Optical, electro-optical, electrical and dielectric characterization of nematic liquid crystal (E7) layers doped with graphene nanoparticles for electro-optics

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Abstract. Thin (7 µm) layers of nanocomposites from graphene nanoflakes (GrFs) dispersed at concentrations of $10^{-3}$ wt.% into the nematic liquid crystal (NLC) E7 were characterized by various investigation techniques, such as Raman spectroscopy, impedance measurements and dielectric spectroscopy, as well as by electro-optical measurements (optical transmittance of the NLC layers versus the voltage of the applied external AC electric field). Conducting behaviour, dielectric permittivity and electric energy loss of our planar-aligned NLC layers at room temperature were analysed as a function of frequency in the range from 0.5 Hz to 1 MHz. The analysis of experimental data indicates that the molecular alignment through GrFs/NLC surface interactions is responsible for the reduction of the ionic conductivity of E7 NLC in the presence of GrFs. As compared to pure LC E7, this leads to improved characteristics for the studied nanocomposites, necessary in their practical applications in electro-optics.

1. Introduction

A new topic and currently trending approach to discover new interesting and practically useful properties of the liquid crystals (LCs) is their modification by addition of nanoparticles (NPs), such as graphene NPs (GrNPs) and NPs of graphene derivatives. The research on these advanced and multifunctional nanocomposite materials [1-8] demonstrated that one can broaden in this way the LCs usage in display technology area (notebooks, computer displays, and TVs), sensitive screens, a variety of other electro-optical (EO) devices and technical applications, as well as in sensorics, optics and organic electronics (e.g., in the field of organic light-emitting devices).

Usually, the LC materials for such applications are multi-component mixtures of different compounds thus utilizing their optimal combination of physico-chemical parameters, properties and characteristics (phase transition, dielectric and optical anisotropy, viscosity, etc.) that determine their EO response relevant to device applications. The doping of LC materials with small amounts of GrNPs can improve their EO and other responses [1,3,5,8], in particular due to the controllable change in their complex refractive index, complex dielectric permittivity, complex electrical conductivity, etc.
In the last decade, such nano-induced modifications are object of growing scientific interest, because the doping with GrNPs brings new important features of the LCs.

In the presented work, we have added graphene nanoflakes (GrFs) to the room-temperature nematic LC (NLC) mixture E7 (widely used in LC devices) in order to produce a nanocomposite material with improved electrical, dielectric and EO properties. Our attention was focused on the effect of the presence of a diluted concentration (10^{-3} wt.%) of GrFs on the transport of ions in the E7 NLC, as well as on the dielectric characteristics of the produced NLC nanocomposites (nanocolloids). Recently, the investigations on alternating-current (AC) electrical conductivity and dielectric characteristics of such NLC material formed as dispersion of GrNPs into E7 showed that all dielectric parameters are strongly influenced by frequency and applied bias voltage [1]. Whereas in the latter study the concentration of GrNPs was 5×10^{-3} wt.%, we have further reduced the concentration of the functional carbon nanostructure materials, in our case – GrFs.

2. Experimental

The NLC used is the well known eutectic mixture E7 with a positive dielectric anisotropy (Δε > 0). This cyano-biphenylic LC was purchased from Merck Eurolab (Darmstadt, Germany) and was used as received, without any further chemical purification. GrNPs (nanoflakes, GrFs, with an average thickness of 12 nm) were commercially obtained from Graphene Supermarket, Inc., in the form of nanopowder (Grade AO-3). The powder was dried in an oven to evaporate any residual moisture, then the GrFs were ball milled in a few drops of ethanol (wet milling) using a Fritsch pulverisette machine. The GrFs/ethanol suspension was steered in an ultrasonic bath for 30 min and added into E7 LC in its nematic state. To obtain a homogeneous solution, the mixture was sonicated for 1 h. Next, the ethanol was evaporated at an elevated temperature of 80°C for 8 hrs. The GrFs concentration in the LC E7 was 10^{-3} wt.% relative to the total mass of the LC.

We used commercially available empty glass cells KSRP-07/B107P6NTS05 Up/Low (E.H.C. Co., Ltd, Tokyo, Japan) with a cell gap of 7 μm, optically-transparent indium-tin oxide (ITO) contacts and alignment layers of polyimide, parallel-rubbed in order to achieve a planar orientation of the NLC content of the cells. The GrFs/E7LC dispersion was capillary filled (in the isotropic phase of E7) into the LC cells. For reference measurements, identical empty cells were filled with undoped NLC E7. Micro-Raman spectra were obtained in backscattering geometry by HORIBA Jobin Yvon Labram HR visible spectrometer equipped with a Peltier-cooled CCD detector. The 632.8-nm line of a He-Ne-laser was used for photo-excitation. Using microscope optics, the laser beam was focused on the sample surface to a spotsize of about 10 μm in diameter. The peak frequencies were determined using calibration with neon lines by least-squares fit to Voigt profiles. The absolute accuracy of the measurements was 0.5 cm^{-1}. The optical transmittance of the NLC layers versus the voltage of the applied external AC electric field (the Fréedericksz transition) was measured as described in [9]. The complex electrical impedance and dielectric spectroscopy measurements were performed as in [10].

3. Results and discussion

Raman spectroscopy has great potential in the studying of nanostructured LCs at molecular level. In our case, we used the Raman spectra to obtain rapid information on the sample content and to look for the changes of the host NLC E7 upon mixing with GrFs. We had to deal with intense Raman lines from the LC phenyl rings and much weaker Raman signal from GrFs. Figure 1(a) reports the micro-Raman spectra of our samples, as recorded under identical experimental conditions. The samples were studied as prepared, i.e., in their initial planar configuration. The E7 response can be recognized by the four sharp and intense Raman lines at 1183, 1286, 1608 and 2231 cm^{-1}. In the Raman spectrum of GrFs-doped E7 a clearly discernible shoulder at the low-frequency side (∼ 1582 cm^{-1}) (shown with arrow in figure 1a) of the characteristic E7 peak marks the presence of GrFs. Due to the relatively low percentage of dispersed GrFs, the change of the Raman spectrum of E7 resulting from the addition of GrFs is a little, to negligible. That is why, no other spectral peculiarities were observed, as well as no change in the intensity, spectral positions and the widths of the E7 Raman lines.
The EO transmittance characteristics of our samples of pure and GrFs-doped NLC E7 were also measured to be compared (figure 1b). To avoid the screening effect, the EO activation of the samples was driven by 1 kHz AC voltage when the voltage-dependent intensity of the transmitted light (He-Ne laser beam) through the LC cells between crossed polarizers was measured. Our EO measurements of the voltage-dependent transmittance of the examined GrFs-doped E7 samples upon AC electric field indicated a well pronounced GrFs-produced change - the Fréedericksz transition for the GrFs-doped E7 samples was characterized with a higher threshold voltage \( U_{F} \) than that of the pure E7 measured under the same experimental conditions. The Fréedericksz transition is the molecular reorientation of the NLCs in the presence of an external electric field [11]. When the NLC possesses a positive dielectric anisotropy \( \Delta \varepsilon > 0 \), the nematic director is forced to be oriented along the applied field. Fréedericksz thresholds of pure and nanostructured E7 are obtained by extrapolation of the steep parts of the transmittance curves to the initial, low-voltage transmittance. In the representative example in figure 1(b) one can adopt the \( U_{F} \)-values of 0.77 V and 0.86 V (RMS), for pure E7 and GrFs-doped E7, respectively. The observed change suggests a GrFs-induced over-alignment of the LC molecules and enhancement of their orientational order even at the very low concentration (10^{-3} wt.%) of GrFs nanodopants we have employed here. The increase of threshold \( U_{F} \) could be associated with a possible modification of LC order parameter \( S \). \( U_{F} \) of a strongly anchored planar nematic layer depends mainly on two material parameters - the splay elastic constant \( K_{11} \) and dielectric anisotropy \( \Delta \varepsilon \) [12]. Taking into account that \( K \propto S^2 \) and \( \Delta \varepsilon \propto S \) [13], \( U_{F} \) can be expressed as \( U_{F} \propto \sqrt{S} \). Thus, the increased \( U_{F} \) measured for GrFs-doped E7 might suggests an increased \( S \) in this nanocomposite, as compared to the undoped E7 NLC. But in view of the weak (square root of \( S \)) dependence of this effect on \( S \), an additional enhancement in the planar anchoring due to adsorption of flakes over electrode surfaces could not be excluded.

Further, we compared the electrical responses of pure and GrFs-doped E7 NLC samples. In particular, by use of complex electrical impedance spectroscopy applied for characterization of both materials in a broad frequency range, we observed a clear effect from GrFs nanodopants in E7 NLC. Nyquist plots (the imaginary part, \( Z_{i} \), vs the real part, \( Z_{r} \), of the complex electrical impedance) display semicircles and almost vertical straight lines for both kinds of samples (figure 2). The studied nematic layers demonstrate a relatively high electrical impedance of the order of mega-ohms. A considerable shift between these curves is seen that displays the effect from GrFs nanodopants. Essentially, figure 2 shows that the resistance of the samples increases by doping with GrFs. Because the value of the bulk resistance \( (R_{b}) \) of the material is associated with the point of intersection of the semicircle with the \( Z_{r} \)-axis (the low-frequency end of the semicircle) [14,15], one can conclude from figure 3, that our GrFs-
doped E7 samples exhibit a lower electrical conductivity (ionic conductivity) than the undoped reference E7 samples. This effect comes from the reduction of the concentration of the free ions in the NLC E7 – the known and complex ion-trapping process reported by other authors for GrNPs inclusions in NLCs [5,8,16,17]. Note that the ionic concentrations in both GrFs-doped and undoped E7 NLCs cells are the same due to the use of the same LC material and identical cells.

Figure 2. Nyquist complex impedance plots for temperature 25 °C.

In the considered NLC nanocomposites, by the GrFs is realized trapping of mobile ions, and thereby, a reduction of their diffusivity in the bulk. The corresponding physical mechanism is complex [5,8,16,17]. Most likely this occurs through π-π electron stacking and interfacial interactions (LC-graphene anchoring [17,18], similar to other such mechanisms of surface interactions known for carbonic NPs [19-23]). In this way, the introduction of GrFs nanodopants into NLCs should improve the EO performance of the doped NLCs. As known, the high concentration of free ion charges (excessive ionic impurities) in the NLCs is unwanted because it leads to problems such as slowing down reactions, retention of images, long-term effects of image tracking and short-term vibrations in LC displays and in other NLCs-based EO devices [24,25].

Figure 3. The Bode plots in log-log scale of the real (a) and imaginary (b) parts of the complex dielectric permittivity for planar layers of GrFs-doped NLC E7 and undoped E7, both in the nematic phase at 25 °C; (c) The Cole-Cole plots of the same dielectric spectra given in (a) and (b).

The analysis of dielectric spectra can be also useful for the consideration of the effect of GrFs inclusions in the NLC E7. The real (the storage component $\varepsilon'$) and imaginary (the loss component $\varepsilon''$) parts of complex dielectric permittivity of the material in alternating electric fields can be evaluated from real ($Z_r$) and imaginary ($Z_i$) parts of the complex electrical impedance. Figure 3(a,b) presents the variation of the dielectric components $\varepsilon'$ and $\varepsilon''$ of the measured NLC layers (perpendicular
components, according to geometry of measurements) as a function of the frequency \( f \) of the AC electric field applied on the layers. As compared to \( \varepsilon' \) of the undoped E7 layers (figure 3a), the lower value of \( \varepsilon' \) for GrFs-doped E7 layers in the low-frequency region (in our case from 1 Hz to 100 Hz) corroborates the above conclusion that the planar alignment of the NLC molecules is improved by the doping with GrFs. Regarding the frequency behavior of \( \varepsilon'' \), one can note the shift of the relaxations peaks (figure 3b). Two dielectric relaxations were present. At the high-frequency region \( (f > 100 \text{ kHz}) \) of the dielectric loss, the dielectric relaxation is referred to reorientation around the short molecular axis [6] and is not of importance for our present considerations. The low-frequency relaxations (a few Hz) is relevant to ionic contribution to the observed dielectric relaxations. It is seen that the GrFs nanodopants do shift the low-frequency relaxation peak towards the lower frequencies, which suggests a decrease of the number of free ions, and hence a decrease of cut-off frequency.

The Cole-Cole plots (the graphs of \( \varepsilon''(f) \) vs \( \varepsilon'(f) \) of both kinds of samples under study is shown in figure 3(c). From this diagram one can find the relaxation frequency \( (f_R) \) of ion polarization. The value of \( f_R \) corresponds to the top points of the semicircle curves of the Cole-Cole plots. At this frequency, the ions can no more follow the electric field and the dielectric heating is maximum. From figure 3(c) we determined that \( f_R \) (2.39 Hz) for GrFs-doped NLC E7 layer is lower than \( f_R \) (4.14 Hz) for undoped E7 layers, both at 25°C. The observed change of \( f_R \) is related to the ion mobility and the diffusion constant \( (D) \). Most likely, the decrease of \( f_R \) in GrFs-doped NLC is due to trapping of ions. These ions respectively exhibit larger inertia for the electric driven oscillations and are less mobile. The reduction of \( f_R \) corresponds to this.

Since the LCs are anisotropic media, one has to consider the LC alignment [2,26]. As might be expected, some of the GrFs should be localized at the aligning boundary interfaces, hence affecting the LC anchoring. This leads to improvement of the planar alignment [5,17,18,27,28]. The directional anchoring and LC alignment effect by GrNPs has been partly explained by \( \pi-\pi \) stacking interactions \( (\pi-\pi \text{ anchoring}) \) [19,21,29-31]. On the other hand, the diffusion constant \( D \) is anisotropic, being related to the complex dielectric permittivity and electric conductivity of the medium. For instance, by impedance measurements in the range of 0.1 Hz – 1 MHz it was shown that impurity ions exhibit different transport behaviors along and perpendicular to the molecular axis, leading to anisotropy od \( D \) [32]. In fact, the diffusion constant along the molecular axis is greater than in perpendicular direction [12,32]. The anchoring modification and molecular orientation have important contributions to \( D \). In considered GrFs-doped E7 NLC layers, the GrFs deposited on the boundary surfaces can quite possible decrease the pretilt angle, approaching to perfectly aligned planar cell. As a consequence, \( D \) in the direction perpendicular to the layer plane becomes smaller. This explanation is consistent with our dielectric and conductivity observations. Thus, the modification of the dielectric properties of the GrFs-NLC system is induced by the coupling of the molecular orientation of the NLCs with the GrFs properties. Accordingly, the dielectric response of the GrFs-NLC system can be modified and finely tuned by incorporating various amounts of GrFs.

4. Conclusion
We have studied the room-temperature EO, electrical and dielectric response of NLC nanocomposite materials (in 7 \( \mu \text{m} \) thin nematic layers) produced by dispersion of graphene nanoflakes (GrFs, graphene forms promising for nanoelectronics) into NLC E7. The results obtained by complex impedance and dielectric spectroscopy show that a sizable reduction of diffusivity of the free ions in the NLC E7 is possible even at the extremely low concentration of GrFs, equal to \( 10^{-2} \text{ wt.}\% \). This happens by altering the molecular alignment through GrFs/LC surface interactions. The addition of this carbon nanomaterial to E7 NLC does influence the orientational order of the NLC, actually the graphene nanoflakes do increase the nematic ordering.

At the very low concentration of the carbonic nanodopants we have used, the material properties of the NLCs are not changed, the threshold voltage is slightly increased, but one can achieve a significant reduction of the transport of the mobile ions. Such positive effect is of great importance for LC displays and other NLCs-based EO devices, where the presence of ions of impurities is very
problematic because it leads to an image sticking/flickering, changing the gray level, and slowing down of the switching response. Complementary measurements and further analyses are necessary to clarify all aspects of the GrFs-induced alignment and its relationship with the reduction of the ion diffusivity in the considered graphene-LC nanocomposites (work in progress).

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