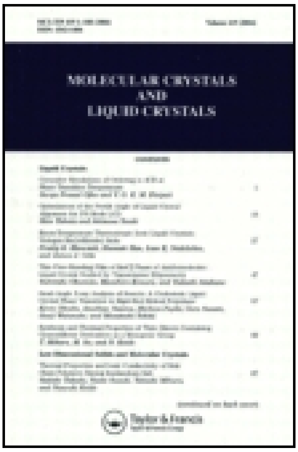

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Electro-optics of LC-Aerosil-Photopolymer Composites

S. Zakrevska [a], Yu. Zakrevskyy [a], A. Nych [a], O. Yar0Shchuk [a] & U. Maschke [b]

[a] Institute of Physics, NASU, Prospect Nauki 46, Kyiv, 03028, Ukraine

[b] Laboratoire de Chimie Macromoléculaire, CNRS, Universite des Sciences et Technologies de Lille, Villeneuve d'Ascq, 59655, France

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Electro-optics of LC-Aerosil-Photopolymer Composites

S. ZAKREVSKA[a], YU. ZAKREVSKYY[a], A. NYCH[a],
O. YAROSHCHUK[a*] and U. MASCHKE[b]

[a]*Institute of Physics, NASU, Prospect Nauki 46, 03028 Kyiv, Ukraine, and*
[b]*Laboratoire de Chimie Macromoléculaire, CNRS, Universite des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France*

Electroopic properties of LC-Aerosil-Photopolymer composites are studied in a wide concentration range of the mixture components. The main results relate to the dynamic parameters describing response to an applied electric field. An increase of the aerosil content results in a decrease of the rise and decay times (except samples with PDLC morphology), whereas an increase of the concentration of photopolymer causes an increase of these parameters. Variation of the transmittance, caused by an alternative voltage consists of alternative and direct components depending on the frequency of the applied voltage. The obtained results are explained based on the structural peculiarities of the LC-Aerosil-Photopolymer composites. The set up designed for the electrooptic measurements is described.

Keywords: liquid crystal; aerosil; polymer network; electrooptics.

INTRODUCTION

Filled liquid crystals (LC), suspensions of small particles in LC, form a separate class of heterogeneous composite materials. An

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[*] Corresponding author. E-mail: olegyar@iop.kiev.ua.

example of this class of systems consists of a suspension of needlelike ferromagnetic particles in LC and was suggested in the 70's by Chen et al.[1] to enhance magnetic sensitivity of LCs. The interest to these suspensions arose further in the beginning of 90's, when Eidenschink and de Jeu[2] and later Kreuzer *et al.*[3] and Guba *et al.*[4] reported unique electrooptic properties of suspensions of aerosils in LC. The term "filled LC" was then suggested for the first time for this kind of suspensions and their properties were studied for nematic[2-4], cholesteric[5] and smectic mesophases[6]. Recently, systems containing new fillers (titanium dioxide, carbon black[6], clay[7] and styrene[8] particles) were considered and new nanoparticles were suggested along the lines of advances in nanotechnologies.

The vast majority of filled LCs attract great attention due to the effect of electrically controlled light scattering that was previously intensively studied for PDLCs[9]. Compared to PDLCs, the LC-aerosil composites demonstrate wider spectrum of electrooptical parameters. For instance, the electro-optical response can be either practically reversible or highly irreversible with a strong memory. The efficiency of memory depends on the concentration of filler, the interfacial interaction LC-filler and the parameters of the applied electric field[10]. The main drawback is the high degree of phase separation for low aerosil concentrations. A way to circumvent this problem was suggested in[11]. It consists in the formation of polymer network in LC-Aerosil suspension. This network serve to stabilize the system and to diminish the memory effect.

In the present paper the electrooptical properties of LC-Aerosil-Photopolymer composites in a wide range of aerosil and photopolymer concentrations are studied. This is an extension of recent work[12] where we addressed the properties of fascinating objects like filled LC with polymer network and encapsulated LC filled with aerosil. In contrast to previous studies, we intend here to elucidate mainly the dynamics of the electrooptical response of the LC-Aerosil-Photopolymer composites. In addition we use the composites in which the aerosil structure is fixed by the polymerization of aerosil particles without adding a photopolymer component. The results of electro-optical investigations are used to interpret structural peculiarities of the studied objects. The original set up serving in electrooptical studies of LC cells is described.

EXPERIMENTAL PART

Samples

The eutectic LC mixture E7 by Merck was used to prepare the composites. This mixture possesses a nematic order in the range –62° ÷ 59 °C. The pre-polymer consists of an aromatic polyester acrylate (Rahn AG, Switzerland) diluted with tripropyleneglycoldiacrylate purchased from USB, Belgium. The UV polymerization was initiated by adding 0.8 wt-% of the photo-initiator 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173, Merck Darmstadt, Germany).

Mixtures LC - Aerosil with an aerosil concentration of c_a=5, 10, 15 weight % were prepared where $c_a=m_a/(m_a+m_{LC})$, m_a and m_{LC} being the weights of aerosil and LC, respectively. Two types of aerosil, R812 and R711 (Degussa) were used. The hydrophobic aerosil, R812 did not cause any bonds with polymer. In contrast, R711 contained $-CH=CH_2$

as surface groups capable of polymerizing with each other or with the pre-polymer agent. To initiate polymerization of R711 a small amount (1 wt-%) of photoinitiator was added to the aerosil.

Mixtures with photopolymer were prepared as follows. The pre-polymer at concentration of c_p= 0.5, 10, 20, and 45 weight % was added to the LC+Aerosil mixture with $c_p=m_p/(m_p+m_m)$, m_p and m_m are the weight of polymer and LC+Aerosil components, respectively. A small amount of spacer (*d* = 20μm) was introduced into the mixture to fix the thickness of the tested layers. The suspension was placed between two glass substrates covered with ITO layers from the inner side. The substrates were pressed and glued by an epoxy glue. The mixture and cell preparation processes were carried out at the red light in order to prevent photopolymerization. The samples containing pre-polymer and the E7-R711 composites doped with photoinitiator were irradiated with the mercury lamp (4 mW/cm^2, 20 min) in order to provide photopolymerization.

Experimental set up

The electroopic characteristics of the samples were measured using the original set-up which was designed by the Kyiv authors. The schematic diagram of the set-up is presented in Figure 1. The computer was programmed so that at the output, we have a signal with a given shape, amplitude and frequency (10…2000Hz). In the present experiments, sinusoidal voltage was applied to the samples. The signal was amplified using a wide-band amplifier. The active value of the voltage applied to the cell was controlled by a computer. The averaged transmittance signal was detected by a photodiode also connected to the computer. The sample transmittance was defined as the ratio I_{out}/I_{in}, were I_{in} and I_{out} are the intensities of the probe beam before and after passing through the sample. The non-scattered light and the light scattered within the angle of 2^0 was detected with a photodiode. The T-V curves were measured automatically by the discontinuous change of the applied voltage for a given frequency. Since some probes demonstrate memory effect, the T-V curves were measured twice - as the voltage increase to the saturation of T, as the voltage decreases to 0 and again as the voltage increases to the saturation level. The switch on and switch off characteristics T(t) were measured by step-wise switching of the applied voltage (f=2 kHz) between 0 and 200 V. The frequency

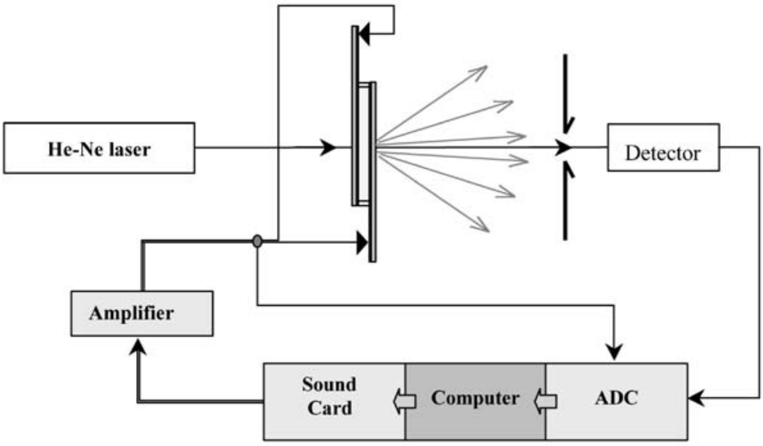

FIGURE 1 The electro-optic set-up.

dependencies of the transmittance were measured using the oscilloscope program specially developed for this purpose.

RESULTS AND DISCUSSION

T-V curves

Two types of T-V curves were obtained. In the first case, the T-V curve is characterized by the high residual transmittance after the electric field is removed (Figure 2a). Such a T-V curve is peculiar to E7-R812 composite for a low aerosil content (c_a=5 wt-%). In the second case the T-V curve is reversible. It is characterized by a pronounced hysteresis (Figure 2b). This type is inherent to all composites containing polymer as well as to the composites based on the aerosil R711.

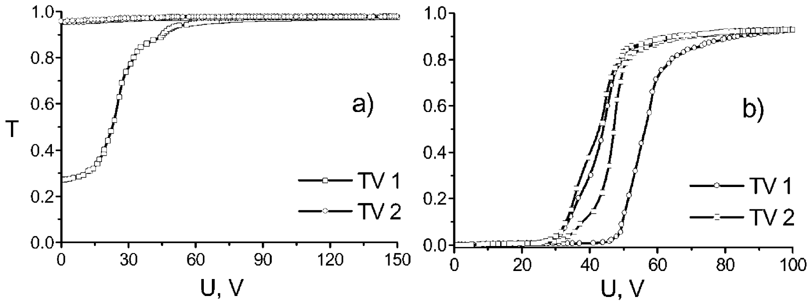

FIGURE 2 Transmittance vs voltage curves. a) E7-R812 (c_a=5 wt-%); b) E7-R711 (c_a=5 wt-%, UV irradiated).

The following properties are given in Tables 1 and 2. One finds the initial zero-field sample transmittance, T_{00} (the transmittance before the first voltage increase), the zero-field transmittance after the voltage application (memory transmittance), T_0, the saturation transmittance,

TABLE 1. Electrooptic parameters of „E7-R812-Photopolymer“ composites.

No	c_p, %	c_a, %	T_{oo}, %	T_o, %	T_s, %	CR	$U_{0,9}$, V	$\Delta U_{0,5}$, V	τ_{on}, ms	τ_{off}, ms	f, Hz	d, μ
1.1	0	5	68	88	99	1.1:1	36	5.3				20
1.2	0	10	3	4	99	25:1	54	12	<10	20	400	20
1.3	0	15	1	1	95	95:1	160	25	<10	<10	900	20
1.4	5	5	6	6	96	16:1	51	13	<10	38	700	20
1.5	5	10	1	1	96	96:1	135	29	<10	18	2000	20
1.6	5	15	1	1	92	92:1	186	27	<10	17	1500	20
1.7	10	5	57	61	98	1.6:1	30	8	10	220	100	20
1.8	10	10	1	1	95	95:1	103	23	10	40	200	20
1.9	10	15	1	1	96	96:1	179	37.6	<10	30	1400	20
2.10	45	0	3	5	97	19:1	65	25	10	100	100	20
1.11	45	5	2	19	99	19:1	34	10	10	730	100	20
1.12	45	10	22	75	97	1.3:1	51	17	<10	157	200	20

TABLE 2. Electrooptic parameters of „E7-R711-Photopolymer“ composites.

No	c_p, %	c_a, %	T_{oo}, %	T_o, %	T_s, %	CR	$U_{0,9}$, V	$\Delta U_{0,5}$, V	τ_{on}, ms	τ_{off}, ms	f, Hz	d, μ
2.1	0	5	1	1	93	93:1	54	5	<10	<10	450	20
2.2	0+	5	10	11	95	9:1	118	18	20	147	200	20
2.3	5	5	5	5	89	18:1	50	7	20	350	100	20
2.4	5	10	1	1	95	95:1	155	48	20	60	100	20
2.5	5	15	1	1	90	90:1	163	31	10	40	200	20
2.6	20	5	3	4	88	22:1	85	34	20	50	150	20
2.7	45	0	3	5	97	19:1	65	25	10	130	100	20
2.8	45	10	2	5	96	19:1	84	33	10	470	200	20
2.9	45	15	1	1	94	94:1	136	45	<10	230	600	20
2.10	45	0	3	5	97	19:1	65	25	10	100	100	20

T_s, the controlling voltage, $V_{0,9}$ (corresponding to T=0,9 T_s), the hysteresis, $V_{0,5}$ (the width of hysteresis loop at T=0,5T_s), and the switching contrast $CR=T_s/T_0$. The results concerning E7-R812 and

E7-R711 composites are shown in Table 1 and Table 2, respectively. The data are presented for both LC-Aerosil and LC-Aerosil-Photopolymer composites.

Analyzing the data of Table 1 and Table 2, one concludes that memory of filled liquid crystals can be suppressed by adding the pre-polymer and its subsequent polymerization. Moreover, the same result can be obtained by polymerization of the aerosil particles (through the polymerization of the surface -$CH{=}CH_2$ groups). Following the model of memory effect[3,4] the origin of the residual transmittance is associated with the destruction of the aerosil structure under the LC re-orientation in the electric field. The new aerosil skeleton formed in the oriented LC matrix stabilizes the LC alignment when the field is removed. This mechanism can be realized when the aerosil skeleton is weak. At the high aerosil content (10-15 wt-%) the aerosil skeleton is fairly strong and the memory effect is not observable. For the same reason, the memory is suppressed in the suspensions containing polymer or polymerized aerosil particles.

Instead of the residual transmittance, the T-V curves of the samples exhibiting a reversible response are characterized by hysteresis (Figure 2b). This hysteresis increases with the aerosil and/or polymer concentration. This shows that hysteresis grows with the decrease of the size of LC domains separated by the parts of the solid skeleton. The higher the dispersion of LC, the stronger the interfacial surface between LC and solid skeleton. P. Drzaic[14] has suggested that hysteresis in PDLC is due to a thin layer of LC at the interface of polymer and LC, which is not oriented by the field in the same manner as in the bulk of

LC drops. According to this model, the increase of interfacial surface should cause an increase of hysteresis.

Assuming that LC domains shrink with the polymer and aerosil content, one can explain other tendencies, such as the increase of controlling voltage, lowering of the initial transmittance and the corresponding increase of the switching contrast.

Dynamic characteristics

To study the dynamics of electrooptic responses, two types of characteristics have been measured. The first one was the dependence of the sample transmittance T on frequency of applied electric field f. It was observed that the transmittance obtained under the application of the sinusoidal voltage consists of an alternative T_a, and a current T_c components. The typical T_a vs f, T_c vs f and $T=T_a+T_c$ vs f curves are represented in Figure 3. The $T_a(f)$ curve monotonously decreases, whereas the $T_c(f)$ curve monotonously grows with the field frequency. In contrast, the total transmittance is practically constant. This result was earlier obtained for LC-Aerosil system[4]. The T_a component was assigned to the LC domains capable to reorient in time following changes in the electric

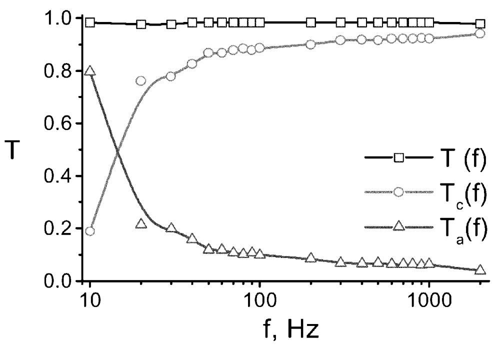

FIGURE 3 Frequency dependencies $T(f)$, $T_a(f)$ and $T_d(f)$ for the E7-R711 composite (c_a=10wt-%, c_p=5wt-%).

field. In turn, the T_c component was assigned to large domains, which can not follow changes of the electric field. The constant value of T was explained assuming a fixed amount of LC aggregates. Increasing the frequency leads to a decrease of the part of the LC domains that are sensitive to changes in the electric field while the rest of LC domains are not sensitive to such changes. Similar frequency characteristics were also obtained for LC-Polymer composites having the swiss-cheese PDLCs morphology[15]. The present results show that the described properties are common for LC-Aerosil - Polymer composites. Based on $T_a(f)$ curve the relaxation frequency f_r was estimated (see Table 1 and Table 2).

The time dependence of the sample transmittance following a step-wise switching on and switching off the applied voltage was also investigated. Typical curves obtained from our samples are presented in Figure 4. The rise time, τ_{on}, and the decay time, τ_{off}, measured for various concentrations are presented in Tables 1 and 2. The rise time was estimated roughly to be less then 10 ms. The more precise values of τ_{on} can be obtained

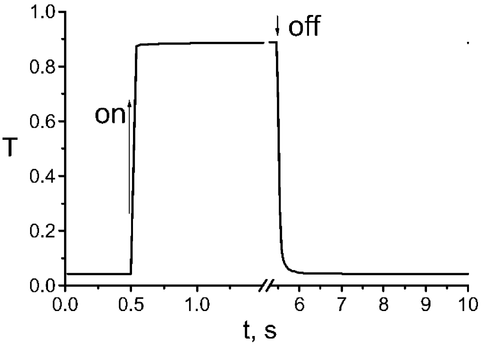

FIGURE 4 Rise and decay kinetic of the sample transmittance at the step-wise switching on (1) and switching off (2) of the applied voltage (155 V, 2 kHz). Sample: E7-R711-Polymer (c_a=10 wt- %, c_p=5 wt- %).

from the relaxation frequency as $\tau_{on}=1/f_r$, since the relaxation of LC domains is determined by the domain response to the applied electric field. The obtained value of τ_{on} is of the order of several milliseconds and decreases as the aerosil content increases. This means that the domains of LC become smaller knowing that τ_{on} and the domain size are related by[16]

$$\tau_{on}^{-1} = [\frac{1}{\eta}(\Delta\varepsilon E^2 + \frac{K(l^2-1)}{a^2})] \qquad (1)$$

where η represents the rotational viscosity coefficient, ΔE is the anisotropy of the dielectric constant, E is the applied electric field, K is an effective deformation constant, $l=a/b$ is the aspect ratio of the elongated droplet, a and b are the lengths of the semi-major and semi-minor axes, respectively. This is confirmed with the direct observation of the suspension layers under polarized microscope.

Tables 1 and 2 also show that the decay time of the LC domains τ_{off} decreases with the increase of aerosil concentration. It can be determined from [16]

$$\tau_{off} = \frac{\eta a^2}{K(l^2-1)} \qquad (2)$$

Assuming that the dependence of LC constants η and K on the aerosil concentration is not crucial one can conclude that the decrease of τ_{off} with the content of aerosil is caused by the reduction of LC domains. This agrees well with the observation made above for the rise time.

One can also admit that both rise and decay times depend on the concentration of photopolymer. In contrast to dependencies on the aerosil concentration, τ_{on} and τ_{off} become larger by increasing the photopolymer content or by photopolymerisation of the aerosil particles. We believe that this effect is mainly caused by the modification of liquid crystal properties with the photopolymer remaining in LC after the photoinduced phase separation. This statement was additionally confirmed by the electro-optic studies of LC doped with small amount of photopolymer (c_p=1-2 w-%). Hence, the polymer dopant preventing phase separation in LC-Aerosil composites enhances response times of the system.

Variation of the system morphology

Increasing the polymer content strongly changes morphology of the composite. At small polymer concentrations (5-20wt-%) the pre-polymer forms rigid networks during photo-polymerization in LCs[17]. These composites are known as polymer network liquid crystals (PNLC). At the higher polymer concentration (c_p>40wt-%) the LC ejected from polymer forms droplets of different shape and different director configuration[9,18,19]. Such materials are known as polymer dispersed liquid crystals (PDLC).

Let us consider the obtained results from the point of view of the influence of aerosil on the electro-optical properties of LC-Polymer composites. For the composites having PNLC morphology, insertion of aerosil enhances the contrast ratio, decreases rise and decay times. These changes can be considered as advantages of PNLC. On the other hand, the composites doped with aerosil shows higher controlling voltage. This is a drawback of the aerosil containing PNLCs. PDLC systems containing aerosil demonstrate substantially enhanced contrast but with the drawback of increased controlling voltage and decay time.

The latter effect is however not quite clear and will be further elucidated by studies of the morphology of LC-Aerosil-Polymer composites.

CONCLUSIONS

The electro-optical properties of LC-Aerosil-Photopolymer composites strongly depend on the properties of the components and their concentrations. An increase of the aerosil content causes a decrease of the rise and decay times, except samples with PDLC morphology in which aerosil dopant increases the decay time. In contrast, an increase of the concentration of photopolymer causes higher values of both τ_{on} and τ_{off}. These dependencies can be explained assuming splitting of LC domains (as the aerosil concentration increases) and modification of LC properties with the pre-polymer composition (by increasing the polymer content). Variation of the transmittance with the applied voltage can be decomposed into an alternative and a direct component. These can be assigned to the LC domains that are either sensitive or not to changes in the electric field. The dynamic parameters obtained from the frequency dependence agree well with the parameters obtained from the switching characteristics.

Acknowledgments
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