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Electrooptic properties of liquid crystals filled with silica nanoparticles of different sorts

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Abstract In this work we investigate electrooptic properties of nematic liquid crystal (LC) E7 from Merck filled with two types of silica nanoparticles (NPs). The particles of these types are of similar size and shape, however, they are made by different methods. The NPs of the first type, aerosil (A), are prepared by a high-temperature hydrolysis of chlorosilanes. The second type of NPs, based on hydrolysis and controlled precipitation of tetraethyl-orthosilicate in alcohol, yields monodispersed NP (MNPs) of silica. Transmittance versus applied voltage curves of the suspension layers are measured and analyzed. Our results show a strong dependence of the electrooptic properties on the particle preparation method. The contrast ratio (CR) 61:1 of LC-A suspension is achieved at relatively low A content (17 wt %). Unlike it, the value of the CR of LC-MNP suspensions is low (about 2:1) even

at 30 wt % of MNPs in the mixture. Both types of suspensions show electrooptic memory. The maximum of the memory efficiency of LC-A suspensions is detected at 4 wt % of A, while for LC-MNP suspensions the maximum is achieved at 15 wt % of MNPs. The difference in the results for the LC-A and LC-MNP series of composites is caused by much stronger aggregation of MNPs compared with A in the LC matrix. Moreover, reactive particle fusion and formation of silica microcrystallites substantially enhances the effect caused by MNP aggregation. These processes deteriorating electrooptic performance may be stabilized by introduction of a polymer network in LC-MNP suspensions.

Keywords Silica · Aerosil · Nanoparticles · Filled liquid crystal · Memory

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Introduction

In some applications, LCD panels based on heterogeneous liquid-crystal (LC) composites may replace traditional ones based on oriented LC layers. The composite-type LCD usually work in light scattering mode, and so they do not require polarizers, orientation surfaces, and strong uniformity of sample thickness. In addition, the panels possess enhanced viewing angle,

brightness, and electrooptic response times faster than for oriented LC layers.

A new type of LC composites is a filled LC, which is a suspension of fine particles, usually aerosils (As), in a liquid-crystal matrix [1, 2, 3]. These composites are being rapidly developed now for several reasons. First, they combine simple preparation and excellent electrooptic performance. Second, development of filled LCs is stimulated by modern nanotechnologies providing a

wide variety of fillers. Along with classical A suspensions, considerable interest has been shown in the last few years in LC composites based on the new types of fillers, above all colloid nanoparticles [4, 5, 6].

The intensive light scattering of filled LCs in the field-off state is mainly caused by a large number of orientational defects in LCs generated by dispersed solid particles. In the field-on state, the layer of filled LC becomes transparent owing to orientation of the LC and diminution of the number of defects. A specific property of filled LCs is the essential residual transmittance after the field is switched off (memory effect) [1, 2, 3]. The residual transmittance of a LC filled with A is explained by stabilization of the oriented LC state with an A skeleton, which is formed by hydrogen bonding between primer A particles [2, 7, 8].

The electrooptic performance of filled LCs strongly depends on the physical and chemical properties of both components, the concentration as well as on the parameters of applied electric field [3]. High switching contrast is realized in LCs containing cyanobiphenyl derivatives characterized by strong dielectric anisotropy and optical birefringence. The effective memory of these filled LCs is explained by the ability of LC molecules to create intermolecular bonds of hydrogen type [7, 8]. Filler properties are also of great importance. It has been shown that electrooptic performance depends on the state of the filler surface [9], filler concentration [3] and filler material [10, 11].

In this work we show that even particles of the same material, similar size and shape, may have different memories, if they are made by different methods. This is shown by the use of silica particles of several types suggested by modern nanotechnologies.

Experimental

Nanoparticles

A and monodispersed nanoparticles (MNPs), both made of silica, were used as liquid-crystal fillers. Both products consist of spherical particles with a size of 10–20 nm; however, the preparation methods of A and MNP are quite different.

A is a white, fluffy powder produced from chlorosilanes, which were hydrolyzed in an oxygen–hydrogen flame. The resultant silicon dioxide occurs in the form of an aerosol and was subsequently separated from the gaseous phase [12].

MNPs of silica were produced by hydrolysis and controlled precipitation of tetraethylorthosilicate in an alcohol medium. In this case, at first, the nuclei of the particles are born and then they grow until the required size [13, 14]. The particles obtained are of equal size, because in the process of particle growth the small

particles grow faster than the big ones. In contrast to As, which may exist as powders, MNPs usually exist in colloidal solutions. The evaporation of liquid, in which MNPs are stabilized, leads to particle fusion and so to formation of material inclusions of macroscopic size.

We used aerosil A300 produced by Degussa and silica MNP MT-ST from Nissan Corporation. The A was obtained in the form of a powder with a size of primer particles of about 10 nm [12]. The MNPs were dispersed in methanol at a concentration of 30 wt % [13]. We used nematic liquid crystal E7 from Merck, which is a mixture of cyanobiphenyl mesogenic derivatives.

Samples

For preparation of E7-MNP suspensions, E7 was intensively mixed with a methanol dispersion of MNPs. During the mixing, methanol was evaporated. The complete removal of alcohol was achieved by vacuuming the suspension at a pressure 10^{-2} torr for 1 h. The precise weighing of the composites controlled the amount of alcohol that remained. In the vacuumed suspensions, the concentration of alcohol was less than 0.1 wt %.

To equalize the preparation processes of the two types of suspensions, A was preliminarily dispersed in methanol. Before dispersing, it was baked at 180 °C for 1 h to evaporate water adsorbed on the particles. The following process of the preparation of E7-A composites was similar to that described earlier for E7-MNP suspensions.

To find the range of optimized electrooptic parameters, we investigated mixtures with different filler concentrations C_f . The concentration of A and MNPs was varied between 0.5 and 20 wt % and between 5 and 35 wt %, respectively.

The suspension was placed between two glass substrates covered with conductive indium/tin oxide layers from the inner side. A small number of spacers ($d=25\ \mu\text{m}$) were introduced into the mixtures to fix the thickness of the layers tested. The substrates were pressed and glued by an epoxy glue. The cell gap was controlled by the interference method.

Method

The sample transmittance T versus applied voltage U curves were measured at room temperature using the computer-conjugated measuring system described in Ref. [15]. The sample transmittance was defined as the ratio

$$T = \frac{I_{\text{out}}}{I_{\text{in}}}, \quad (1)$$

where I_{in} and I_{out} are the intensities of the probe beam before and after passing through the sample. In the latter case, the nonscattered light and the light scattered within an angle of 2° were detected with a photodiode. The T - U curves were measured two times: by the voltage increase and, subsequently, by the voltage decrease. In this process, the voltage was varied in the range 0–200 V, whereas the frequency was fixed at 2 kHz. From the curves obtained, electric field switching contrast and memory efficiency were calculated.

Results and discussion

The typical T - U curves for the suspensions E7-A and E7-MNP are shown in Fig. 1a and b, respectively. In the initial state the samples are characterized by the initial transmittance T_0 . With increasing applied voltage (curve 1), the transmittance of the samples reaches a

saturation level, T_{sat} . At the following voltage decrease to zero (curve 2), the system turns to the state with residual transmittance T_m .

As commonly accepted, the ratio

$$CR = \frac{T_{sat}}{T_0} \quad (2)$$

is defined as the switching contrast. This parameter is strongly influenced by the value of the initial transmittance, which is in the denominator of the expression. As in our previous works [3, 7, 8], the memory efficiency is determined as

$$M = \frac{T_m - T_0}{T_{sat} - T_0} \times 100\%. \quad (3)$$

In the case of $M=0\%$ the electrooptic response is completely reversible, whereas $M=100\%$ implies that an ideal memory cell is realized.

T_0 , T_{sat} and CR as functions of nanoparticle concentration for both E7-A and E7-MNP composites are presented in Fig. 2a and b, respectively. Compared with E7-MNP composites, the data for the E7-A series are presented for a smaller range of particle concentrations, because of dielectric breakdown in the samples with high C_f . One can see that the concentration dependencies of T_{sat} for E7-A and E7-MNP composites are similar and that T_{sat} weakly depends on C_f . At the same time,

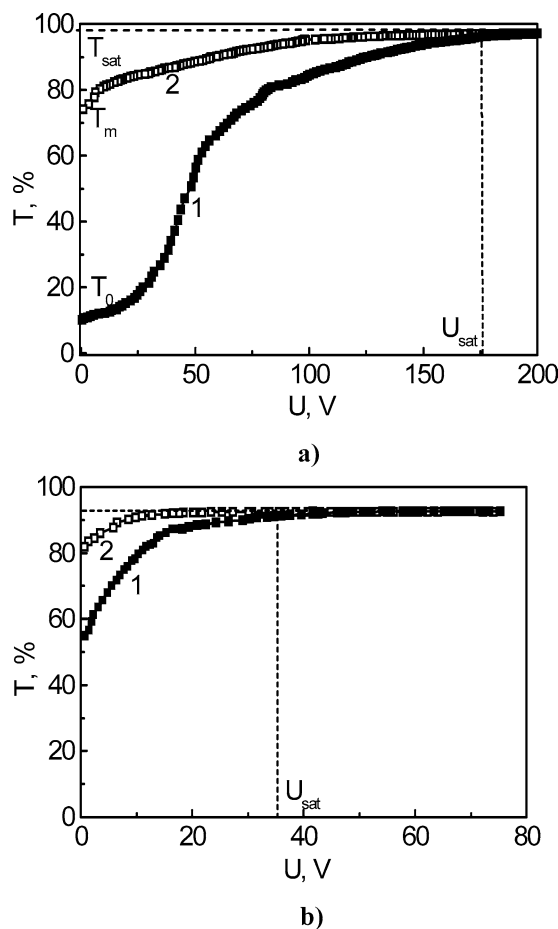


Fig. 1 Transmittance versus voltage curves for two types of suspensions: **a** E7-A300 ($C_f=5$ wt %); **b** E7-SiO₂ monodispersed nanoparticle (MNP) ($C_f=25$ wt %). Voltage increase—1; voltage decrease—2

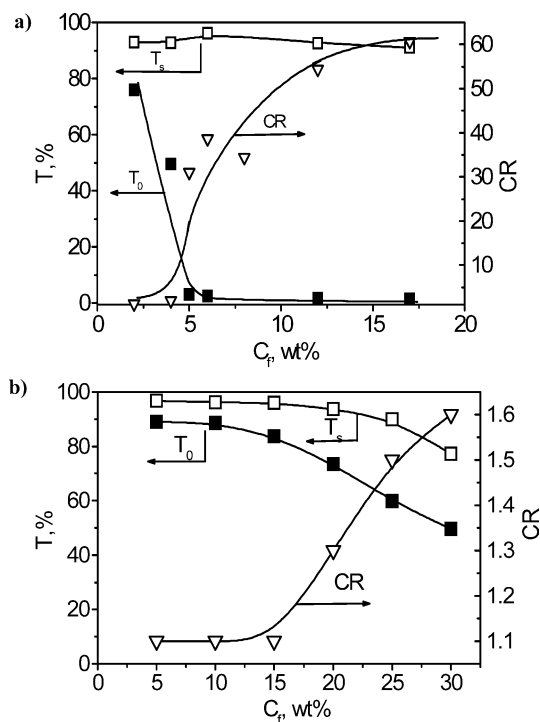


Fig. 2 T_0 , T_{sat} and contrast ratio (CR) as functions of filler concentration for **a** E7-A300 and **b** E7-SiO₂ MNP composites

a distinctive difference is observed in the data for T_0 ; the $T_{\text{sat}}(C_f)$ curve for the E7-A series decreases steeply, while only a slight decrease is observed for the $T_{\text{sat}}(C_f)$ dependence for E7-MNP composites. The behavior of the $T_0(C_f)$ and $T_{\text{sat}}(C_f)$ curves results in a rapid increase of switching contrast of E7-A composites, reaching 61:1 at $C_f = 17$ wt %. At the same time, poor (about 2:1) and slightly variable contrast is observed for the E7-MNP series. It is also noteworthy that the controlling voltage for E7-MNP composites is lower than for E7-A ones.

The M versus C_f curves for LC-A and LC-MNP composites are presented in Fig. 3. From these results, several conclusions can be made.

1. The $M(C_f)$ curves go through a maximum for both types of composites.
2. The maximum of the $M(C_f)$ curve for the LC-A series is reached for a lower concentration than for the LC-MNP series.
3. The maximal value of M obtained for the LC-A series is higher than for the LC-MNP series.

To interpret the results obtained, we refer again to the microscopic model, which assumes that light scattering in filled LCs is caused by distortion of the LC director with dispersed particles and their aggregates. Until the distortions caused by different inclusions (particles or their aggregates) overlap, the scattering intensity should be proportional to the concentration of these inclusions. Naturally that distortion ability of the filler is enhanced with the increase of the efficiency of its fragmentation. Indeed, the higher is the number of particles, the bigger is number of scattering centers in the filled LC. This may be one of the reasons for the difference in the results obtained for the two series of samples, since A and MNP have different particle sizes. Because of this difference, an equal mass of A and MNP brings different numbers of particles into the LC. In the case of nonporous particles, the ratio of the number of spherical particles of the two different sorts, obtained from the same mass of the filler material, can be expressed through the ratio of the particle radii:

$$\frac{N_1}{N_2} = \left(\frac{r_2}{r_1}\right)^3. \quad (4)$$

By setting $r_A \approx 10$ nm and $r_{\text{MNP}} \approx 15$ nm in Eq. (3) one can obtain $N_A/N_{\text{MNP}} = 3.4$. This means that the number of A particles is 3.4 times higher than the number of MNP particles of the same weight. Of course, this estimate is quite rough, since averaged particle sizes are used and possible particle porosity is not taken into consideration. Nevertheless, this estimate shows that the concentration curves should be shifted to higher weight concentrations for E7-MNP composites compared with E7-A composites. It is in agreement with the $M(C_f)$ curves obtained experimentally for the two kinds of samples, Fig. 3. Apparently, the bigger the particle size, the higher is the weight concentration of filler in the LC at which the particle network is formed.

Following the same logic, suspensions E7-A and E7-MNP with the ratio of filler concentrations $C_{\text{MNP}}/C_A \approx 4$ should be characterized by similar electrooptic contrast. Surprisingly, the CR values of E7-MNP suspensions are very low and poorly dependent on the MNP concentration. This implies a primer MNP aggregate. Moreover, the aggregation rate is substantially higher than for A particles. This is confirmed by the sample observation in a polarizing microscope. Figure 4a shows that A particles are strongly and uniformly dispersed in the LC. At the same time, E7-MNP samples demonstrate textures with relatively large grains that reflect enhanced aggregation of MNP, Fig. 4b. In some samples we even see microcrystallites of silica (Fig. 4c), which can be formed by the reactive particle merging. Thus, by replacing methanol with a LC, we provoke particle aggregation and merging. This implies that, in contrast to A, MNPs are chemically active and LC E7 is a much weaker particle stabilizer than methanol. It is known that nanoparticles can be well stabilized in solvents with high polarity. The permittivity of methanol ($\epsilon = 33.7$) is substantially higher than the average permittivity of E7, $\langle \epsilon \rangle = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp}) = 9.8$ ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are permittivities along and perpendicular to the LC director, respectively). This explains why a LC is not a sufficiently good stabilizer for colloidal particles. It should be mentioned here that the authors of Refs. [4, 5] did not notice the problem of particle fusion in the LC suspensions based on MNP of organic origin. This might have been caused by the low concentration of the particles in LC composites as well as by their low chemical activity, as compared with the inorganic MNPs we utilized.

To improve stability of LC-MNP suspensions, we applied the method proposed earlier for LC-A suspensions [15, 16]. It involves the introduction of a pre-polymer composition to the suspensions. The role of this composition is the formation of a polymer network and, possibly, covering of the dispersed particles with

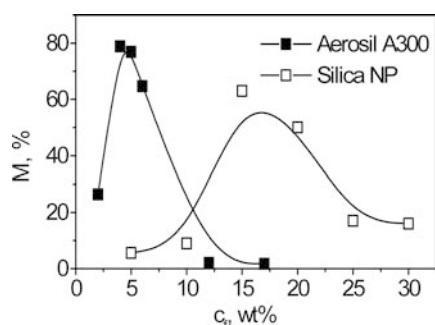
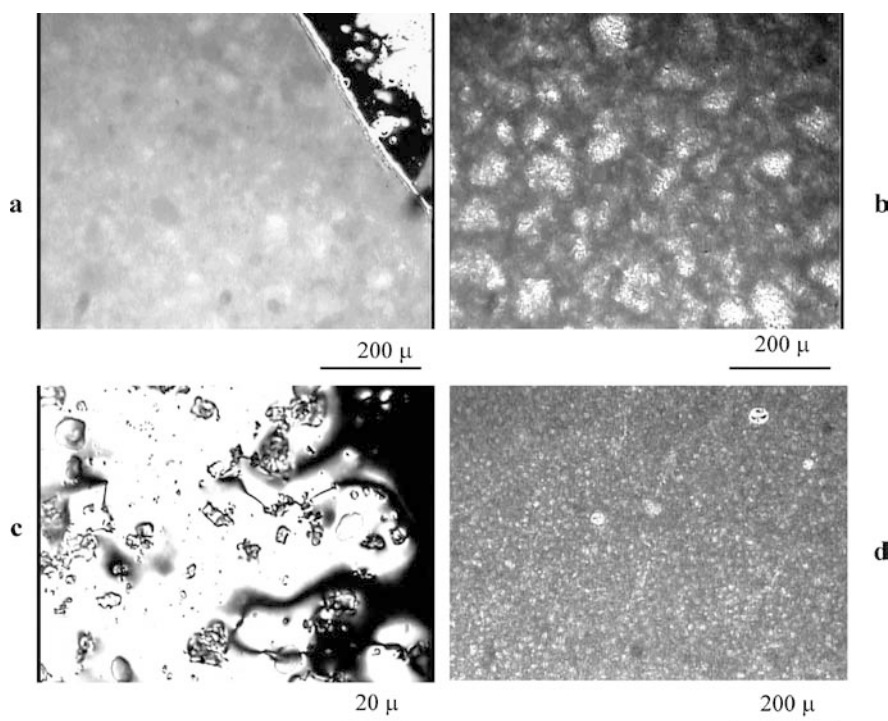


Fig. 3 Memory efficiency as a function of filler concentration for E7-A300 and E7-SiO₂ MNP composites

Fig. 4 Microscope pictures of the filled liquid crystal layers:
a E7-A300 ($C_f=20$ wt %),
b E7-SiO₂ MNP ($C_f=20$ wt %), **c** E7-SiO₂ MNP layer ($C_f=20$ wt %) demonstrating silica crystallites formed owing to chemical merging of MNP; **d** polymer-stabilized E7-SiO₂ MNP suspension ($C_f=20$ wt %, $C_p=5$ wt %)



polymer. These factors prevent aggregation and merging of the particles. To realize this idea, E7-MNP suspensions were doped with 5 wt % of photocurable prepolymer composition no. 65 from Norland. Subsequently, the samples were exposed to UV light from a mercury lamp (100 mW/cm², 20 min) in order to provide photopolymerization and corresponding structuring of the polymer phase. Figure 4d shows that the filler in this sample is dispersed substantially better than in the sample without polymer dopant (Fig. 4b). Electrooptic curves for the polymer-doped E7-MNP composite are shown in Fig. 5. One can see that the CR strongly improves and it is comparable with that for E7-A suspensions. On the other hand, the memory effect

practically vanishes. This makes polymer-doped LC-MNP composites quite attractive for applications in which a reversible electrooptic response is utilized.

Conclusions

The results obtained allow us to conclude that the preparation method strongly influences the structure and properties of LCs filled with nanoparticles. A, obtained and stored in the form of a powder, demonstrates highly dispersive and uniform distribution in LCs. By contrast, chemically active monodispersed silica particles, existing only in the form of colloidal solutions, demonstrate enhanced aggregation and even reactive merging when they are mixed with LCs. In electrooptic experiments it becomes apparent in the drastic decrease of switching contrast and in the concentration delay of the efficiency of memory. To make LC-MNP composites attractive for applications, a highly dispersed state of the solid phase should be stabilized, for instance, by a polymer network. We believe these results will be useful for the development of new composites based on the variety of fillers supplied by modern nanotechnologies.

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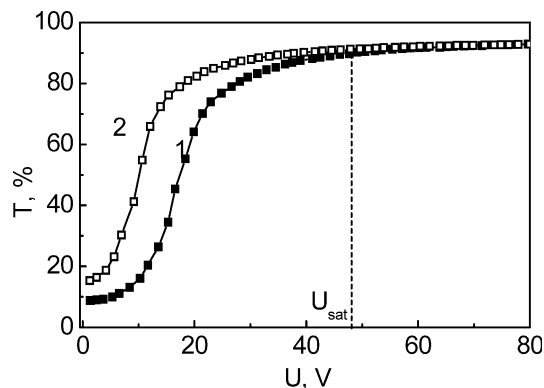


Fig. 5 Transmittance versus voltage curve for polymer-stabilized E7-SiO₂ MNP composite ($C_f=20$ wt %, $C_p=5$ wt %)

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