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Original paper

NEW WAY TO CREATE HIGH-SPEED LCD'S BASED ON THE USE OF MODIFIED NANOMATERIALS

VALERI I. LAPANIK, ANATOL P. LUGOVSKY, SERGEI N. TIMOFEEV

A. N. Sevchenko Institute of Applied Physical Problems of Belarusian State University, Minsk, Republic of Belarus

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Abstract. The object of research is liquid crystal materials of the nematic and smectic types containing modified nanoparticles of detonation diamonds, partially reduced graphene and nanoclay. The purpose of the work is the development of new functional materials with improved physicochemical and electro-optical characteristics. During the study, methods for chemical modification of the surface of nanoparticles were developed; the mesomorphic, dielectric and electro-optical properties of nematic and ferroelectric compositions, doped with modified nanomaterials are studied. It has been established that the effect of modified nanodiamonds on the mesomorphic, dielectric, and electro-optical properties of liquid crystals is large and depends on the size of these particles and the type of grafted functional groups. Small-sized diamond nanoparticles do not significantly affect the properties of liquid crystals. At the same time, conglomerates based on nanodiamonds with a diameter of about 50–100 nm can increase or decrease the dielectric anisotropy and the response time of liquid crystals by 1,5–2,5 times, depending on the polarity of the functional groups. It has been experimentally shown that the addition of a small amount of graphene flakes to nematic and ferroelectric liquid crystals can significantly improve the electro-optical response time (up to 2 times depending on concentration). There is a decrease in threshold (by 7–30 %) and saturation voltages (by 11–31 %). For ferroelectric liquid crystals, the addition of graphene leads to an increase in the tilt angle and a spontaneous polarization.

Keywords: liquid crystal composites, dielectric constant, electro-optical parameters, detonation nanodiamonds, graphene, nanoclay.

Conflict of interests. The authors declare no conflict of interests.

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Introduction

Liquid crystals (LCs) currently play a very important role in nanoscience and nanotechnology. Nanoscale particles (NPs) do not cause significant distortions in the LCs. Therefore, various nanomaterials were dispersed in LCs to improve their physical and electro-optical properties. Liquid crystal suspensions with metal, dielectric, semiconductor [1–3], as well as ferroelectric nanoparticles were studied. In particular, it was reported that the doping of nematics with ferroelectric NPs increases dielectric and optical anisotropy, improves the electro-optical response. Suspensions of para-

and ferromagnetic particles in nematics are promising candidates for magnetically tunable structures, doping ferroelectric LCs with metal nanoparticles and silicon dioxide nanoparticles can increase spontaneous polarization and dielectric constant and reduce switching times [4–5]. Gold NPs were also used to extend the temperature range of the cholesteric blue phases [6]. Finally, the distribution of semiconductor quantum dots in smectic LC polymers makes it possible to achieve positional ordering of nanoscale particles [7–8].

The aim of our work is to attach functionalized organic groups to the surfaces of various nanomaterials and study the physical and electro-optical properties of nanocolloidal dispersions of modified in this way detonation nanodiamond, partially reduced graphene oxide and nanoclay in some nematic and ferroelectric LCs, respectively, and compare them with the properties of pure liquid crystals.

Methods

For research, test cells with a cell gap of 4–8 μm were made. The thickness of the test cells was measured by the interferometric method using a spectrometer. The alignment quality and morphology of the samples were determined by observation in a polarizing microscope (ML9400, MEIJI Techno Co., LTD, Japan) in transmitted white light with crossed polarizers. Dielectric measurements were performed using a HP 4192A LF Impedance Analyzer at a frequency of 1 kHz. All measurements were carried out at a room temperature of 20 °C. Electro-optical parameters were measured using a setup consisting of the following functional parts: light source, polarizer, liquid crystal cell, photoelectric light flux converter, IOtech DaqBoard/2000 multifunction data acquisition board, PC and software for control and graphical presentation of measurement results.

Results, Discussion

Ultradispersed diamond or detonation nanodiamond (DND) − nanodiamond produced by the explosion in a closed volume of condensed explosives with a negative oxygen balance. This is a typical nanomaterial with an average grain size of 4–6 nm, having a polyhedral shape that is close to spherical. Each DND particle consists of a superhard and inert diamond core coated with an amorphous carbon shell, and of various functional groups that determine the chemical state of the surface of the DND. The presence of a large number of functional surface groups leads to the fact that DNDs are prone to aggregation, and typical commercial suspensions of DNDs contain larger aggregates up to several hundred nanometers in size (which can withstand ultrasonic processing).

Detonation nanodiamonds were obtained by detonation synthesis, followed by purification of the charge from other allotropic modifications of carbon by oxidation with nitric acid. For the functionalization of nanodiamonds, we focused on the attachment of several carboxyl groups to the DND surface. Activation of COOH-surface functional groups made it possible to attach various organic tails [9].

In the experiments, both homogeneous nanoparticles with a modified surface of 4–6 nm (N-1) and aggregates with an average size of 50 nm (N-2) and 100 nm (N-3), based on 4-cyano-4'-diphenyl ester DND, as well as aggregates based on 4-octylphenyl ester DND, approximately 50 nm in size, (N-4) were used. For the experiments, three base (parent) nematic liquid crystalline (NLC) mixtures, containing various polar components, were prepared: M-1 based on compounds with a CN-terminal group, M-2 based on compounds with an OCF_3-terminal group and M-3 based on compounds with a NCS-terminal group.

To prepare suspensions, a small amount of nanodiamond powder was first dispersed in propanol and stirred using a micro-homogenizer with a diameter of 5 mm at 35000 rpm for two hours, followed by sonication in an EMMI-20 ultrasonic cleaner for 1,5 hours. This process reduces the tendency to aggregation, creating a uniform mixture of DND + propanol. Next, the base nematic compositions were added to the mixture of DND and propanol and stirred on a vortex mixer for 0,5 h at 2000 rpm, then sonicated for 1,5 h. Further, propanol was slowly evaporated at a temperature of 70 °C and was degassed under vacuum (1–3 mbar) for one hour. For compliance, “pure” liquid

crystal compositions were treated in the same manner, in particular dissolved in propanol, followed by slow evaporation and degassing.

It was found that the effect of DND on the mesomorphic, dielectric and electro-optical properties of liquid crystals is large and depends on the size of the nanoparticles and the type of attached functional group. As expected, small nanoparticles (4–6 nm) do not have a significant influence on the physical properties of NLCs, regardless of the magnitude of their dielectric anisotropy. The addition of such nanoparticles slightly increases the phase transition temperatures of the NLC. At the same time, larger aggregates (50–100 nm) can, depending on the polarity of the attached functional groups, increase or decrease the dielectric anisotropy and the switching time of the NLCs up to 1,5–2,5 times (table 1).

Table 1. Effect of DND aggregates (N-4) on the value of dielectric constant, dielectric anisotropy and electro-optical parameters of the compositions

Mixture	$\varepsilon_{\|\|}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	V_{10}, V	V_{90}, V	τ_{on}, ms	τ_{off}, ms
M-1	12,1	3,2	8,9	1,65	2,49	1,1	47,9
NHL-4	12,6	2,6	10,0	1,46	2,24	0,9	42,0
M-2	15,2	4,8	10,4	1,82	2,44	1,8	40,3
NHL-8	15,7	4,4	11,3	1,64	2,18	1,1	28,3

Doping the LCs with 4-cyano-4'-diphenyl ester DND and 4-octylphenyl ester DND reduces (Fig. 1) and increases, respectively, the dielectric anisotropy and the switching time of the NLCs. The change in dielectric anisotropy and switching time is proportional to the concentration of DND particles.

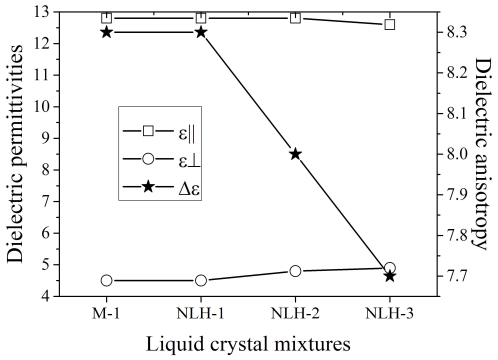


Fig. 1. Dependence of dielectric permittivity and dielectric anisotropy of M-1 on the size of the nanoparticles

Graphene is a layered structure or a one-atom-thick planar nanosheet of sp^2-bonded carbon atoms packed in a honeycomb crystal lattice.

Studies of LC + graphene suspensions or composites based on LCs and graphene oxide are quite rare today. For the E7 nematic mixture (Merck), an increase in the threshold voltage was reported [10], while for a 5 CB + graphene suspension a decrease in the orientational order was shown [11]. More recently [12], a decrease in switching time and a decrease in rotational viscosity has been reported for the 5 CB + graphene system. On the other hand, for the zero-dimensional derivative of graphene, graphene quantum dots, an improvement in electro-optical properties and a decrease in the threshold voltage are shown [13].

For research, we used partially reduced graphene oxide samples provided by colleagues from the Heilongjiang Institute of Petrochemistry (HINH, Harbin, China).

For experiments with graphene, nematic (NLC + graphene) and smectic (FLC + graphene) suspensions were prepared. The suspensions of LC + graphene were prepared similarly to the preparation of suspensions of NLC + DND.

Doping of graphene in nematic compositions lowers the clearing point. However, as the measurement results show, there is an optimal concentration of graphene (about 0,5 wt %), above which the temperature does not change by more than 1 %. It was experimentally shown that doping a small amount of graphene flakes into nematic and ferroelectric liquid crystal materials can significantly improve the electro-optical response time (up to 2 times depending on concentration). The threshold voltage also decreases by 7–30 % and the saturation voltage by 11–31 %. This is due to the strong influence of graphene on the visco-elastic properties of NLC

compositions, in particular, on rotational viscosity. Obviously, a significant decrease in rotational viscosity is associated with a decrease in the number of free ions in the mixture and, possibly, with an increase in the anchoring energy of LC molecules with the alignment layer due to the doping of graphene flakes.

The measurement results (Fig. 2) clearly indicate that a cell filled with FLC + graphene (GF-1, GF-4) switches much faster than a cell filled with "pure" ferroelectric LC (F-1 and F-4), respectively.

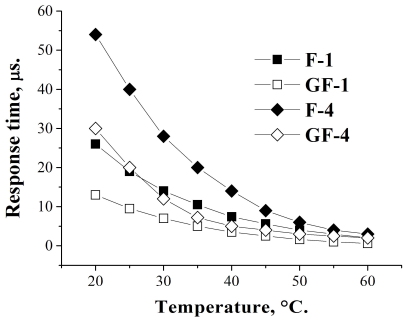


Fig. 2. Dependence of response time on temperature

The optical response time τ of an FLC is proportional to the rotational viscosity and inversely proportional to spontaneous polarization:

$$\tau = \frac{\gamma}{P_s E}, \quad (1)$$

where γ − rotational viscosity of the FLC; P_s − spontaneous polarization; E is the applied electric field.

According to this formula, an increase in the spontaneous polarization and a decrease in the rotational viscosity will result in a faster optical response with a constant applied voltage E. For this reason, we measured the spontaneous polarization P_s of "pure" FLC mixtures (F-1, 2, 3, 4) and mixtures of FLC + graphene (GF-1, 2, 3, 4). The results are presented in table 2.

Table 2. Physical and electro-optical parameters of ferroelectric LC doped with graphene

Composition	P_s, nC/cm^2	Tilt angle, deg	Response time, μs
F-1	10	23	22,0
GF-1	13	28	12,0
F-2	9	23	220
GF-2	12	27.5	92
F-3	52	20	9,8
GF-3	58	22,5	7,2
F-4	13	23	54,0
GF-4	18	25	28,0

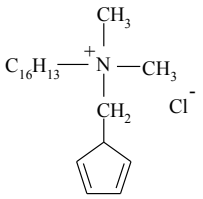
Samples of smectic LC doped with graphene are characterized by large spontaneous polarization P_s in comparison with "pure" FLC. This result indicates a structural modification, especially in the order parameter, of the chiral smectic phase C due to the addition of graphene flakes. Since the order parameter in ferroelectric liquid crystals is proportional to the spontaneous electric polarization of the crystal, a higher value of P_s proves an improvement in ordering in the smectic C* phase.

Thus, it was established that for ferroelectric liquid crystals doping of graphene leads to an increase in the tilt angle in the LC layer and an increase in spontaneous polarization, which is associated with an improvement in both the positional and tilted orientational ordering of the molecules in the LC layers due to aromatic $\pi - \pi$ interactions between the benzene rings of the LC molecules and the honeycomb structure of graphene.

Nanoclay is a very promising candidate for the creation of liquid crystal composites due to the high cation exchange capacity, very small plate size and large surface area. In addition, the chemical nature and porous structure of the surface of the nanoclay, which determine the strength of adhesion with liquid

crystal molecules, can be easily modified, which allows increasing the stability of LC suspensions.

As a component for the creation of organophilic nanostructures, natural aluminosilicate with a layered structure − montmorillonite was used. In its natural state, montmorillonite has a two-layer structure consisting of plates with transverse dimensions of 70–150 nm and a thickness of 1 nm. Isomorphic substitution within the layers (Mg_2+ replaces Al_3+ in octahedral or Al_3+ replaces Si_4+ in tetrahedral structures) generates negative charges that are electrostatically balanced by alkali or alkaline earth metal cations located in the interlayers. Inorganic cations inside the interlayers may be replaced by other cations. Substitution with cationic surfactants, such as bulk ammonium and phosphonium ions, increases the space between the layers, reduces the surface energy of the clay and gives the clay surface a hydrophobic character. Quaternary ammonium salts of the formula I and II were used as a modifier of the nanoclay.



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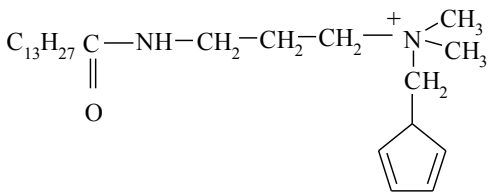

II

Synthesis of organoclays was carried out by the method of replacing alkali metal cations located in the interplanar layers of the mineral. The aqueous dispersion of montmorillonite was alkalized to pH = 8,5 with sodium carbonate and treated at a temperature of 40 °C with an aqueous solution of quaternary salts I or II. As a result, as organoclay is formed, due to its hydrophobicity, it floats to the surface of the water. The upper layer was collected, wring out and dried.

The suspensions of FLC + nanoclay were prepared similarly to the preparation of suspensions of NLC + DND and FLC + graphene.

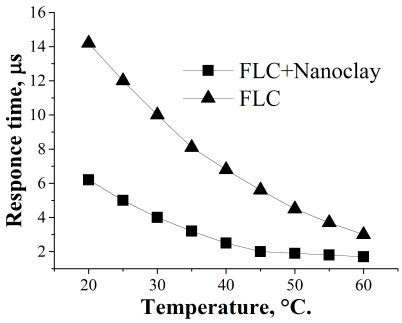

Fig. 3. The response time of FLCs and FLCs doped with modified nanoclay

Fig. 3 and table 3 show the results of measurements of the main physical and electro-optical parameters of FLC + nanoclay composites. Samples of FLCs doped with modified nanoclay at concentrations up to 2,2 wt % are characterized by larger values of the spontaneous polarization and tilt angle compared to "pure" FLCs.

A significant decrease in the response times, observed in experiments, is obviously associated with a significant decrease in rotational viscosity upon addition of modified nanoclay.

Table 3. Effect of modified nanoclay on physical and electro-optical parameters of FLC

Mixture	SmC* range, °C	P_s, nC/cm^2	Tilt angle, deg	t_{rise}, µs	t_{decay}, µs
FLC	61	27	26	12,8	26,2
FLC+Nanoclay (0,2 %)	61,6	28	26,5	10	21
FLC+Nanoclay (0,7 %)	62,3	30	28	7,2	16
FLC+Nanoclay (1,2 %)	62,8	31	28,5	6,6	14
FLC+Nanoclay (1,7 %)	63,1	32	29	6,2	13
FLC+Nanoclay (2,2 %)	63,1	32	29	6,2	13

Conclusion

It was established that the influence of modified DND on the mesomorphic, dielectric, and electro-optical properties of liquid crystals is large and depends on the size of the nanoparticles and the type of grafted functional groups. Nanoparticles of small size (4–5 nm) do not significantly affect the parameters of LCMs. At the same time, the conglomerates based on DND of about 50 nm or about 100 nm in diameter can increase or decrease the dielectric anisotropy and the response time of LCMs to about 1,5–2,5 times, depending on the polarity of the tails.

It has been experimentally shown that the addition of a small amount of graphene flakes to the nematic and ferroelectric liquid crystal material can significantly improve the electro-optical response time (up to 2 times depending on the concentration). The threshold voltage also decreases by 7–30 % and the saturation voltage by 11–31 %, due to the strong influence of graphene on the viscoelastic properties of LC compositions, especially on rotational viscosity. Obviously, a significant decrease in rotational viscosity is associated with a decrease in the number of free ions in the mixture and, possibly, with an increase in the anchoring energy of LC molecules with the alignment surface due to the addition of graphene flakes.

For ferroelectric liquid crystals, the addition of graphene leads to an increase in the tilt angle in the LC layer and an increase in spontaneous polarization, which is associated with an improvement in both the positional and tilted orientational ordering of the molecules in the LC layers due to aromatic $\pi - \pi$ interactions between the benzene rings of the LC molecules and the honeycomb structure of graphene.

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Authors contribution

Lapanik V.I carried out scientific management of the research, carried out the formulation of research tasks and the interpretation of experimental data.

Lugovsky A.P. developed methods for chemical modification of the surface of nanoparticles, the synthesis of modified nanomaterials.

Timofeev S.N. performed experimental studies, analysis and synthesis of data obtained as a result of the research.

Information about the authors

Lapanik V.I., Head of the Laboratory of Condensed Matter Optics A.N. Sevchenko Institute of Applied Physical Problems of Belarusian State University.

Lugovsky A.P., Leading Researcher of the Laboratory of Spectroscopy A.N. Sevchenko Institute of Applied Physical Problems of Belarusian State University.

Timofeev S.N., Senior Researcher of the Laboratory of Condensed Matter Optics A.N. Sevchenko Institute of Applied Physical Problems of Belarusian State University.

Address for correspondence

220045, Republik of Belarus,
Minsk, Kurchatova st., 7,
A.N. Sevchenko Institute of Applied
Physical Problems of Belarusian State University
tel. +375-17-398-43-82;
e-mail: lapanik@bsu.by;
lapanik@yahoo.com
Lapanik Valeri Ivanovich