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Anisotropic cellulose-derived matrix for dispersed liquid crystals

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New cellulose-derived dispersed liquid crystal free-standing thin films were prepared by a shear-casting technique from anisotropic and isotropic solutions of thermotropic (acetoxypropyl)cellulose in *N*,*N*-dimethylacetamide with different amounts of the nematic E7. For films prepared from anisotropic solutions, dispersed nematic E7 droplets of micron and submicron size were found to coexist, with the band texture characteristic of polymer liquid crystals after shearing. Mechanical properties including Young's modulus and stress–strain curves were determined along and perpendicular to the shear direction, and revealed the anisotropic behaviour of films prepared from lyotropic solutions. The nematic E7 component appears to promote chain mobility and rearrangement of the polymer matrix and to modify the viscoelastic properties of the matrix.

1. Introduction

Polymer–dispersed liquid crystals (PDLCs) have attracted great interest due to their applications [1–4]. The role of the polymeric matrix in these composites is very important with respect to the stabilization and orientation of the low molar mass (LMMLC) dispersed liquid crystal droplets. LC/cellulose-derived composites have been used to produce electro-optical devices [5]. The cellulose derivative-based PDLC-like optical cell (CPDLC) [6–8] consists of a thin rugged polymeric film covered on both surfaces with a liquid crystal layer and placed between two conductive transparent substrates. The nematic LC may also be phase-separated as droplets distributed in the cellulosic polymer [9].

It was found that films of cellulose derivatives [10] can exhibit anisotropic mechanical properties, reflecting the state of molecular orientation resulting from the flow of the liquid crystal state under shear stress experienced during the film's preparation. (Acetoxypropyl)cellulose (APC) exhibits both lyotropic and thermotropic chiral nematic phases at room temperature: the cellulose backbone provides sufficient stiffness for near-parallel arrangements of the chains; the macroscopic helicoidal structure is a consequence of the chirality of the anhydroglucose units, whereas the flexible side chains inhibit crystallization and allow the molecules sufficient mobility to achieve their preferred orientation. It is of particular interest to investigate the mechanical properties [11] of structurally phase-separated PDLCs composed of fluid LC droplets embedded in a polymeric matrix. The performance of the PDLCs is influenced by the geometry and orientation of the LCs, which can be modified by applying a mechanical field. In this work we present a new type of polymer-dispersed liquid crystal free-standing film, consisting of micron and sub-micron size nematic droplets dispersed in an APC matrix. The films were prepared by shearing from both anisotropic and isotropic solutions of APC, with and without the nematic liquid crystal E7. The tensile properties were studied along and transverse to the shear direction. The role of the LC component in the cellulose composite on the resulting mechanical properties is discussed.

2. Experimental

(Acetoxypropyl)cellulose was synthesized as previously described through the acetylation of (hydroxypropyl)-cellulose (HPC) (Aldrich, nominal $M_w=100{,}000$, molar substitution equal to four, as determined by ^{1}H NMR) [12]. The number of acetyl groups per residue evaluated by ^{1}H NMR was two. The commercial liquid crystal mixture E7 was purchased from Merck, UK. The liquid crystalline (60 wt% of polymer) and isotropic (30 wt% of polymer) solutions were prepared by placing APC and *N*,*N*-dimethylacetamide (DMAC) in glass vials (5 ml). These containers were sealed and well mixed by

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centrifuging to obtain uniform solutions. To these solutions different amounts (10, 12 and 15 wt%) of low molar mass liquid crystal E 7 were added. The resulting solutions were allowed to stand for a few weeks in order to homogenize thoroughly. 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^{-1}. The films were stored at room temperature for about two weeks. The thickness of the dried films was $10 \pm 2\,\mu m$.

The morphology of the films was observed using a polarizing optical Olympus microscope (POM). The mechanical properties of the samples were registered with a home made extensiometer using a XFTC 300 force sensor (GS Sensors) coupled to an optical bench (HeNe laser $\lambda = 545.5$ nm), allowing simultaneous light scattering measurements. The films were cut into $10 \times 5\,mm^2$ 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^{-1}, along the longest sample dimension.

3. Results and discussion

In figure 1 the optical photomicrograph taken between crossed polarizers of a composite film obtained from a thermotropic cellulose derivative with dispersed E7 droplets is presented. Micron and submicron size droplets, dispersed homogeneously in the matrix, can be observed. A band texture perpendicular to the shear can be seen in the matrix. It is well established for specific shear flow conditions, that cholesteric liquid crystalline cellulose derivatives exhibit an unwinding of the cholesteric helix and a cholesteric-to-nematic transition [13, 14]. In addition it is also well known that under certain shear flow conditions thermotropic and lyotropic liquid crystalline polymers, after the cessation of the shear stress, can develop a periodic oscillation of the molecular director, which is at the origin of the band texture running perpendicular to the shear flow [13]. The band texture formation has proved to be a challenging subject of study over many years [15, 16]. APC has also received much scientific interest from this point of view [17]. For HPC solid thin films prepared from aqueous solutions it was found that the band size constitutes a controlling factor in the anisotropy of the mechanical properties [10]. For these films brittle behaviour along the shear direction and ductile behaviour in the transverse direction were found. The films based on APC studied here also show these two characteristics. Stress–strain curves were measured for 12 samples with different LC contents and distinct precursor APC–DMAC solutions. Typical results are shown in figures 2 and 3 for films prepared from anisotropic (I) and isotropic (II) solutions, respectively. Young's modulus, and the stress- and strain-at-break evaluated from the tensile results are given in table 1 and presented graphically in figures 4 and 5.

The 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 $(L - L_0)/L_0$, where L is the final length and L_0 is the initial length.

The values of the Young's modulus, as expected are lower for our (acetoxypropyl)cellulose material than

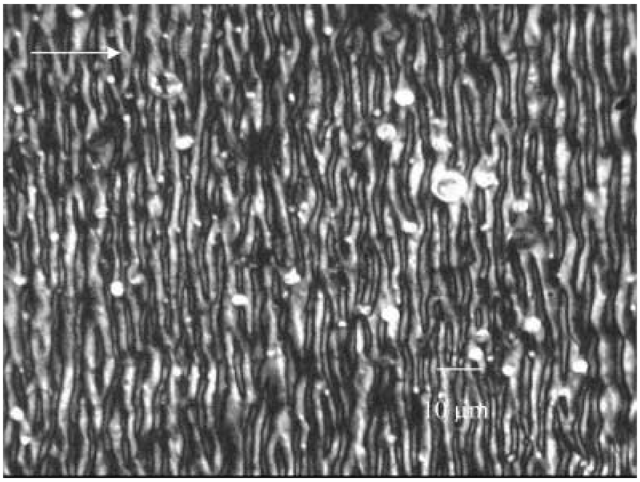

Figure 1. Optical microphotograph of an anisotropic film of APC and 12% low molecular weight liquid crystal E7. The arrow indicates the shearing direction.

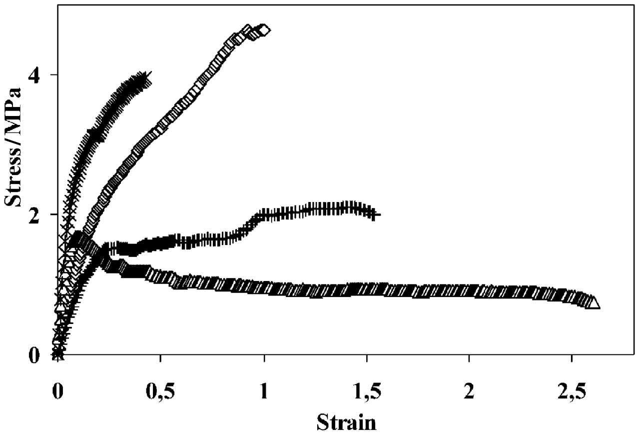

Figure 2. The stress–strain curves of the composite anisotropic films (I), parallel and perpendicular to the shear direction: ◇=15% E7 parallel; △=15% E7 perpendicular; *=0% E7 parallel ; +=0% E7 perpendicular.

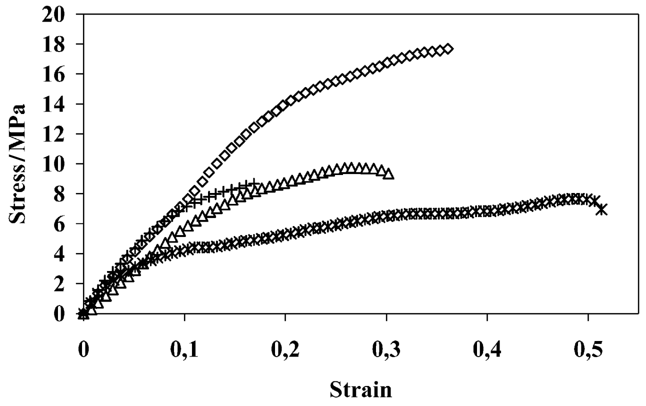

Figure 3. The stress-strain curves of the composite isotropic films (II), parallel and perpendicular to the shear direction: *=15% E7 parallel; +=15% E7 perpendicular ; ◇=0% E7 parallel; △=0% E7 perpendicular.

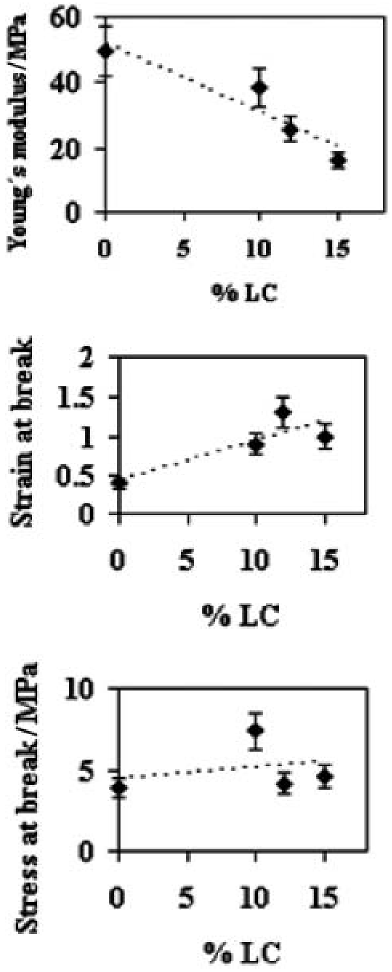

Figure 4. Young's modulus, strain-at-break and stress-at-break vs concentration of the LC for anisotropic films evaluated in the parallel direction with respect to the shear.

those found in the literature for (hydroxypropyl)cellulose [10, 18]. This result may be explained by the thermotropic liquid crystalline phase state of APC at room temperature, induced by the presence of side groups which act as a solvent disrupting the hydrogen bonding. Comparing the results from the 0% LMMLC content films of types I and II, we observe that in the type I sample a large anisotropy (estimated as in table 1, see the values of Δ_{modulus}, Δ_{strain} and Δ_{stress}) between the parallel and perpendicular values of the Young's modulus (129%) and stress-at-break (64.4%) is observed. In the type II sample, however, a vanishing value (−2.1%) is found for the Young's modulus and for the stress-at-break a smaller value is also recorded (−45%). These results are in agreement with those found for HPC [10] and reflect the fact that for type I films the polymeric chains are on average packed along the shear direction, giving a brittle behaviour along this direction and a ductile behaviour in the perpendicular

Table 1. Mechanical properties of the APC- based composite films.

Sample Type %E7	Direction	Modulus/ MPa	Δ_{modulus}, [a]/%	Strain-at-break	Δ_{strain}, [a]/%	Stress-at-break/ MPa	Δ_{stress}, [a]/%	$\sigma^* \times \varepsilon^*$/ MJ m^{-3}
I	Along	15.8	−86.5	1.0	−88.9	4.7	141.8	—
15%	Transverse	39.9		2.6		0.8		0.2
I	Along	25.7	19.6	1.3	−103.7	4.2	129.4	—
12%	Transverse	21.1		4.1		0.9		0.3
I	Along	38.4	70.9	0.9	−80	7.4	125.3	—
10%	Transverse	18.3		2.1		1.7		0.4
I	Along	49.5	129	0.4	−115.8	3.9	64.4	—
0%	Transverse	10.6		1.5		2		0.4
II	Along	15.5	−62.5	0.3	40	2.8	3.6	—
15%	Transverse	29.6		0.2		2.7		—
II	Along	37.1	−2.1	0.3	−28	7.9	−45	—
0%	Transverse	37.9		0.4		12.5		—

[a] Anisotropies Δ_{modulus}, Δ_{strain}, Δ_{stress} are estimated as the ratio $\frac{(along-transverse)}{along+transverse} \times 2$.

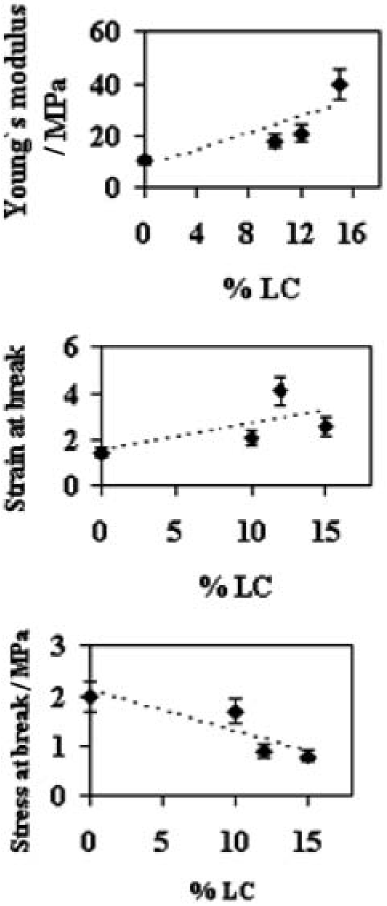

Figure 5. Young's modulus, strain-at-break and stress-at-break vs concentration of the LC for anisotropic films evaluated in the perpendicular direction with respect to the shear.

direction, as seen in the strain-at-break anisotropy (−115.8%), while for type II films this anisotropy is noticeably smaller (−28%). The addition of the nematic E7 strongly influences the mechanical properties of types I and II films. In figures 4 and 5 the Young's modulus, strain-at-break and stress-at-break are plotted as functions of concentration of the LC for type I films stretched in parallel and perpendicular directions, respectively, with respect to the shear.

The mechanical properties are affected in both directions by adding the LC component. The Young's modulus and stress-at-break show differing tendencies in the two directions: the Young's modulus decreases along the shear direction but increases in the transverse direction. Stress-at-break for the films stretched in the parallel direction slightly increases with increasing amount of LC, whereas in the perpendicular direction it decreases with increasing concentration of the LC. Strain-at-break, in both directions shows an increasing tendency with increasing concentration of LC. These results clearly show that the low molar mass liquid crystal component modifies the viscoelastic properties of the cellulose derivative matrix. The liquid crystal appears to act as a lubricant to the anisotropic cellulose matrix, allowing a better alignment along the shear direction; it also promotes packing in the transverse direction that translates into an increase of the Young's modulus and a decrease of the stress-at-break along this direction.

For films prepared from isotropic solutions (type II), the initial shear breaks the symmetry of the chain alignment, creating a preferential direction that is only revealed when LMMLC is added. A stronger effect of the lubricating action of the LMMLC is expected, and observed in the large decrease of the Young's modulus along the shear direction.

For both anisotropic and isotropic films, the fluid LC E7 changes the elasticity of the matrix. This is important when PDLCs with interesting new possible applications are required [19]. When comparing the results of anisotropic films with those of isotropic films, it appears that the most important modifications in mechanical stretching occur in the transverse direction for anisotropic films, suggesting the strong modification in molecular orientation state in this direction when subjecting to a mechanical field. The presence of the band texture running perpendicular to the shear direction determines, to a great extent, the mechanical behaviour in the perpendicular direction, making it different from that in a parallel direction with respect to the shear.

For films stretched along the shear direction the mechanical field could, in principal, have only the effect of enlarging the already aligned domains with no significant effect on molecular orientation. Perpendicular to the shear direction there is also the band texture which, as described already, represents a periodic oscillation of the director orientation. The higher the 'polydomain' characteristic in the matrix with high amplitude of director oscillation, the lower is the difference between the properties in the two directions. The less viscous LMMLC dissolved in the polymeric matrix may give rise to larger oscillations of the director within the bands; therefore the increasing Young's modulus for anisotropic films with LC, stretched perpendicular to the shear, could be a consequence of this effect. In this way the LC constitutes another factor influencing the anisotropy of this type of material.

By adding the nematic LC, the material becomes tougher. The area under the stress–strain curve, defined as the modulus of toughness, corresponding to the anisotropic film with 0% LC stretched along the shear direction (1.2 MJ m^{-3}) is lower than the corresponding area estimated for the anisotropic film with 15% LC (3 MJ m^{-3}), indicating that the LC reduces the brittle behaviour in this direction in the films. In the transverse direction the stress–strain curves show a totally different behaviour, the material is ductile with cold flow phenomena and high strains. The LC component enhances the matrix-yielding by modifying the disentanglement rate. The product of the yield stress (σ*) and the yield strain (ε*) (see table 1) decreases with increasing amount of LC, highlighting its role in the brittle–ductile transition [20]. For PDLC materials with incompressible phase-separated liquid crystal filled cavities causing strain–energy concentration in the matrix, an amplified strain rate dependence of the elastic modulus was revealed [21]. This strain concentration is responsible for the permanent deformation of the droplets. The observed stress–strain behaviour of our composite material comprises the contributions of both the dissolved LC in the bulk polymer and the phase-separated LC droplets.

The type I film samples with LC in the transverse direction have higher values of the strain-at-break and lower values of the stress-at-break, indicating an increase of the drawability of the films associated with an increase of the molecular mobility important in achieving highly oriented structures. High strains lead, as a result, to high reorientation and alignment of the polymer chains. The plateau appearing in the stress–strain curves corresponding to highly oriented polymeric chains may be associated with the polydomain–monodomain transition occurring in liquid crystalline elastomers [22].

In figure 6 the ratio of the uniaxial stress applied in the parallel and perpendicular directions with respect to the shear flow for type I film samples with different concentrations of the LMMLC, as a function of the strain are presented.

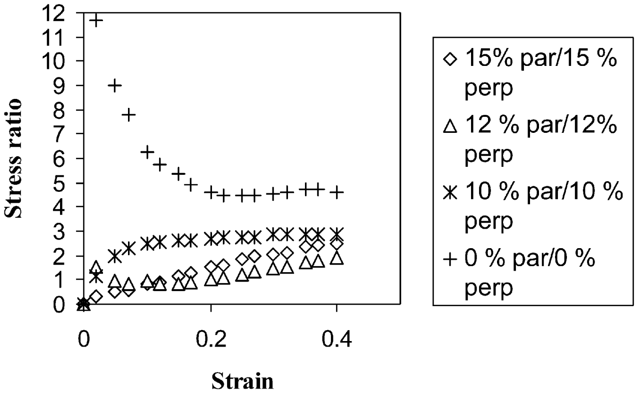

Figure 6. Stress ratios ($\sigma_{\mathrm{parallel}}/\sigma_{\mathrm{perpendicular}}$) of composite anisotropic films with different LC contents, as a function of strain.

It may be noted that the mechanical anisotropy is strongly affected by the LC. The films with LC show a reduced mechanical anisotropy when compared with the stress ratio behaviour of the 0% LC content anisotropic film sample. The stress ratio of the films with LC shows a slight increase with the applied strain and thereafter remains constant. The anisotropic film without LC, at the beginning at low strains, shows a marked decrease of the stress ratio up to a constant value slightly higher than those of the anisotropic films with LC. The abrupt decrease observed in the sample with 0% LC content may be explained by the strong molecular reorientation which occurs in the initial stage of stretching, in the case of the sample stretched perpendicular to the shear direction. The addition of the lubricating LC strongly reduces the initial anisotropy.

4. Conclusions

A new type of thin free-standing film based on an (acetoxypropyl)cellulose matrix and dispersed nematic E7 liquid crystal droplets is discussed. The mechanical properties studied along and transverse to the shear direction revealed the anisotropy of the properties of the films prepared from lyotropic solutions of APC in *N*,*N*-dimethylacetamide. The fluid LC component in the composite, by changing the viscoelastic properties and favouring chain mobility and rearrangement of the polymeric matrix, was found to affect the anisotropy of the mechanical properties and may be used to fine tune the mechanical properties of the composite films.

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