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Carbon Nanotubes as Reinforcement of Cellulose Liquid Crystalline Responsive Networks

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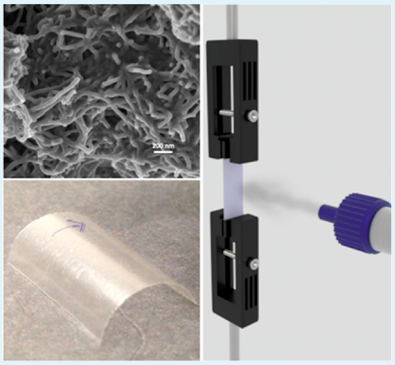
Supporting Information

ABSTRACT: The incorporation of small amount of highly anisotropic nanoparticles into liquid crystalline hydroxypropylcellulose (LC-HPC) matrix improves its response when is exposed to humidity gradients due to an anisotropic increment of order in the structure. Dispersed nanoparticles give rise to faster order/disorder transitions when exposed to moisture as it is qualitatively observed and quantified by stress−time measurements. The presence of carbon nanotubes derives in a improvement of the mechanical properties of LC-HPC thin films.



KEYWORDS: *cellulose derivative, polymer liquid crystal, carbon nanotubes, humidity-responsive, actuator, soft motor*

The demand of finding environmentally friendly materials together with seeking for simplicity have put the focus on the nature as a rich inspiration for the development of environmentally responsive systems.[1−5] A good example that combines both premises can be found in plants. They possess structures that transform humidity into mechanical motion.[2,6] Cellulose, which is the structural component of plants, and its derivatives have received extensive attention and postulate as promising material for mimicking nature.[7] For instance, Hydroxypropylcellulose (HPC), a commercially available derivative of cellulose, is capable to form lyotropic liquid crystalline phases in water solutions, at room temperature and for a certain concentration range (42−70 wt %).[8] The hydrophobic groups of the semicrystalline polysaccharide promote the formation of rigid rods like fragments that associate, become parallel and additionally exhibit a twist of the molecules perpendicular to the vertical axis, giving rise to a chiral nematic liquid crystal domains or cholesteric structure.[9] Polymeric Liquid Crystal (PLC) actuators or liquid crystalline elastomers (LCE), are a class of soft actuators consisting of a network of polymerized mesogenic molecules presenting orientational order.[10−13] These materials are anisotropic, and the alignment of the molecules can be influenced to obtain specific properties.[14,15] In the case of HPC, the mesogenic rigid segments are the molecule's fragments responsible for the orientational order in the system.[16] In fact, it was demonstrated that films produced from HPC/water solutions, form networks similar to elastomers, when prepared from liquid crystalline (LC) solutions.[17] These liquid crystal networks (LCN) can be further manipulated in order to produce helicoidal structures and spirals[18] able to respond to external stimuli, generating bending, unbending and torsion motions, similar to movements found in live plants. Taking advantage of the unusual characteristics of these materials, a soft-motor (an anisotropic HPC film actuator capable to transform humidity into mechanical motion) was assembled.[17] The mechanism behind the motion of the motor is based on an order/disorder transition induced by water molecules. Thus, the objective of this study is to improve the responsiveness of LC-HPC anisotropic films, and consequently the actuator performance, by altering the order parameter of the anisotropic network. A recent work based on the humidity responsiveness of microfibrilated cellulose films[19] opened a field in which high anisotropic materials can be used as reinforcement materials for the proposed objective. In this line of thought, we have chosen Carbon Nanotubes (CNT), that have been widely used for the reinforcement of polymer matrix and stimuli responsive systems, as the filler for polymer composite materials

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development.[20−22] Therefore, in this work we prepared composites of LC-HPC and multiwalled carbon nanotubes (CNT) and determined if the incorporation of these anisotropic and high aspect ratio nanoparticles, actually improves the orientational order and thus the responsiveness of the thin solid films.

For this work lyotropic aqueous solutions of 50 wt % of HPC were prepared with three different CNT concentration (0.01, 0.05, 0.1 wt %) added to the solution (no dramatic changes of the precursor solution viscosity are induced (Figure S1)). All the prepared samples show polygonal textures typical of cholesteric structures (Figure S2) indicating that the presence of CNT does not affect the cholesteric phase of HPC.

In Figure 1A, a SEM micrograph of the cross-section of a LC-HPC film depict the characteristic periodic structures formed

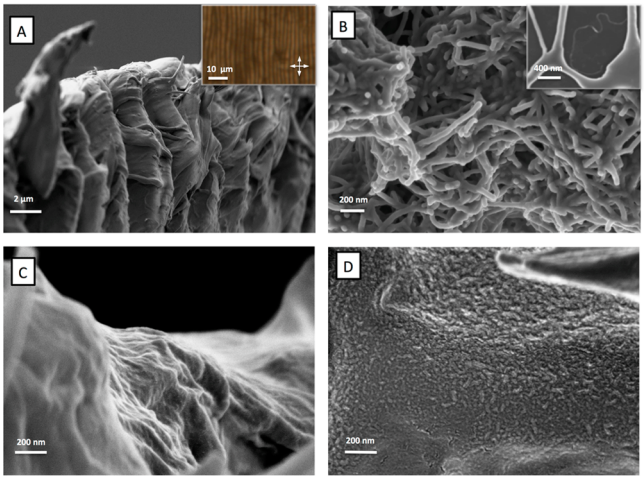

Figure 1. (A, C) SEM micrographs of the cross-section of an LC-HPC (50 wt %) film. Cross-polarized microscopy (POM) image of an LC-HPC (50 wt %) film is shown in the inset of A. (B) SEM micrograph of MWCNT and the inset shows an isolate CNT, (D) SEM image of LC-HPC-0.01 wt % CNT film's cross-section.

and locked within the polymer after the evaporation of water and already studied in depth by Godinho et al.[23] These bands are confirmed by POM (inset of Figure 1A) and are also present in all the prepared LC-HPC composites (Figure S3). The commercial multiwalled CNT (Figure 1B) incorporated in the LC-HPC (50 wt %) solutions present dimensions of 10−20 nm in diameter and 0.5−10 μm of length. A qualitative first indication of the presence of CNT in the LC-HPC matrix is given by its morphology study, when CNT are added to the LC-HPC solution, a noticeable change of roughness is observed for LC-HPC/CNT (0.01 wt %) film (Figure 1D and Figure S4) compared to the LC-HPC (50 wt %) film (Figure 1C).

Considering that the objective of the study is to optimize the soft motor's performance, an improvement may also come from its anisotropic mechanical reinforcement. In this line, the results regarding the mechanical properties performed to LC-HPC and LC-HPC composite films in both directions perpendicular and parallel to the casting shear are gathered in Table 1. As observed, when compared to the LC-HPC values, the addition of 0.01 wt % CNT provokes an increase on the Young's modulus as well as on the tensile strength by a factor of 2.2 and 1.9, respectively, for film measured parallel to the shear, and 2.3 and 2.6, respectively, for perpendicular measurements. Thus, another indirect indication of the presence and influence of CNT in the LC-HPC polymer matrix is its mechanical properties enhancement. Nevertheless, the improvement of these properties achieves its maximum level for the polymer with the lowest CNT content. The increment of CNT to the LC-HPC and the improvement of their mechanical properties are not directly proportional. As seen from Table 1, when the amount of CNT in the matrix increases to 0.05 and 0.1 wt %, both Young's modulus and tensile strength values decrease. This result could be indicative of a critical CNT content between 0.01 and 0.05 wt %. Above this critical value the filler (CNT) would act as an impurity. The reinforcement role of the CNT is less evident, although they still present higher values from those of LC-HPC without CNT. This interesting result points out the extraordinary influence that a low CNT content can have in this system. Focusing now on the effect that the addition of 0.01 wt % has in the elongation at break of the polymeric thin film, different results are obtained when tested in the direction parallel or perpendicular to the casting shear direction. Essentially, CNT contribute to improve the elongation at break in the direction parallel to the casting shear by a factor of 1.5 whereas in the direction perpendicular to the shear, they induce a decrease of the elongation at break by a factor of approximately 3. These interesting results indicate that the preparation method, which is shear casting (Experimental Section), is helping for the highly anisotropic CNT to be preferentially oriented in the direction of the shear induced by the polymeric chains under uniaxial shear and thus contributing to the intrinsic orientational order of the film, which is paramount for the enhanced responsiveness of the soft motor as will be further demonstrated. For the sake of comparison mechanical properties of HPC/SDS sample (without CNT) is also collected in the Table 1 and as expected, they decrease dramatically because SDS may act as a

Table 1. Young's Modulus (E), Tensile Stress (σ_s), and Strain Deformation (ε) of the Films Prepared from HPC (50 wt %) and HPC (50 wt %) with 0.01, 0.05, and 0.1 wt % CNT Water Liquid-Crystalline Solution[a]

	E (MPa)		σ_s (MPa)		ε (%)		
CNT (wt %)	Par.	Per.	Par.	Per.	Par.	Per.	thickness (μm)
0	98 ± 21	72 ± 14	11.6 ± 2.8	3.1 ± 0.4	57 ± 10	73 ± 20	19 ± 1
0.01	218 ± 36	168 ± 15	21.2 ± 3.0	8.2 ± 1.0	84 ± 15	25 ± 9	18 ± 2
0.05	191 ± 26	132 ± 35	18.3 ± 3.0	6.8 ± 0.9	60 ± 10	30 ± 10	14 ± 2
0.10	175 ± 27	120 ± 35	18.5 ± 3.0	6.2 ± 2.0	60 ± 10	33 ± 15	16 ± 3
*HPC/SDS	71 ± 10	43 ± 14	7.0 ± 1.2	2.1 ± 0.7	77 ± 0.4	90 ± 1	18 ± 2

[a]Par and Per indicates the direction at which the mechanical stress-strain measurements where performed, parallel and transverse to the shear casting direction, respectively. The shear direction is represented in each film with an arrow. Thickness of films was measured. *HPC/SDS reference sample with no CNT content is presented for comparison purposes.

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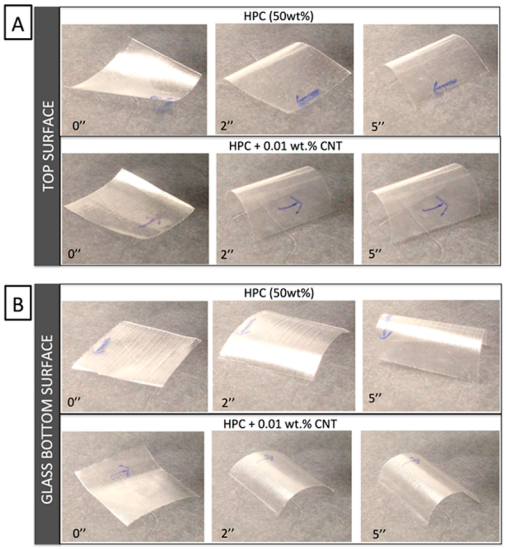

C

CNT [wt.%]	σ [MPa]	Responsiveness [Pa/s]	Relaxation [Pa/s]
0	0.13±0.01	47823±5079	2201±313
0.01	0.20±0.03	115466±4290	5331±921
0.05	0.21±0.01	72934±15491	4918±496
0.1	0.27±0.01	66616±16664	7310±953

D

CNT [wt.%]	σ [MPa]	Responsiveness [Pa/s]	Relaxation [Pa/s]
0	0.13±0.01	46541±3698	2366±112
0.01	0.12±0.03	59409±7202	2242±335
0.05	0.19±0.01	51956±11117	3956±1025
0.1	0.18±0.01	68686±6670	5849±972

Figure 2. Bending of free-standing films of HPC/water (50 wt %) and HPC-0.01 wt % CNT performed by applying water vapor to both (A) the top surface and (B) the bottom surface of the films. The arrows indicate shear direction. Data tables corresponding to the evolution of stress with time, in response to the applied vapor stimuli and subsequent relaxation performed for the (C) top surfaces and (D) bottom surface.

plasticizer of the polymer. Our main goal is the optimization of a soft-motor in terms of responsiveness, which requires at least the mechanical properties of the HPC matrix or even better to improve them for the mentioned applications; therefore, the use of HPC/SDS is not suitable for our purpose.

When free-standing LC-HPC and LC-HPC/CNT composite films are exposed to water vapor, they bend as depicted in Figure 2. As was verified, the bend direction is directly dependent on the triggered surface. When water vapor penetrates the top surface (facing up during solvent evaporation) of the film, the sample bends around the shear direction. These results were already explored and explained for a similar systems (LC-HPC 60 wt %) and are related to the expansion of the surface in the direction perpendicular to the shear. This expansion is due to a reduction in the order parameter provoked by the presence of water molecules between the polymeric chains, that increases the thickness of the rodlike fragments.[17]

Focusing on the top surface response of the films and comparing the LC-HPC/CNT (0.01 wt %) film with the LC-HPC one (Figure 2A) it is found that the film containing 0.01 wt % CNT fully bends after just 2 s of exposure to vapor (Video S2), whereas the LC-HPC films requires 5 s (Video S1) to have the same effect. To quantify this responsiveness of the composite films top surface and subsequent relaxation, we follow along time, the force (N) generated by the film and transformed into stress (divided by the cross-section of the area) when it is activated with vapor (application time 3 s, see Scheme S1), and its subsequent relaxation when the applied stimuli is removed. The responsiveness (Pa s^{-1}) of the LC-HPC and composite films is obtained from the first slope of the stress tension vs time plot described in Figure S5A. As shown in Figure 2C (and Figure S6), the sample containing 0.01 wt % performs a much faster response when compared to the reference (0% CNT) and also to the composite films with higher CNT content. This result highlights LC-HPC/CNT (0.01 wt %) sample as the most interesting for the soft motor optimization. Also very interesting (and included in the system's responsiveness) is the capacity of the sample to relax after the stimulation. This will be another determinant part of the mechanism behind the motion. Here again, the sample containing 0.01 wt % of CNT presents a better performance when compared to LC-HPC film, although the sample with 0.1 wt % CNT gives better relaxation results. The reason for a faster response is found in a higher orientational order of the liquid crystalline polymer induced by the presence of a low amount of CNT. In addition, CNT could also hamper the interchain hydrogen bonds formation, which may leave the hydroxyl groups as available sorption sites for the caption of water molecules, responsible of the order/disorder transition mechanism behind the motion.[24]

The bottom surface (facing down and in contact with the glass substrate, during solvent evaporation) is less responsive when compared with the top surface. In fact, it seems to give rise to a less pronounce bending when CNT are added (Figure 2B). The responsiveness and subsequent relaxation of the composite films show similar results (Figure S5B), indicating a similar behavior, with no noticeable improvement with respect to LC-HPC except for the sample containing 0.1 wt % of CNT (Figure 2D). The different response between both film surfaces is directly related to the presence of the periodic bands on the top surfaces developed during solvent evaporation, as previously reported and well-known.[17,23]

We have demonstrated that it is possible to improve the response to humidity of a LCN by the incorporation of a small amount of highly anisotropic nanoparticles into LC-HPC matrix. This nanoparticles do not affect the cholesteric structure of the LC-HPC, which is paramount for its further response to external stimuli. This simple and effective approach allows CNT to be well-dispersed and oriented in the direction of the shear, giving rise to faster order/disorder transition when exposed to humidity, in addition to improving the thin film's mechanical properties.

EXPERIMENTAL SECTION

Materials. Hydroxypropylcellulose with a molecular weight, M_w = 100.000 Da and M_S = 3 was purchased from Sigma-Aldrich and used as received. Commercial Multi-Wall Carbon Nanotubes were purchased from Sigma-Aldrich. For this study 0.01, 0.05, and 0.1 wt % CNT were mixed with water and Sodium Dodecyl Sulfate (SDS) surfactant in a

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1:10 ratio (CNT to SDS ratio); CNT/SDS/water solutions were sonicated during 1 min and let rest for 1 min, this process was repeated 4 times (in total 4 min of sonication). Then, solutions were left in an ultrasound bath for 1h. HPC powder was dissolved in the solution containing CNT at 50 wt %. The prepared samples were sealed, kept in the dark to avoid light damage, and stirred every 2 days. A complete dissolution of HPC/CNT was obtained in 4 weeks.

Methods. Films were prepared by shear-casting method. LC-HPC composite solutions were shear-casted by using a calibrated Gardner knife from Braive Instruments at a constant velocity of 1.25 mm s^{-1}. The films were allowed to dry at room temperature for 2 weeks before any measurement was performed. The thickness of the dried films was estimated by averaging 10 measurements in different positions of each sample, with a Mitutoyo digital micrometer.

The textures of the prepared LC-HPC composite solutions and characteristic periodic bands of LC-HPC composite films were observed using an Olympus BX51 microscope equipped with cross polarizers and an Olympus DP73 camera.

The morphology of LC-HPC composite films were examined by scanning electron microscopy (SEM, Zeiss AURIGA) after coating the dried sample with a thin layer of gold.

The mechanical properties of the samples were registered with a tensile testing machine from Rheometric Scientific (Minimat Firmware Version 3.1). Small rectangular pieces of LC-HPC composite films (2.5 cm × 1.0 cm) were cut in two orthogonal directions with the longest dimension of the sample parallel or perpendicular to the direction of the shear. In addition, the film was stretched uniaxially at a rate of 5 mm min^{-1} along the longest sample dimension. The values of the mechanical properties of a given sample were taken to be the average of the results of ten successful measurements. For the quantification of the LC-HPC composite films responsiveness and relaxation we used a homemade apparatus with the capability of imposing certain strain and record the involved force with the precision of 1 cN. The solid LC-HPC film is clamped and subjected to an initial force value of 5 cN. Moisture is applied to the film for 3 s and the temporal evolution of the force is recorded during 60 s, period of time enough to observe the material response and further relaxation. The presented stress tension values were obtained by dividing the force by the cross-section area of each sample.

Bending experiments (Figure 2, Videos S1 and S2) were carried out for free-standing films with dimensions of 1.5 cm × 1.5 cm at which moisture is applied in both surfaces to induce bending of the film.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05881.

Evolution of the viscosity with shear rate for the LC-HPC/CNC solutions; POM pictures of LC-HPC/CNT precursor solutions and films; additional SEM images of the cross-section of LC-HPC-0.01 wt % sample; evolution of stress with time of the LC-HPC and LC-HPC/CNC films when top surface and bottom surface in contact with the glass substrate are subjected to moisture; maximum stress, responsiveness and relaxation of LC-HPC/CNC films as a function of carbon nanotubes content; experimental set up used to quantify the responsiveness of the composite films top surface and subsequent relaxation; (PDF)

Video S1 recording the responsiveness of LC-HPC films (AVI)

Video S2 recording the responsiveness of LC-HPC/CNC (0.01 wt %) films (AVI)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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