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Influence of modified detonation nanodiamonds on electro-optical properties of nematic liquid crystals

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Abstract. To modify the structure of detonation nanodiamonds (DNDs) several carboxylate groups were added to DNDs. Activation of COOH-surface functionalized groups allowed attaching of various organic tails to molecules. It was investigated that dielectric and electro-optical properties of nematic liquid crystalline mixtures (LCMs) doped with modified DNDs (MDNDs). It is established that the effect of DNDs on mesomorphic, dielectric and electro-optical properties depends on the size of nanoparticles (NPs) and the type of tail-like organic molecules grafted to DNDs. It is found that NPs of a small size (5–6 nm) do not significantly affect on the parameters of LCMs. At the same time conglomerates of a larger size (50 and 100 nm) depending on the tails polarity can increase or decrease the dielectric anisotropy and response time of LCMs in about 1.2–1.4 times.

1. Introduction

Dispersion of different NPs aimed to improve electro-optical properties of liquid crystals (LCs) have attracted attention of many researchers in recent years [1-4]. The influence of metal particles Ag, MoS and semiconductor particles MnO_2, WS_2 on ferroelectric LCs (FLCs) has been reported lately. According to the research, that was conducted, the rise and decay times of FLCs where Ag metal nanowires had been added did not significantly differ from those of the original FLCs (the nanowire size is about 40-70 nm) [1]. Ag NPs didn’t improve the characteristics of FLCs due to the low activity of Ag which is located almost in the end of the series of chemical activity of metals.

The research of Ni particles with a size of 2-8 nm and a concentration of 0.5% showed that the optical transmittance improved and the optical response time of FLCs reduced [2]. The authors suppose that the improvement of properties of FLCs doped with metal NPs is due to the appearance of particles dipole moment, which is explained by their interaction with LC molecules (the dipole moment of Ni NPs is 10 Debye [2]). When voltage was applied, Ni NPs aligned with force lines, attracting LCs, which affected on the temporal characteristics of LCs and promoted better light transmission.

As a result of doping nematic LCs (NLCs) with Ti NPs the optical response time reduction can also be observed [4]. If Ti NPs doping concentration ranges from 0.1 to 1.0 wt% and the size of Ti NPs is 100 nm, then the optical response time reduces twice from 15 ms to 7.5 ms. The authors of this paper propose two mechanisms of Ti NPs interaction with NLC molecules. In the first case though there is no electric field in the conductive metal particle, the electric field density around it increases, which makes NLC molecules move faster. In the second case the screen effect is suppressed due to the presence of ionized impurities in the NLC. Adsorption of impurities around Ti NPs in the absence of the electric field leads to their neutralization, reducing the optical response time.

Nanodiamonds are unique carbon NPs because of their intrinsic hydrophilic surface. The surface contains a complex array of chemical groups, including carboxylic acids, esters, ethers, lactones and amines. Alteration of DNDs surface can lead to a bunch of chemical properties, that can be compared with nanoscale diamond powders, since almost 15% of all atoms in the DND primary particle are located on the surface and, therefore, can dissolve. DNDs show potential for applications in energy storage, composites and catalysis. Besides, DNDs can be used in electroanalysis, electrochemical doublelayer capacitors and batteries. Other potential is biomedical applications including usage of nanodiamonds as supporters for solid-phase peptide synthesis and as sorbents for detoxification and separation [5].

We were interested in characterizing suspensions using a special class of nanodiamond materials having a size of 4–5 nm often called in literature as ‘ultradispersed diamonds’ or ‘detonation nanodiamonds’ produced *via* detonation of carbon-containing explosives. Complex research of the effect of modified DNDs on electro-optical characteristics of NLCs was carried out. In the continuation of studies [6] and to test the impact of such NPs on the parameters of compositions based on compounds with different polar groups compositions based on compounds with a isothiocyanates polar group (NCS) and with cyano group (CN) and F atoms were investigated. DNDs of various doping concentrations were dispersed in NLCs cells. The dependence of mesomorphic, dielectric and electro-optic properties of LCs on the NPs size and a type of organic molecules grafted to DNDs was shown.

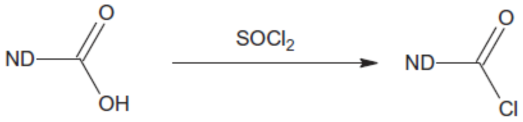
2. Materials and methods

2.1. Ozonolysis

The DNDs suspension with a concentration of 5 g per liter (water) was poured into the apparatus, producing ozone at a flow rate of 10–15 ml/second, leading to 3–5% of ozone in the gas mixture. Before using, the prepared ozone was purified by means of a concentrated sulphuric acid in the flask and then it was passed through granulated potassium hydroxide. The latter was able to oxidize the intermediate-formed ozonide into a carboxyl group, whereas hydrolysis of the ester bond led to the formation of a carboxylate group. About 0.1 g of caustic soda was added to the water suspension of DNDs under constant stirring. Thereafter, ozone was passed through the suspension for 2 hours (more than 300 times). The final oxidation was reached by adding 30 ml hydrogen peroxide (30%) while incubating the mixture for 1 hour. Then, 10% aqueous hydrochloric acid was added until 2–6 pH acidification was reached. Finally, the upper clear layer was carefully decanted and the precipitate was centrifuged with subsequent washing with water 8–10 times. Residual water was removed by washing the precipitate with dioxane two times. After drying overnight at room temperature, the content of carboxyl groups was determined. This procedure caused 2-3 times increase of the carboxylate groups content. The molecular weight (excluding the sorbed water) was between 1300 and 1560, depending on the kind of experiments

2.2. The activation of COOH-surface functional groups

The activation of COOH-surface functional groups was done by acylchloride obtained by boiling nanodiamonds and $SOCl_2$:

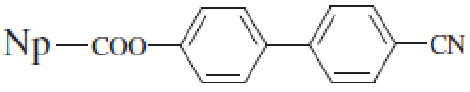


2.3. Acid chloride DND

2 ml thionylchloride was added to 1 g suspension of ozonized DNDs in 30 ml dichloroethaneand it was heated for 1 hour under reflux. After cooling, the product was separated by decantation and washed with dichloromethanetwo times.

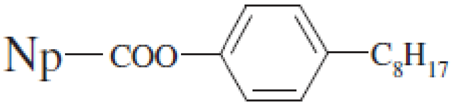
2.4. Dicyano-4-4'-diphenyl DND

A mixture of 1 g DND chloride and 0.1 g 4-hydroxy-4′-cyanobiphenyl dissolved in 20 ml pyridine and was heated at 25°C for 3 hours. Then, the ester of the DND was separated and washed with distilled water, with dimethylformamide (DMF) two times and with dichloromethane three times. The resulting ester was dried in the air at 60°C for 3 hours.



2.5. 4-Octylphenyl DND

A mixture of 1 g chloride of the DND and 0.1 g of 4-octylphenol dissolved in 20 ml of pyridine was heated at 25°C for 3 hours. Then, the ester of DND was separated and washed with distilled water, twice with DMF and three times with dichloromethane. The resulting ester was dried in the air at 60°C for 3 hours.



2.6. Preparation of testing mixtures

For the LC base two mixtures with different polar liquid crystalline compounds were prepared. M-1 is the mixture based on the compound with the NCS end group, M-2 is the mixture based on the compound with the CN end group (50%) and F atom (50%). The selection of two mixtures was made in order to verify the effect of modified DNDs (MDNDs) on parameters of LCs with different polar groups. Dicyano-4-4'-diphenyl DNDs having a small size (5-6 nm, N-1), and conglomerates on the basis of dicyano-4-4'-diphenyl DNDs with a size of about 50 nm (N-2) and 100 nm (N-3) were investigated. The conglomerates based on 4-octylphenyl DNDs with a size of about 50 nm led to N-4. DNDs particles and LCs were manually mixed in certain proportions and then subjected to ultrasonic agitation for 20 min in EMMI-20. 0.5% of N-1, N-2, N-3, N-4 were added to the mixturesM-1 and M-2, leading to NLH-1, NLH-2, NLH-3, NLH-4 and NLH-5, NLH-6, NLH-7, NLH-8,respectively. N-4 with concentrations of 0.2%, 0.4%, 0.6%, 0.8%, 1% were added to M-1 for more detailed study of the influence of the MDND conglomerates amount on dielectric properties of LCMs. As a result, NLH-4a, NLH-4b, NLH-4c, NLH-4d, NLH-4e were obtained. Cells with a thickness of 7 µm were filled with mixtures thus prepared. The quality of LCs alignment and sample uniformity were studied using a polarized optical microscope (Olympus BX-51P). Electro-optical parameters were measured using a setup consisting of a He–Ne laser (λ = 632.8 nm), a rotating table, a thermostatic camera (Linkam LTS 350) coupled with a temperature controller (Linkam CI 94, with an accuracy of ±0.1ºC), a function generator (HP 33, 120A) and a digital oscilloscope (HP Infinium). The frequency and the voltage of the sinusoidal electric field were 1 kHz and 10 V for all electro-optical measurements.

3. Results and discussion

It was interesting to us to study the impact of different MDNDs on the dielectric characteristics of LCMs. Figure 1 shows the results of measurements of dielectric permittivity for LCMs with MDNDs and conglomerates of MDNDs modified by dicyano-4-4′- diphenyl. It is seen that small MDNDs had no effect on these parameters independent of the LCMs dielectric anisotropy magnitude. Any polar dopant having a concentration of 0.5% cannot change the LC matrix parameters.

Dielectric permittivity of pure LCMs and that of LCs containing conglomerates (50 nm, 100 nm in diameter) of MDNDs were different. The difference is due to long-chain conglomerates of MDNDs that have a permanent dipole moment parallel to the surface. This assumption is based on the fact that functionalized organic groups attached to the surface of DNDs and carrying a permanent dipole moment are parallel to the LCs molecules alignment plane. This alignment is the result of elastic interactions between LC molecules and functionalized organic groups molecules. In this case, long-chain conglomerates of MDNDs are able to change the polarisability anisotropy of mixtures, i.e. the perpendicular component can increase. When the electric field was applied, conglomerates of MDNDs did not reorient like LC molecules, rather their organic tails on the surface became a little bit tilted. Therefore, parallel dielectric permittivity and, consequently, the magnitude of dielectric anisotropy decreased (Figure 1).

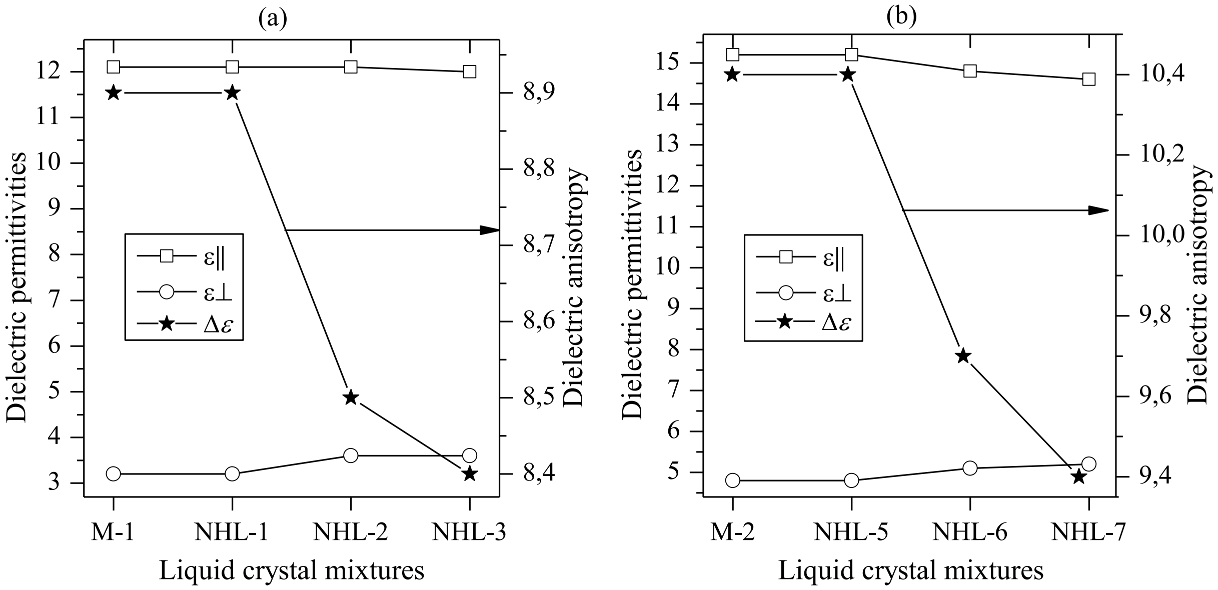


Figure 1. Dependence of dielectric permittivity and dielectric anisotropy of M-1 (a) and M-2 (b) on the size of NPs.

One should note that the influence of MDNDs on the parameters of LCMs with different polar compounds was the same. Naturally, the dielectric anisotropy decrease caused the switching time increase, in particular, the fall time increase. Table 1 shows that the switching time remained virtually unchanged for LCMs with small MDNDs, and it reduced 1.2–1.4 times for LCMs with conglomerates of MDNDs.

Table 1. The switching time of M-1 and M-2.

Mixture	τ_{rize}, ms	τ_{fall}, ms
M-1	1.14	47.87
NHL-1	1.2	50.34
NHL-2	1.32	53.84
NHL-3	1.48	58.62

Mixture	τ_{rize}, ms	τ_{fall}, ms
M-2	1.82	40.3
NHL-5	1.88	43.3
NHL-6	1.98	48.6
NHL-7	2.12	55.7

Similar studies were conducted with LCMs to which conglomerates of MDNDs with non-polar tails had been added. The effect of such conglomerates was opposite compared to the one of conglomerates of MDNDs that had polar tails. Of course, the dielectric permittivity for pure LCMs and LCM nanocolloids with N-4 was also different. This behaviour can be explained by assuming that such particles have the form of long chains. In this case they have a permanent dipole moment which is directed at some angle to the long chain of N-4. According to this assumption, one can explain the reduction of the dielectric anisotropy value of LCMs. Experimental data showed that the polarisability anisotropy of mixtures, i.e. the perpendicular component had decreased. In the case where the electric field was applied, we assumed that N-4 was not totally reoriented together with LC molecules and, therefore, parallel dielectric permittivity also slightly increased. Consequently, the magnitude of dielectric anisotropy also increased (Table 2). The results presented in Table 2 show that the switching time decreased for mixtures with 0.5 % of N-4 as expected.

Table 2. Dependence of dielectric permittivities, dielectric anisotropy and electro-optical parameters of M-1 and M-2 on the conglomerates of N-4.

Mixture	$\varepsilon_{\|\|}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	V_{10}, V	V_{90}, V	τ_{rize}, ms	τ_{fall}, ms
M-1	12.1	3.2	8.9	1.65	2.49	1.14	47.87
NHL-4	12.6	2.6	10.0	1.46	2.24	0.87	42.04
M-2	15.2	4.8	10.4	1.82	2.44	1.82	40.3
NHL-8	15.7	4.4	11.3	1.64	2.18	1.12	28.3

Finally, the experiments with LCMs having different concentrations of N-4 were performed. Figure 2 shows a strong influence of MDNDs conglomerates on the main parameters of LCMs at concentrations below 0.75 %, i.e. NLH-4a, NLH-4b, NLH-4c.

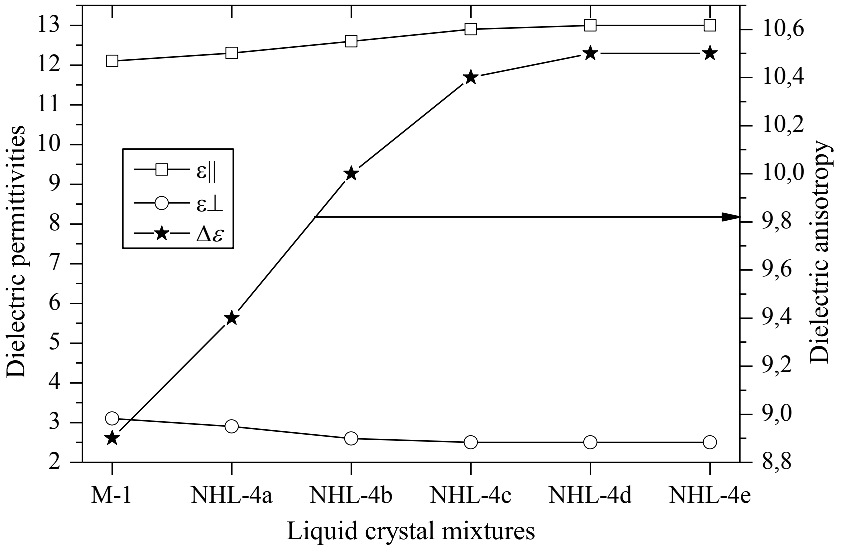


Figure 2. Dependence of dielectric permittivities and dielectric anisotropy of M-1 on the concentration of N-4.

4. Conclusions

It is established that the effect of DNDs on mesomorphic, dielectric and electro-optical properties depends on the size of NPs and a type of tail-like organic molecules. As expected, nps of a small size (4–5nm) don’t significantly affect physical properties of LCMs regardless of the value of their dielectric anisotropy. The addition of particles slightly increases the phase transition temperature of

LCMs. At the same time conglomerates of a larger size (50 and 100 nm) depending on the tails polarity can increase or decrease about 1.2–1.4 times the dielectric anisotropy and response time of LCMs. Dicyano-4-4′-diphenyl DNDs and 4-octylphenyl DNDs decrease and increase the dielectric anisotropy and switching time of LCMs, respectively. The change of the dielectric anisotropy and switching time is caused by the increase of the amount of DND particles.

References

[1] Rajh D. 2013 *Physica Status Solidi (A)* **210** 2328
[2] Neeraj K, Raina K 2013 *Optical Materials* **35** 531
[3] Al-Hazmi F, Al-Ghamdi A A, Al-Senany N, Alnowaiser F, Yakuphanoglu F. 2014 *J Mol Liq* **190** 169
[4] Ha Y S, Kim H J, Park H G, Seo D S. 2012 *Opt. Express* **20** 6448
[5] Mochalin V.N., Shenderova O., Ho D., Gogotsi Y. 2011 *Nat. Nanotechnol.* **7** 11
[6] Lapanik V., Lugouskiy A., Timofeev S. and Haase W. 2014 *Liq. Cryst.* **41** 1332