The addition of the nematic E7 strongly influences the mechanical properties of type I (anisotropic) and type II (isotropic) films by modifying the viscoelastic properties of the matrix. The stress-strain behaviour observed in our composite material is the result of the contributions of both the dissolved part in the bulk polymer of the LC component and the phase separated LC droplets with the strain-energy concentrated in the matrix due to the incompressible phase separated cavities filled with liquid crystal [28].

Larger values of strain are found (see Figs. 3a and 3b); the LC component acts as a lubricant improving the draw ability of this material by increasing the chain mobility essential in achieving highly oriented structures. Consequently, slider elements are introduced into the mechanical model. High strains as a result have high reorientation and alignment of polymer chains.

For anisotropic films based on (hydroxypropyl)cellulose, the band size was found to constitute a controlling factor in anisotropy [26]. In our case, for the anisotropic type I films, adding the less viscous LC increased the “polydomain” characteristic of the matrix allowing larger director fluctuations to occur. The mechanical properties are affected in both directions, reducing the anisotropy of the material [29] and consequently affecting the brittle-ductile transition [30]. The estimated values for the Young’s modulus anisotropy (see Table I) decrease by adding nematic E7.

For stretching along the shear direction, the mechanical field mainly has the effect of extending the already aligned domains, with no considerable effect on molecular orientation. Deeper modifications with the mechanical stretching occur in the transverse direction for anisotropic films, sug-

\[
\text{TABLE I. Mechanical properties of the film samples studied.}
\]

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Direction</th>
<th>Modulus, MPa</th>
<th>Δσ/ɛ modulus, %</th>
<th>Strain at break</th>
<th>Stress at break, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) 0% E7</td>
<td>Along</td>
<td>49.5</td>
<td>129</td>
<td>0.4</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Transverse</td>
<td>10.6</td>
<td>1.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(I) 15% E7</td>
<td>Along</td>
<td>15.8</td>
<td>-86.5</td>
<td>1.0</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>Transverse</td>
<td>39.9</td>
<td>2.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>(II) 0% E7</td>
<td>Along</td>
<td>37.1</td>
<td>-2.1</td>
<td>0.3</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Transverse</td>
<td>37.9</td>
<td>0.4</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>(II) 15% E7</td>
<td>Along</td>
<td>15.5</td>
<td>-62.5</td>
<td>0.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Transverse</td>
<td>29.6</td>
<td>0.2</td>
<td>2.7</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{a anisotropies } \Delta_{\text{modulus}} \text{ are estimated as the ratio } \left(\frac{\text{along} - \text{transverse}}{\text{along} + \text{transverse}}\right) \times 2.\)

\[\text{FIGURE 3. Stress-strain curves parallel and perpendicular to the shear direction of a- composite anisotropic films (I): } \bigtriangleup 15\% \text{ E7 parallel}; 15\% \text{ E7 perpendicular}; \times 0\% \text{ E7 parallel}; \times 0\% \text{ E7 perpendicular}; \text{ b- composite isotropic films (II): } \ast 15\% \text{ E7 parallel}; + 15\% \text{ E7 perpendicular}; \bigtriangleup 0\% \text{ E7 parallel}; 0\% \text{ E7 perpendicular.}\]
suggesting a strong modification in the molecular orientation state in this direction when subjecting the film to a mechanical field, thus emphasizing the role of the band texture running perpendicular to the shear direction. For the films stretched perpendicular to the shear direction, the plateau occurring in the stress-strain curves corresponding to highly oriented polymeric chains resembles either the polydomain-monodomain transition occurring in polydomain samples of liquid crystalline elastomers [11] or the director rotation in monodomain samples. The anisotropy in the stress-strain results, along and perpendicular to the shear direction strongly favour the latter hypothesis.

Thin solid films prepared from lyotropic solutions of cellulose derivatives can be used as alignment layers for low molecular weight liquid crystals [21,31]. Studies were also performed on the effects of the polymer orientation surrounding droplets of low molecular weight liquid crystal in a cellulose polymer surface [32], and a strong influence over the liquid crystal orientation within the droplet was found [32,33]. There have also been many basic studies of liquid crystal alignment in spherical and elliptical droplets in elastomeric matrix [34]. 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 [35]. Uniaxially stretched phase separated polymer films can be used as nonabsorbing polarizers which efficiently reflect or backscatter light rather than absorbing it [35].

We used [36] polarizing optical microscopy and small angle light scattering experimental techniques to investigate the effect of elongation parallel and perpendicular to the shear direction on the morphology of the thin composite films (10 ± 2 µm) of cellulose derivative liquid crystalline. For the nematic ellipsoids dispersed in the matrix, the anisotropy ratio was found to be around 1.23. The main axis is oriented on the average 28° away from the shear direction. It was found that stretch along the shear, with strain equal to 0.8, seems to have no effect on the banded structure of the matrix, while the nematic liquid crystal ellipsoids slightly orient the main axis to the stress direction, and their shape anisotropy increases by a factor of 2. In the direction transverse to the shear direction the applied mechanical field induces a deep change of the polymeric matrix, and a fibrillar structure is found at the end. The evolution of the nematic ellipsoids is noteworthy with respect to this direction: the main axis of the ellipsoids almost aligns along the stretch direction and the shape anisotropy increases to a value equal to 5.5.

The anisotropic polymer matrix alignment dramatically influences not only the droplet shape anisotropy and orientation but also the liquid crystal alignment within the droplets. The droplet shape can be regarded as a sensor for the stress tensor in the material. The results obtained for our system suggest that before stretching the molecules of the nematic liquid crystal droplets tilt at the surface and that after stretching a more homogeneous surface alignment can be obtained.

Figures 4a, 4b, 4c show the POM and SALS results on the composite films of liquid crystalline cellulose derivative, stretched parallel and perpendicular to the shear direction, showing the change of the droplets anisotropy and shape and direction, along with the modification of the light-scattering patterns. From Fig. 4c the results show the profound changes that occur when stretching in a perpendicular direction with a strong increase in shape anisotropy and orientation of the main axis to the stress direction.

4. Conclusions

New phase-separated liquid crystal bioelastomers based on cellulose derivative are obtained. The precursor solutions are important in determining the mechanical properties of this new soft material. The thin films prepared from lyotropic so-
olutions have anisotropic mechanical properties. It seems that
the added low molecular weight LC constitutes another tun-
ing factor for mechanical anisotropy. It acts as a lubricant in-
ducing slider elements in the mechanical model. By stretch-
ing these thin films, the resulting polymeric chain align-
ment provokes changes in the LC droplet orientation, shape
anisotropy, as well as subtle changes inside the droplets. As is
well-known, one of the key features of the LC displays is the
alignment of the LCs. Our new PDLC seems to be promising
well-known, one of the key features of the LC displays is the
anisotropy, as well as subtle changes inside the droplets. As is

Acknowledgment

Dr. D. Filip wishes to thank the Portuguese Science
Foundation (FCT) for the fellowship granted,
SFRH/BPD/19722/2004. This work was par-
tially supported by projects POCTI/CTM/56382/2004,
POCTI/CTM/37435/2001 and by the FCT through Pluri-
annual contracts with CENIMAT.

* Corresponding author. Maria Helena Godinho:
mhg@fct.unl.pt.
1. S.J. Park, M.K. Seo, M. Han, and J.R. Lee Opt. Mater. 21
3. M. Jazbinsek, I. D. Olenik, M. Zgonik, A.K. Fontecchio, and
4. J.L. Figuerinhas, P.L. Almeida, and M.H. Godinho, Electro-
Optical Properties of Cellulose Derivatives, in Polysaccharides:
Structural Diversity and Functional Versatility, edited by S.
Dumitriu (New York : Marcel Dekker, 2005) 1123.
11. M. Warner and E.M. Terentjev, Liquid Crystal Elastomers (Ox-
13. J. Watanabe, Y. Fukuda, R. Gehani, and I. Uematsu, Macro-
molecules 18 (1986) 2141.
16. J.B. Riti, M.T. Cidade, M.H. Godinho, A.F. Martins, and P.
594.
296.
31. N. Mori, M.Morimoto, and K. Nakamura, Macromolecules 32
32. N. Mori, M. Morimoto, and K. Nakamura, Adv. Mater. 11
34. O.A. Aphonin, Yu. V. Panina, A.B. Pradin, and D.A. Yakolev,
35. I. Animori, N.V. Priezjev, R.A. Pelcovits, and G.P. Crawford,