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Optical transmittance and electric conductivity in nematic dispersions containing carbon nanotubes and organomodified montmorillonite

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Optical transmission and electric conductivity were measured for dispersions of multi-walled carbon nanotubes (MWCNT), organomodified montmorillonite (MMT) and for hybrid dispersions of MWCNT+MMT in 5CB nematic liquid crystal (LC). The optical transmittance jump at the nematic-isotropic transition was observed in MMT+LC (~0.1 % wt. of MMT). This behaviour was qualitatively similar to that of reported earlier for MWCNT+LC (~0.1 % wt. of MWCNT) nanocomposites, suggesting exfoliation of the organoclay plate-like particles and their incorporation into the orientationally ordered nematic structure. In hybrid dispersions the effect of MWCNT and MMT on optical transmission was additive. Noticeable differences in the electric conductivity behaviour for composites filled with MWCNTs and organomodified MMT were observed. It was shown that MWCNTs facilitated and MMT hindered the electric field-induced transition from planar to homeotropic state in the LC cell.

Исследовано оптическое пропускание и электропроводность дисперсий многостеночных углеродных нанотрубок (НТ), органомодифицированного монтмориллонита (ММТ) и гибридных дисперсий НТ+ММТ в нематическом жидком кристалле (ЖК) 5CB. Наблюдался скачок оптического пропускания при нематико-изотропном переходе в ММТ+ЖК (~0.1 % ММТ). Такое поведение качественно подобно ранее описанному для нанокомпозитов НТ+ЖК (~0.1 % НТ), что позволяет предположить расслаивание плоских частиц органоглины и их встраивание в ориентационно упорядоченную нематическую структуру. В гибридных дисперсиях влияние НТ и ММТ на оптическое пропускание аддитивно. Отмечены существенные различия в поведении электропроводности между композитами, заполненными НТ и органомодифицированным ММТ. Показано, что НТ облегчают, а частицы ММТ затрудняют индуцированный электрическим полем переход из планарного в гомеотропное состояние в жидкокристаллической ячейке.

Dispersions of carbon nanotubes (CNTs) in liquid crystals (LC) have recently become a subject of extensive research as promising objects for liquid crystal science, nanophysics, and physics of colloidal systems; a detailed analysis of the state-of-art can be found in the reviews [1–3]. A simple and straightforward method for evaluation of the degree of incorporation of CNTs into the orientationally ordered structure of the nematic mesophase was recently proposed [4–6]. The method involves comparison of the optical transmission jump at the nematic to isotropic phase transition for LC dispersions doped and undoped with CNTs. Studies of electric conductivity of CNTs+LC nanocomposites as function of CNTs concentration and the applied voltage allowed further clarification of the general picture of supramolecular arrangement in these dispersions.

Another example of anisometric particles which, when dispersed in liquid crystals, could form ordered supramolecular arrangements resulting in peculiar optical properties and electrooptical effects is presented by organomodified layered silicates such as montmorillonite [7–9]. In this case, the dispersed anisometric aluminosilicate particles are of plate-like shape; if nanotubes can be considered as rod-like ("calamitic") non-mesogenic dopants of large size, montmorillonite particles can be presented, in a similar model, as "discotic" quasi-mesogens. The hybrid materials filled with both organoclays and CNTs can demonstrate improved thermal stability, electrical and mechanical properties, and even synergetic effects arising from the combination of plate-like and rod-like fillers [10, 11, 12].

In this study, we carried out optical transmission and conductivity measurements in nematic dispersions of organomodified montmorillonite (MMT) under experimental conditions similar to those used by us in [6] for nematic dispersions of multiwalled carbon nanotubes (MWCNTs). To get a further insight into the structure and properties of such systems, similar experiments were carried out using hybrid dispersions containing both MWCNTs and organomodified MMT particles jointly distributed in the same nematic matrix. The LC host used was 4-pentyl-4'-cyanobiphenyl- a typical nematic substance with dielectric anisotropy $\Delta\varepsilon > 0$ (5CB, Chemical Reagents Plant, Kharkiv, Ukraine).

The MWCNTs were obtained from TMSpetsmash Ltd., (Kyiv, Ukraine). They were prepared from ethylene using the chemical vapour deposition (CVD) method with $FeAlMo_{0.07}$ as catalyst and subsequent treatment by concentrated alkali (NaOH) and acid (HCl) solutions was followed by filtering and repeated watering until the pH value of the filtrate became the same as that of the distilled water [13]. The residual mass content of the mineral additives was <1 %. The MWCNTs involved typically had the outer diameter d_e of about 10–20 nm, while their length ranged from 5 to 10 μm.

The crude MMT of Pyzhevskii deposit (Ukraine) was initially refined from impurities and transferred into the sodium form by multiple treatments in 0.1 molar solution of NaCl for 24 h at 70°C to obtain a homoionic clay. The prepared clay samples contained highly pure MMT as revealed by X-ray and chemical analysis. Then MMT was washed several times with deionised water to remove surplus of salt. The prepared MMT had the exchange capacity of 1.05 μmole-equ/g, the specific surface (determined by adsorption of methylene blue) of 640 m^2/g. The organomodified MMT was prepared in the ion-exchange reactions. The long chain cetyl trimethyl ammonium bromide ions ($CH_3(CH_2)_{18}NH_3^+ \cdot Cl^-$, CTAB, Merck) were chosen because they had been shown to favour the formation of exfoliated LC nanocomposites [7, 8]. The aqueous solution of CTAB (1 % wt.) was slowly added to the aqueous MMT dispersion (1 % wt.) and stirred vigorously at 370 K for 24 h. The quantity of solutions corresponded to the required 1:1 stoichiometric ratio of exchange capacity of clay and CTAB. After incubation, the dispersion was filtered using a disc filter funnel, centrifuged, and the obtained organomontmorillonite was freeze-dried.

The MWCNT+LC, MMT+LC and hybrid MWCNT+MMT+LC nanocomposites were obtained by adding the appropriate weights of NTs and/or MMT to the LC solvent in the isotropic state with subsequent sonication of the mixture using a UZDN-2T ultrasonic disperser, in accordance with procedure essentially similar to the previously described [4–6].

The optical transmission spectra were measured in a 50 μm thick cell using a Hitachi 330 spectrophotometer. The studied dispersion was introduced between the cell walls by the capillary forces at a temperature above the nematic-isotropic transition point (35°C for 5CB).

Before introduction of the nanocomposites into the cell, the cell walls were treated with polyvinyl alcohol water solution and, after drying, rubbed in one direction similarly to the standard procedure of obtaining the cholesterics with planar texture. The resulting alignment was believed to be close to planar.

All optical transmission data were measured at 700 nm. This wavelength was chosen as optimal because it was well above the absorption region of the studied LC solvent. The parallel experiments were done under identical conditions for a LC dispersion (T) and the undoped liquid crystal (T_o).

The home-made cell, used for measurement of electrophysical characteristics, included a grounded guard ring, which reduced the influence of the edge effects. The cell was a capacitor with metal plates, covered by a polyvinyl alcohol film rubbed in one direction for ensuring the planar texture. The cell thickness (50 μm) was set by a Teflon spacer. Before the measurements, the cell parts were washed in hexane and dried at 390 K. After assembling, the cell was connected to E7-12 LCR-meter (KALIBR, Belarus), to make sure that tgδ of the empty cell did not exceed 0.0001. The liquid crystal system in the isotropic state was introduced into the pre-heated cell by the capillary forces at a temperature 5–10 K above the nematic-isotropic transition point.

For conductivity and capacitance measurements, the ac voltage of 0.25 V and 1 MHz was used, which should not affect the LC director field. The experimental setup provided application of DC bias voltage up to 40 V to the cell. The external DC voltage could align the molecules, thus leading to re-orientation of the nematic director and corresponding changes in dielectric properties and conductivity. The difference $T_0 - T$ between transmittances of the LC solvent and a filled LC composite can serve as a measure of contribution of the dispersed nanoparticles to the total value of $(1-T)$ (i.e., absorption + reflectance/scattering) of a composite at the given wavelength [4–6]. The nematic-isotropic transition commonly results in a step-wise increase of the optical transmittance T. Impregnation of MWCNTs into a LC matrix enhances such transitional behaviour, with higher optical transmittance jumps observed at larger concentration of MWCNTs. This was explained by deep integration of MWCNTs into orientationally ordered nematic LC matrices [4–6]. Such integration possibly reflects the existence of a strong binding interaction between the surface of hydrophobic MWCNT nanoparticles and LC molecules [14].

Fig. 1 shows typical dependences of $T_0 - T$ as function of temperature t for 5CB doped with organomodified MMT in the nematic and isotropic phases (the nematic-isotropic transition point for pure 5CB is 35°C). The directly measured optical transmittance T vs. t plots for these composites and pure 5CB are shown in insert in Fig. 1. The recorded change in $T_0 - T$ at the nematic-isotropic transition (transmittance jump) increases with increasing of MMT concentration. This behaviour of the studied MMT+LC composites was essentially similar to that observed for the MWCNT+LC composites [6]. This suggests that organomodified MMT plate-like particles are also integrated into the LC matrix and there exist noticeable interactions between the surface of MMT and molecules of LC. This result is consistent with the earlier reported data [7, 8]. However, it should be noted that at low concentrations of MMT (<1 % wt.) the effect of organomodified MMT on transmission jump was several times weaker as compared with that observed for MWCNT+LC composites. On the other hand, in MMT+LC composites reliable and reproducible optical measurements could be carried out up to much higher concentrations of organomodified MMT (>2.5 %). The optical experiments for opaque MWCNT+LC composites are usually restricted to low concentrations of MWCNT (<0.2 %). In the nematic phase the optical transmittance T decreases with increasing organomodified MMT concentration. This is in full agreement with the results of [7, 8], where the measured transmission did not exceed several per cent for ~4 % dispersions of organomodified MMT in 5CB.

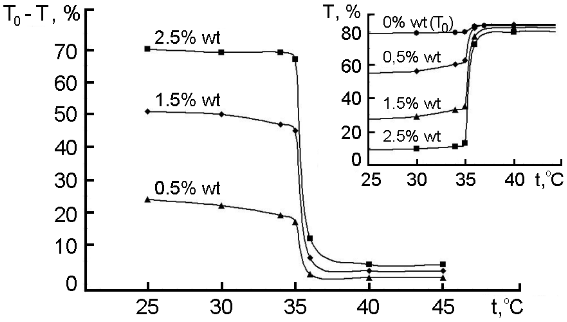

Fig. 1. Difference in transmittances of the nematic matrix 5CB (T_0) and the organomodified MMT+5CB composites (T) as function of temperature t. Insert shows the directly measured optical transmittance values.

Fig. 2 shows $T_0 - T$ as function of temperature t for MMT(0.1 %) + LC, MWCNTs (0.1 %) + LC and hybrid MMT(0.05 %) + MWCNTs(0.05 %) + LC composites. It should be noted that the transmittance jump for MMT+LC nanocomposites was much smaller than for MWCNT+LC composites. This possibly suggests weaker structure organisation in MMT+LC composites due to different nature of interface interactions between organomodified MMT particles and the nematic LC, the influence of particle shapes and their aspect ratios on structure organization, etc. In hybrid MWCNT+MMT+LC nanocomposites, the transmittance proper-

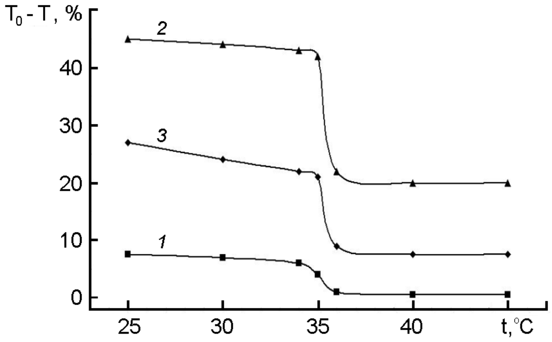

Fig. 2. Differences in transmittance (T_0–T) as function of temperature t for 5CB doped with anisometric particles: 0.1 % organomodified MMT (*1*), 0.1 % MWCNTs (*2*), 0.05 % organomodified MMT+0.05 % MWCNTs (*3*).

ties show an approximate additivity, suggesting the absence of any synergetic effect related with interactions between MWCNTs and particles of organomodified MMT.

Fig. 3 shows electric conductivity σ as a function of the applied DC voltage U for the studied MWCNT+LC, MMT+LC and hybrid MWCNT+MMT+LC nanocomposites at 0.1 % wt content of each filler component. The electric conductivity increases with applied voltage U, and a certain threshold on σ(U) plots was observed. This threshold at U_{th} evidently reflects the transition from planar to homeotropic texture of LC. At small voltage (at $U<U_{th}$) the initial planar texture in LC are fixed by near-surface interactions of LC with the rubbed polyvinyl alcohol films. In the high external field (at $U>U_{th}$), homeotropic alignment of 5CB molecules with positive dielectric anisotropy occurs.

For pure 5CB and composite impregnated with MWCNTs the threshold voltages are minimal (~2 V). In nanocomposites, the integrated anisometric nanoparticles tend to follow the LC director, and the observed conductivity behaviour reflects the re-orientation of 5CB molecules along the electric field and corresponding re-organisation of spatial arrangement of nanoparticles.

Impregnation of electrically conductive MWCNTs into 5CB results in the conductivity rise, and above some threshold concentration of MWCNTs (≈0.1 %) the percolation threshold into the highly conductive state is observed [4–6]). For the MWCNT+LC composite, the threshold voltage Uth is minimal (1.8 V), so the presence of MWCNTs facilitates the reorientation of 5CB molecules from planar to homeotropic state (curve *2* in Fig. 3).

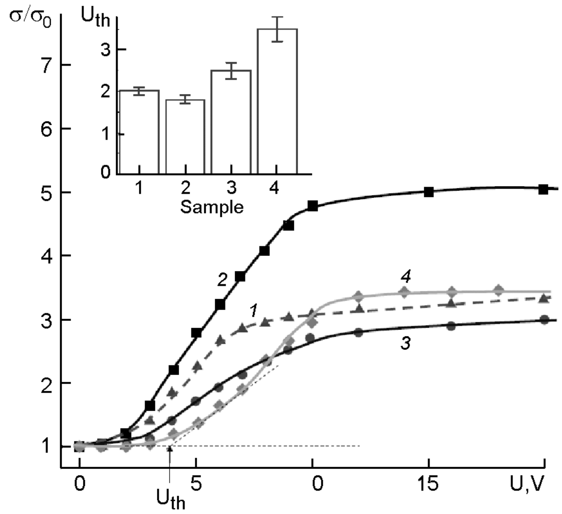

Fig. 3. Relative changes in electrical conductivity on application of d.c. voltage for the measurement cell containing undoped nematic 5CB (*1*) and 5CB doped with 0.1 % MWCNTs (*2*), 0.1 % organomodified MMT (*3*), and 0.1 % MWCNTs+0.1 % organomodified MMT (*4*). Insert shows the threshold voltages U_{th} for samples 1–4.

On the contrary, the introduction of non-conductive organomodified MMT particles (line *3* in Fig. 3) results in an increase of the threshold voltage U_{th} up to ≈2.5 V (Insert in Fig. 3) and hinders the rise of electric conductivity with voltage as compared with pure 5CB (line *1* in Fig. 3). For the MMT+LC composite the final relative conductivity increase at high voltages (≈20 V) was even weaker than that observed for undoped 5CB.

In the hybrid MWCNT+MMT+LC nanocomposites (curve *4*), the effects on electric conductivity can be considered as "positive" as compared with curve *3* (MMT+LC) or "negative" as compared with curve *2* (MWCNT+LC). Note also that the hybrid composite demonstrates the largest threshold voltage of ~3.5 V.

It should be noted that these differences in conductivity behavior for MWCNT+LC, MMT+LC and their hybrid composites may reflect details of composite supramolecular organisation, degree of mutual integration, intrinsic electric conductivity of the nanoparticles, inequality in percolation or sol-gel behaviour, shape of particles and nature of interfacial interactions. Due to strong van-der-Waals interactions the nanoparticles are also predisposed to adhere on cell surfaces. For example, the formation of organo-clay film may enhance the surface field stabilizing the initial planar texture in LC at small U and hinder the transition to the homeotropic orientation at high U.

For the first time, the comparative optical transmittance and electric conductivity studies of liquid crystal composites filled with particles of different shapes (carbon nanotubes, organomodified montmorillonite plates) were carried out. The data showed the presence of deep integration of the studied fillers into nematic LC. The electric conductivity data evidenced the presence of noticeable differences in field induced changes for composites filled with MWCNTs and organomodified MMT: nanoparticles of MWCNTs facilitated the re-orientations of 5CB molecules, while nanoparticles of organomodified MMT hindered the transition from planar to the homeotropic state.

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Оптичне пропускання та електропровідність нематичних дисперсій, що містять вуглецеві нанотрубки та органомодифікований монтморилоніт

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Досліджено оптичне пропускання та електропровідність дисперсій багатостінкових вуглецевих нанотрубок (НТ), органомодифікованого монтморилоніту (ММТ) та гібридних дисперсій НТ+ММТ у нематичному рідкому кристалі (РК) 5СВ. Спостерігали стрибок оптичного пропускання при нематико-ізотропному переході у ММТ+РК (~0.1 % ММТ). Така поведінка якісно подібна раніше описанії для нанокомпозитів НТ+РК (~0.1 % НТ), що дозволяє припустити розшаровування пласких частинок органоглини та їх вбудовування в орієнтаційно впорядковану нематичну структуру. У гібридних дисперсіях вплив НТ та ММТ на оптичне пропускання був адитивним. Відзначено істотні відмінності у поведінці електропровідності між композитами, заповненими НТ та органомодифікованим ММТ. Показано, що НТ полегшують, а частинки ММТ утруднюють індукований електричним полем перехід від планарного до гомеотропного стану у рідкокристалічній комірці.