Flexoelectro-Optical Behaviour of Layers Formed by Polymer-Liquid Crystal Phase-Separated Composites*

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Abstract. The flexoelectro-optical behavior of layers formed by a liquid crystal (LC)-polymer phase-separated composite was investigated by flexoelectric spectroscopy. The composite layers with a thickness of 6 μm contain micrometer-sized droplets of LC E7 dispersed in a transparent polymer matrix. The layers were prepared between glass substrates with Teflon nanolayers initially deposited. Thus, LC-polymer composite layers with well ordered and aligned droplet morphology were obtained. The dispersed LC droplets were spherical in shape, with a mean size of about 14 μm. The flexoelectric response of LC droplets in this structure was studied as depending on both temperature and applied voltage.

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1 Introduction

In recent years, material scientists have devoted substantial efforts to the development and improvement of soft-solid materials for optical and electro-optical applications. Operating through an electrically-controllable scattering effect, the microscale systems of liquid crystals (LCs) dispersed in polymeric binders have found a number of advanced applications ranging from "light valves" in integrated circuits to large area flexible displays and intelligent glass facades [1–6]. Such LC-polymer composite layers consist of micrometer-sized droplets of LC

*In memoriam Assoc. Prof. Dr. Marin D. Mitov (1951-2011) – one of the founders of the world-wide recognized method for the measurement of the bending rigidity of lipid membranes by means of analysis of the thermally induced shape fluctuations of quasispherical lipid vesicles.

dispersed in a solid optically-transparent polymer matrix. Sandwiched between two electrically-conductive and optically-transparent substrates, by applying an external electric field the composite LC-polymer dispersions can be switched electrically from a light scattering "OFF-state" to a highly transparent "ON-state". The electro-optical properties of these smart materials are currently of growing interest for various new light-control applications [7–14]. In this report, we present an experimental study on the flexoelectro-optical response of layers of LC-polymer phase-separated composites as investigated by flexoelectric spectroscopy. The flexoelectricity signifies macroscopic spontaneous polarization developed in elastically deformed liquid crystals. This effect has been early investigated by researchers from Sofia, the Laboratory of Liquid Crystals at the Institute of Solid State Physics (Bulgarian Academy of Sciences). Important points of their research are: the discovery of gradient flexoeffect [15], the study on the one-dimensional dielectric-flexoelectric deformations in nematic layers [16] and the electric field-induced texture changes in nematic layers [17]. Further contribution from the researchers of this group to the LC physical science related to the flexoelectricity is the study on the parallel surface-induced flexoelectric domains (flexo-dielectric walls) [18] and the setting-up the flexoelectric spectroscopy, subsequently applied for investigation of flexoelectric properties of continuous nematic layers [19, 20] and soft-solid systems [12, 13]. The subject of present flexoelectric spectroscopy study is a microscale LC-polymer composite layer prepared as sandwiched between glass substrates beforehand treated by Teflon. Our aim is to inspect the effect of the deposited Teflon nanolayers in the twisted cell configuration on the morphology of the composite layer, as well as the effect of the distribution of both LC droplets and the nematic director on the flexoelectro-optical response of the layer.

2 Experimental

In our study, the sample was a thin layer with a thickness of 6 μm, prepared as composite of the nematic LC E7 and the photo (UV)-curable polymer NOA65. The commercial Norland Optical Adhesive product NOA65 is a polymer that is transparent in the visible. The refractive index (1.52 at the wavelength $\lambda = 633$ nm) of the cured NOA65 is close to the refractive index of glass and matches the refractive index of many commercial LC mixtures. Catalogue data for E7 LC mixture: E7 MERCK Art. 28658, 4-pentyl-4'-cyanobiphenyl plus 4-heptyl-4'-cyanobiphenyl. The E7 mixture is capable of giving a nematic phase of high chemical and photochemical stability at room temperature. Its nematic-isotropic phase transition (clearing point) is at about 59°C. The nematic E7 is characterized by the following refractive indices at 20°C and $\lambda = 633$ nm: $n_0 = 1.5185$ and $n_e = 1.737$ (ordinary and extraordinary refractive indices, respectively) [21] and has positive dielectric anisotropy, $\Delta\epsilon_{\parallel} = 19$ and $\Delta\epsilon_{\perp} = 5.2$ (at 20°C and 1 kHz frequency) [22]. The LC E7 was used without any further treatment. E7 has a good solubility in the prepolymer NOA65. Both compounds were mixed in the weight ratio 50:50% and heated above the isotropic clearing temperature to achieve a homogeneous mixing. Then, the mixture in its isotropic phase was filled by capillary action into the empty cell. After the filling, the sample was cooled slowly to a nematic phase. The cell was constructed from two 1 mm-thick glass slides each coated inside by a thin transparent conductive layer of indium tin oxide (ITO). A 6 μm-thick Mylar spacer was used. The size of the sample was 1×1 cm. In order to modify the morphology of the formed layer, a preliminary treatment of the substrates was undertaken. Both ITO glasses were covered by Teflon. A nanometer-thick layer of Teflon was deposited by the method of rubbing a preheated glass by a piece of Teflon [23]. A twisted cell was assembled by crossing both Teflon-rubbed ITO glass plates at 45° before the cell assembly. The sample was prepared by photo-polymerization induced phase separation technique. For the purpose, an UV-light illumination was used (mercury vapor lamp with a continuous action). To cure the polymer NOA65, the strong spectral line at the wavelength of 365 nm was employed, with intensity 0.9 mW/cm^2. The UV curing time was 15 minutes. The morphology of the prepared layer of LC-polymer phase-separated composite was characterized by transmission optical microscopy (Zeiss NU-2 Universal Research Microscope). The microscope images were recorded by a Hitachi VK-C150ED video camera and computer. The flexoelectro-optical behavior of the sample was investigated by flexoelectric spectroscopy [20].

The experiment set-up is schematically shown in Figure 1. Laser light (wavelength of 630 nm) was used to probe the flexoelectro-optic response of the sample placed between two crossed polarizers. The frequency dependence of modulated light transmitted through the layer (or scattered from the layer in the forward direction) was measured by lock-in amplifier (SR830, Stanford Research Systems) controlled by a computer. The frequency of the sinusoidal voltage applied to the ITO electrodes of the LC cell was in the range from 3 Hz to 3×10^3 Hz. The sample was heated by a hot stage (Mettler FP82). The temper-

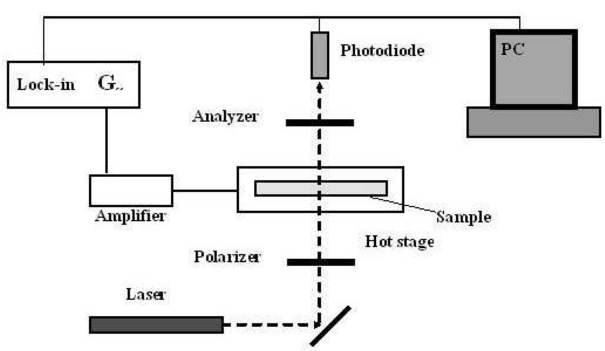

Figure 1. Schematic of the experimental set-up used in this work.

ature of the sample in the range $20 \div 40$°C was controlled with an accuracy of 0.1°C.

3 Results and Discussion

Figure 2 shows micrographs of the sample placed between two crossed polarizers. As observed by optical microscopy, the obtained soft-solid composite material is a fine dispersion of the nematic E7 LC in an optically-transparent and isotropic solid polymer matrix. The layer contains LC droplets with spherical (slightly flattened) shapes, with a mean size of about 14 μm. It is also seen that the droplets are dispersed in a 2D layer. Similar single layers of LC-polymer compositions have been previously investigated [24, 25]. It is noteworthy to mention that the LC-polymer dispersion exhibits homogeneous droplets distribution.

The pair (a,b) of the polarizing microscopy images in Figure 2 illustrates a quenching of the transmitted light. The light quenching is well observable for all LC droplets, thus the layer is characterized by uniform director along the rubbing direction. Rotating the cell, the maximum of the light transmission occurs at 45° for all LC droplets in the layer, *i.e.* a planar nematic orientation is evident. Also in Figure 2 one can see that when an electric field with a sufficient strength is applied to the cell, the director configuration is altered from planar to homeotropic for all LC droplets. All the droplets are affected by the electric field in a similar manner, they have almost the same electro-optical behaviour,

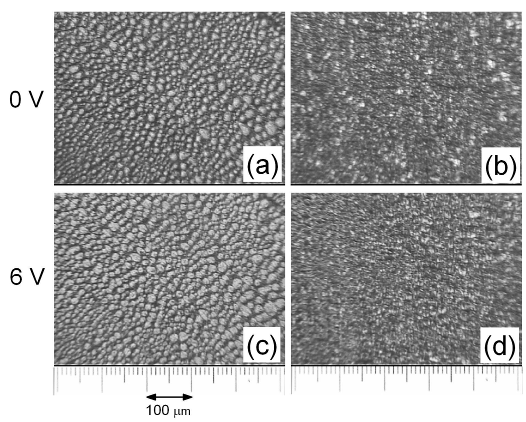

Figure 2. Optical polarizing microscopy images of the LC-polymer composite layer prepared in twisted cell. The pictures are taken when the cell is placed between two crossed polarizers: (b,d) the direction of the rubbed grooves coincide with one of the optical axes of the polarizers; (a,c) the cell is rotated at 45°. Applied voltage: 0 V (a,b); 6 V at frequency 25 Hz (c,d). The temperature of the sample was fixed at 20°C.

thereby their electro-optical response is matched. Obtained by use of modified substrates (additional nano-structured surfaces), the structure formed in the examined LC-polymer composite layer is specific. The Teflon-rubbed surface on the glass plates has unidirectional groove relief that is able to impose planar LC orientation conditions [26]. The employed twisted cell imposes a droplets arrangement along the rubbing grooves, as well as a director alignment along the grooves. Through the Teflon-manipulation of the substrate plates, an efficient modification of the droplet nematic director field was achieved. In this way, after the substrate treatment, a microscale soft-solid material in the LC-polymer composite layers confined by Teflon nanolayers was obtained that exhibits not only well-ordered LC droplets, but also aligned LC. The LC-polymer composite structure under study was excited by transversal ac electric field. The flexoelectro-optical response of the sample was registered as linear electro-optic modulation. The flexoelectric origin of the induced electro-mechanical oscillation is discussed elsewhere [27]. The main feature of the flexoelectricity [28] is that positive and negative voltages cause opposite flexo-deformation, infer producing of a first harmonic electro-optic oscillations.

Figure 3 represents flexoelectro-optical spectra (the first harmonic of the flexoelectric oscillations) of the sample. The amplitude of transmitted light modulation versus the electric-field frequency is given as measured by varying the voltage applied and temperature. In the spectra are seen peculiar minima, characteristic of the confined nematic system [29]. The spectral position and the depth of the minima strongly depend on both temperature and applied voltage. These notch-filter-like spectral shapes are consistent with the features previously reported [24, 25]. The flexoelectric oscillations (Figure 3) display a spectral

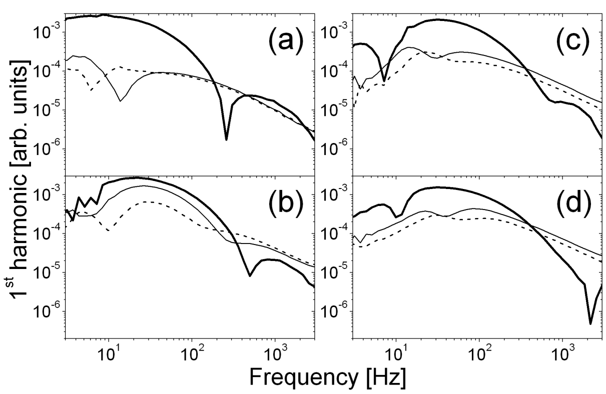

Figure 3. Flexoelectro-optical response of the examined LC-polymer composite layer in twisted cell. The 1st harmonic spectra are plotted for various values of the applied voltage: 3.6 V (dashed line); 4.8 V (thin line); 9.6 V (bold line). The temperature of the sample: 22°C (a); 30°C (b); 35°C (c); 40°C (d).

shift of the minima to the higher frequency by increasing both voltage and temperature. At increasing voltages, the minima become deeper and narrower, in contrast to the case when the temperature is increased. At higher temperature some new minima appear which are missing at room temperature. To describe the flexoelectro-optical spectra of polymer-dispersed LCs, a model of vibrating central sphere and orientationally-anchored spherical shell was proposed [27]. It is best applicable for a normally anchored LC droplets with a central point defect. This model is based on the idea of selective diffraction filtering of propagated light due to formation of an internal refractive index contrast in the LC droplets of the LC-polymer dispersions. The detailed analysis is rather complicated. In this case, besides the surface-driven flexoelectric oscillations, a bulk contribution of the gradient flexoelectric effect has to be also considered. As indicated our research on single layers of polymer-dispersed LCs, a specificity in the time dependency of the light transmittance takes place for these soft-solid materials that can be attributed to optical interference effects [14, 30]. For such confined systems, a deviation of the switching times as measured against the droplet mean diameter is found that does not match the theoretical predictions [31]. Moreover, as analyzed and explained in [32], the optical interference in single layers of polymer-dispersed LCs may result in an effective decrease of the switching time. Most probably, the peculiarities and modifications observed for the spectral shapes in Figure 3 as characteristics of the flexoelectro-optical response of the present LC-polymer composites, reflect such optical interference effects. Further systematic investigation and analyses are necessary to elucidate this point (work in progress).

4 Conclusions

By the method of photopolymerization-induced phase separation, thin single layers of LC-polymer composites were fabricated, having nematic (E7) droplets dispersed in the photopolymer NOA65. The nematic orientation in these layers was efficiently modified by rubbed Teflon nanolayer deposited on the cell substrates (ITO glass plate). Owing to the substrate treatment by Teflon, composite layers of well-ordered droplets and aligned nematic director in a single layer were obtained. The dispersion exhibits a nearly uniform distribution of the LC droplets, as well as a planar configuration of the nematic director. The LC-polymer composite single layers were characterized by the first-harmonic flexoelectro-optic spectra (the amplitude of transmitted light modulation versus the electric-field frequency). Sample prepared in a twisted cell was measured as varying the applied voltage and temperature. The peculiar minima (and their transformation and shift) observed in the spectra may be related mainly to the effect of the selective diffraction.

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