

## Dispersions of carbon nanotubes and organomodified clay platelets in cholesteric liquid crystals

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Comparative studies were carried out of cholesteric liquid crystal dispersions of anisotropic nanoparticles of different types, namely, essentially rod-like carbon nanotubes (CNT) and plate-like exfoliated particles of organo-modified Laponite and montmorillonite clays. The characteristic properties under study were selective reflection spectra of the cholesteric planar structure and optical transmission changes at the transition temperatures to the isotropic phase. Marked differences were noted in CNT-containing systems for purely steroid matrices and nematic-cholesteric mixtures with nematic 5CB, which presumably reflected differences in CNT interaction with aromatic and non-aromatic molecules. Effects of clay platelets upon selective reflection spectra were much smaller as compared to CNTs, in agreement with our assumption that dispersed plate-like particles should stabilize the planar cholesteric texture. The processes of CNT aggregation were markedly slower in cholesteric matrices as compared with nematics due to higher effective viscosity.

Проведены сравнительные исследования дисперсий анизотропных частиц различных типов в холестерических жидких кристаллах, а именно, стержнеобразных углеродных нанотрубок (УНТ) и пластинчатых эксфолиированных частиц органо-модифицированных глин — лапонита и монтмориллонита. Для характеристики использованы спектры селективного отражения холестерической плоской текстуры и величина изменения оптического пропускания при температуре перехода в изотропную фазу. Отмечены значительные различия для систем с УНТ на основе чисто стероидных матриц и нематико-холестерических смесей с нематическим 5CB, которые, вероятно, отображают различия во взаимодействии УНТ с ароматическими и неароматическими молекулами. Влияние пластинок глин на селективное отражение было значительно меньшим по сравнению с УНТ, что можно объяснить стабилизирующим действием плоских частиц на планарную холестерическую текстуру. Процессы агрегации УНТ проходили в холестерических матрицах значительно медленнее, чем в нематиках, вследствие более высокой вязкости.

## 1. Introduction

Dispersions of carbon nanotubes (CNT) and other types of anisometric micro- and nanoparticles in liquid crystalline (LC) media have rapidly developed into a new class of composite materials with broad prospects of their practical application [1–4]. CNT dispersions in nematic LC have been thoroughly studied in many works, including our previous papers ([5–9] and references therein). Also known are nematic dispersions of montmorillonite (MMT) and other similar clay-like substances [10, 11]. One should also note works on "hybrid" nematic dispersions comprising both types of particles [4, 12]. Much less attention was paid to dispersions of anisotropic nanoparticles in cholesteric liquid crystals (CLC). We could note only five publications on CLC+CNT dispersions [13–17], and only two of them explicitly consider selective reflection [13, 17]. In all these cases, just some qualitative effects were noted for arbitrarily chosen systems, with no systematic analysis of the mechanisms involved. As for CLC+MMT dispersions, no studies have been reported by the present time.

In the present work, we attempted to carry out comparative studies of CLC dispersions of carbon nanotubes (essentially rod-like particles) and plate-like particles of organo-modified Laponite (LapO) and montmorillonite (OMMT) under similar experimental conditions, using cholesteric matrices of different chemical composition.

## 2. Materials and methods

Two different cholesteric hosts were used: (1) a "steroid" cholesteric mixture of 80 % COC (cholesteryl oleyl carbonate, Aldrich, USA) and 20 % CC (cholesteryl chloride, Chemical Reagents Plant, Kharkiv, Ukraine), hereafter referred to as COC/CC, and (2) a "nematic-cholesteric" mixture of 70 % COC/CC and 30 % nematic 5CB (4-pentyl-4'-cyanobiphenyl). The multi-walled carbon nanotubes of diameter  $d \sim 10$  nm and length  $l \sim 5\text{--}10$   $\mu\text{m}$  were obtained from Arry, Germany. The samples of organo-modified clays, LapO and OMMT, were prepared by ion-exchange reactions with clays (Laponite and Pyzhevsky MMT, respectively) using the surfactant cetyltrimethylammoniumbromide (CTAB,  $\text{C}_{16}\text{H}_{33}\text{-N}(\text{CH}_3)_3\text{Br}$ , Fluka, Germany) with 99.5 % purity [10, 11]. The CLC+CNT and CLC+LapO and CLC+OMMT dispersions were obtained by adding the appropriate

weights of the dispersed substance to CLC solvent in the isotropic state with subsequent 20–30 min sonication of the mixture using a UZDN-2T ultrasonic disperser, in accordance with procedure essentially similar to that used in our previous works [5, 8, 12, 13].

The optical transmission spectra were measured using a Hitachi 330 spectrophotometer in a 50 mm thick cell with temperature controlled by a water thermostat. The studied dispersion was introduced between the cell walls by the capillary forces at a temperature above the cholesteric-isotropic transition point. The cell walls were treated with polyvinyl alcohol water solution and, after drying, rubbed in one direction to obtain the planar texture [13]. The regions of the measured spectra corresponding to selective reflection bands of cholesteric planar texture were used to determine the wavelength of maximum selective reflection  $\lambda_{max}$  ( $\lambda_{max} = np$ , where  $p$  is the helical pitch, and  $n \sim 1.5$  is the average refractivity index). In another set of experiments, the optical transmission values were determined at 800 nm, i.e., well above the absorption and selective reflection bands of the CLC solvents used. The change in the optical transmission values at the transition temperature from cholesteric to isotropic phase (the transmission "jump") was considered as a measure of incorporation of anisometric particles into the orientationally ordered liquid crystal structure [5, 6]; in some cases, not just the "jump", but the difference between optical transmission values in the cholesteric phase at room temperature and in the isotropic phase could be taken as a more adequate measure of the characteristic value.

## 3. Results and discussion

Fig. 1 shows the wavelength of selective reflection maximum  $\lambda_{max}$  as function of temperature for the studied cholesteric mixtures containing (dashed lines) and not containing (solid lines) dispersed carbon nanotubes. Upon addition of CNT, the general character of the  $\lambda_{max}(t)$  plots remains the same, with a very slight decrease of the isotropic phase transition temperature. The  $\lambda_{max}$  values are changed by  $\sim 10$  nm, and it should be noted that direction of this shift is different for "steroid" and nematic-cholesteric mixtures. This obviously reflects different character of intermolecular interaction between carbon nanotubes and molecules of different chemical nature in CLC

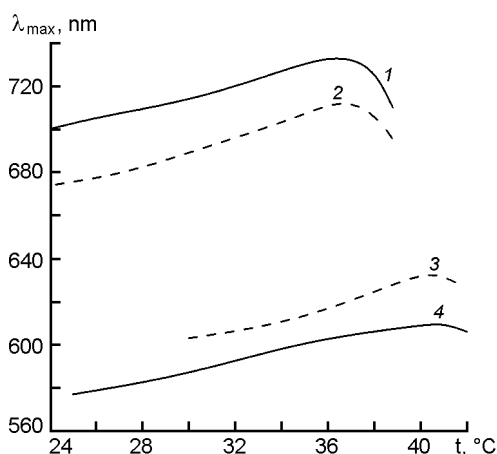


Fig. 1. Selective reflection maximum as function of temperature for cholesteric mixtures doped with carbon nanotubes: 1 — nematic-cholesteric mixture (70 % [COC/CC 80:20] and 30 % 5CB), undoped; 2 — the same mixture with 0.1 % CNT; 3 — steroid cholesteric mixture (COC/CC 80:20) with 0.1 % NT; 4 — the same mixture, undoped.

mixtures (aromatic 5CB and aliphatic cholesterol derivatives).

In Fig. 2, selective reflection spectra are shown for the nematic-cholesteric mixture doped with CNT, LapO and OMMT. Plots 1–4 were obtained at 35°C, i.e., rather close (within 5°C) to the isotropic transition temperature. It can be seen that plate-like particles of LapO (curve 2) and OMMT (curve 3) practically do not affect the shape of the initial peak, i.e., do not deteriorate the planar cholesteric texture. It can be assumed that the plate-like particles of LapO and OMMT are oriented normally to the helical axis by the planar helical arrangement of the host. Such integration of plate-like particles can even improve the planar texture induced by the appropriately treated cell surfaces, largely compensating for possible negative effect on the orientational ordering.

From the other side, much smaller quantities of carbon nanotubes slightly, but obviously affect the liquid crystal ordering, which results in broadening of the selective reflection peak (curve 4). Moreover, under cooling to lower temperatures the peak becomes even more smeared with a tendency to gradual appearance of two separate peaks at lower temperatures (curve 5). This also is a manifestation of different character of CNT interaction with aromatic and non-aromatic host molecules.

Figs. 3, 4 show optical transmission vs. temperature data for the studied nematic-

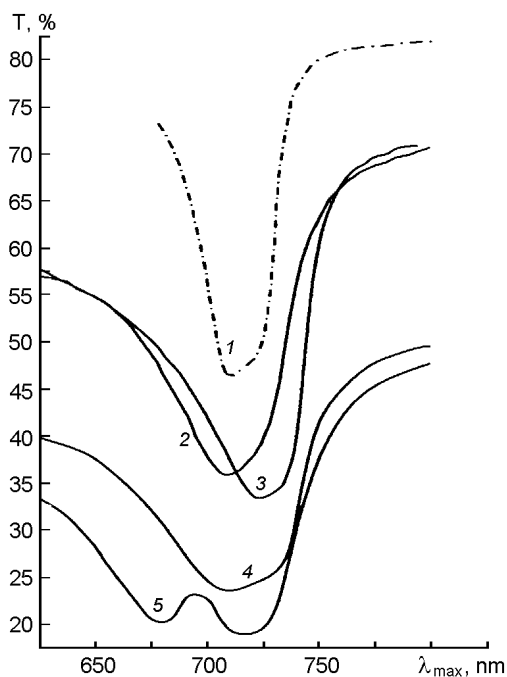


Fig. 2. Selective reflection spectra of the nematic-cholesteric mixture (70 % [COC/CC 80:20] and 30 % 5CB) at 35°C (1 — undoped mixture; 2 — mixture with 2 % LapO; 3 — mixture with 2 % OMMT; 4 — mixture with 0.1 % CNT) and at 25°C (5 — mixture with 0.1 % CNT).

cholesteric mixtures (COC+CC+5CB) doped by carbon nanotubes with two different concentrations of CNT. The CNT concentration of 0.01 % is below the critical point of aggregation [7, 9], and the effects of nanotube aggregation could be expected to be negligible. In this case (Fig. 3), the change ("jump") in optical transmission at the temperature of phase transition to the isotropic phase (at ~39°C) noted for the undoped mixture (curve 1) somewhat increases upon addition of CNT (curve 2). The viscosity of the nematic-cholesteric mixtures was rather high as compared with pure 5CB, and in accordance with expectations, after the sample storage no signs of CNT aggregation were observed by optical microscopy. However, after 2 h storage of the sample this "jump" becomes more pronounced (curve 3), especially when we take into account the overall increase in the temperature range from ~25°C to the isotropic phase. This behavior can be related to much higher viscosity of the cholesteric mixture as compared with pure 5CB — the process of homogenization of the dispersion is rather slow and continues for some time after ultrasonication (a certain analogy can be made, e.g., with processes during "dark storage" after

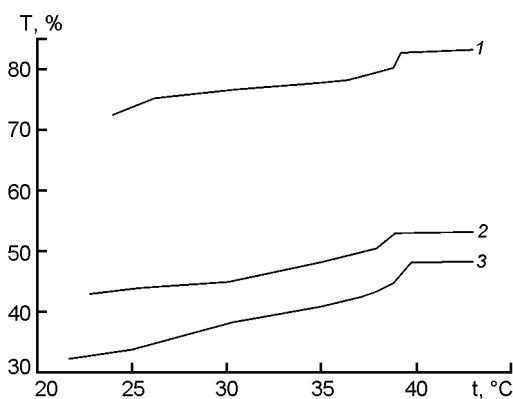


Fig. 3. Optical transmission as function of temperature for nematic-cholesteric mixture (70 % [COC/CC 80:20] and 30 % 5CB): 1 — undoped mixture; 2 — mixture with 0.01 % dispersed carbon nanotubes after ultrasonication; 3 — the same mixture after 2 h storage at room temperature.

UV irradiation). As it could be expected, no signs of CNT aggregation were noted in optical microscopy observations.

At CNT concentration of 0.1 %, i.e., above the nanotube aggregation threshold, the observed behavior was essentially different (Fig. 4). The transmission jump is noticeably increased upon introduction of nanotubes, and after the storage it becomes smaller, just as in the "standard" case of CNT dispersed in a nematic matrix. It can be assumed that this (as in the "nematic" case) reflects the process of aggregate formation. The aggregates formed can be seen in the optical microscope; it can be noted that the aggregation in the nematic-cholesteric mixture goes less intensively as compared with the pure nematic matrix. A similar behavior was observed for CNT dispersions in the "steroid" (COC/CC) matrix, but with much weaker effects, presumably due to larger viscosity of the matrix and weaker interaction of nanotubes with the liquid crystal host.

### 3. Conclusions

The reported preliminary results of our work allow us to formulate at least three "points of novelty":

— Dispersions of exfoliated platelets of organo-modified clays (montmorillonite and Laponite) in cholesteric liquid crystals (CLC) were studied for the first time, and their stabilizing effect on cholesteric planar texture was established.

— Dispersions of carbon nanotubes in CLC were studied using two types of

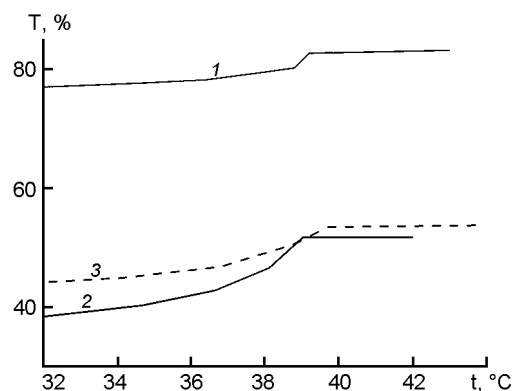


Fig. 4. Optical transmission as function of temperature for nematic-cholesteric mixture (70 % [COC/CC 80:20] and 30 % 5CB): undoped mixture (upper curve); mixture with 0.1 % of dispersed carbon nanotubes after ultrasonication (lower curve); the same mixture after 2 h storage at room temperature (dashed curve).

cholesteric hosts: mixtures of cholesterol derivatives and nematic-cholesteric mixtures containing cyanobiphenyl nematic 5CB. It has been shown that selective reflection spectra of such systems are sensible to the interactions between carbon nanotubes and molecules of different chemical nature.

— Processes of nanotube aggregation are qualitatively similar in both nematic and cholesteric dispersions, though higher effective viscosity of cholesteric mesophase results in slower aggregation.

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## **Дисперсії вуглецевих нанотрубок та платівок органомодифікованих глин в холестеричних рідких кристалах**

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Проведено порівняльні дослідження дисперсій анізотропних частинок різних типів у холестеричних рідких кристалах, а саме, стрижнеподібних вуглецевих нанотрубок (ВНТ) та платівкоподібних ексфолійованих частинок органомодифікованих глин — лапоніту та монтморилоніту. Для характеристики використано спектри селективного відбивання холестеричної планарної текстури та зміни величини оптичного пропускання при температурі переходу в ізотропну фазу. Відзначено значні відмінності для систем з ВНТ на основі суто стероїдних матриць та нематико-холестеричних сумішей з нематичним 5СВ, які, вірогідно, відображають різницю у взаємодії ВНТ з ароматичними та неароматичними молекулами. Вплив платівок глини на селективне відбивання був значно менший у порівнянні з ВНТ, що можна пояснити стабілізуючою дією плоских частинок на планарну холестеричну текстуру. Процеси агрегації ВНТ в холестеричних матрицях йдуть значно повільніше, ніж у нематиках, внаслідок більш високої ефективної в'язкості.