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Physical properties of cholesteric liquid crystals – carbon nanotube dispersions

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Abstract. The mesomorphic and visco-elastic properties of cholesteric liquid crystal – multi-wall carbon nanotube dispersions were investigated with respect to temperature and nanotube concentration. The important rheology characteristics, such as dynamic viscosity, elastic modulus and loss modulus were studied. For the first time a 3D-model of cholesteric liquid crystal at the temperature of cholesteric phase existence was obtained by molecular dynamics simulation method. A weak effect of nanotube on the molecular orientation of the liquid crystal molecules in the N* phase was found.

1. Introduction

Anisotropic structures – liquid crystals (LC) have a number of unique properties that made it possible to use them as easily manageable materials, e.g. for electronics. Helical liquid crystal phases are the most promising but the least studied in this aspect. The perspective of their application is caused by the presence of spontaneous ordering of electric dipoles in the ferroelectric liquid crystal phase, which gives an opportunity to create systems for optical information processing [1]. One of the ways to optimize properties of mesogenic and other materials is creation of compositions based on them.

Setting a task of studying the compositions of helical LC phases with multi-walled carbon nanotubes (MWCNTs), we considered MWCNTs as sensitizers having unique physical characteristics in terms of electrical conductivity, developed surface area, stability under physical and chemical stresses. We suggested that the creation of MWCNT dispersions in these materials optimizes some of their parameters and leads to new spheres of application.

Previously, we investigated phase transition temperatures, electro-optic and dielectric properties of ferroelectric liquid crystal – multi-wall carbon nanotubes dispersions [2]. In this paper we summarize the results of the study of MWCNTs impact on the molecular orientation of the liquid crystal molecules, mesomorphic and visco-elastic properties of cholesteric mesophases, specifically in N*-phase, as the function of nanotube concentration and temperature.
2. Materials and methods

The representatives of cholesterol esters – cholesteryl oleate I (Cr – 5 °C N* 35.2 °C Iso); cholesteryl tridecylate II (Cr 63.3 °C SmA 78.8 N* 84.2 °C Iso); and cholesteryl myristate III (Cr 71.4 °C SmA 79.3 °C N* 84.0 °C Iso) were chosen as liquid crystal host materials:

I: \( R = \text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{COO}^- \)

II: \( R = \text{CH}_3(\text{CH}_2)_{11}\text{COO}^- \)

III: \( R = \text{CH}_3(\text{CH}_2)_{12}\text{COO}^- \)

The multi-wall carbon nanotubes (MWCNTs, Taunit-M) with an outer diameter of 8-15 nm, an inner diameter of 4-8 nm and a specific surface area of 300 m²/g were provided by Nanotechcenter, Tambov, and were used as active dopants. They were produced by chemical vapour deposition using a Ni/Mg catalyst [3]. To identify the carbon nanotube, Raman spectroscopy before sonification (HoribaJobin Yvon LabRam HR800 spectrometer equipped with a He–Ne laser (λ=633 nm) operating at 20mW) and atomic force microscopy (Veeco Nanoscope Dimension 3100 AFM operating in the tapping mode with Si cantilever) were employed. The most probable length of the nanotubes was approximately 900 nm [4].

The ChLC–MWCNTs dispersions were prepared using an ultra sound sonication method [4]. The phase transition temperatures of all ChLC–MWCNTs dispersions were determined using a Leitz LaborLux 12 Pol polarizing microscope combined with a Mettler FP–82 hot stage.

The viscoelastic parameters of the respective materials depending on temperature and nanotube concentration were investigated using RheoStress RS 600 rheometer (Haake) with a cone-and-plate sensor system (cone angle – 1°, diameter – 20 mm, gap size between the cone and the plate – 0.055 mm) in the oscillation test mode. The measurements were carried out in the SmA and N* temperature range at 6.28 rad/s (1 Hz) angular velocity. The temperatures were controlled by TC501 Haake controller within 0.1 °C. During the harmonic oscillation mode measurements the samples were exposed to sinusoidally varying voltage [5]. This mode belongs to the class of non-destructive measurement of the material [6].

The initial experimental data to analyze the ChLC-compositions behaviour were the temperature dependence of elastic modulus \( G' \), loss modulus \( G'' \) and complex viscosity \( \eta^* \).

Modulus \( G' \) (elastic or storage modulus) is a measure of stored and released energy for the oscillation period per volume unit of this material. Modulus \( G'' \) (the viscous or loss modulus) is a measure of the energy transformed to heat during one period of sinusoidal strain.

The value of the complex viscosity \( \eta^* \), describing the total resistance to a dynamic shear, can also be obtained from oscillatory tests [6]:

\[
\eta^* = \frac{G^*}{\omega},
\]

where \( G^* \) – complex modulus, \( \omega \) – angular velocity [rad/s]; \( \omega = 2\pi f \), where \( f \) – frequency [Hz].

The molecular dynamics simulations of pure ChLC sample (cholesterol myristate) as well as its composition with a carbon nanotube were carried out with a MDsimGrid software [7] and software modules [8, 9] on the Intel Core i7-960 computer system, equipped with two GeForce GTH 580 graphics controllers. To accelerate the calculations of van der Waals forces we used an algorithm with Verlet lists (Verlet Neighbour Lists) [10] and transferred the computational tasks from the CPU to the GPU [11]. The system of classical equations of atoms motion was solved taking into account the AMBER force field (Assisted Model Building with Energy Refinement) [12].
3. Results and discussion

3.1. Effect of MWCNTs on mesomorphic properties of ChLC

Studies of mesomorphism and phase transition temperatures of the ChLC–MWCNTs mixtures (I–III) showed that the doping of MWCNTs into the ChLC matrix (0.005 ÷ 0.04 wt. %) leads to a shift of the phase transition temperatures into lower temperature region and significantly influences the SmA–Cr transition temperature. The temperature range of the SmA phase for compounds II and III essentially expands (approximately 13 ºC) with increasing nanotube concentration [3]. It was confirmed by DSC technique, which determines phase transition more precisely compared to microscopy.

At the same time optical polarizing investigations showed that the LC phases textures of pure and doped materials were identical. It means that the MWCNTs did not disturb liquid crystal molecular orientation at the scale of optical wavelengths or larger. However, the polygonal texture of the crystalline phase of compounds II and III with MWCNTs, which is formed on cooling, obtained periodic striations resembling "fingerprint" texture that was not observed in the individual compounds (figure 1).

![Figure 1](image1.png)

Figure 1. Photographs of polygonal texture of crystalline phase: a) individual compound II; b) composition of compound II with nanotubes (MWCNTs concentration – 0.01 wt. %), on cooling, crossed polarizers, × 250 [3].

3.2. Visco-elastic properties of ChLC– MWCNTs dispersions

Focusing on the ChLC visco-elastic characteristics can be explained by practical importance of these properties, which determine LC material behavior in external (e.g., shear) fields.

A representative of cholesterol esters – cholesteryl myristate III was selected as the ChLC matrix. The measurements of the visco-elastic parameter of the given material and its composites with MWCNTs were carried out in the deformation mode within a wide temperature range of LC phases existence and at different frequencies.

Figure 2 shows temperature dependence of dynamic moduli and complex viscosity of compound III at angular velocity $\omega = 6.28$ rad/sec (1 Hz) and 0.01° amplitude [5].
The graph shows that the temperature dependences of $\eta^*$, $G'$ and $G''$ of ChLC have qualitatively similar appearance, while the temperature curve corresponds to the general tendency to decreasing of the material order parameter with temperature increasing. Loss modulus $G''$ prevails over storage modulus $G'$ in the temperature range of isotropic phase existence, which indicates the behaviour of a viscous material. However, with temperature decrease in the transition region into N* phase, the reaction of the sample on the sinusoidal voltage exposure changes from viscous to elastic ($G' > G''$), later on, at the phase transition of the second order from N* to SmA the material becomes more viscoelastic. Most importantly, the increase of the dynamic moduli $G'$ and $G''$ in SmA phase as compared to N* phase is over an order of magnitude larger [5]. Such behaviour of ChLC materials under dynamic test mode was also mentioned in [13, 14].

The visco-elastic properties of ChLC compositions with respect to temperature and nanotube concentrations (0.01 and 0.02 wt. %) (figure 3) at different frequencies were investigated for the first time [5].

**Figure 2.** Temperature dependences of the dynamic moduli and complex viscosity of the cholesteryl myristate III.

**Figure 3.** Temperature dependences of the complex viscosity of the ChLC – MWCNTs nano-composites with different MWCNTs concentrations (wt. %).
Doping of the nanotubes into the studied ChLC sample at concentration ≤ 0.02 wt. % does not affect the complex viscosity in the temperature range of the isotropic phase existence, however, it leads to a 25%-increase of $\eta^*$ in N* phase and to an almost double increase in SmA phase [5, 15].

The experimental data on the temperature dependence of dynamic moduli of $G'$ and $G''$ of ChLC – MWCNTs compositions are shown in figure 4. The peculiarity of the results obtained during the research of the samples was the increase of the elastic modulus $G'$ value with a simultaneous decrease of the viscous modulus $G''$ value in the isotropic phase when adding MWCNTs (figure 4). Thus, in the Iso-phase at a certain concentration of carbon nanotubes, the LC material exhibits viscoelastic behaviour, which is probably caused by the formation of an additional spatial structure by the particles of the filler (percolation mesh). It is most likely that the rheological behaviour of the ChLC composites in the isotropic phase is determined by MWCNTs interaction [5].

![Figure 4](image)

**Figure 4.** Temperature dependence of dynamic moduli of the ChLC – MWCNT dispersions at different MWCNTs concentrations (wt. %).

This assumption confirms the need of introducing CNTs in the LC material at the mesomorphic state temperatures to implement the process of disaggregation of the carbon dopant and its stabilization in the volume of the matrix [19]. At the same time, the introduction of MWCNTs into ChLC at a concentration of 0.02 wt. % leads to ~ 25% increase of $G'$ and $G''$ in N* phase and to their 2.5-times increase in SmA phase. This probably indicates more efficient incorporation of MWCNTs into smectic phase [5, 15].

The frequency dependence of the studied viscoelastic characteristics, especially at low frequencies, is of a particular interest in the estimation of the dynamic investigation results [6]. Since MWCNTs introduction into the ChLC–matrix has no significant impact on the viscoelastic properties of N* phase, we studied the behaviour of the dynamic parameters $\eta^*$, $G'$ and $G''$ of the investigated ChLC samples in the frequency range from 0.1 to 20 Hz in the temperature range of SmA phase existence $T–T_c = –8 ^\circ C$ (figure 5) [5].
Figure 5. Frequency dependence of the complex viscosity (a) and dynamic moduli $G'$ and $G''$ (b) of ChLC–MWCNTs dispersions.

The investigation of the dynamic characteristics of the compositions with MWCNTs in SmA phase showed that at the increase of the deformation frequency from 0.01 to 20 Hz the value of $\eta^*$ for the ChLC materials linearly decreases by more than two orders of magnitude (figure 5), while the storage and loss moduli get approximately twice as big. The $G''(f)$ curve increases faster than the $G'(f)$ curve, thus showing that at high frequencies the ChLC composite tends to exhibit viscous flow [5].

3.3. Molecular dynamics simulation of the ChLC–CNT system

The investigation of the supramolecular organization of compound III (cholesteryl myristate) and its composite with CNT was conducted using MDsimGrid software which makes calculations on the graphics processing units [7–9].

The molecular dynamic simulation of the pure material and its composition with CNT of chair type (a length of 40 Å and a diameter of 10 Å) was performed in the following way: preliminary optimized models of 524 molecules (60260 atoms) of the test compound (in case of the one-component system) or 524 molecules with a single-walled CNT (in case of the composition with the nanotube) were placed in the cubical box of side L about 75 Å. In order to prevent the influence of the initial arrangement of molecules on further calculations, the systems were "annealed": the simulation was performed at the temperature of 1000 K during 1500 ps under the periodic boundary conditions. Then the systems were driven to local thermodynamic equilibrium in the canonical NPT–ensemble under the external pressure of 1 atm. and the given temperature [16].

The molecular dynamics simulations were performed under cooling in the temperature range of isotropic, cholesteric, smectic A and crystalline phases during 1500 ps. The radial distribution of the centres of mass of the molecules was recorded in the course of the numerical experiments.

The simulations resulted in radial distribution functions (RDF) of the centres of mass of the molecules or pair correlation functions $g(r)$ [17]:

$$g(r) = \frac{\rho(r)}{\rho} = \frac{1}{4\pi r^2 \rho} \frac{dN(r)}{dr},$$

where $\rho(r)$ – local number density of points in a spherical shell of thickness $dr$, at a distance $r$ from a fixed point, $\rho$ – average density, $dN(r)$ – the number of points in a spherical shell of volume $dV$.

The RDF describes the correlation between arbitrarily chosen atomic positions (centres of mass of the molecules) at different moments of time, in other words, it characterizes the most probable
distances between molecules. Exploring the given graphics of the correlation functions for height and width of the maxima it is possible to describe the peculiarities of the nearest neighbours in the simulated system, and identify the trends in the particle packing changes, depending on temperature.

Figure 6 shows the radial distribution functions of cholesterol myristate as an individual compound (figure 6a) and its composition with CNT (figure 6b).

![Figure 6](image)

**Figure 6.** Radial distribution functions of cholesteryl myristate (a) and composite with CNT on its base (b) at a temperature of existence of isotropic (150 °C), cholesteric (81 °C), smectic A (60 °C) and a crystalline (– 25 °C) phases.

On curve 1, corresponding to the RDF at the temperature of isotropic liquid in the range from 5 to 15 Å, there are two peaks of approximately equal amplitude: \( r = 7.2 \) and 14.4 Å, describing the short-range order of molecular arrangement. At large distances (over 20 Å) there is no correlation between the molecules, which describes the isotropic phase state. Besides the two initial peaks, there appear another two in the range from 4 to 6 Å on curves 2 and 3, respectively corresponding to N* and SmA LC phases. The first peak with the position of the molecular mass centre \( r = 4.3 \) Å corresponds to molecular thickness, while the second one with \( r = 5.7 \) Å corresponds to molecular width. However, since the RDF value in these points is small (\( g(r) = 0.33 \) and 0.64, correspondingly), it is unlikely that the molecules will be located at such distances from each other. In the crystalline state, there is splitting of the first and second intensive peaks on curve 4, which corresponds to a change in the short-range order and is characterized by molecular mobility decrease. It can be noticed that there is some periodicity in the distribution of the molecular mass centres compared to the RDF of certain mesophases, corresponding to the crystalline state.

Analyzing the results obtained, we can assume that the two distinct peaks: \( r = 7.2 \) and 14.4 Å (with the value of \( g(r) > 1 \)) describing the short-range order of molecules arrangement express the two stable states corresponding to the arrangement of the molecules relatively to each other. Given that \( r = 14.4 \) Å is half the length of the molecule, the spatial arrangement of the molecules will look as in figure 7 and, finally, determines the anisotropy of the properties in the system [16].
A visual analysis of the simulated system made it possible to get additional data about the supramolecular organization of the studied compound in the cholesteric phase. In order to do it, a vector between two atoms $i$ and $j$ was selected as conditional direction of the molecule axis, which characterizes the molecule orientation in space (figure 8).

As a result of the molecular dynamic calculations, using the distribution vector, we got for the first time a 3D–model of a one-component system for compound III (figure 9) (at the temperature of the cholesteric liquid crystalline phase existence) [16].

As it can be seen in the schematic representation, a periodically ordered structure with an element of chirality (twisted nematic), corresponding to its mesomorphic state, is clearly observed in the volume model of the ChLC sample obtained during the experiment.

In order to determine the impact of the nanotube on the orientation order of the molecules in N* phase, we introduced the order parameter $S'$ showing the orientation of the long molecular axis in its relation to the nanotube (4).

The order parameter of the neat ChLC material was calculated according to equation:

$$S = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{3} \approx 0.44 ,$$

where $\theta$ is the angle between the long molecular axis direction and the director.

For the system with single wall CNT:

$$S' = \frac{3}{2} \langle \cos^2 \beta \rangle - \frac{1}{3} \approx 0.15 ,$$

where $\beta$ is the angle between the long molecular axis direction and the axis directed along nanotube.
Based on the numerical calculations, we draw a conclusion that in the N* phase CNT has a weak impact on the orientation of the ChLC molecules and probably locates in the liquid crystal defects [16].

4. Conclusions
1. Doping of MWCNTs into the ChLC-matrix (0.005–0.04 wt. %) leads to significant expansion of the temperature range of SmA phase existence with preservation of LC-textures, typical for pure compounds. Polygonal texture of crystalline phase displays “fingerprint” striations which were not observed in pure ChLC material.
2. For the first time the visco-elastic properties of ChLC–MWCNT compositions have been investigated with respect to temperature and nanotube concentration and at different frequencies. At the addition of MWCNTs the increase of the elastic modulus $G'$ value with simultaneous decrease of viscous modulus $G''$ values were established in isotropic phase. In N* phase an increase of $G'$ and $G''$ values (up to 25%) and in SmA phase – by 2.5 times was found.
   At the increase of the deformation frequency from 0.01 to 20 Hz the value of $\eta^*$ linearly decreases by more than two orders of magnitude, while $G'$ and $G''$ moduli increase ~by 2 times.
3. For the first time the 3D-model of pure ChLC compound III (at the temperature of cholesteric mesophase existence) was obtained. On the basis of numerical calculations slight impact of CNT on orientation of ChLC molecules was established.

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