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# Carbon nanotubes doped liquid crystals: Robust composites with a function of electro-optic memory

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## ABSTRACT

This paper describes effect of electro-optic memory in the carbon nanotubes (CNTs) doped liquid crystals (LCs) and recent trends in optimization of these composites for practical use. The memory effect consists in irreversible increase of light transmittance through the homeotropically aligned layers of LC-CNTs composites placed between two crossed polarizers due to the electric field application cycle. The irreversibility of electro-optic response is caused by stabilization of LC planar alignment realized in the electric field by a network of CNTs acting as a spatially distributed aligning surface. This network reveals itself in percolation behavior of electric conductivity of LC-CNTs samples. By using nematic mixtures MLC6608 and MLC6609 from Merck developed for vertical alignment, a number of essential improvements of the LC-CNTs composites are obtained such as a room temperature operation, reduced controlling voltage and switching time. Efficiency of electro-optic memory of these composites was further doubled by doping LC with small amount of chiral agent. The developed samples give real application prospect to the memory type LC-CNTs composites, especially in the information displaying and storage systems based on the LC materials.

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## 1. Introduction

Due to a unique structure and high length-to-diameter ratio (typically, 500–1000), CNTs are characterized by extremely high anisotropy of physical properties. To utilize these properties in functional materials and devices the assembly and alignment of nanotubes should be thoroughly controlled. In particular, the alignment of CNTs is highly demanded for such applications as sensors, field emitters and nanoelectronics.

The methods of CNTs alignment can be divided in two groups. First of all, the alignment can be controlled in a process of synthesis. This can be, for example, achieved by growing nanotubes in nanopores [1], realizing very dense packaging of the growing tubes forcing them to align parallel to each other [2], creating directionality of the tube growth by electric field [3] or collimated flux of particles containing carbon [4].

However, many potential applications of CNTs require postsynthesis manipulation of CNTs including their alignment. The methods earlier proposed for this purpose are based on direct influence on individual nanotubes or their ensembles with mechanical stress, magnetic field, etc. [5,6]. Usually these methods are not very effective and/or suffer from different limitations.

Unique solution of this problem was recently suggested by using liquid crystals (LCs) [7]. Having molecular shape similar to CNTs, LCs perfectly incorporate CNTs into own structure. In the aligned LC layers the CNTs are aligned too and this alignment can be patterned by pattering alignment of LC host [8]. Furthermore, the alignment direction of CNTs can be easily driven by the LC reorientation in the external field [9]. Finally, by removing LC pure aligned CNTs can be obtained [7].

On the other hand, CNTs change essentially the viscoelastic [10], electrical [11,12] and electro-optical properties of liquid crystals [13,14] improving their potential for various applications. Besides, incorporation of CNTs in LC host leads to number of new effects. These results are summarized in several recent reviews [15–17].

Among the recently described effects there is an effect of electrooptic memory. It was observed for the suspensions of multiwalled CNTs in nematic LC ethoxybenzylidene-*p*-*n*-butylaniline (EBBA) with negative dielectric anisotropy [18,19]. The effect consists in irreversible homeotropic-to-planar alignment transition of LC–CNTs composites under the electric field. The memorized random planar state demonstrates bright appearance in the crossed polarizers. In the transmittance vs. voltage plot, it reveals itself in the residual transmittance  $T_m$  after the field is ramped down to zero. The induced memory state can be erased by the mechanical or thermal action on the suspension.

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The discovered effect of electro-optic memory attracts considerable application interest because of its potential application in the information displaying and storage systems based on the LC materials. It excels in simplicity of materials and electro-optic cells, low driving signals, and use of well established LCD technologies. However, further optimization of the LC-CNTs composites is needed for the above mentioned potential applications. First of all, LC EBBA is not suitable for practical use. This material is in a solid crystalline state at the ambient temperatures (the nematic mesophase is in the 36–77.5 °C temperature range) and thus it should be heated for operation in a LC state. It possesses low dielectric anisotropy ( $\Delta \varepsilon = -0.13$ ) that increases driving voltage. Finally, it reacts with water and oxygen and thus is unstable in atmosphere. The other problems of EBBA-CNTs composites are low efficiency of memory effect and long switching time.

This paper describes two stages of further optimization of memory type LC-CNTs composites. The first stage is connected with substitution of LC EBBA with more practical nematic mixtures from Merck. It yields composites operable at ambient temperatures and with substantially improved switching parameters. The second stage is aimed on maximization of memory efficiency and concerns LC composites with slight chirality. The combination of these approaches gives obvious improvement of the memory type LC-CNTs composites. The mechanisms of the enhanced memory are also discussed.

### 2. Experimental

# 2.1. Samples

In present studies, nematic mixtures MLC6608 and MLC6609 from Merck developed for a vertical alignment mode of LC displays have been used instead of nematic LC EBBA. These mixtures exhibit wide temperature range of nematic mesophase fully covering the range of room temperatures. The clearing temperatures of MLC6608 and MLC6609 are at 90 °C and 91.5 °C, respectively. The dielectric anisotropy of MLC6608 and MLC6609 mixtures,  $\Delta \varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ , where  $\varepsilon_{||}$  are permittivities of LC along and perpendicular to the alignment axis, are correspondingly -3.7 and -4.2.

The LCs were doped by chiral dopant (ChD) S811 from Merck ( $c_{ch} = 0-0.3 \text{ wt.\%}$ ) and subsequently mixed with multiwalled CNTs (SpetsMash, Russia) by using ultrasonic mixer. The concentration of CNTs, *c*, was varied in the range 0-1.0 wt.%. The used nanotubes were prepared from ethylene by the chemical vapor deposition method [20]. Typically, they had an outer diameter of about 15 nm and the length of about 5 µm. The samples with a zero concentration of chiral dopant were considered as the reference one when studying an influence of chiral dopant on the electro-optic performance.

The electro-optical cells were made from glass substrates containing patterned ITO electrodes. The electrode pattering was made to minimize breakdown probability, to exclude edge area with a glue path in dielectric measurements and to observe visually the contrast between the areas with initial and memorized alignment. The electrodes were coated with aligning layers of polyimide SE5300 (Nissan, Japan) developed for homeotropic alignment. The polyimide layers were rubbed by a fleecy cloth in order to provide a uniform planar alignment of LC in a field-on state. The cells were assembled so that the rubbing directions of the opposite aligning layers were antiparallel. A cell gap was maintained by 16  $\mu$ m glass spacers. The cells were filled by the LC–CNTs composites using a capillary method.

## 2.2. Methods

The electro-optical measurements were carried out using the experimental setup described in [21]. The cell was set between two crossed polarizers so that the angle between the polarizer axes and the rubbing direction was 45°. The sinusoidal voltage 0–60 V (at a frequency f=2 kHz) was applied to the cell. Two voltage switching

regimes were employed. To measure the transmittance vs. voltage curves, the voltage was stepwise increased from 0 to 60 V and then decreased back to 0. In turn, to estimate a switching time of the memory state, the voltage was abruptly increased to 30 V, kept at this value over definite time and then abruptly decreased back to zero.

In dielectric studies the parallel connected *R*–*C* circuit was used as an equivalent scheme of the cell and the *R* and *C* data were measured using the oscilloscopic method [22]. In these measurements the tested cell was subjected to electric voltage of triangle form with varied frequency and amplitude fixed at 0.25 V. Based on *R* and *C* data the values of the real (capacitive)  $\varepsilon'$  and imaginary  $\varepsilon''$  components of the permittivity  $\varepsilon = \varepsilon' + i\varepsilon''$  of the composites were calculated as functions of voltage frequency *f*. The  $\varepsilon'(f)$  and  $\varepsilon''(f)$  curves for selected concentration of CNTs are presented in Fig. 1. Based on  $\varepsilon''$  data the sample conductivity  $\sigma$  was determined using a formula

$$\sigma = 2\pi\varepsilon_0\varepsilon' f,\tag{1}$$

where  $\varepsilon_0$  is a dielectric constant. The frequency f = 50 Hz was used for this estimation. It fell in the range corresponded to linear part of double logarithmic plot of  $\varepsilon''(f)$  (Fig. 1b). This implied that conductivity in this range was frequency independent. At rather high CNTs concentration (c > 0.5 wt.%) this was, however, not the case, because of pronounced change of  $\varepsilon''(f)$  curve due to occurrence of new conductivity processes [12].

The structure of the composites was monitored by observation of the filled cells placed between two crossed polarizers, both by naked eye and with an optical polarizing microscope.



**Fig. 1.** Dielectric spectra  $\varepsilon'(f)$  (a) and  $\varepsilon''(f)$  (b) for pure LC MLC6608 and LC MLC6608 doped with CNTs (0.05 and 0.5 wt%).



**Fig. 2.** The transmittance vs. applied voltage curves for the cells filled with LC MLC6608 (a) and MLC6608–CNTs (c=0.05 wt.%) suspension (b). The arrows point directions of voltage ramping up and down.

# 3. Results and discussion

# 3.1. Memory of LC-CNTs composites

The effect of electro-optic memory in MLC6608–CNTs and MLC6609–CNTs composites was preliminarily detected in [19]. A present study is aimed on optimization of the memory response in these composites and clarification of underlying physical processes.

Since the results appeared to be quite similar for the MLC6608 and MLC6609 based composites, we will further present results for only MLC6608–CNTs series.

The transmittance *T* vs. applied voltage *U* curves for the MLC6608– CNTs (c = 0.05 wt.%) composite, typical for the composites of this sort, are presented in Fig. 2b. For comparison, Fig. 2a presents the T(U) curves for the reference sample containing neat LC MLC6608. The oscillations of T(U) curves are caused by a phase incursion higher than  $\pi/2$  appeared during the homeotropic-to-planar reorientation in an electric field. In contrast to neat LC, MLC6608–CNTs suspension demonstrates irreversible electro-optic response; instead of falling down to the initial value  $T_{0}$ , the sample transmittance keeps at the level  $T_m \gg T_0$  after the field is off. This state persisted over several months of our monitoring.

The memory efficiency was characterized by the memory parameter *M*:

$$M = \frac{T_m - T_0}{T_{\max} - T_0},$$
(2)

where  $T_{\text{max}}$  is a maximum value of transmittance (Fig. 2). Coefficient *M* appears to range from 0 to 1. For MLC6608–CNTs sample, M = 0.44, while for the neat MLC6608 sample M = 0.

According to measurements of T(U) curves, a memory state of the MLC6608–CNTs samples is induced at the voltages capable to reorient a major part of LC (U=6–8 V). This voltage is about one order of magnitude lower than the memory recording voltage for the EBBA–CNTs composites [18,19].

The change in transmittance for the MLC6608–CNTs samples is clearly evident by a naked eye; the samples become brighter in the areas subjected to the electric field cycle (Fig. 3b). In contrast, no any transmittance change is detected in the reference samples based on the neat LC (Fig. 3a). The microscopic observation of the lightened areas revealed islands of LC in a random planar state surrounded with the areas of homeotropic alignment (Fig. 4, b). This means that a visual lightening is associated with a partial stabilization of the state of random planar alignment realized in an electric field.

The T(U) curves were measured for a series of LC–CNTs composites with various concentrations of CNTs, c, and based on this results memory parameter M was estimated as a function of c. The M(c) curve for the MLC6608–CNTs series is presented in Fig. 5. There is evident that M steeply grows with CNTs concentration reaching saturation at  $c \approx 0.1$  wt.%.

Fig. 5 also presents a concentration dependence of electric conductivity  $\sigma$ . In full accordance with the M(c) dependence, the  $\sigma(c)$  curve rapidly grows on the initial stage (at c = 0-0.1 wt.%) and slows down at higher concentrations of CNTs. This behavior reflects percolation transition in the system caused by formation of continuous network of CNTs [11,12]. At low concentration of CNTs (c < 0.01 wt.%)



**Fig. 3.** The cells filled with LC MLC6608 (a), MLC6608–CNTs (c=0.05 wt.%) (b) and MLC6608–ChD–CNTs (c=0.05 wt.%,  $c_{ch}$ =0.1 wt.%) (c) suspensions viewed between a pare of crossed polarizers. The rectangular areas in the middle of the cells correspond to pixels preliminarily subjected to cycle of electric field (30 V, f=1 kHz, 20 s).

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**Fig. 4.** Microphotographs of two cells filled with MLC6608–CNTs (*c* = 0.05 wt.%) (a, b) and MLC6608–ChD–CNTs (*c* = 0.05 wt.%, *c*<sub>ch</sub> = 0.1 wt.%) (c, d) composition, respectively. The photos (a) and (c) show the cells before a field application, while the photos (b) and (d) show the same cells after the field application cycle (30 V, 1 kHz, 20 s).

the nanotubes predominately exist in a form of isolated aggregates and the main type of electrical conductivity is the ionic conductivity of LC phase. A further growth of *c* leads to growing of CNTs aggregates and formation of their continuous network. This creates new conductivity channel associated with nanotubes. Within this channel the charges travel along the single nanotubes. The charge transfer between the single nanotubes seemingly occurs due to a hoping mechanism and direct transfer in case of tightly connected nanotubes [11,12]. Since quasimetallic conductivity of CNTs is much higher than conductivity of LC, the  $\sigma(c)$  curve sharply increases in the concentration range of nanotubes corresponding to their percolation transition. Note that a sharp increase of the memory efficiency *M* occurs in the same concentration range. This gives a ground to suggest that, similarly to



Fig. 5. Dependences of memory parameter *M* and conductivity  $\sigma$  of MLC6608–CNTs suspensions on the CNTs concentration.

LC-aerosil composites [23,24], a nanotube network plays an important role in stabilization (memorization) of the LC alignment state realized in the electric field. This network acting as a spatially distributed surface in the LC host overcomes the alignment force of the boundary substrates between which the layer of LC suspension is confined.

The percolation behavior of CNTs allows us to assume that fine CNT network exists in parallel with massive CNT aggregates visible in optical microscope. The big aggregates decompose under the electrohydrodynamic (EHD) flows developing in LC phase and thus feed the CNT network. This is confirmed by strong (in several order of magnitude) increase of electric conductivity detected after keeping samples in EHD regime [18,19]. The EHD flows were observed in the MLC6608 and MLC6609 based composites too, but their intensity was considerably lower than in the EBBA based samples. Usually they develop in the vicinity of CNTs aggregates. These peculiarities can be assigned to lower concentration of ionic impurities in the MLC6608 and MLC6609 based composites and the enhanced concentration of these impurities in the sites enriched with CNTs. Fortunately, dispersion of CNTs in MLC6608 and MLC6609 is better than in EBBA so that the fine nanotube network is formed even without intensive EHD flows.

A switching time of the memory state was measured by applying a U-type pulse of the voltage 30 V (2 kHz) with a variable duration  $\tau$ . The *M* vs.  $\tau$  curve for the sample MLC6608–CNTs (c=0.05 wt.%) is presented in Fig. 6. According to this curve, switching time of the memory state is about 2 s. This is 25 times faster than for the EBBA–CNTs composites [15]. The value of  $\tau$  slightly grew with a further increase of CNTs concentration.

# 3.2. Memory of LC-CNT composites with induced chirality

According to M(c) curve (curve 1 in Fig. 5), a saturation value of memory is about 0.55 that roughly is just a half of its highest possible value. To approach this maximum we induced chirality in the LC

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**Fig. 6.** Memory parameter *M* as a function of voltage application time  $\tau$ . *U*=30 V, *f*=1 kHz.

material assuming that the twisting force will additionally stabilize a state of random planar alignment realized in an electric field. In these experiments we used composites with c = 0.05 wt.% even though the value of *M* at this concentration of nanotubes is somewhat smaller than the maximal value (0.44 vs. 0.55). It was motivated by several

reasons, such as increased breakdown probability [25] and enhanced light scattering at higher concentrations of CNTs.

At first concentration of chiral dopant,  $c_{ch}$ , was optimized. The increase of  $c_{ch}$  strengthens twisting tensions in the LC. Fig. 7 demonstrates that at  $c_{ch} \le 0.1$  wt.% anchoring forces of boundary substrates satisfactorily balance these twisting tensions thus stabilizing homeotropic alignment. At  $c_{ch} \ge 0.15$  wt.%, the anchoring forces cannot restrain the twisting force anymore that leads to formation of various helical structures. At  $c_{ch} = 0.15$  wt.% the filamentary texture is formed. At  $c_{ch} \ge 0.2$  wt.% it transforms in the periodic fingerprint texture with a period inversely proportional to ChD concentration and twisting power of the chiral dopant. The concentration  $c_{ch} = 0.1$  wt.% was selected for further preparation of LC–ChD–CNT samples. It was the maximal value at which a uniform homeotropic alignment was preserved and formation of helix pitch was suppressed.

The T(U) characteristics for the MLC6608–ChD–CNTs sample, as well as for the reference MLC6608–ChD sample are given in Fig. 8. As is evident, the MLC6608–ChD sample demonstrates reversible response. In turn, transmittance of MLC6608–ChD–CNTs sample changes irreversibly showing high residual value in a zero field. The memory parameter for this sample estimated according to formula (2) is M=0.82, i.e. twice higher than the value for corresponding MLC6608–CNTs sample with equal concentration of nanotubes.

The strengthening of the memory effect in the samples doped by ChD can also be seen clearly by a naked eye (Fig. 3). The observation in



**Fig. 7.** The cells filled with MLC6608–ChD compositions viewed between a pare of crossed polarizers. The chiral dopant concentration is 0, 0.1, 0.15 and 0.2 wt% in (a), (b), (c) and (d), respectively. The cases (1) and (2) correspond to viewing by a naked eye and in polarizing microscope (×100 magnification).

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Fig. 8. The transmittance vs. applied voltage curves for the cells filled with MLC6608-ChD (c<sub>ch</sub>=0.1 wt. %) (a) and MLC6608-ChD-CNT (c=0.05 wt.%, c<sub>ch</sub>=0.1 wt.%) (b) compositions. The arrows point directions of voltage ramping up and down.

polarizing microscope demonstrates that in contrast to island structure typical for MLC6608-CNT samples the MLC6608-ChD-CNTs samples demonstrate continuous planar alignment in the area pretreated with an electric field (Fig. 4). This explains the increased memory efficiency of the LC-ChD-CNT samples.

Switching time of the memory state was estimated to be about 3 s. This means that a minute amount of ChD did not influence essentially switching characteristics of LC-CNTs composites.

As we previously assumed, the enhanced affinity of LC-ChD-CNT samples to planar alignment can be explained by an enhancement of forces resulting in the planar alignment. In the LC-ChD-CNT samples. the force associated with a CNT network is magnified by a twisting force, which eventually destroys homeotropic alignment. It worth mentioning that, in spite of the memory enhancement of LC-CNT samples, the twisting force by itself does not cause a memory effect (the case of LC-ChD samples, Fig. 8a). This suggests that the described memory effect is an intrinsic feature of CNTs containing samples.

## 4. Conclusions

In summary, this paper suggests several important steps towards optimization of the memory types LC-CNTs composites for the practical use. It is demonstrated that replacement of LC EBBA for which the memory effect was discovered by the commercial LC mixtures MLC6608 and MLC6609 developed for the homeotropic-to-planar switching in LCDs gives number of important advantages such as a room temperature operation, reduced driving voltage and switching time. On the other hand, the electro-optic memory of LC-CNTs suspensions can be essentially (at least by a factor of 2) enhanced by doping them by small amount of chiral agent. This occurs due to a twisting tensions caused by the chiral dopant, which, together with the elastic force of CNTs network, maintains the planar alignment state of LC formed in an electric field. The realized advances give a real application prospect to the memory type LC-CNTs composites, especially in the information displaying and storage systems based on the LC materials.

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## References

- [1] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, Science 283 (1999) 512.
- X. Wang, Y. Liu, D. Zhu, Chem. Phys. Lett. 340 (2001) 419.
- [3] V.I. Merkulov, A.V. Melechko, M.A. Guillorn, M.L. Simpson, Appl. Phys. Lett. 80 (2002) 4816.
- S. Orlanducci, V. Sessa, M.L. Terranova, M. Rossi, D. Manno, Chem. Phys. Lett. 367 [4] (2003) 109.
- T. Hertel, R. Martel, P. Avouris, J. Phys. Chem. B 102 (1998) 910.
- [6] B.W. Smith, Z. Benes, D. Luzzi, J.E. Fischer, D.A. Walters, M.J. Casavant, J. Schmidt, R.E. Smalley, Appl. Phys. Lett. 77 (2000) 663.
- M.D. Lynch, D.L. Patrick, Nano Lett. 2 (2002) 1197. [7]
- I. Dierking, G. Scalia, P. Morales, D. LeClere, Adv. Mat. 16 (2004) 865. [8]
- I. Dierking, K. Casson, R. Hampson, Jpn. J. Appl. Phys. 47 (2008) 6390. [9]
- S.Y. Jeon, S.H. Shin, J.H. Lee, S.H. Lee, Y.H. Lee, Jpn. J. Appl. Phys. 46 (2007) 7801. [10] N. Lebovka, T. Dadakova, L. Lysetskiy, O. Melezhyk, G. Puchkovska, T. Gavrilko, [11] J. Baran, M. Drozd, J. Mol. Struct. 877 (2008) 135.
- [12] A. Kovalchuk, L. Dolgov, O. Yaroshchuk, Semicond. Phys. Quantum Electron. Optoelectron. 11 (2008) 337 http://journal-spqeo.org.ua/n4\_2008/v11n4-08-p337-341.pdf.
- W. Lee, C.-S. Chiu, Opt. Lett. 26 (2001) 521. [13]
- W. Lee, C.-Y. Wang, Y.-C. Shih, Appl. Phys. Lett. 85 (2004) 513. [14]
- J.P.F. Lagerwall, G. Scalia, J. Mater. Chem. 18 (2008) 3277 [15]
- [16] M. Rahman, W. Lee, J. Phys. D. Appl. Phys. 42 (2009) 063001.
- [17] H. Qi, T. Hegmann, J. Mater. Chem. 18 (2008) 3288.
  [18] L. Dolgov, O. Yaroshchuk, N. Lebovka, Colloid J. 73 (2009) 603.
- [19] L. Dolgov, O. Yaroshchuk, N. Lebovka, Mol. Cryst. Liq. Cryst. 496 (2008) 212.
- [20] A.V. Melezhyk, Y.I. Sementsov, V.V. Yanchenko, Appl. Chem. 78 (2005) 938. [21] O. Kovalchuk, S. Zakrevska, O. Yaroshchuk, U. Maschke, Mol. Cryst. Liq. Cryst. 368A (2001) 129.
- A.J. Twarowski, A.C. Albrecht, J. Chem. Phys. 20 (1979) 2255. [22]
- M. Kreuzer, T. Tschudi, R. Eidenschink, Mol. Cryst. Liq. Cryst. 223 (1992) 219. A. Glushchenko, H. Kresse, V. Reshetnyak, Y. Reznikov, O. Yaroshchuk, Liq. Cryst. [24] 23 (1997) 241.
- [25] V. Jayalakshmi, S. Krishna Prasad, Appl. Phys. Lett. 94 (2009) 202106.