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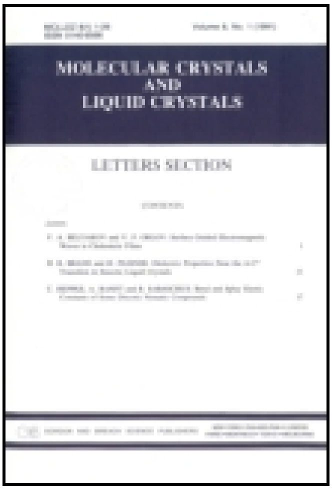

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Great Effect of Laponite Nanoplatelets on Structure and Optical Properties of Liquid Crystal-Carbon Nanotube Composites

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Great Effect of Laponite Nanoplatelets on Structure and Optical Properties of Liquid Crystal–Carbon Nanotube Composites

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By using several optical methods, dramatic improvement of dispersion of carbon nanotubes (CNTs) in nematic liquid crystal (LC) E7 is found by adding a small amount (0.1 wt.%) of Laponite particles modified with an ionic surfactant CTAB to the LC-CNT composite. This effect is explained by surrounding the nanotubes by Laponite particles that promoted their disaggregation. The enhanced dispersion of CNTs was accompanied with essential changes in electro-optical properties of the colloids, namely, in greatly improved optical transmittance and electro-optic contrast, as well as in reduction of Fredericks threshold.

Keywords carbon nanotubes; liquid crystals; dispersions; structure; electro-optics

1. Introduction

Inclusion of nanoparticles of inorganic materials in liquid crystals (LCs) has several motivations. The first is the aspiration to expand the range of LC properties, which is significantly limited by the organic nature of such substances. This idea came from Brochard and de Gennes [1] still at the very beginning of active practical application of LCs. Thereafter, “ferromagnetic” [1, 2], “ferroelectric” [3] and “metallic” [4] LC composites were proposed with the properties unimaginable for conventional LCs. The second is the desire to eliminate the intrinsic weak points of LCs as electro-optic materials for displays, shutters and other devices. Lowering of Fredericks threshold and residual DC voltage is described. And thirdly, anisotropic LC matrices can be used to orientationally order ensembles of anisometric particles to gain unique properties of these particles.

All of these reasons fully relate to carbon nanotubes (CNTs) that explains huge interest to their dispersions in LCs. CNTs well integrate in LC order so that these systems demonstrate high anisotropy of physical properties that opens new horizons for their optical, electro-optical and electronic applications [5, 6]. Besides, doping of LCs with a minute amount of CNTs ($\sim$0.005 wt%) leads to lowering of Fredericks’ reorientation threshold and residual DC voltage, which determines image sticking problems in the LC displays [7].

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The problem that does not allow getting the benefit of such systems is insufficient dispersion of CNTs. They bundle and cluster together in disordered agglomerates. This leads to different problems, such as disruption of optical homogeneity and high scattering losses.

To solve this problem, several approaches have been recently proposed, which relate to optimization of LC materials and dispersing conditions [8], *in situ* electro-hydrodynamic (EHD) dispergation [9, 10], debundling of CNTs in high electric fields [11], chemical linking of various functional fragments to CNTs via covalent bonding and π-π stacking [12]. Despite significant progress in dispersion particles using these approaches, none of them provides a high efficiency combined with dispersion stability in a wide range of particle concentrations. Thus, obtaining highly dispersed and stable suspensions of CNTs in LC remains a topical problem.

To improve the dispersion of CNTs in LC we test a new approach that has proven itself for water and polymer dispersions of CNTs. It implies assistance of CNT dispersion by nanoparticles of another type, which demonstrate high affinity to carbon nanotubes. This stabilization principle was for the first time demonstrated by Tohver et al. [13], who observed stabilizing effect of highly charged nanoparticles on aqueous dispersion of colloidal spheres. The nanoparticles formed a kind of halo around the spheres (haloing effect) preventing their coagulation. Later on, this approach was proved to be quite effective for CNT dispersions in water [14] and some polymers [15]. Recently, we have attempted to apply this approach to stabilization of CNTs in a LC by using particles of natural clay montmorillonite (MMT). In some cases, we were able to achieve a positive result, but in general the effect of MMT was not pronounced and poorly reproducible [16].

In the present paper, this approach is implemented through the use of particles of synthetic clay Laponite. The particles of this sort are obtained in a well controllable synthesis. Their longitudinal size is much smaller than the size of MMT particles ($\sim$25 nm vs. $\sim$1 μm), but it is commensurable with the transversal size of CNTs. This simplifies dispersing and facilitates their interaction with CNTs. With several optical techniques we have proved significant improvement of dispersion of CNTs in LC in a presence of Laponite. This, in turn, leads to a dramatic improvement of electro-optical characteristics of the LC+CNT suspensions.

2. Experimental

2.1. Samples

We used nematic mixture E7 from Merck with the temperature of nematic-to-isotropic transition at 58°C and dielectric constants in the directions parallel and perpendicular to the LC director $\varepsilon_{\parallel} = 19$ and $\varepsilon_{\perp} = 5.2$, respectively. As CNTs we utilized the multi-walled carbon nanotubes (MWCNTs) from Spetsmash Ltd. (Kyiv, Ukraine) produced from ethylene by the chemical vapor deposition method [17]. These CNTs had an outer diameter 20–40 nm and the length ranged from 5 to 10 μm. The specific electric conductivity σ of the powder of compressed CNTs was about 10 S/cm.

The synthetic clay was Laponite from Rockwood Additives Ltd., U.K. This is the material in a form of powder with the chemical formula $Na_{0.7}[(Si_8Mg_{5.5}Li_{0.4})O_{20}(OH)_4]$. The primer particles of Laponite are the disc-like nanoplatelets, which tend to form stacks. The thickness and diameter of these discs are about 1 nm and 25–30 nm, respectively. The platelets of original Laponite were modified according to procedure described in [18] by ionic surfactant cetyltrimethylammoniumbromide (CTAB, $C_{16}H_{33}$-$N(CH_3)_3Br$, Fluka, Germany) with 99.5% purity. The resultant material will be further called the organomodified Laponite (LapO).

The studied dispersions were obtained by adding CNTs, LapO or both of them to LC E7 in appropriate weights; the concentration of CNTs, C, ranged from 0.025 to 0.5 wt.%, while loading of LapO was fixed at 0.1 wt.%. The mixture was sonicated at $T = 60^\circ$C for 10 min using an ultrasonic disperser at the frequency of 22 kHz, incubated at room temperature for 24 hours and then sonicated for 2 min again. The resultant dispersion was loaded by capillary forces into the cells.

The cells were made from glass substrates containing patterned ITO electrodes and rubbed layers of polyimide AL3046 (JSR, Japan) for planar alignment. The cells were assembled so that the rubbing directions of the opposite aligning layers were antiparallel or perpendicular to each other, so that the antiparallel or twisted cells were obtained. The structure of all samples was studied by optical microscopy. The twisted cells were also used for electro-optical measurements. The cell gap d was maintained by 20 μm glass spacers.

2.2. Methods

The macroscopic alignment uniformity in the cells was checked using a light box equipped with two polarizers. The microstructures were studied using optical polarization microscope Polam L-213M equipped with digital camera conjugated with personal computer.

The size distribution and mean radius of CNT aggregates R_m were determined by cluster analysis of black and white microscopic optical images using Hoshen-Kopelman (HK) algorithm [19]. Within this approach, the clusters were labeled and the radius of cluster with label k was determined as its radius of gyration:

$$R_k = \sqrt{\frac{1}{N_k}\sum_{i=1}^{N_k}\left(\overrightarrow{r_i^k} - \overrightarrow{r_m^k}\right)^2}, \tag{1}$$

where $\overrightarrow{r_m^k} \equiv \{x_i^k, y_i^k\}$ defines position of the pixel with coordinates x_i^k and y_i^k, N_k is a number of the pixels, and the value of

$$\overrightarrow{r_m^k} = \frac{1}{N_k}\sum_{i=1}^{N_k}\overrightarrow{r_i^k} \tag{2}$$

defines the position of the center of the cluster with label k.

These data were used to obtain cumulative $F(R)$ and differential $f(R) = dF/dr$ distribution functions for the clusters of some microscopic picture. Then the mean radius of the aggregates R_m can be estimated as

$$R_m = \frac{\int Rf(R)dR}{\int f(R)dR} \tag{3}$$

In electro-optical tests, the transmittance of the twisted cells placed between two parallel polarizers was measured as a function of applied AC voltage ($f = 2$ kHz) ramped

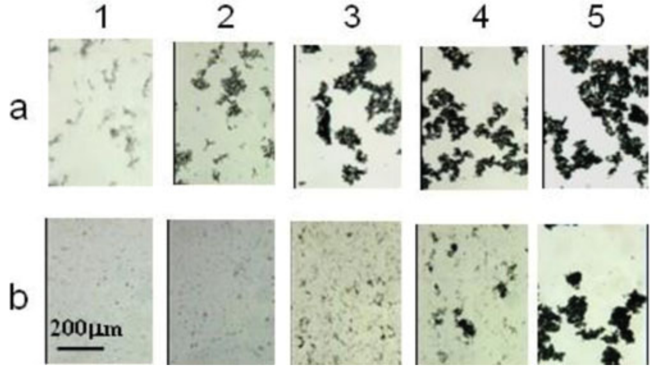

Figure 1. Microscopic pictures of the layers of (a) E7+CNT and (b) E7+CNT+LapO (0.1 wt.%) suspensions. Concentration of CNTs in the samples 1, 2, 3, 4 and 5 is 0.025, 0.05, 0.1, 0.3 and 0.5 wt.%, respectively.

up from 0 to 30 V. The cells worked in a waveguide regime (the Mauguin's regime) so that polarization of testing light followed director of LC, experiencing rotation in 90°. For this purpose we used in-house made electro-optic setup earlier described in [6]. All experiments were carried out at room temperature.

3. Results and Discussion

3.1. Structure

The microscopic images corresponding to E7+CNT and E7+CNT+LapO series of the cells are presented in Figs. 1a and 1b, respectively. These images were analyzed in terms of two processes, LC alignment and structuring of nanoparticles. The planar alignment provided by rubbed PI substrates was maintained in all samples. The E7+LapO samples demonstrated high alignment uniformity, but the alignment worsened in E7+CNT and E7+CNT+LapO suspensions due to director perturbations caused by the particle aggregates.

An interesting difference between the cells with parallel and twisted alignment configuration is the formation of linear defects in the twisted cells, Fig. 2. The defects cling to the particle aggregates and so are rather stable. They disappear after application of electric

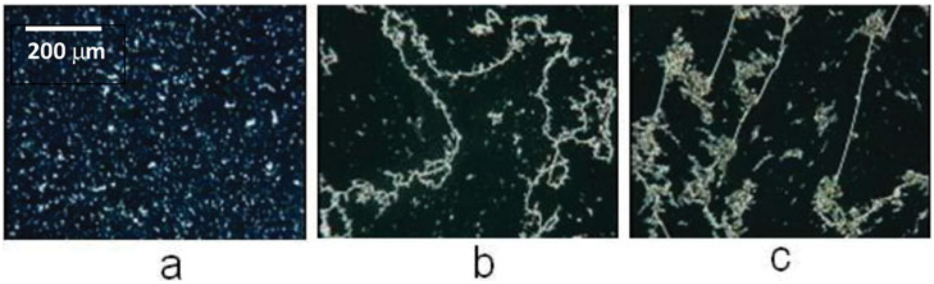

Figure 2. Dark state of parallel (a) and twisted (b,c) cells viewed in polarizing microscope. The cells are filled with E7+CNT (0.1 wt.%)+LapO (0.1 wt.%) (a,b) and E7+CNT (0.1 wt.%) (c) suspensions.

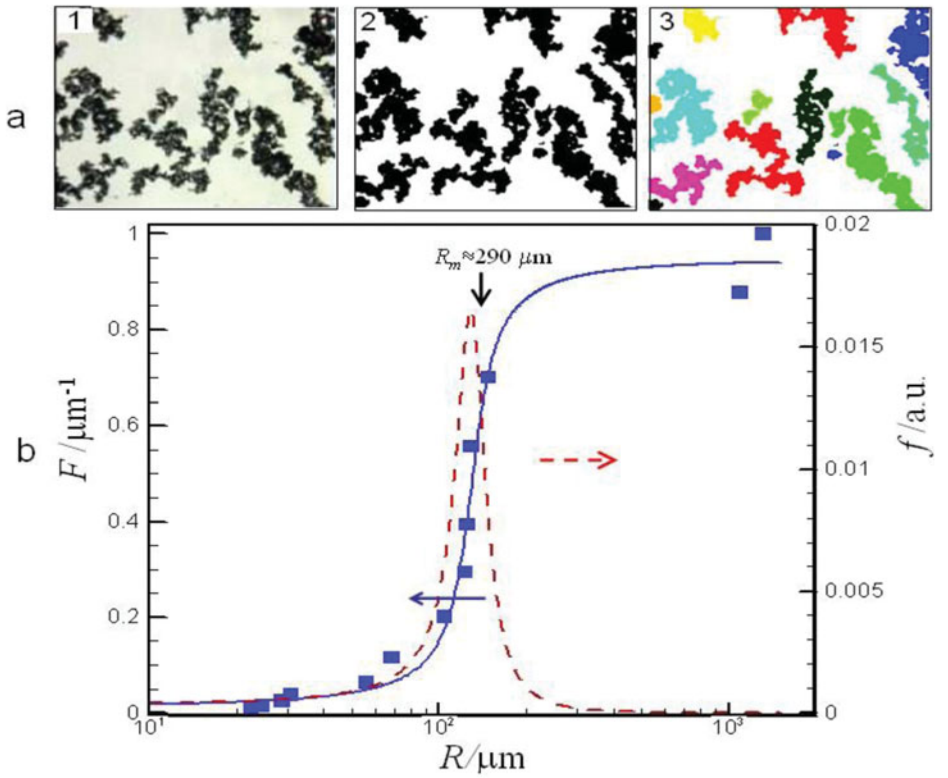

Figure 3. (a): Microphotograph (photo 4a in Fig. 1) (1), its black and white image (2) and the image with labeled clusters (3). (b): Cumulative, *F(R)*, and differential, *f(R),* size distribution functions corresponding to image (a).

field, but form again after heating the cell above T_c and subsequent cooling to the nematic state. The nature of these defects may be similar to that in cholesteric LCs [20].

According to Fig. 1, increase of CNT concentration leads to growing of particle aggregates. However, this growth is much more pronounced for E7+CNT series. In turn, in case of E7+CNT+LapO series it is strongly hampered by LapO particles. This conclusion is well supported by the results of image processing by using Hoshen-Kopelman (HK) algorithm. As example, Figs. 3a and 3b, respectively, demonstrate the processed images of picture 4a in Fig. 1 and corresponding size distribution functions. The concentration dependences of the mean radius of CNT aggregates R_m and the half-width of the size distribution cumulative function ΔR, determined by cluster analysis of Fig. 1, are presented in Fig. 4. Obviously that growth of this curve for the E7+CNT+LapO series is much slower in the range of CNT concentrations 0–0.1 wt. %. This implies stabilizing role of LapO platelets for CNTs.

The much improved dispersing of CNTs in the presence of LapO platelets can be explained by haloing effect. This is due to the fact that LapO particles demonstrate high affinity to both components of LC+CNT suspensions. The affinity to LC results in good exfoliation of LapO stacks in this host. In turn, high affinity to CNTs means that the energy of LapO+CNT interaction is considerably higher than the energy of the weak van der Waals

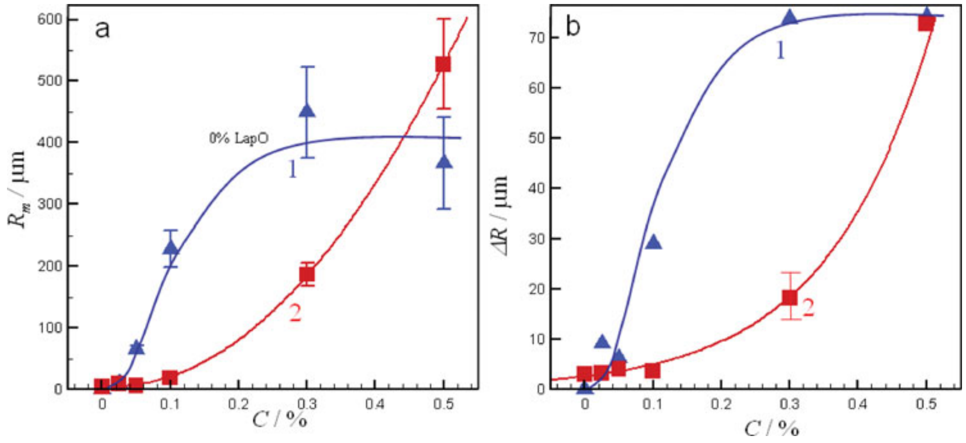

Figure 4. Mean radius of the CNT aggregates R_m (a) and half-width of the size distribution ΔR (b) as functions of CNTs concentration. Curves 1 and 2 correspond to E7+CNT and E7+CNT+LapO (0.1 wt.%) series, respectively.

interaction of nanotubes. In view of this, LapO platelets surround the nanotubes and screen the nanotube interaction. This prevents formation of big aggregates of CNTs.

3.2. Electro-Optical Properties

Structural changes of LC+CNT composites in the presence of LapO particles result in radical change of electro-optical characteristics. Figure 5 shows transmittance vs. applied voltage curves for pure E7, E7+CNT (0.05 wt%) and E7+CNT (0.05 wt%)+LapO

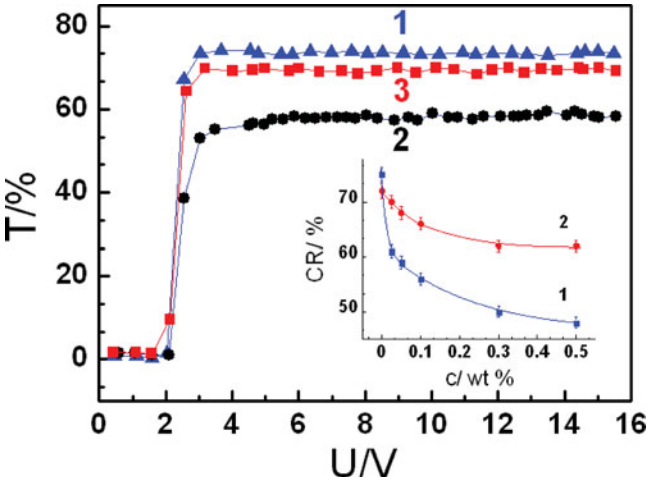

Figure 5. Transmittance vs. voltage plots for the E7 (1), E7-CNT (0.1 wt.%) (2) and E7+CNT (0.1 wt.%) (2) and E7+CNT (0.1 wt.%)+LapO (3) samples. The inset shows contrast ratio vs. CNT concentration curves for the E7-CNTs (1) and E7-CNTs-LapO (2) series.

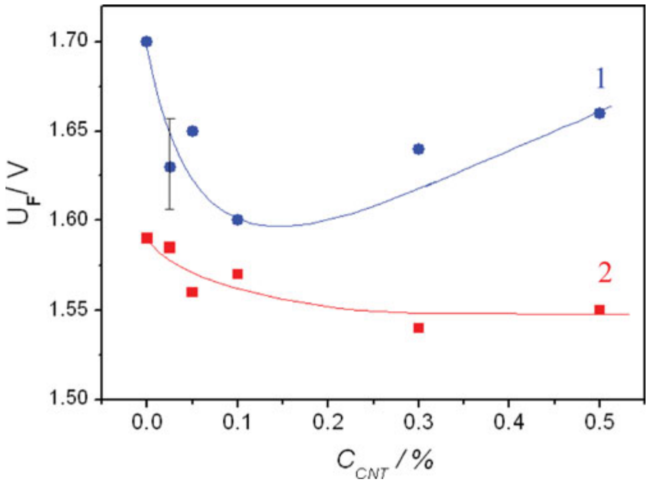

Figure 6. Fredericks threshold voltage vs. CNT concentration curves for the E7+CNTs (1) and E7+CNTs+LapO (2) series.

(0.1 wt%) samples. One can notice pronounced difference in the saturation values of transmittance, T_s. The lowest value is observed for the E7+CNT sample. In contrast, T_s for the E7+CNT (0.05 wt%)+LapO (0.1 wt%) sample is close to corresponding value for pure E7. The essential difference in T_s causes distinct difference in switching contrast, considered as a ratio T_s/T_0, where T_0 is the initial transmittance. The contrast value is essentially higher for the Laponite containing counterparts. Generally, changing of the contrast with concentration of CNTs is considerably weaker for the LapO assisted series. These features can be easily explained taking into account increasing of absorption and scattering loses by strengthening of aggregation of CNTs.

Figure 6 shows Fredericks threshold voltage, $U_F(c)$, as a function of concentration of CNTs. The $U_F(c)$ curve for the E7+CNT series demonstrates non-monotonic behavior; after initial decrease the curve goes into growth. The initial, descending part can be caused by shunting of near-electrode double electric layers, leading to higher actual voltage applied to LC bulk [6, 7] and the increase in dielectric anisotropy [5], while the ascending character can be attributed to essentially enhanced orientational elasticity in the samples with highly percolated structure of CNTs. The $U_F(c)$ curve for the E7+CNT+LapO (0.1 wt%) series shows monotonic decrease, caused by the above mentioned reasons and absence of percolation of CNTs.

4. Conclusion

In summary, the effect of organomodified Laponite on structure and electro-optic response of LC dispersions of CNTs is studied. It is shown that LapO promotes effective dispergation of CNTs in rather wide range of CNT concentrations ($c = 0$–0.1 wt.%). This apparently occurs due to high affinity of LapO to CNTs, resulting in haloing of the nanotubes by LapO platelets that prevents their effective interaction.

Improved dispersing of CNTs in presence of LapO leads to essential changes in electro- optic response. Reduced optical absorption in the samples with fine aggregates causes essential enhancement of electro-optic contrast, which approaches values typical for pure LC. Besides, insertion of LapO platelets enhances tendency to lowering of the Fredericks voltage by adding of CNTs to LC.

Acknowledgment

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