PHOTOCONDUCTIVITY AND DIELECTRIC PROPERTIES OF (C$_{60}$+C$_{70}$) — FERROELECTRIC LIQUID CRYSTAL COMPOSITE

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A composite stable in time of fullerene (Fn) and a ferroelectric liquid crystal (FLC) has been obtained. It is shown that the illumination by the focused light of a halogen lamp results in changes of the complex dielectric permittivity components only in the low-frequency range. The interrelation between dielectric permittivities measured under illumination and those measured in dark depends on the type of the mesophase of FLC. The illumination results in the formation of an additional channel through the fullerene for the electron exchange between ions and the electrode.

Introduction

Since the majority of liquid crystals (LC) do not absorb light in the visible spectrum range, the investigation of their composites with photosensitive materials is important from the scientific and technological point of view. For the successful studies of such composites, it is necessary to dissolve a photosensitive material in LC. However, due to a weak polarity of most LCs, there are no many photosensitive chemical compounds which would be rather easily dissolved in LC. Therefore, it is very important to develop technological processes of dispersion or distribution of some part of the molecules of photosensitive compounds in an LC matrix. Such photosensitive nanoparticles as fullerenes could be used for the creation of heterogeneous media including nonuniformities with dimensions as small as possible. However, the aggregation of solid particles in a liquid matrix remains an important factor for the composite stability.

We have shown that it is possible to obtain a stable composite Fn—FLC [1] by varying the component concentration and studied its dielectric properties. At temperatures $T >$ 329 K, the composite conductance is determined by the conductance of fullerene. At 344 K, the composite conductance is $3.2 \times 10^{-8}\ \Omega^{-1}m^{-1}$, and the activation energy for the temperature dependence of conductance is 0.99 eV. At temperatures below 329 K, the composite dielectric properties are determined by the properties of LC, as confirmed by the existence of a dispersion area due to the rotation of dipole moments around a helicoid (the Goldstone mode) axis. Almost equal values for the relaxation times of such a dispersion for homeotropically oriented LC and for Fn—FLC composite lead us to the conclusion that the presence of fullerene does not substantially change the LC parameters.

In the present work, we investigate the photoelectric properties of the above composite and study the connection between these properties and dielectric processes occurring in the composite.

Materials and Methods

In our studies, we used a fullerene mixture Fn from the MER Corporation with the following composition: 76%C$_{60}$, 22%C$_{70}$, and 2% higher-order fullerenes. A ferroelectric liquid crystal mixture was used, where the FLC is an eutectic mixture of 4-n-hexyloxyphenyl 4'-n-decyloxybenzoate and 4-n-hexyloxyphenyl 4'-n-octyloxybenzoate with LUCH-15 polar chiral additive [2]. Pure FLC has the following changes of phases and phase temperatures (K):

$$\text{IP} \xrightarrow{358} \text{Chol} \xrightarrow{349} \text{SmA} \xrightarrow{345} \text{SmC}^* \xrightarrow{313} \text{Cr}.$$

To obtain Fn—FLC composites at temperatures where LC remains in the isotropic phase (IP), the
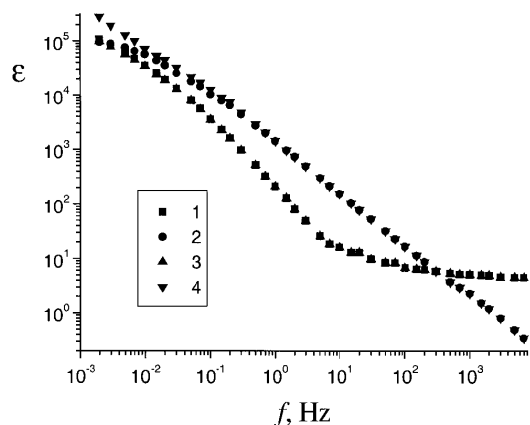
Fig. 1. Frequency dependences for ε' (*1,3*) and ε'' (*2,4*) of FLC + 0.43 wt.% $C_{60}+C_{70}$ composite corresponding to the measurements in dark (*1,2*) and under illumination by focused light (*3,4*), $T = 359$ K (IP FLC)

Fig. 2. Frequency dependences of the ratios $\varepsilon'_P/\varepsilon'_D$ (*1*) and $\varepsilon''_P/\varepsilon''_D$ (*2*) of FLC + 0.43 wt.% $C_{60}+C_{70}$ composite, $T = 359$ K

components were mixed and grinded in a mortar during one hour. The composite obtained was placed between two glass slides, and its stability was tested with a microscope. The observations showed that the aggregation did not take place at Fn concentrations of above 40 wt.%, i.e. a stable system is formed. The fullerene content of 43 wt.% was selected for all our experiments. The studies were carried out with the use of sandwich cells. Transparent layers of In_2O_3 deposited on glass slides were employed as electrodes. Each electrode was divided by etching into central (measuring) and external (protecting) sections. The protecting electrode was grounded during the measurements. The thickness of the composite layer d in the range of 30—50 μm was obtained by introducing a Teflon film between the glass slides over the protecting electrode. Due to a high composite viscosity, filling the cells was achieved by pressurizing the Fn—FLC composite between the electrodes bearing the Teflon film. An empty (composite-free) volume was left, where d was measured by interferometry. The cell assembled was sealed on its perimeter with a glue.

Temperature stabilization with an error below 0.2 K was carried out in a custom-designed thermostat having a low level of electromagnetic noises. The measurements were performed in the temperature range 315—370 K. The sample capacity C and resistance R were measured in the frequency range 10^{-3}—10^6 Hz by means of the oscilloscopic method [3, 4]. The signal measured had the triangular shape. The peak voltage value was 0.25 V. Based on the data obtained, we analyzed the frequency dependence of the ε' and ε'' components of complex dielectric permittivity.
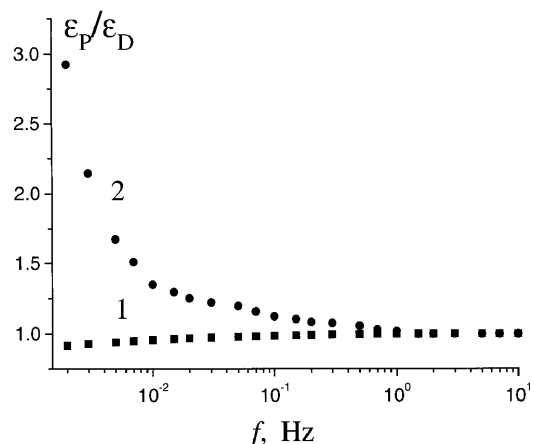
The measurements of the frequency dependences of ε' and ε'' were carried out both in dark and under illumination by the concentrated light from a halogen lamp with a power of 100 W.

Experimental Results

Fig. 1 shows the frequency dependences for ε' (*1,3*) and ε'' (*2,4*), corresponding to the measurements in dark (*1,2*) and under illumination by a focused light (*3,4*). From these results, we can conclude that a larger difference between the dielectric permittivity measured under illumination ε_P and the one measured in dark ε_D is observed for the low-frequency range.

Fig. 2 presents the frequency dependences of the ratios $\varepsilon'_P/\varepsilon'_D$ (*1*) and $\varepsilon''_P/\varepsilon''_D$ (*2*). It is clear that the illumination results in an increase of ε''. The changes in ε' are even lesser in the low-frequency range. With the increase in the frequency f, the ratio $\varepsilon_P/\varepsilon_D$ decreases and $\varepsilon_P = \varepsilon_D$ for $f > 1$ Hz.

Fig. 3 shows the temperature dependences of the ratios $\varepsilon'_P/\varepsilon'_D$ (*1*) and $\varepsilon''_P/\varepsilon''_D$ (*2*) at a frequency of $2 \cdot 10^{-3}$ Hz. From the data obtained, one can observe a monotonous temperature dependence for $\varepsilon''_P/\varepsilon''_D$. The bigger value of $\varepsilon''_P/\varepsilon''_D$ (more than 3) has been obtained for the isotropic phase. The value of $\varepsilon''_P/\varepsilon''_D$ decreases with temperature. It is important to note that the sharp changes of $\varepsilon''_P/\varepsilon''_D$ are observed in the region of phase transitions. It seems that the LC structure rather than the photosensitive fullerene component influences the photoprocesses in the Fn—FLC composite.

For the ratio $\varepsilon'_P/\varepsilon'_D$, no monotonous temperature dependence is observed. Depending on the LC phase,

the illumination results in increasing (the SmC*-phase) or decreasing ε' (the IP-, Chol-, and SmA-phases).

In order to explain the mechanism of light influence on the studied composites, it is very important to understand which processes are associated with the in the chemical composition changes: the ones which occur near the electrode or the ones in the bulk. In this work, the discussion of the experimental data obtained is devoted to such an understanding .

Discussion

From Fig. 1, one can see that the samples have large values of ε' and ε'' (of about 10^5) in the low-frequency range (where the influence of illumination is more essential). Based on the observation of large ε' and ε'' not only in the SmC*-phase, but also in other phases of LC, including the IP, it is believed that they are not associated with spontaneous polarization, but with a non-uniform distribution of the electric field in a sample [4—6]. This implies that the changes of parameters of the studied samples caused by illumination are due to changes in the near-electrode region. Let us see in more detail which processes can be associated with these changes.

As was shown in [6, 7], LC is surrounded by the ions of solvated neutral molecules, which have polarization-related properties (such as electronic polarizability and dipole moment) stronger than those of the main part of molecules. That is why a barrier for the electron exchange between ions and the electrode is formed. The main part of this barrier corresponds to the electron transport from the liquid to the anode. Therefore, at the voltage less than several volts, the electric field is concentrated near the electrode area, mainly at the anode. As was shown in [5, 6], the electron exchange in such an area is described by the theory of Shottky emission through the dielectric layer, and the dependence for the current density J on the applied voltage U is described by the formula

$$J = J_0 \exp(\beta\sqrt{U}). \tag{1}$$

The parameters J_0 and β are

$$J_0 = AT^2 \exp(-\frac{e\varphi_b}{k_B T}), \tag{2}$$

$$\beta = \sqrt{\frac{e}{k_B T}\frac{e}{4\pi\varepsilon_0\varepsilon' d_S}}, \tag{3}$$

where A is a constant, e is the electron charge, φ_b is the barrier height, k_B is the Boltzmann constant, ε_0 is the
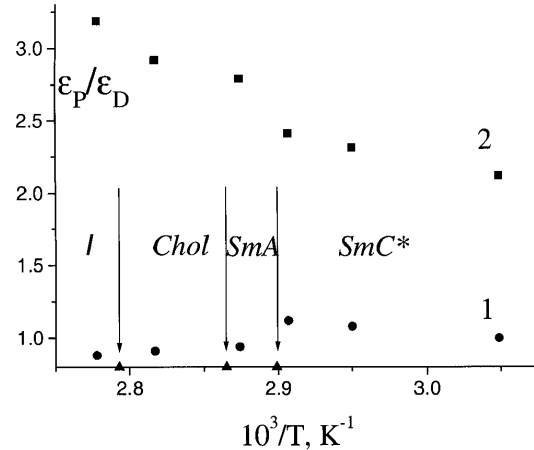

Fig. 3. Temperature dependences of the ratios $\varepsilon'_P/\varepsilon'_D$ (1) and $\varepsilon''_P/\varepsilon''_D$ (2) of Fn—FLC composite, $f = 2 \times 10^{-3}$ Hz. The vertical arrows mark the temperatures of FLC phase changes

dielectric constant, and d_S is the thickness of the electron transport layer.

It was shown in [6—8] that the value of d_S is equal to several nanometers and is of the same order that we have found herein for the studied composites (this result will be shown below). Therefore, the electric field will be large enough in the near-electrode region and can lead to the ionization of a certain number of neutral molecules (electrode polarization). The relaxation of the resulting accumulated charge in the near-electrode region (due to the electron transfer) will occur through the same mechanism, as under the applied electric field. The relaxation process can be described based on the equation of continuity, by considering the process of electron transfer as a one-dimensional problem (in the direction perpendicular to the electrode surface)

$$\frac{\partial\rho_{QS}}{\partial t} + \frac{d}{dx}[J_0 \exp\beta\sqrt{(Ed_S)}] = 0, \tag{4}$$

where E is the electric field intensity which is related to the near-electrode charge density ρ_{QS} by the Poisson equation

$$\frac{dE}{dx} = \frac{\rho_{QS}}{\varepsilon'\varepsilon_0}. \tag{5}$$

Relations (4) and (5) describe the process of electrode polarization, and the relaxation process which causes the low-frequency dispersion of ε' and ε'' (Fig. 1) belongs to it. In [4—7], it was shown that such a relaxation corresponds to the Debye dispersion modified as

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}, \tag{6}$$
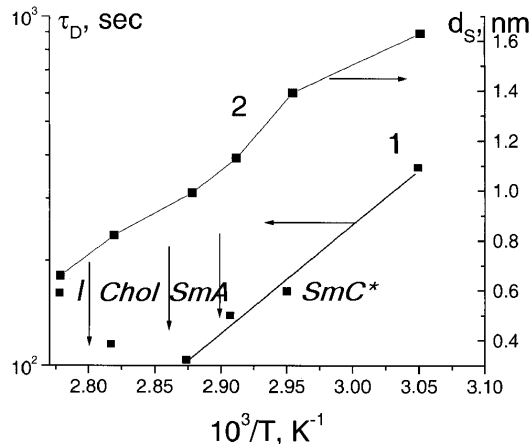
Fig. 4. Temperature dependences of the relaxation time τ (1) and the thickness of the electron transport layer d_S (2) of Fn—FLC composite. The vertical arrows mark the temperatures of FLC phase changes

where ε^* is the complex dielectric permittivity, ε_s and ε_∞ are the dielectric permittivities for the frequencies $f = \infty$ and $f = 0$, respectively, τ is the relaxation time, and α is the Cole—Cole parameter.

The analysis of the frequency dependences of ε' and ε'' for composites LC—Fn has shown that Eq. (6) is correct only for ε_D. For ε_P, the typical Cole—Cole dispersion curve for ε'' (ε') is not observed.

Fig. 4 presents the temperature dependence of τ. From the data obtained, we can conclude that this time corresponds to hundreds of seconds and the ratios $\varepsilon'_P/\varepsilon'_D$ and $\varepsilon''_P/\varepsilon''_D$ are defined by the phases of LC. It is important to note that the exact trend to a reduction of τ with increase in temperature, common for all temperatures, is not observed. The increase of τ, not typical of other parameters, in particular of conductivity, occurs in the regions of the phase transitions SmA − Chol and Chol − IP. The temperature dependence of d_S also is presented in Fig. 3. Like in [4, 5—8], this parameter was determined on the basis of the following assumptions: in the low-frequency range, the total field is applied to the anode, and the dielectric permittivity of the near-electrode region is equal to the dielectric permittivity of the sample bulk. In this case,

$$d_S = d\frac{\varepsilon_\infty}{\varepsilon_S}. \tag{7}$$

The value of d_S is a few nanometers (Fig. 4). Contrary to τ, the common tendency for d_S to decrease with increase in temperature can be observed for all values of T.

We can mention briefly the analysis of the temperature dependence of α. It was found that, as compared to other parameters, the value of α changes insignificantly upon the temperature reduction: at high temperatures, $\alpha = 0.22$, and it is 0.18 at low ones.

Based on the data mentioned above, we can analyze the influence of illumination upon the sample parameters. The most essential change for ε' and ε'' that occurred under illumination in the low-frequency range allows us to consider that the photoexcitation influences the process of electron transfer between ions and the electrode. As fullerene "is introduced" into the layer, through which such a process goes on, then it can be an additional channel for electron exchange. Therefore, it is necessary to include another additional term into Eq. (4) which would describe the charge relaxation. The presence of the additional channel for electron transfer results in the fact that the relaxation process in the case of illumination does not correspond to the Cole—Cole dispersion, as it does in the case of measurements in dark. The presence of the additional channel for electron transfer increases the active component of a current (ε'').

However, as follows from the data of Fig. 1, the illumination also influences ε', whose values are normalized to the thickness and the area of the near-electrode capacity. As follows from the data obtained, the illumination can increase or decrease the capacity, and it depends on parameters of the surrounding medium (LC mesophase). Thus, it is independent of parameters of the external environment (mesophase LC). It is important to note that the increase in the capacity at illumination is observed only for the SmC*-phase. The highest $\varepsilon'_P/\varepsilon'_D$ value was obtained experimentally for the temperature range close to the SmC* − SmA phase transition. In this temperature range, both possibilities are realized: a change of the orientation of molecular dipoles due to the rotation around the helicoid (the Goldstone mode) axes typical of FLC and a change of the orientation in a plane perpendicular to the smectic layer (the soft mode) [9, 10].

Conclusions

1. We have found that the illumination by the focused light of a halogen lamp increases ε'' and changes ε' of the FLC + 0.43 wt. % $C_{60}+C_{70}$ composite. When the frequency increases, the ratio of the dielectric permittivity at illumination, ε_P, to the dielectric permittivity in dark, ε_D, decreases, and $\varepsilon_P = \varepsilon_D$ for $f > 1$ Hz.

2. For a frequency of 2×10^{-3} Hz, the ratio $\varepsilon_P''/\varepsilon_D''$ has the highest value (more than three) for the IP and decreases monotonously with increase in temperature. The illumination decreases ε' for the IP-, Chol-, and SmA-phases and increases ε' for the SmC*-phase. The highest value of $\varepsilon_P'/\varepsilon_D'$ was found in the range of the SmC*—SmA phase transition. From all the data obtained, it follows that the photoprocesses in Fn—FLC composites are essentially influenced by the FLC structure.

3. Low-frequency dispersion of ε_D' and ε_D'' of the composites corresponds to the Cole—Cole dispersion. The relaxation time τ was estimated to be about hundreds of seconds. An increase of τ, non-typical of other parameters (especially of conductivity), was obtained for the SmA—Chol and Chol—IP phase-transition ranges.

4. The reason for the low-frequency dispersion of ε' and ε'' is the presence of a barrier for electron transfer between ions and the electrode. This fact results in the localization of the whole field in the near-electrode area at low frequencies. The thickness of this area d_S is estimated to be of the nanometer order. It is experimentally shown that the value of d_S decreases with increase in temperature.

5. The main cause of the light influence on the composite parameters is the "shunting" on fullerene molecules of the electron transfer between ions and electrode. The presence of the additional channel for electron exchange results in the disagreement of the low-frequency dispersion of ε_P' and ε_P'' of the composites to the Cole—Cole dispersion in the low-frequency range.

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ФОТОПРОВІДНІСТЬ ТА ДІЕЛЕКТРИЧНІ ВЛАСТИВОСТІ КОМПОЗИТІВ (C$_{60}$ + C$_{70}$) — СЕГНЕТОЕЛЕКТРИЧНИЙ РІДКИЙ КРИСТАЛ

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Р е з ю м е

Одержано стабільні в часі композити сегнетоелектричний рідкий кристал — фулерен. Показано, что опромінення сконцентрованим світлом лампи розжарювання приводить до зміни компонент комплексної діелектричної проникності тільки в діапазоні низьких частот. Знайдено, що відношення величин діелектричної проникності, виміряної при освітленні, до діелектричної проникності, отриманої в темноті, залежить від типу мезофази рідкого кристала. Зроблено висновок, що опромінення приводить до створення додаткового каналу для обміну електронами між іонами і електродом через фулерен.