

## Electrooptical and dielectric properties of liquid crystal-aerosil-photopolymer mixture

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Electrooptical and dielectric properties of liquid crystal (LC)-aerosil-photopolymer three-component mixture have been studied in a wide range of aerosil and photopolymer concentrations. Insertion of aerosil into filled LC prevents phase separation usually observed in such compositions. Increase of the polymer content in filled LC results in an improved of the switching contrast in the electric field and shortened switching-off time. At the same time, the controlling voltage increases. At the polymer concentration of 10 to 15 % (mass), the optimal set of parameters set is obtained; the controlling voltage value is comparable with the corresponding values for the polymer free samples dopant, whereas a considerably higher contrast and system stability is reached. Variations of the electrooptical parameters with the increasing polymer content have been established to be caused to a great extent by the change of system morphology. The limiting morphologies are filled LC with incorporated polymer network and capsulated LC filled with aerosil. Dielectric method has been shown to be suitable for the studies of the system morphology.

Исследованы электрооптические и диэлектрические свойства трехкомпонентной системы жидкий кристалл (ЖК)-аэросил-фотополимер в широкой области концентрации аэросила и полимера. Введение фотополимера в наполненные ЖК предотвращает наблюдаемую в них фазовую сепарацию. С повышением содержания полимера улучшается контраст переключения слоев суспензий электрическим полем и уменьшается время выключения. В то же время увеличивается управляющее напряжение. При концентрации фотополимера 10–15 вес. % достигается оптимум, когда управляющее напряжение сравнимо с его значениями для образцов без полимера, в то же время достигается значительное повышение контраста, а также стабильности системы. Установлено, что изменение электрооптических параметров с увеличением концентрации полимера в значительной мере обусловлено изменением морфологии системы, граничными случаями которой являются наполненный жидкий кристалл со встроенной полимерной сеткой и капсулированный ЖК, наполненный аэросилом. Продемонстрирована возможность применения диэлектрического метода для изучения морфологии системы.

Among the wide variety of electrooptical devices based on liquid crystals (LC) [1], it is just the LC-aerosil (LCA) that is produced using the simplest technology [2–4]. It fact, it requires no LC orientation, while that is a requirement of the most importance for other LC-based electrooptical devices. In LCA, no matching of the LC and polymer matrix parameters is necessary, in contrast to devisec using nematics dsipersed in polymers (PDLC). The wide use of LCA, however, is hindered by several drawbacks inherent in all dispersions of micro- and nanoparticles in liquid matrices. The main

of those consists in the solid admixture aggregation and settling (in particular, in external electric fields) and a rather slow relaxation rate.

The purpose of this work was to seek for a simple technology providing a reduced effect of those factors. We have used the method described in [5] to eliminate the memory effect inherent in LCA. In that method, a polymer network is incorporated into the system and so the aerosil structure becomes stabilized. The rigid polymer network was expected to prevent not only the aerosil structure transformation in electric

field but also its separation from the LC. Unlike [5], we have studied the polymer effect on LCA electrooptical and dielectric properties within a wide range of its concentrations.

The LCA-polymer (LCAP) structures were prepared as follows. At the first stage, LCA mixtures were obtained using the procedure described in [2–4]. The aerosil concentration,  $c_A$ , was varied within limits of 2 to 20 % (by mass) with respect to the LC. Hydrophobic R812 aerosil from Degussa (Germany) [6] and the E7 LC mixture from Merck were used. The E7 parameters at 293 K: dielectric constant at the planar molecular orientation  $\epsilon = 5.2$ ; the dielectric constant anisotropy  $\Delta\epsilon = +13.8$ . At the second stage, the photopolymer No.65 from Norland (USA) was added to the LCA mixture. The photopolymer concentration was varied from 5 to 40 % (by mass) with respect to the LC. Moreover, the photopolymer mixture described in [7] was used to prepare PDLc samples. Its concentration in E7 was 45 % (by mass). The LC-aerosil-photopolymer compositions were mixed thoroughly and placed between two glass plates with transparent conductive ITO layers on inner surfaces. To provide the desired composition layer thickness, few spacers were placed onto one plate. The mixture was distributed uniformly over the sample area, then the plates were pressed together in an uniform manner and so fixed using an epoxide adhesive. All operations were carried out under red light illumination to avoid the photopolymer polymerization. The photopolymerization was made using a low pressure mercury lamp of 2 mW/cm<sup>2</sup> for 30 min.

The transmission,  $T$ , as a function of the voltage applied,  $U$ , was measured using a setup with small photoreceiver aperture [4, 8]. The incident light beam from a He-Ne laser passing through the glass plate was normal to the sample under study. The beam reflected from the plate was used to monitor the laser power. The  $T(U)$  measurements were made at 1 kHz frequency, the voltage change rate was less than 0.05 V/s. The  $T(U)$  dependences were registered using a two-coordinate recorder. Three measurement cycles were carried out for each sample: under increasing  $U$  up to  $U_s$  (i.e., the voltage corresponding to  $T$  saturation); under  $U$  decreasing down to 0 at the same rate; and under repeated  $U$  increasing to  $U_s$ . The experiments have shown that the

data obtained at the 2nd and 3rd measurement cycles are reproducible to within 2 %. It is just those data that will be considered in what follows. The following parameters were determined from the obtained  $T(U)$  dependences:  $T_0$ , the transmission at  $U = 0$ ;  $T_{\max}$ , the maximum  $T$  value;  $\Delta U_{0.5}$ , the  $T(U)$  curve hysteresis expressed as the difference between  $U$  values corresponding to  $T = 0.5T_{\max}$  in curves corresponding to 2nd and 3rd cycles;  $U_{0.9}$ , the voltage corresponding to  $T = 0.9T_{\max}$ .

To analyse the transmission kinetics at the voltage switching-on and switching-off, square voltage pulses of the frequency from 0.1 to 10 Hz and with amplitude equal to  $U_T$  were applied to the sample. When considering the oscillograms so obtained, both transmission increase and drop kinetics were assumed to meet an exponential law. Proceeding therefrom, the time constants for transmission increase and drop ( $\tau_{\text{on}}$  and  $\tau_{\text{of}}$ , respectively) corresponding to the voltage switching-on and switching-off were determined. The frequency dependences of the complex dielectric constant components  $\epsilon'$  and  $\epsilon''$  were determined using the procedure described in [9].

The phase separation in the samples was first tested. To that end, the 100 V voltage at 30 Hz and 1 kHz frequency was applied to those for 5 min. The phase separation extent was judged comparing the sample structure observed by optical microscopy prior to and after the test. No substantial structure changes were seen for samples containing the photopolymer. In the polymer-free ones, the aerosil separation took place, being particularly intense at the 30 Hz frequency. This resulted in an irreversible sample brightening and its homogeneity loss. For that reason, all subsequent measurements were made using 1 kHz frequency.

The electrooptical and time parameters for LCA and LCAP samples at different aerosil and photopolymer contents are presented in the Table below. The data are grouped according to the same photopolymer concentration but different aerosil ones. In each group, the aerosil content increase results in an appreciable drop of the initial transmission, while the saturation one varies only slightly. This causes a considerable increase of the switching contrast (exceeding one decimal order for some samples). At the same time, the switching voltage value increases. It is also seen from the

Table. Electrooptical and time parameters of LCA and LCAP layers as functions of aerosil ( $c_A$ ) and photopolymer ( $c_P$ )<sup>\*</sup>

No.	$c_P$ , %	$c_A$ , %	$T_0$ , %	$T_s$ , %	$T_m$ , %	CR	$U_{0.9}$ , V	$\Delta U_{0.5}$ , V	$\tau_{op}$ , ms	$\tau_{off}$ , ms
1	0	5	1.5	94	91	61:1	46		2	200
2	0	10	1.1	89	1.4	81:1	49	0.3	1	100
3	0	20	0.8	90	0.9	120:1	55	5	2	100
4	5	5	7	87	7	13:1	50	2	20	300
5	5	10	5	90	5	18:1	52	7	5	250
6	5	20	2	90	2	45:1	103	11	20	200
7	15	5	1	65	0.8	80:1	20	1.5	2	100
8	15	10	0.5	84	0.5	165:1	30.5	2	10	80
9	15	20	0.1	85	0.4	850:1	50	5	10	100
10	40	5	0.1	65	0.1	650:1	120	2	10	20
11	40	10	0.1	70	0.1	700:1	180	2	10	10
12	40	20	0.05	64	0.07	950:1	190	1.5	20	10
13	45	0	0.13	92	1	710:1	79	21	5	200
14	45	5	0.10	92	0.3	920:1	92	36	2	100

\* concentrations calculated with respect to the liquid crystal mass.

Table that the increase in the aerosil content effects only slightly the response time at the electric field application,  $\tau_{on}$ , but causes a decrease in the relaxation time,  $\tau_{of}$ , by a factor of 1.5 to 2. In photopolymer-free sample series, an effective memory is observed at the aerosil content of 5 % that disappears essentially as the aerosil concentration is increased to 10 %. No memory effect was observed for photopolymer-containing samples, that fact agrees well with results obtained in [5].

The photopolymer introduction causes a very interesting change in the electrooptical properties. At low concentrations (5 %), it reduces the contrast considerably due to increased initial transmission. At the same time, the switching voltage increases. The polymer introduction results in that the switching-on time constant  $\tau_{on}$  increases almost by one decimal order, while the  $\tau_{of}$  value is influenced only slightly. The polymer concentration increase up to 10–15 % causes a sharp contrast increase while the switching voltage becomes lowered. The time parameter of the samples are very close to those for polymer-free ones. The

further polymer content increase up to 40 % results in a slight contrast change but the switching voltage is increased substantially. In contrast to the samples with low polymer content, the relaxation constant  $\tau_{of}$  is several times shorter. In the last series of PDLC, the aerosil incorporation results in an improved sample homogeneity, increased switching contrast as well as reduced relaxation time. In parallel, the switching voltage increases.

Considering the data obtained from the practical application standpoint, it is to note that for the LC, aerosil and polymer kinds used in this work, the optimum parameter set is attained in the composition with  $c_A = 5$  to 10 % (by mass) and  $c_P = 15$  % (by mass). This composition provides a rather high contrast value (about 100:1) at relatively low switching voltages (20 to 30 V). The fact that the aerosil incorporation into the PDPL samples improves their homogeneity and contrast as well as reduces the switching-off time is also of practical importance. To improve further the composition parameters, components with characteristics most suitable for specific applications are to be selected. For example, LC with great dielec-

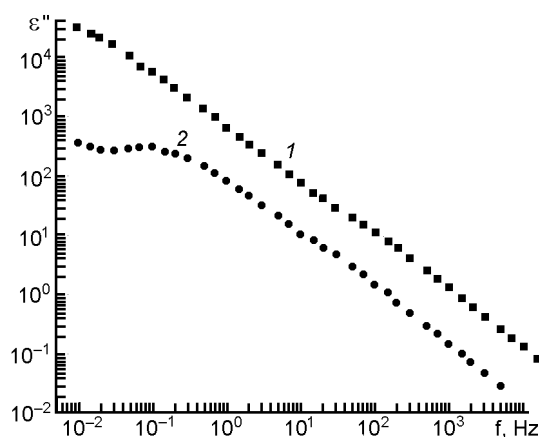


Fig. 1. Frequency dependences of  $\epsilon''$  for samples with  $c_A = 10$  % (mass),  $c_P = 0$  % (1);  $c_A = 10$  % (mass),  $c_P = 40$  % (mass) (2).

tric constant anisotropy are reasonable to be used to reduce the switching voltage. The matching of refractive indices for the composition components is of importance to enhance the contrast.

Some of the results obtained are easy to explain. Let the LCA system be considered as a set of LC domains enclosed in aerosil aggregates [3]. The increased aerosil concentration causes the reduced LC domain size. This explains the switching voltage and contrast increase as well as the relaxation time reduction due to the aerosil content increase. The unmonotonous dependence of electrooptical parameters on the photopolymer concentration is less obvious, additional data on the system, first of all, on its morphology, being necessary to interpret those results. Some of those data can be obtained from dielectric measurements, as will be shown lower.

Fig.1 presents the frequency dependences of  $\epsilon''$  for samples with  $c_A = 10$  %,  $c_P = 0$  (1) and with  $c_A = 10$  %,  $c_P = 40$  % (2). The  $\epsilon''(f)$  curve for the polymer-free sample is seen to drop monotonically. At low polymer concentrations, the curve is similar to the 1. At 40 % polymer, a maximum exists pointing to a new relaxation region. A similar dependence is observed for Samples 13 and 14 which have definitely the PDPL morphology. The dispersion similar to that found by us and often referred to as the Maxwell-Wagner relaxation was observed before in LC confined in porous glasses [10], although the dispersion region corresponds to higher frequencies ( $10^4 < f < 10^6$  Hz). The Maxwell-Wagner relaxation in our case may evidence the tran-

sition from the LC-polymer network structure to that of capsulated (dispersed) LC. Thus, the dielectric measurements could provide an effective control method not only for the photopolymer content in the system but, in some cases, for the structure of the latter.

Thus, it follows from the data obtained that the photopolymer provides the LCAP structure stabilization. As the polymer concentration increases, the electrooptical properties vary unmonotonically: a small polymer additive in the LCA reduces the contrast and increases the switching voltage. At the polymer concentration  $c_P = 15$  %, an optimum is attained where the switching voltage values are comparable with those for polymer-free LCA while the contrast is several times higher. A further  $c_P$  increase results in a substantial switching voltage increase without any substantial contrast changes. At the same time, the relaxation time is reduced by one decimal order. The results obtained may be due to a substantial changes in the sample morphology caused by the polymer concentration variation. The dielectric measurement results show a new relaxation region in samples containing more than 40 % polymer. This may evidence the transition from the LC-polymer network structure to that of capsulated LC.

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## **Електрооптичні та діелектричні властивості сумішірідкий кристал-аеросил-фотополімер**

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Досліджено електрооптичні і діелектричні властивості трьохкомпонентно системи рідкий кристал (РК)-аеросил-фотополімер в широкій області концентрацій аеросилу і полімеру. Внесення фотополімера в наповнені РК усуває фазову сепарацію, що спостерігається для таких систем. Зростання концентрації полімеру призводить до покращення контрасту перемикання шарів суспензій електричним полем та зменшу час вимкнення. Поряд з ним, збільшуться керуюча напруга. При концентрації полімеру 10–15 вага.р % досягається оптимум, коли величина керуючої напруги порівняна з аналогічною величиною для зразків без полімеру, однак досягається значно вищий контраст, а також стабільність системи. Встановлено, що зміна електрооптичних параметрів зі збільшенням концентрації полімера у великій мірі спричинена зміною морфології системи, граничними випадками яко наповнений рідкий кристал із внесеною полімерною сіткою та капсульований РК, наповнений аеросилом. Продemonстровано можливість застосування діелектричного методу для вивчення морфології системи.