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A cellulosic liquid crystal pool for cellulose nanocrystals: Structure and molecular dynamics at high shear rates

Coro Echeverria [a], Pedro L. Almeida [a,b], Gabriel Feio [a], João L. Figueirinhas [c], Maria H. Godinho [a,*]

[a] I3N – CENIMAT, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT/UNL, 2829-516 Caparica, Portugal
[b] Área Departamental de Física, ISEL, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal
[c] Departamento de Física, and CeFEMA, Instituto Superior Técnico, IST/UL, Av. RoviscoPais, 1049-001 Lisboa, Portugal

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ABSTRACT

Cellulose and its derivatives, such as hydroxypropylcellulose (HPC) have been studied for a long time but they are still not well understood particularly in liquid crystalline solutions. These systems can be at the origin of networks with properties similar to liquid crystalline (LC) elastomers. The films produced from LC solutions can be manipulated by the action of moisture allowing for instance the development of a soft motor (Geng et al., 2013) driven by humidity. Cellulose nanocrystals (CNC), which combine cellulose properties with the specific characteristics of nanoscale materials, have been mainly studied for their potential as a reinforcing agent. Suspensions of CNC can also self-order originating a liquid–crystalline chiral nematic phases. Considering the liquid crystalline features that both LC-HPC and CNC can acquire, we prepared LC-HPC/CNC solutions with different CNC contents (1, 2 and 5 wt.%). The effect of the CNC into the LC-HPC matrix was determined by coupling rheology and NMR spectroscopy – Rheo-NMR a technique tailored to analyse orientational order in sheared systems.

1. Introduction

Hydroxypropylcellulose, one of the polymers capable of forming both thermotropic [2] and lyotropic liquid crystalline phases [3,4], extends its range of applications from film forming materials through thickening agents, protective colloids, optical applications, development of textures or the preparation of chirofilters [5–9] among several other applications. Recently it was found that HPC networks can transform energy into motion when triggered by humidity [1] gradients. This interesting behaviour takes places when HPC soft films are prepared from liquid crystalline solutions. A step-forward for this type of responsive HPC polymer liquid crystals (PLC) could come from the reinforcement of the matrix by the incorporation of CNC.

For most plastics, semi-crystallinity is highly preferred, as it associates the strength of the crystalline regions with the flexibility of the amorphous sections of the matrix. The introduction of a small amount of a filler into an amorphous polymer matrix is a common approach to increase material strength and endurance [10]. In this sense, CNC postulate as a good candidate and have been extensively incorporated into polymer matrixes to improve strength and decrease cost for composite applications [11–15] due to the interesting properties that they present: including high aspect ratio, high degree of crystallinity, high elastic modulus, high rigidity, low deformability, optical transparency, anisotropy and excellent properties

* Corresponding author.
E-mail address: mhg@fct.unl.pt (M.H. Godinho).

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of surface derivatization [16,17]. CNC, generated by the removal of amorphous sections of a purified cellulose source by acid hydrolysis, consist of rod-like cellulose crystals and combine cellulose properties with the specific features of nanoscale materials. Most studies on cellulose nanocrystals were focused on their potential application in reinforcing composites, but it has been observed that suspensions of CNC can also self-assemble to give a liquid–crystalline chiral nematic phase. For instance, CNC films produced from liquid–crystalline suspensions are capable of reflecting coloured light [18]. When adding CNC to a LC-HPC matrix, it was found that the incorporation of a small amount (0.1 wt.%) induced iridescence in sheared transparent LC-HPC films [14]. Therefore, the addition of CNC not only affects the mechanical properties but it can also modify the cholesteric structure and texture of the LC-HPC.

Taking profit of these special features (of both LC-HPC and CNC) and the advantage of high compatibility, in this work we prepare an all cellulose-based liquid crystal as a first approach for the optimization of the efficiency of the referred soft motor. For that purpose, in this contribution the objective is twofold: Firstly, we aim to study the effect of addition of CNC into the LC-HPC not only in terms of reinforcement of the matrix (viscoelastic properties) but also focusing in the cholesteric structure that could be differently affected depending on the CNC content. Secondly, we pursue to understand the structure–properties relationship and the mechanisms behind the shear motion by means of a deep study of the cholesteric liquid crystal HPC/CNC/water system using the Rheo-NMR technique in order to determine the structural changes that can be induced by shear flow [19]. The different responses of the all based cellulosic system as a function of the incorporated amount of CNC are also studied.

For the Rheo-NMR study, shear rates between 1 and 50 s^{-1} were investigated. Deuterated water was used as a solvent for the NMR analysis. The obtained NMR spectra allow the identification of different ordering states within shear and relaxation. Preliminary analysis indicates that a 5% of CNC hinders the HPC to reorder during the relaxation process.

2. Experimental part

2.1. Materials

Hydroxypropylcellulose with a molecular weight, Mw = 100,000 Da and MS = 3 was purchased from Sigma–Aldrich and used as received. Cellulose nanocrystals (CNC) were kindly supplied Prof. Derek Gray. For the following study 1, 2 and 5 wt.% of CNC were mixed with deuterated water and sonicated for 5 min. HPC was dissolved in the mixture of CNC/deuterated water (D_2O) at 50% (wt.%). The prepared samples were sealed, kept in the dark to avoid light damage, and stirred every two days. A complete dissolution of HPC/CNC was obtained in 2 weeks.

2.2. Characterization methods

The textures of the prepared HPC solutions were observed using an Olympus BX51 microscope equipped with cross polarizers and an Olympus DP73 camera.

The wavelengths (λ_0) of the maximum selective reflection peaks were recorded with a Jobin Yvon monochromator H10 V, mounted on the microscope stage, equipped with a photomultiplier, and the data was acquired on a computer. The homogenized samples, inside the vials, were used to collect the spectra (see the coloured solutions in the glass vials shown in Fig. 2 (A)).

For the structural characterization of the HPC/CNC/water solution a X'Pert PRO (PANAlytical) X-ray diffractometer (XRD) was used. The measurement were performed using Cu Kα radiation (k = 1.5418 Å) in the range 2θ = 3–70°.

Two different complementary techniques were used to characterize the rheology of this system: Rheo-NMR and Rotational Rheometry. In the Rheo-NMR experiments, the DNMR spectra were recorded on an AVANCE III Bruker NMR spectrometer equipped with a 7.049 T superconducting magnet, corresponding to a deuterium resonance frequency of 46.072 MHz, with a Couette-flow device and a saddle coil. The Couette cell consists of an outer cylinder with an inner diameter of 19 mm and a rotating inner cylinder with a diameter of 17 mm. The symmetry axis of the coaxial cylinders is parallel to the magnetic field. The mechanical motion in the device is originated from a pulse-programmer-controlled stepper motor placed on the top of the magnet. The following shear rates were selected for the study: 1, 3.75, 10, 20 and 50 s^{-1}. The protocol used for the measurements proceeds as follows: the solution was subjected to a pre-shear, with a shear rate of 3 s^{-1} during 1 min and let rest during 1 h in order to get a stabilized isotropic NMR spectra. That protocol allows obtaining a reproducible initial state for every run. This preparation process gives rise to a polydomain liquid crystal solution composed of randomly oriented cholesteric domains that were formed when the aligned nematic state structure is allowed to relax back to the cholesteric equilibrium state [14,20]. After attaining the polydomain cholesteric state the shear measurement is started with acquisition of NMR spectra during a period of time at a selected constant shear rate. The relaxation process after cessation of the imposed shear was monitored for a long period of time. The rheological characterization of the HPC/CNC solutions was performed using a stress-controlled rheometer Bohlin Gemini HR nano, with a cone-plate (20 mm diameter and 2° cone). Temperature of the test was kept at 25 °C. A solvent trap was used in order to avoid evaporation. The evolution of viscosity with shear rate was recorded at room temperature for a shear rate range of 0.1–500 s^{-1}. Dynamic measurements after cessation of shear were performed at a non-destructive frequency of 1 Hz and in the linear viscoelastic regime previously determined from strain sweep tests (not shown).