Understanding the influence of highly anisotropic nanoparticles such as carbon nanotubes on the flow behavior of liquid crystalline Hydroxypropylcellulose: A Rheo-NMR study.

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ABSTRACT. Hydroxypropylcellulose (HPC) is an important cellulose derivative that has been widely studied due to its water-solubility, biocompatibility and biodegradability, but even more significant due to its ability to form liquid crystalline phases. HPC is able to form, under certain conditions, chiral nematic (cholesteric) structures in water solutions. Previous work confirmed that films prepared from liquid crystalline HPC/water solutions (LC-HPC) gave rise to anisotropic networks with similar mechanical and optical characteristics of Liquid Crystalline Elastomers (LCE) capable to respond to humidity. It was also demonstrated that the incorporation of carbon nanotubes (CNTs) significantly

improved the actuator responsiveness [1, 2]. Considering that the movement of the actuator arises from an induced order-disorder transition, it becomes crucial to understand the effect of the CNTs in LC-HPC under shear stress (and its consequential relaxation). Therefore, in this work we investigate how highly anisotropic nanoparticles, such as carbon nanotubes, affect the flow behaviour of liquid crystalline hydroxypropylcellulose solutions. Therefore, in the present work we aim to understand how the incorporation of a small amount of highly anisotropic nanoparticles, CNTs, affects the structure-properties relationship of the LC-HPC-CNTs actuator at a molecular level. For that purpose, we performed a detailed Rheo-NMR analysis.

1. INTRODUCTION.

Currently, the development of so called “green materials” has gained significance due to the consequences of global warming and the energy crisis [3]. Such demand requires of a great effort for the replacement of fossil fuels (which still accounts for 74% of global energy consumption [4] with materials provided by renewable sources [5]. In this respect, cellulose, which is the major constituents of plants is the most abundant renewable organic material in the world (5×10^{11} tons/year). This polysaccharide composed of anhydroglucopyranose units, presents a backbone chain decorated with free hydroxyl groups that are susceptible to undergo a chemical substitution, enabling the production of several functional derivatives [6].

Hydroxypropylcellulose (HPC) is an important cellulose derivative in which some of the hydroxyl groups have been hydroxypropylated. This cellulose derivative has been widely studied due to its water-solubility, biocompatibility and biodegradability, but even more significant due to its ability to form liquid crystalline phases either within a temperature range (thermotropic) or within a concentration range (42-70 wt%) in an aqueous solution

(lyotropic).[7, 8] When in a water solution, within the specified concentration range, HPC forms lyotropic chiral nematic (cholesteric) structures.

Knowing that cellulose is the major constituents of plants, and inspired by the ability of plants to perform movements (due to their sensitiveness to environmentally external stimuli), a new humidity responsive cellulosic soft motor (actuator) was developed by our group [1]. This *soft-motor* was capable of transforming the humidity into mechanical motion. This achievement was made possible by using thin films prepared from liquid crystalline HPC/H₂O solutions (LC-HPC). Such anisotropic films preserved in the dry solid state (after solvent evaporation), the cholesteric order of the LC-HPC/H₂O solutions giving rise to a Liquid Crystal Network (LCN) similar to a liquid crystalline elastomeric network. As explained in a previous study, the working mechanism behind the soft motor is based in an order-disorder transition induced by the water molecules that permeate the film [1]. The optimization of the soft motor in terms of responsiveness came from the incorporation of highly anisotropic nanoparticles as multiwall carbon nanotubes (CNTs) [2]. The incremented LC-HPC system anisotropy, due to the presence of CNTs, gave rise to a faster order-disorder transition, and therefore, an enhanced response of the soft-motor toward humidity gradients [1]. Thus, it was confirmed the positive influence of CNT in the soft-motor performance from a macroscopic point of view.

Nevertheless, the performance of the actuator is not exclusively dependent on its composition, indeed the method by which the LC-HPC solutions are processed in order to obtain the thin film (actuator) is also determinant to its final properties. To produce the thin films, a calibrated Gardner knife is used (linear shear-casting). By moving it at constant speed, a film is deposited onto a substrate and after solvent evaporation, originates the thin solid film. When shear-casting the LC-HPC solutions, the applied shear rate induces a structural transformation from chiral nematic polydomains to a

nematic monodomain. This phenomenon had been theoretically predicted and was recently disclosed experimentally [9-11]. For the first time, for the LC-HPC system, the undergoing elastic change of LC-HPC system during the uncoiling of the helix was experimentally evidenced [12]. The shear induced structure transformation of pure LC-HPC was also studied at a molecular level by Rheo-NMR, combining rheology and Deuterium NMR [13-16], where it was established a critical shear rate at which the cholesteric-to-nematic transition occurred and it was also analysed the ability of the system to recover its initial cholesteric structure [17-21].

When highly compatible Cellulose nanocrystals (CNCs) were incorporated in LC-HPC solutions it was found that CNCs restrained the movements of the polymeric chains, which strongly influenced their mobility. It was determined that strain was necessary to induce the helix uncoiling when shearing, but the recovery of the cholesteric structure was favoured after cessation of shear [14, 22]. In definitive, the obtained results helped to establish structure-properties relationships that lead to the improvement of the processing strategies for the preparation of materials with controlled alignment and topography. Considering that the movement of the actuator derives from an induced order-disorder transition, it became crucial to understand the effect of CNTs in LC-HPC under shear (and its consequential relaxation). Therefore, the present work is an attempt to better understand how the incorporation of small amounts of highly anisotropic nanoparticles, CNTs, in LC-HPC solutions can affect the structure-properties relationships of the LC-HPC-CNTs actuators at a molecular level.

2. EXPERIMENTAL PART

Materials. Hydroxypropylcellulose (HPC) was purchased from *Sigma-Aldrich* ($M_w = 100.000$ Da and $MS = 3$) and used as received. Commercial Multi-Walled Carbon

Nanotubes were purchased from *Sigma-Aldrich*. For the following studies HPC was dissolved in a water dispersion containing CNT. (i) Preparation of CNT/D₂O dispersions: 0.01, 0.05, and 0.10 wt% CNT were mixed with deuterated water D₂O and Sodium Dodecyl Sulfate (SDS) surfactant in a 1:10 ratio (CNT:SDS); CNT/SDS/H₂O dispersions were then sonicated during 1 min and let to rest for 1 min, this process was repeated 4 times (in total 4 min of sonication). In addition to that, CNT/D₂O/SDS dispersions were left in an ultrasound bath for 1 h. (ii) Preparation of LC-HPC/CNT solutions: HPC powder was dissolved in the CNT/D₂O dispersion at 50 wt%. The prepared samples were sealed, kept in the dark to avoid light damage, and stirred every 2 days. The total dissolution was achieved after 4 weeks and confirmed by the observation of the typical polygonal texture characteristic of liquid crystalline polymers (LCP).

Methods. A Polarized light Optical Microscope (POM) was used to observe the textures of HPC and HPC/CNT solutions for what an *Olympus BX51* microscope, equipped with cross polarizers and an *Olympus DP73* camera, was used. The viscoelastic properties of the LC-HPC and the LC-HPC/CNT solutions were evaluated by means of dynamic oscillatory measurements using a stress-controlled rotational rheometer (*Bohlin Gemini HR Nano*). Frequency sweep scans were performed for all samples at room temperature using a cone/plate geometry (2 ° and 20 mm of diameter), at a constant strain value within the linear viscoelastic range. For the determination of the linear viscoelastic range (LVR), strain sweep tests at a non-destructive constant frequency (1 Hz) were performed at room temperature using the same geometry. For the cessation after shear experiments, time sweep test were performed. The protocol of the measurement was as follows: We pre-shear the sample during 1 minute, stop the shear and follow the evolution of the elastic

modulus with time. This was performed for all the samples and for the shear rates of 0.1, 1.0 and 10.0 s^{-1} .

The D-NMR experiments were performed on a 7.049 T (300 MHz) *Bruker Avance III* NMR spectrometer equipped with a 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, being the symmetry axis of the coaxial cylinders is parallel to the magnetic field. The mechanical motion in the device originates from a pulse-programmer-controlled stepper motor placed on the top of the magnet.

To ensure the reproducibility of the measurements an initial protocol was applied to all the samples; solutions were subjected to a pre-shear of 3.0 s^{-1} for 1 min and left at rest for 1 hour in order to get a stabilized isotropic initial NMR spectrum (single peak), so that an equilibrium state, where a polydomain liquid crystal solution composed of randomly oriented cholesteric domains is formed [20, 23]. After this initial protocol, deuterium spectra were collected while shearing the sample at the certain constant shear rate during a defined period of time (up to 7000 seconds). Further, the subsequent relaxation process was monitored and deuterium spectra regarding the relaxation process (after the previously applied shear rate) were collected until the complete relaxation of the sample occurs (complete evolution towards a single peak). We executed this process for the same sample using 7 different low shear rates: 0.1, 0.3, 0.6, 0.8, 1.0, 5.0 and 10.0 s^{-1} .

The transverse relaxation time T_2 , for each studied solution, was determined using the *Carr-Purcell-Meiboom-Gill* (CPMG) sequence. The following parameters of the CPMG sequence were used: deuterium frequency resonance: 46.072 MHz, recycle delay: 5 s, time to allow pulse ringdown: 50 μs , duration of FID: 300 μs , and pulse widths at $\pi/2$ and π of 125 and 250 μs respectively, both using a RF power of 50 W. The total number of

scans for each measurement was 4, each scan having a total of 80 acquired echoes. The acquisition of the T_2 data was performed using specific delays between measurements during the shear and subsequent relaxation processes. All the NMR measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Since the objective of the incorporation of CNTs, in this study, is not to evidence the mechanical reinforcement the material, but to reveal the increase of the anisotropy of the system while preserving the cholesteric structure of HPC/D₂O solutions, at rest, the amount of CNTs incorporated in the LC-HPC/D₂O solution is low. Figure S1 depicts the obtained Polarized Optical Microscopy (POM) images of a pristine LC-HPC solution and LC-HPC solutions containing 0.01, 0.05 and 0.10wt.% of CNTs. As observed, all the samples present the typical polygonal texture, characteristic of a cholesteric structure [24] (Figure S1 of the supplementary information), which confirms that the incorporation of CNTs does not affect the cholesteric structure, as it was envisioned [2]. We have also analysed the effect of adding 0.01, 0.05 and 0.10 wt.% of CNT in LC-HPC solution by oscillatory rheology (Figure S1). As one can perceive from the figure that there is no significant change on the viscoelastic properties with the incorporation of CNTs. Indeed, a slight decrease of both elastic and viscous modulus is observed when the amount of CNTs in the solution increases. This could be attributed to a plasticizing effect that is induced by the presence of the CNTs.

As stated in the introduction, in a previous study regarding the development of LC-HPC based actuator, it was demonstrated that the incorporation of CNT improved significantly the performance of the humidity driven sensor, by increasing the degree of order in the system[2]. However, it is crucial to better understand the phenomenology and

molecular mechanisms behind such improvement. For that reason, in this work an effort was made in order to understand the influence of the CNTs in the flow behaviour of LC-HPC/D₂O, by performing a detailed Rheo-NMR analysis of this system.

For the study of LC-HPC/CNT system under shear flow we selected the following shear rate range: 0.1 to 10.0 s⁻¹. This range corresponds to the regime I and II of the typical “three-regime curve” characteristic of liquid crystalline polymers (LCP) viscosity/shear rate curves [12, 25-28]. As determined in previous work by oscillatory rheology and confirmed by Rheo-NMR, the transition from cholesteric polydomain to a nematic monodomain was found to occur around 15 s⁻¹ for LC-HPC (50%wt.). Since our purpose is to understand how the incorporation of CNT affects the cholesteric structure of LC-HPC under shear flow, a Rheo-NMR study was performed at shear rate regimes (I and II) where the cholesteric polydomains of LC-HPC system reorganized, flow over each other and/or start to uncoil but all prior to the cholesteric-to-nematic transition occurs.

Figure 1 shows representative plots corresponding to the evolution of D₂O spectra collection with time during shear, at a constant shear rate of 0.8 s⁻¹, and during relaxation process for both LC-HPC and LC-HPC/CNT samples. The relevant information comes from the analysis of the behaviour associated to the evolution of the single peak signal (isotropic state arising from a polydomain liquid crystal solution composed of randomly oriented cholesteric domains) toward its quadrupolar splitting. This is related to the degree of order/disorder that D₂O molecules may experience and thus to the polymer chains behaviour under shear; D₂O molecules act as a probe of the polymer movements and molecular configurations. After the initial protocol, already described in the experimental part, samples present a single peak spectrum. This central peak corresponds to a disordered D₂O environment related to the cholesteric structure of the LC-HPC and LC-HPC/CNT [16]. As time grows, and thus the applied strain units increase, the

quadrupolar peak splitting occurs as a consequence to some degree of order experienced by the D₂O molecules. After cessation of the applied shear, during the relaxation process, the observed peak splitting (ordered D₂O environment) evolves toward the initial single peak (disordered D₂O environment) in the studied timeframe. This indicates the recovery of the initial cholesteric structure at that timeframe.

From Figure 1 it is confirmed the influence of CNTs in the LC-HPC flow behaviour both during shear (at a constant shear rate of 0.8 s^{-1}) and during the subsequent relaxation process. When observing the spectra evolution during the shearing of the samples at a constant shear rate of 0.8 s^{-1} it is perceived that the quadrupolar peak splitting occurs at shorter times for the samples containing CNTs. This first result is indicative of the contribution of the CNTs to the higher degree of order achieved during shear, when compared with the sample without CNTs. Similarly, and for the same reason, CNTs contribute to reduce the time that LC-HPC system needs to relax after cessation of shear.

Figure 1 : NMR spectra evolution with time of LC-HPC and LC-HPC-CNT samples in D₂O during shear and further relaxation process after cessation of applied shear rate of 0.8 s^{-1} .

To better observe and interpret the flow behaviour of LC-HPC and LC-HPC/CNT systems, in Figure 2, the evolution of quadrupolar peak splitting with time during shear

and subsequent relaxation process is given, for each studied sample and shear rates. As predicted and by analogy with previous studies, the shear was found to induce a degree of order (inferred by the quadrupolar peak splitting) in the system, which increases as the applied shear rate increases. Besides, after cessation of the applied shear, during the relaxation process, all studied samples evolve to the initial single peak representative of the recovery of the cholesteric structure as stated above. However, differences are observed associated to the presence of CNTs in the LC-HPC matrix.

Figure 2: Peak splitting evolution with time extracted from deuterium NMR spectra during shear and relaxation process after applied shear rates of 0.1, 0.3, 0.6, 0.8, 1.0, 5.0 and 10.0 s⁻¹ for the following samples: (A) LC-HPC/D₂O, (B) LC-HPC - 0.01 % CNT, (C) LC-HPC- 0.05 % CNT and (D) LC-HPC - 0.10 % CNT.

In order to more accurately analyse the information obtained from the Rheo-NMR study collected in Figure 2, the analysis of the results of this study of the LC-HPC and LC-HPC/CNTs systems was divided into two sections: (i) flow behaviour under shear and (ii) after cessation of shear, during the relaxation process.

(i) Effect of the CNTs content in the shear dependence behaviour of LC-HPC studied by Rheo-NMR. In Figure 3, a representation the maximum splitting achieved at each shear rate (during shear) is presented and plotted against the imposed shear rate. Interestingly, these type of plot allows the better observation of the impact of adding small amounts of CNTs in the LC-HPC flow behaviour. When comparing the maximum splitting reached at each one of the applied shear rates, it is very clear how the attained degree of order is higher as the amount of CNTs increases. This dependence is attributed to the high anisotropy of CNTs that contribute to enhance the polymer flow behaviour. When shearing the LC-HPC/CNTs system, at a constant shear rate, the CNTs align in the direction of shear and thus contribute to the increase of the degree of order, as shown in Figure 3. This increment is clear when 0,01 and 0.05 wt% of CNTs are incorporated in the system. However the addition of 0.10 wt% presents no significative differences with respect LC-HPC sample containing 0.05wt% CNT.

Figure 3: Evolution of the maximum peak splitting with the applied shear rate for the LC-HPC/D₂O sample and LC-HPC/D₂O sample containing 0.01, 0.05 and 0.10 % CNT.

To have a more clear picture on the influence of the CNTs in the LC-HPC system during shear, the spin-spin transverse relaxation times, T_2 , was determined using the *Carr-Purcell-Meiboom-Gill* (CPMG) sequence. Similarly and using the same procedure as described in previous work [15], T_2 values were calculated by fitting each CPMG measurement to the following exponential decay function:

$$M_x(t) = M_x(0)e^{\left(\frac{-t}{T_2}\right)} \quad (\text{eq. 1})$$

where $M_x(t)$ is the remaining magnetization at a given time t after application of the Radio Frequency (RF) pulse, $M_x(0)$ is the magnetization amplitude immediately after application of the RF pulse and T_2 is the spin-spin relaxation time.

In Figure 4A is a representation of the obtained T_2 values as a function of time for the LC-HPC and the LC-HPC/CNTs samples, measured at three different constant shear rates: 0.1, 1.0, and 10.0 s⁻¹. By the interpretation of these plots, were evaluated both the

effect of the applied shear and the CNTs content, in the spin-spin relaxation time T_2 , and they represented in Figure 4B and Figure 4D, respectively. When analysing the evolution of T_2 as a function of the applied shear rate (Figure 4B), T_2 presents an expectable augment with the increase of the applied shear in all the studied samples. At low shear rates the value of T_2 is low, thus reflecting a more “solid” like system, however, as the shear rate increases T_2 also increases being an indication of a more “liquid” like system. As determined in previous work, increasing the shear rates contributed to orientation of the LC-HPC polymer chains increasing their mobility [15]. Interestingly, T_2 evolution with shear describe a change of slope (or a Jump in the trend) similar to a transition. This occurs close to shear rates of $0.6\text{-}1.0\text{ s}^{-1}$ and is in accordance to the shear induced helix uncoiling that was recently detected experimentally [12]. The shear induced helix uncoil (and further alignment of polymer chains) favours the flowing of the system, therefore this fact can be at the genesis of such a clear T_2 transition (jump) from a more “solid” like to a more “liquid” like behaviour. Regarding the effect of the CNTs content, from Figure 4C, the incorporation of CNTs results in a decrease of T_2 . CNTs are hampering the mobility of LC-HPC chains and thus giving rise to a more “solid” like system. But, above $0.05\text{ wt\%}$ of CNTs, the evolution of T_2 tend to achieve a constant value similar to what was observed regarding the reached maximum splitting (Figure 3). Besides, this effect is more significant in the LC-HPC flow behaviour under higher shear rates, as is also shown in Figure 4C. If we observe, for instance, the evolution of T_2 as a function of CNT for LC-HPC/CNT samples sheared at 0.1 s^{-1} , the variation is almost null and the value almost constant. However, if we observe the evolution of T_2 as a function of CNT for LC-HPC/CNT samples sheared at 1.0 s^{-1} and 10.0 s^{-1} , the variation of the plot describes a curve with an exponential decay.

Figure 4.: (A) Representative graphs corresponding to the evolution with time of the transversal relaxation times, T_2 , for LC-HPC/D₂O and LC-HPC/D₂O-CNT samples during application of constant shear rate of 0.1, 1.0 and 10.0 s^{-1} , respectively. (B) Evolution of the transversal relaxation time T_2 (extracted from (A) taken at 2000 seconds of the measurement) as a function of applied shear rate for LC-HPC/D₂O and LC-HPC/D₂O-CNT samples. (C) Representative plots regarding the evolution of T_2 with CNT content measured during shearing at 0.1, 1.0 and 10.0 s^{-1} .

(ii) Relaxation process influenced by the presence of CNT nanoparticles: Rheo-NMR, transverse relaxation times, T_2 , and viscoelastic properties. In order to analyse the relaxation process and how the CNT presence influence the LC-HPC behaviour after cessation of shear, in Figure 5A-C experimental data based on graphs shown in Figure 2 are presented. In Figure 5A is given a plot of the time needed for the system to relax and recover from the reached degree of order (maximum quadrupolar peak splitting) to the initial disorder environment, and thus the cholesteric structure full recovery (single peak

in the deuterium spectra). As a general behaviour, all samples present similar relaxation trends with respect to the previously applied shear rate. At low shear rates, below 0.6 s^{-1} , the time required for the system to relax increases with the previously applied shear, but at higher shear rates (above 0.6 s^{-1}) the trend changes and as the previously applied shear rate increases, less time is required for the system to relax. The results evidence a transition for a shear rate close to 0.6 s^{-1} in the flow behaviour of LC-HPC system, which is coincident with the transition or jump observed during shear when analysing the T_2 shear dependence, during shear.

As for the effect of CNTs in the LC-HPC relaxation behaviour, we observe that the sample containing the lowest amount of CNTs (0.01 wt%) requires less time to recover the initial cholesteric structure. This evidence is more significant at high shear rates (above 0.8 s^{-1}). LC-HPC solution, which contains 0.05wt% CNTs presents similar recovery times as pure LC-HPC. In contrast, LC-HPC sample with of 0.10 wt% of CNTs (the highest amount) requires more time than the pristine LC-HPC sample to recover to the initial state. The incorporation of higher amounts of CNTs is hampering the mobility of LC-HPC polymer chain in the relaxation process. To enlighten this influence, the spin-spin transverse relaxation times T_2 was determined during the relaxation process, for all the studied samples and shear rates. In Figure 5B a plot of the evolution of T_2 (measured at the time where the system relaxes from an ordered to a disordered state, that is, from having a NMR peak splitting to a single peak in the deuterium spectra), with respect to the previously applied shear rate, is presented. As a general trend, all samples present a decrease of T_2 as the shear rate increases up to a minimum value of T_2 , found close to the shear rate of 0.6 s^{-1} . This implies that the relaxation process generates a more “solid” like system as the previously applied shear rate increases. Above this critical shear rate, the value of T_2 increases, which indicates that the relaxation process generates a less “solid”

like system when recovering from previously applied higher shear rates. Interestingly, this critical shear rate is coincident with the observed in Figure 4A and the one determined in previous works, which is always related to the start of the LC-HPC helix uncoiling [12]. To better evidence the effect of the CNTs the obtained T_2 values as a function of CNTs, for three different shear rates, were plotted. Similarly, to what was observed before, the deviations in the T_2 values trend with the amount of CNTs are more significant at higher shear rates. By analysing the results obtained for the samples sheared at 1.0s^{-1} , it was observed that the incorporation of 0.01 wt% CNTs provokes a decrease in T_2 , which is an indication of a more “solid” like system behaviour. The evolution (decrease) of T_2 values with the CNTs content tend to a constant behaviour for samples containing 0.05 % and 0.10 wt% of CNT.

Figure 5: (A) Evolution of the time needed for the LC-HPC/D₂O and LC-HPC/D₂O-CNT samples to relax (from 2 peaks to a single peak) as a function of the previously applied shear rate. (B) Evolution of the

transversal relaxation time T_2 determined at the time where the recovery of the sample occurs in the relaxation process as a function of previously applies shear rate (after cessation of shear) and (C) as a function of CNT wt% content.

It was also performed the analysis of the relaxation behaviour of LC-HPC samples at a macroscopic level by means of a rotational rheometer. As so, in Figure 6A-C is presented a representation of the evolution of the elastic modulus G' with time, recorded after the application of a pre-shear of 0.1, 1.0 and 10.0 s^{-1} in order to evaluate the influence of the applied shear on the recovery of the cholesteric structure [19]. As observed, after the application of a low pre-shear rate (0.1 s^{-1}) the elastic modulus recovery is not very significant; LC-HPC/CNTs samples depict an almost constant value compared with the small increase observed for initial LC-HPC solution. The applied pre-shear is not enough for the helix to uncoil and being so, the cholesteric structure is not affected. As the applied pre-shear increases, the effect of CNTs in the LC-HPC relaxation process becomes more significant as it is the case for the samples pre-sheared at 10.0 s^{-1} . After a pre-shear of 10.0 s^{-1} the elastic modulus of LC-HPC and LC-HPC/CNT recovers almost two orders of magnitude. This recovery takes close to 300 seconds for the LC-HPC sample to occur which is in contrast with LC-HPC/CNTs samples that G' recovery starts at a shorter time (approximately 100 s). These results are in agreement with the conclusions drawn from Rheo-NMR experiments; the incorporation of CNTs in the LC-HPC matrix contributes in the recovery of the cholesteric structure being more evident when the relaxation process is preceded by the application of high shear rates.

Figure 6: Evolution of the normalized elastic modulus G' with time after cessation of applied shear rates of: 0.1, 1.0 and 10.0 s^{-1} for LC-HPC and LC-HPC/CNT samples containing 0.01 wt%, 0.05 wt%, 0.10 wt%.

4. CONCLUSION

In this work, by taking advantage of Rheo-NMR and Rheology techniques it was demonstrated how the incorporation of small quantities of highly anisotropic nanoparticles such as carbon nanotubes can modify the flow behaviour of the LC-HPC system under shear, and consequently, the relaxation process. The experiments were performed in the shear rate range between 0.1 and 10.0 s^{-1} , which corresponded to the Regime I and II of the “three-regime” curve characteristic for LC-HCP, in order to ensure that the analysis was performed before the cholesteric-to-nematic transition occurs. This work allows the better understanding of adding CNTs to a cholesteric liquid crystalline cellulosic solution, while shearing and during relaxation processes.

Regarding the effect of the amount of CNTs in the LC-HPC flow behaviour under shear, when analysing the obtained deuterium spectra collection, it was demonstrated that the maximum splitting reached at each one of the applied shear rates increased as the amount of CNTs increases. This could be due to the high anisotropy of CNTs that contribute in the polymer flow. We consider that when shearing the LC-HPC/CNTs system at constant shear rate, the CNTs align in the direction of shear and thus contribute to increase the degree of order of the system. This increment in the degree of order was more evident as the applied shear rate increases, since there is more energy available to promote that alignment. The analysis of the T_2 measurements revealed that the incorporation of CNTs derives in a decrease of the T_2 values and indicating the formation of a more “solid” like system. This implies that CNTs are hampering the mobility of LC-HPC chains. Moreover, the analysis of the T_2 values evolution as a function of applied shear rate evidenced a transition for the shear rate close to $0.6\text{-}1.0\text{ s}^{-1}$, at which the variation tendency of T_2 changed. This transition was associated to an incipient cholesteric uncoiling that was experimentally determined in previous work [].

Concerning the relaxation process and how the CNTs content might influence the LC-HPC behaviour after cessation of shear, it was concluded that the sample with lowest CNTs content influenced the most. In fact, the incorporation of 0.01 wt% of CNTs favours a faster recovery from the previous sample deformation. This is in agreement with the results obtained regarding the influence of the CNTs content in the improvement of the actuator responsiveness studied in previous work. In that study, the lowest amount of CNT provided the better results. Therefore, the incorporation of 0.01 wt% of CNTs contributes to the flow behaviour and thus the processing of the LC-HPC solution, but higher content of CNTs might severely hamper the mobility of LC-HPC or even destroy the cholesteric structure which is undesirable for the actuator purpose.

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