Mol. Cryst. Liq. Cryst., Vol. 321, pp. 15–30
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Printed in Malaysia.

Memory Effect and Structure of Filled Nematic Liquid Crystals

A.GLUSHCHENKO, H.KRESSE[a], G.PUCHKOVS'KA, V.RESHETNYAK[b], YU.REZNIKOV and O.YAROSHCHUK*
Institute of Physics, Nation. Acad. Sci., prospect Nauki 46, Kyiv, 252650 Ukraine; [a]Martin-Luther-Universität, Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, D-06108 Halle, Germany; [b]Institute of Surface Chemistry, Nation. Acad. Sci., prospect Nauki 31, Kyiv, 252650 Ukraine; *to whom correspondence should be addressed; e-mail: olegyar@marion.iop.kiev.ua

The irreversible electro-optical response (memory effect) in suspensions of liquid crystals (LCs) and aerosil was investigated. Thereby the influence of the intermolecular interaction in liquid crystals, of the aerosil concentration and its surface treatment and of electric field parameters on the efficiency of the memory effect was studied. The experimental results are discussed in the frame of a model where the filled nematic LC is considered as a system of aerosil agglomerates in a liquid crystal matrix stabilised by elastic forces.

Keywords: liquid crystals, aerosil, filled nematic liquid crystals, electro-optic effects.

INTRODUCTION

The electric field controlled light scattering in heterogeneous media based on liquid crystals provokes interest. They are muddy in the initial state and clear up in electric fields. Usually, such systems go back to its original state after removing the electric field. In the some cases the partially cleared up state may remain. Such effect is known as *memory effect* of the heterogeneous media. The description of the memory effect for the encapsulated nematic LCs with the definite structure (polymer ball structure) is well known in the literature[1-2]. However, the efficiency of the memory effect in the such media is not high.

Filled LCs (suspended small hard particles in LC) presents a good example of a media with the high memory effect. The first studies of the such systems have shown that the cleared up state may remain without changes after the electric field is switched off[3-4]. Aerosil was used as stuffing for these studies. The memory effect of filled LCs was also observed using other stuffings (for example, clay particles [5]). We have ascertained formerly for the system LC-aerosil that the characteristics of the memory effect depends on the chemical nature of both, aerosil surface and LC molecules [6,7]. The aim of this work is to study the influence of chemical modification of aerosil surface, aerosil concentration and electric-field parameters on the memory effect. The structure of the aerosil particles in a suspension and its influence on the memory efficiency will be considered.

EXPERIMENT

Samples and measurements

Three types of nematic LCs, namely 5CB (NIOPIK, Russia) with a dielectric anisotropy $\Delta\varepsilon=7$, ZhKM-1285 (NIOPIK, Russia) with $\Delta\varepsilon=11{,}8$ and ZLI-4801 (Merck, Germany) with $\Delta\varepsilon=5{,}1$ were used. The LCs 5CB and ZhKM-1285 contain molecules which can form hydrogen bonds. This specific kind of interaction is not possible for ZLI-4801. In order to prove the importance of the hydrogen bonds on the memory effect 0,5 weight percent of di-n-nonyl-4-(4-cyanobenzoyloxy) benzylidenemalonate (BM) were added to ZLI-4801.

Aerosils A300 and R812 (DEGUSSA, Germany) were used as stuffing [8]. The surface of aerosil A300 contains about 5 OH-groups/nm^2 whereas for aerosil R812, which was modificated with hydrophobic polymethylsiloxanes fragments, only a density of 0.29 OH/nm^2 was measured[9].

Suspensions with various aerosil concentrations c_a=2-25 weight % ($c_a=m_a/(m_a+m_m)$, where m_a and m_m are the weights of both, aerosil and the mixture, respectively) were prepared by mingling the components in an ultrasonic mixer. Suspension layers of 10 μm thickness placed between two glass substrates with transparent ITO-electrodes were investigated. The microscopic observation of the suspensions in a polarized light shows the chaotically disordered texture of LCs containing aerosil agglomerates with a size up to several microns.

The experimental set up is described in previous papers[6,7]. Thereby the intensity of the He-Ne-laser light beam transmitted through the sample, I_{out}, is measured within the cone of 2°. From these data the transmittance of the sample, $T=I_{out}/I_{in}$, is calculated (I_{in} is the intensity of the incoming beam). Based on these data the transmittance-voltage ($T(U)$) and transmittance-frequency ($T(\nu)$) characteristics are obtained for various LC-aerosil systems with different aerosil concentrations. To describe the memory effect a memory parameter $M=(T_m-T_o)/(T_s-T_o)$ was introduced. Here T_o, T_s and T_m are the initial transmittance of the sample, the saturation value of the transmittance at high voltages and the residual transmittance after removing the field, respectively.

The dependence of the memory parameter on the suspension composition

The dependence of $M(c_a)$ for various LC-aerosil combinations at a frequency of 2 kHz is given in Fig.1. Three parts can be distinguished in the curves: a) increase of M with the increase of aerosil concentration, b) maximum of the memory effect and c) decrease of M and transition to a reversibility regime.

The highest memory parameter ($M\approx70\%$) was observed for the combination "nonmodificated aerosil-5CB", where the components can form hydrogen bonds with aerosil (curve 1)[*]. The curve $M(c_a)$ is shifted to higher concentrations of c_a and broadened as result of the hydrophobic treatment of aerosil (curve 2). It is important to note, that a rather large contrast, $k=T_s/T_o$ (50:1 or more), was observed for the switching process. We did not detect a memory effect for the mixture of "A300-ZLI-4801" (curve 3). However, by adding of BM the memory parameter increases and the corresponding curve 4 has the similar shape as the curve 1.

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[*] The dependence of $M(c_a)$ for "A300-ZhKM 1285" system is similar to curve 1. Therefore, it is not shown in Fig.1.

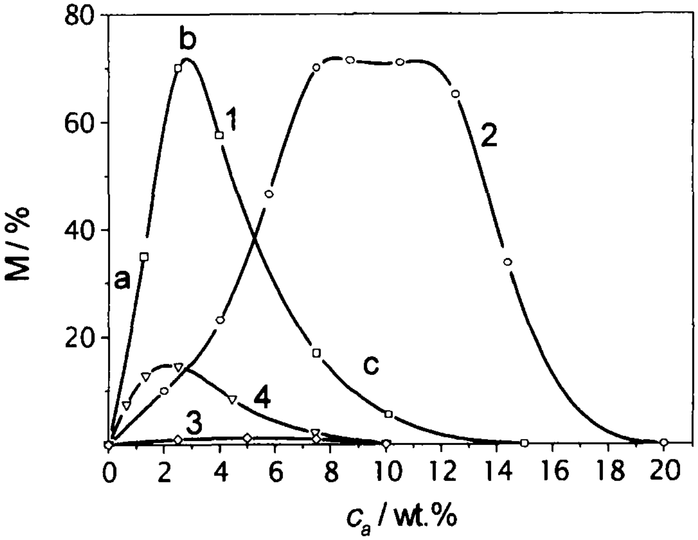

FIGURE 1. The dependencies of $M(c_a)$ for various pairs of LC-aerosil. 1-"5CB-A300"; 2-"5CB-R812"; 3-"ZLI 4801-A300", 4-"ZLI 4801 with BM-A300". The frequency of the applied field f=2kHz. The saturation value T_s corresponds to the applied voltage, U=60V.

The dependence of M on the parameters of electric field

The frequency and voltage of the applied electric field were varied to investigate the influence of field parameters on M. The electro-optical response drastically differs between low ($f \leq 500$Hz) and high ($f > 1000$ Hz) frequencies of the electric field. At low frequencies the electric field causes the appearance of flow and the separation of the suspension components. Microscopic observations show the appearance of turbulent flows of the LCs and a motion of the aerosil particles upon switching on of the electric field. Increasing voltage at a fixed frequency results in an increase of the turbulence which involves bigger agglomerates in the motion. Furthermore break-up of the largest agglomerates was observed.

The time for the appearance of the hydrodynamic effect is of several seconds. A "boiling" of the suspension takes place all the time under electric field and does not prevent the transition to the transparent state of the cells after the field is switched off. Observations by a polarizing microscope show that the transparent state of the cells is caused by both, the orientation of the LC and the separation of the two phases. The effect of the phase separation is specially strong for the non-modificated aerosil and can be observed after some seconds under the electric field. A much longer time is needed for the separation of the modificated aerosil from the LC.

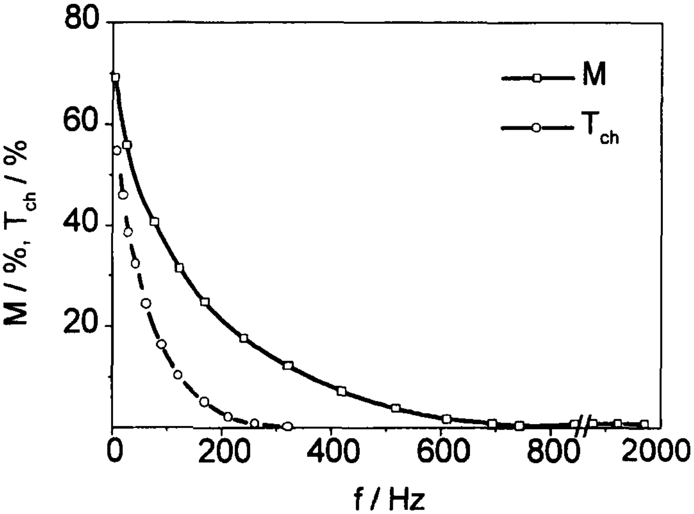

FIGURE 2. Dependencies of the memory parameter and variable component of the transmittance on the frequency of the electric field.

With increasing frequency at fixed voltage the aggregates went out from the motion, starting from the biggest one. Concurrently the variable component of the light transmittance, T_{ch} and memory parameter M decrease (Fig.2).

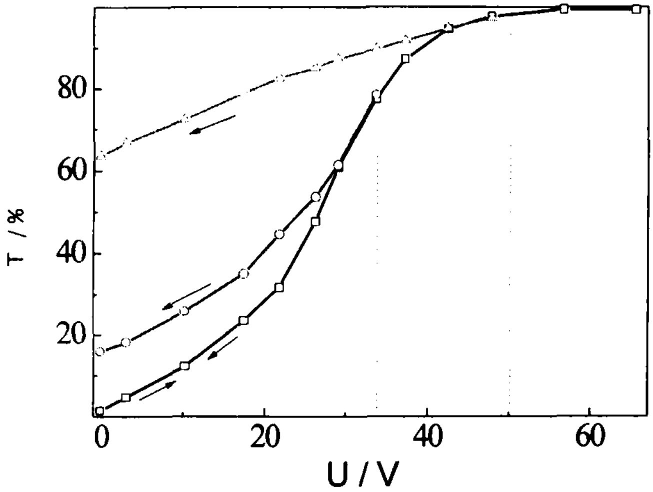

FIGURE 3. The dependence of the transmittance of the cell on the voltage of electric field for suspension "5CB-R812" (c_a=5 wt.%) measured by decreasing applied voltage beginning from U=20;35;50V (f=2kHz).

There are no hydrodynamic effects in the high frequency region. Moreover, we did not find any phase separation for all the suspensions being investigated. The transparency of the cells is caused by the reorientation of LC molecules due to the electric field. Fig.3 shows the transmittance-voltage curves for "5CB-R812 (hydrophobic aerosil)" suspension (c_a=5 wt.%) measured with decreasing voltage. It is seen that the memory effect becomes sufficiently high for voltages corresponding to the saturation of the curve *T(U)*. The saturation value at about *T*=90 % does not depend on concentration, but the saturation voltage increases with the increase of aerosil concentration. This is common behavior for all investigated suspensions.

Characteristic switching times from dark to transparent state in the high frequency region are about some milliseconds. The time of the memory effect development is of the same order of magnitude.

DISCUSSION

A microscopic mechanism for the origin of memory effect has been proposed by R.Eidenschink, M.Kreuzer et al [3-4]. They supposed that aerosil forms a network structure in a LC matrix where individual aerosil particles are connected with hydrogen bonds. By applying the electric field LC molecules orient toward the field and involve the aerosil network into the reorientation process. The former aerosil network is being broken and a new stable network is being formed. The latest network has an anisotropic structure being oriented in the direction of electric field. The network keeps the director of the LCs parallel to the vector $\vec{E}$, that results in the stable transparent state of the system. Thus, LC orientation is stabilized by the aerosil network in the transparent state.

At the same time, our tentative studies by ultrasonic spectroscopy show that up to c_a=10 wt. % aerosil forms separate agglomerates in the investigated suspensions[11]. The structure and size of the agglomerates depend upon the value of c_a. The estimation show that the typical average size of agglomerates is about 1000Å at c_a=(5-10) wt. % and the distance between the agglomerates is of the same order[11,12].

The structure of the agglomerates in the suspension might be stabilised by elastic forces of the LC. Certainly, the aerosil agglomerates are in the anisotropic surrounding. Therefore, it can be expected that the agglomerates also are anisotropic. The reorientation of the anisotropic agglomerates out of the equilibrium state is prevented by the elastic torque being appeared in the surrounding LC. In turn, the agglomerates can be considered as spatially-distributed aligning surface stabilising the LC orientation. Thus, just the LC's elasticity keeps the transparent state while the electric field is switched off.

Let us consider in first approximation an anisotropic aerosil agglomerate in a homogeneously oriented nematic LC matrix and try to estimate the energy needed to turn the agglomerate or to reorient the director of LC from its equilibrium state. One can describe the aerosil agglomerates as elongated dielectric rods with the length L and the transverse size R. Both, L and R, are presumed to be much greater than the dimensions of the molecules of the LC, so they are macroscopic objects. Since the typical size of LC molecules is about 20Å and R >300Å, this assumption is valid. Furthermore we will restrict our consideration to two boundary cases known from the literature [13,14].

In the one elastic constant approximation the free energy of the long rod (relative geometrical anisotropy $d_d/L = (L - R)/L \approx 1$) has the form [13]

$$F = F_{\perp} + (F_{\parallel} - F_{\perp})\cos^2\theta, \qquad (1)$$

where θ denotes the angle between the rod with the director of the nematic LC far from the agglomerate $\vec{d}_0$, $F_{\perp}$ is a free energy of LC while a long axes of the rod is lined up perpendicular to $\vec{d}_o$, $F_{||}$ is a free energy while a long axes is lined up parallel to $\vec{d}_o$. The components of F can be written

$$F_{\perp} = \pi KL\left[-\ln(1-p^2)+\frac{1}{2}\xi(1-p)\right],$$

$$F_{||} = \pi KL\frac{\xi}{1+\xi}, \xi = \frac{W\,R}{K},$$

$$p = \frac{2}{\xi}\left[\sqrt{1+\frac{1}{4}\xi^2} - 1\right].$$

For a typical value of the elastic constant K=10^{-6} dyne, the anchoring energy W=10^{-2} erg/cm^2, a minimal size of R=3·10^{-6} cm and the anchoring parameter of $\xi \approx 3\cdot 10^{-2} << 1$ the difference is

$$\Delta F = F - F_{\perp} = \pi KL\xi\frac{\cos^2\theta}{2} \approx 3\cdot 10^{-13}\,\text{erg}. \qquad (2)$$

This value is one order of magnitude larger than the energy of thermal fluctuation in the system being $k_B T = 4\cdot 10^{-14}$ erg.

Equation (2) shows that the larger the size of the agglomerate the more stable is the transparent state. To estimate the influence of the agglomerate anisotropy on the system stability let us explore the model of inventively strong anchoring of LC with the anisotropic rod[13]. The energy needed to turn the such rod in a homogeneously oriented LC is proportional to geometrical anisotropy d_a and θ^2:

$$F \approx K d_a \theta^2 \qquad (3)$$

For K=10^{-6} dyne this formula also leads to the value $F \approx 10^{-13}$ erg >> $k_B T$ at the extremely small anisotropy $d_{\grave{a}} = 10^{-7}$ cm.

So, the transparent state of the suspension containing non-interacted aerosil particles should be stable and cannot relax back to the initial state.

Let us estimate the agglomerate concentration when the regions of the director field distortion caused by different agglomerates begin to overlap.

One of the possible director distributions $\vec{d} = (\cos\Phi, \sin\Phi, 0)$ has the form

$$\Phi(r,\varphi) = -\arctan\frac{(R/r)^2 p\sin 2\varphi}{1-(R/r)^2 p\cos 2\varphi}, \quad p = \frac{2}{\xi}\left[\sqrt{1+\frac{1}{4}\xi^2} - 1\right]. \quad (4)$$

From last formula one can see that a deviation from $\vec{d}_0$ is small at $r > 3R$. Therefore, the critical concentration of the agglomerates per unit volume can be estimated as follows:

$$c \sim \frac{1}{(4/3\pi)(3R)^3} \approx 10^{-2}\frac{1}{R^3}cm^{-3} \qquad (5)$$

The size R of the agglomerates is assumed to be $(3\text{-}10)\cdot 10^{-7}$ cm. In this case cooperative effects should be essential at the concentration of agglomerates $c_a = (10^{13}\text{-}10^{14})$ cm^{-3}. It corresponds to the most effective memory effect observed [*].

Thus, the above estimations show that the main parameters determining the stability of a transparent state are the size and the anisotropy of the agglomerates, the distance between the agglomerates and the anchoring strength of a LC molecules at the agglomerates surface. The increase of agglomerates size and anisotropy as well as of aerosil concentration should stabilize the transparent state. The same effect should be provided with the increase of the anchoring strength. Let us consider the

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[*] It should be noted that one can expect negligible influence of the cell orienting surfaces on the LC director orientation at such aerosil concentrations when average distance between agglomerates is smaller than cell thickness. It means that memory explanation made here will do also for a space limited system

correspondence of these tentative conclusions with the obtained experimental results.

The size of agglomerates is small at small aerosil concentrations. In turn, a distance between agglomerates is large. So, the structure of agglomerates do not play important role in LC orientation. The orientation influence of the cell substrates is more essential in this case. It results in a reversible response of a cell (part **a** of the curves M(c_a) in Fig.1). The increase of the aerosil concentration results in the increase of the size of aerosil agglomerates as well as in a decrease of the inter-agglomerate distances[15]. In this case an orientation influence of agglomerate substrates increases and finally it suppresses the influence of the cell substrates. This leads to a stabilization of the transparent state and an amplification of memory parameter with the increase of c_a (part **b** of the curves M(c_a)). Nevertheless one can see that at high concentrations the memory parameter goes down (part **c** of the curves M(c_a)). We explain it from investigations of the IR spectra [10] The shape of OH stretching vibration band of filled LC can be separated in a few simple bands. The concentration dependency of the intensities of several bands for the suspension "5CB-A300" is presented in Fig. 4. The band at 2500 cm^{-1} corresponds to the polymer type OH...OH stretching vibrations and could be assigned with aggregation of aerosil[10]. Bands at 3614 and 3540 cm^{-1} correspond to OH..π vibration modes. They are assigned to interactions between aerosil surface OH groups and benzene rings of LC molecules. It is important to point out that curves 1-3 have a maximum at the same concentration c_a=3 wt.% as memory parameter *M*. The nonmonotonic behavior of curves 1-3 indicates a structure transition near c_a= 3 wt.%. We suppose that the transition from branched agglomerate structure (Fig.5,a) to more close packed structure takes place when the suspension consists of quasi spheres of aerosil

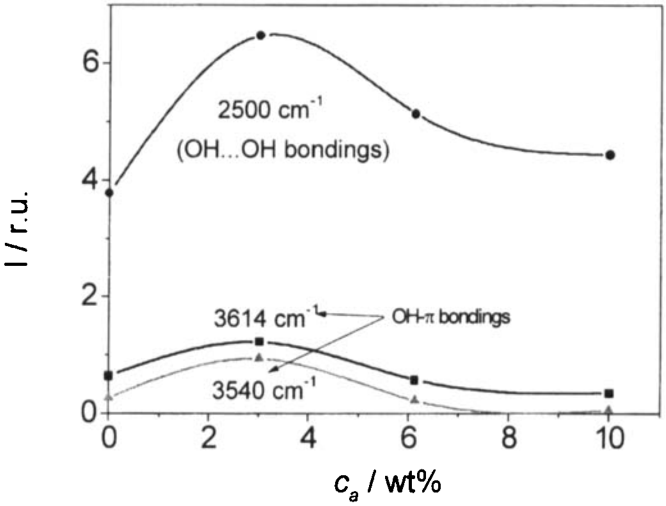

FIGURE 4. The dependence of intensities of several IR bands for the suspension “5CB-A300” on the aerosil concentration

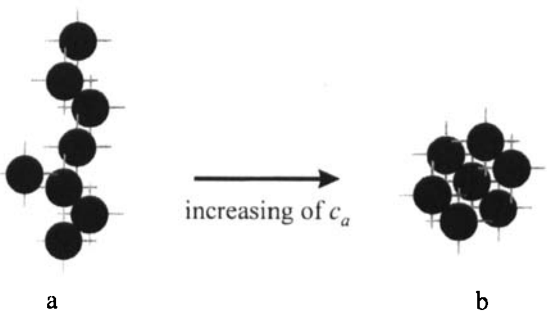

FIGURE 5. a - branched agglomerate structure; b - close packed structure.

agglomerates in the LC matrix (Fig.5,b). Such transition may result in the decrease of agglomerate size and its anisotropy at high aerosil concentration. As the result it depletes the memory effect.

Experimental results show the influence of a surface treatment of the aerosil surface. From this it can be concluded that the anchoring strength is important for the memory effect. Certainly, the efficiency of the memory effect strongly depends on the presence of H-bonds in the system. This is caused by two facts. Firstly, the effective interaction of LC molecules with the aerosil particle surface, i.e. high anchoring strength is possible owing to hydrogen bonds. Secondly, the ability to create H-bonds promotes aerosil particles to agglomerate. In this way the stability of transparent state is also supported. Actually, the most effective memory is realized for the "A300 (nonmodificated aerosil)-5CB" system. Such a system is characterized by greatest quantity of hydrogen bonds between the aerosil particles and by the effective anchoring of LC molecules with the aerosil particle surface. As it was pointed out above, this anchoring is due to the presence of hydrogen bonds of the aerosil surface OH-groups with benzene rings of 5CB molecules. The hydrophobic treatment of aerosil and reducing of the number of the surface OH-groups decreases the probability for H-bondings between the aerosil particles and between aerosil and LC molecules as well. It results in the decrease of the memory parameter of the suspension and in the shift of the curve $M(c_a)$ to larger concentrations c_a (compare the curve 1 with the curves 2 in Fig.1). In opposite, on addition of hydrogen bonds initiator incrases the effective memory parameter (curve 4, Fig.1).

CONCLUSIONS

The efficiency of the memory effect in filled nematic LCs depends on the aerosil surface properties, aerosil concentration and parameters of the electric field (frequency and voltage). Hydrogen bonds between the aerosil and liquid crystal as well as between aerosil particles play an important role for the memory effect.

The obtained results can be described qualitatively in the frame of a model where the filled LC is considered as a system of aerosil agglomerates in a liquid crystal matrix. The geometrical anisotropy, sizes and inter particles distances depend upon the total concentration of aerosil in the matrix and surface properties of aerosil. The shape and size of aerosil agglomerates could be essentially changed with increase of aerosil concentration. It may cause the decrease of memory parameter at higher concentrations of aerosil.

Under electric field the LC molecules orient toward the field and involve aerosil aggregates into the reorientation process. The efficiency of the aerosil motion is determined by the LC anchoring at the agglomerate surfaces as well as by voltage and frequency of the applied field. The produced transparent state is stabilised by the elastic forces of the liquid crystal and interaction between LC and macroscopic agglomerates.

Acknowledgements

The research was supported in part by Grant No. 2.4/923 from the Ukrainian State Found for the Fundamental Studies Support.

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