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Electrooptical Properties of Three-Component Compositions "Liquid Crystal-Aerosil-Photopolymer"

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Electrooptical properties of three-component mixture "liquid crystal (LC)-aerosil-photopolymer" are investigated in a wide concentration region of aerosil and photopolymer. Polymer structure formed under UV irradiation prevents separation of aerosil and causes improvement of several performance characteristics- increase of the switching contrast and contraction of the switching off time. At the same time, controlling voltage increases with the increase of polymer concentration. At the polymer concentration of 10-15 % by weight optimal set of the parameters is obtained; the value of controlling voltage is comparable with the corresponding value for the samples without polymer dopant, whereas considerably higher contrast and system stability are reached. Variation of the electrooptic parameters with the increase of polymer part in the system is supposed to be caused not only by higher fraction of polymer but also by the change of system morphology. Special cases of such morphology presumably are filled LC with incorporated polymer network and capsulated LC filled with aerosil.

Keywords: aerosil; liquid crystal; polymer; electrooptics

INTRODUCTION

There are two main operation principles of modern LCDs. They are associated with electrically controlled birefringence of properly oriented LC layers and electrically controlled light scattering of the layers of heterogeneous materials with participation of LC. Last principle is quite attractive, since no polarizer system is implied and uniformity of the cell thickness is not a critical requirement. A well-known representative of the class of heterogeneous LC materials is polymer dispersed LC (PDLC) ^[1]. Recently, new heterogeneous system was proposed which consists of small solid particles dispersed in LC ^[2-4]. Aerosil, highly dispersed modification of silica, is usually used as a filling material. Preparation technology of filled LCs is much more simple then for other heterogeneous LCs. In contrast for example to PDLC, refractive indexes matching is not necessary requirement. Besides, the problem of not complete separation of the polymer composition from LC does not arise for filled LCs. The only one principle problem of the studies suspensions is separation of the particles of solid phase especially intensive under the influence of external factors.

The aim of this work is search of the simple method preventing mentioned phase separation. We used approach suggested in ^[5] for elimination of memory effect intrinsic for filled LCs. The basic idea is incorporation of rigid polymer network, which stabilizes the structure of aerosil. In contrast to ^[5], we investigated influence of polymer fraction on the electrooptic parameters of filled LC in the wide concentration region of polymer. Possible morphological modifications are discussed.

EXPERIMENTAL

Sample preparation

Two compositions "LC-aerosil" (LCA) and "LC-aerosil-photopolymer" (LCAP) were investigated. LCA suspensions were prepared as it is described in [3,4]. We used nematic liquid crystalline mixture E7 by Merck and hydrophobic aerosil R812 by Degussa (Germany) [6]. Aerosil concentration was varied within 2 and 20 % by weight calculated with respect to the mass of LC. As a photopolymer agent we used photocuring mixture No 65 by Norland Inc (USA). A polymer concentration was varied in the range of 5-40 wt % (with respect to the weight of LC). Besides, for preparation of the samples with PDLC morphology we used polymer composition earlier described in [7]. Its concentration in LC was about 45wt %. The compositions were thoroughly mixed and placed between two glass slabs covered by ITO from the inner side. Surface of one from the slabs was coated with small amount of glass spacers to maintain thickness of the samples. The slabs were uniformly pressed and glued with epoxy adhesive. Described operations were performed by the red light in order to prevent photopolymerization during preparation of the samples. The photopolymerization was carried out using mercury lamp with the intensity of 2 mW/cm^2 . Irradiation time was 30 min.

Experimental method

A light transmission T versus applied voltage U curves were measured by set up with a small aperture of receiving photodiode [4,8]. Frequency of the applied voltage was 1 kHz. Dependencies $T(U)$ were recorded with a plotter. Three measuring cycles were realized. 1) Voltage increase from zero to U_s corresponding to saturation of T . 2) Voltage decrease from U_s to zero. 3) Second voltage increase from zero to U_s .

From the measured curves $T(U)$ the following parameters were estimated: T_0 – transmittance at $U=0$; T_{max} – maximal value of T ; $\Delta U_{0,5}$ – hysteresis of the curve $T(U)$ determined as a difference of the values of U at which value $T=0,5T_{max}$ is reached in the measuring cycles 2 and 3; $U_{0,9}$ – voltage corresponding to $T=0,9T_{max}$.

Switching on and switching off kinetic curves $T(t)$ were measured by application to the samples rectangular voltage pulses with a frequency of 0.1 Hz and amplitude equal to $U_{0,9}$. On the base of these curves the values of switching on, τ_{on} , and switching off time, τ_{off} , were estimated assuming single-exponential character of the measured curves $T(t)$.

EXPERIMENTAL RESULTS AND DISCUSSION

At first, samples were tested for the purpose of phase separation. In this case electric voltage of 100 V was applied to the samples over 5 min. A field frequency was 30 Hz and 1 kHz. Sample textures before and after application of the field were compared by observation in polarizing optical microscope. In the layers of filled LC we clearly observed separation of aerosil especially intensive at the frequency of 30 Hz. In contrast, in the samples containing photopolymer it was not detected any change of the texture caused by application of the electric field.

The estimated electrooptical parameters of some investigated LCA and LCAP samples are presented in Table 1. The data are divided in groups characterized by the same polymer concentration but various concentration of aerosil. Rise of aerosil concentration in each group of samples leads to considerable reduction of the initial transmittance and, hence, to essential increase of the switching contrast. Simultaneously, controlling voltage increases. Increase of aerosil fraction does not

essentially influence response time τ_{on} , whereas τ_{off} decreases by a factor of 1.5-2. In a series without polymer at the concentration of aerosil of 5 wt % effective memory was observed (Fig.1a). It is practically vanished at $c_a=10$ wt %. In addition, memory was not observed in all samples with a polymer content. This result agrees well with [5].

Table. Electrooptical parameters obtained for the samples with various concentration of aerosil and photopolymers

№	c_p , %	c_a , %	T_0 , %	T_s , %	T_m , %	CR	$U_{0.9}$, B	$\Delta U_{0.5}$, B	τ_{on} , μ s	τ_{off} , μ s
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

At small fraction of photopolymer in composition (5wt %) contrast ratio is essentially decreased because of growth of initial transmittance. Simultaneously, controlling voltage increases. Switching on time, τ_{on} also increases (almost in one order of magnitude), whereas value of τ_{off} changes not essentially. Increasing polymer concentration to 10-15 wt

% leads to sharp increase of the switching contrast and to reduction of

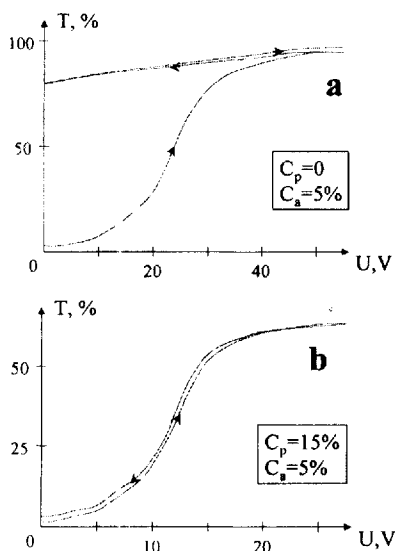


FIGURE 1 Transmittance vs voltage dependencies for LCA (a) and LCAP (b).

the controlling voltage. Time parameters of these samples are similar to that for the samples without polymer. The further increase of the polymer fraction to 40 wt % weakly changes contrast ratio but considerably increases controlling voltage. Comparing with the samples having lower content of polymer, the relaxation time, τ_{off} , reduces in a few times reaching 10 ms.

In the last series corresponding to PDLC, insertion of aerosil improves uniformity of the samples,

increases switching contrast and reduces characteristic time of the system relaxation. Simultaneously, the value of controlling voltage increases.

Analyzing presented results from the point of applications one can admit good optimization of the electrooptical parameters. For the chosen LC, aerosil and polymer the optimal parameters set was obtained for $c_a=5-10$ wt % and $c_p=15$ wt %. In these case fairly high contrast ratio 100:1 was reached at relatively low controlling voltage 20-30 V. It is also important that insertion of aerosil in the samples with PDLC morphology improves its uniformity and performance characteristics.

Some results of our experiments can be easily interpreted in frame of the existing concept of the structure of filled LCs. Let us conceive LCA as a system of LC domains separated by aerosil aggregates. Increase of aerosil fraction in the composition leads to reduction of LC domains. It can be a reason of the experimentally observed increase of controlling voltage and contrast ratio, as well as decrease of the relaxation time. The non-monotonic dependence of some electrooptical parameters on the polymer concentration is not so explicable. We believe that these results are strongly determined by the change of system morphology with the increase of polymer content in studied composition. At the small concentration of polymer (5 wt %) the structure of separated polymer domains is assumed to be formed under UV irradiation ^[9]. At the concentration of 10-15 wt % it is transformed in the structure of persistent polymer network ^[10]. At $c_p=40$ wt % continuous polymer layers should be formed containing cavities filled with LC ^[11]. The studies of LCAP morphology and its evolution under the change of polymer concentration are in progress.

CONCLUSIONS

Thus, composition "LC-aerosil-photopolymer" is a system perspective for modern LCD technologies. Insertion of photopolymer in filled LC leads to stabilization of aerosil structure and prevention of aerosil separation. Increase of polymer fraction in a composition leads to the non-monotonous change of electrooptical parameters. Addition of small amount of polymer deteriorates contrast and increase controlling voltage. At the polymer concentration $c_p = 15$ wt % optimum is reached when values of controlling voltage are comparable with that obtained for the samples without polymer. In addition, contrast ratio essentially

increases. A further increase of c_p leads to increase of controlling voltage without any noticeable changes of the switching contrast. Simultaneously, the time of system relaxation decreases. Observed dependencies presumably are strongly influenced by the change of the system morphology. Particular cases of the realized structures are modified versions of the well-known systems - filled LC with aerosil network and PDLC filled with aerosil. Modified systems have improved performance characteristics compared with its two-component analogs.

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