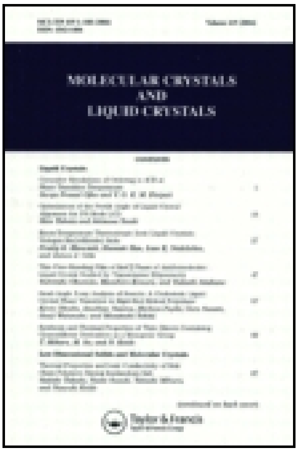

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INFLUENCE OF THE AEROSIL SURFACE MODIFICATION ON ELECTRO-OPTICAL CHARACTERISTICS OF FILLED LIQUID CRYSTALS

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Abstract We have studied the influence of surface state of aerosil on electro-optical characteristics of suspensions 'aerosil-liquid crystal (LC)'. Modification of aerosil surface by hydrophobic fragments improves these characteristics. Also the dependence of a hydrophobic modificator structure on electro-optical characteristics was investigated. Explanation is given on the basis of the influence of the surface structure on the anchoring energy value of the LC-aerosil interface.

From a great amount of different heterogeneous systems based on liquid crystals (LC) [1-3] filled LC -- a suspension of small silica particles (aerosil) in a liquid crystal -- are widely investigated nowadays.[4-6] Electro-optical properties of filled LC (FLC) associated with alteration of a light scattering under the influence of external electric field is of a particular interest. Initial strong light-diffusing on such a system is explained due to the existence of many defects in LC-orientation. These defects are originated by separate silica particles or their aggregations existing due to hydrogen bonds of surface groups.[6] Application of an electric field to the cell with FLC reduces the number of defects and changes their structure that results in an increase of transmission of the medium.

Investigated system intrinsically possesses a highly developed interphase surface between a liquid crystalline phase and a solid one. That's why one can expect that chemical modification of a surface with substances that greatly affect the aerosil-LC-molecules interaction should allow to control electro-optical characteristics of the cell efficiently. Our assumption has also been based upon the results of investigations of filled polymers, which manifested a significant dependence of such compound features on a technique of a stuffing modification.[7] In this publication first results of such treatment and investigations are presented for filled LC.

1. Nematic liquid crystals with great both positive dielectric anisotropy $\Delta\varepsilon$ and birefringence Δn are used.[5] The former is needed for the light transmittance growing while electric field is applied, while the latter is necessary for a sufficient light-scattering in the initial state. In our experiments a regular nematic compound (LCC-1289; $\Delta\varepsilon = 9.8$ and $\Delta n = 0.156$) was used.

A-300 aerosil with particle dimensions about 100-150 Å was used as a stuffing. The presence of OH-groups makes the particle surface to be a hydrophilic one.[8] Aerosil was treated either with hydrophilic and hydrophobic compounds. Monoethanolamin (MEA) was chosen for hydrophilic modification[9] while siloxanes were used for hydrophobic treatment, which gives rise to either linear structures (polymethylsiloxanes -- PMS) or bridge-like ones (octomethyltetrasiloxanes -- OMTS). Possible surface structures of modified aerosil are shown in Fig.1(b-d).[9-11] Suspension of LC and aerosil was made by ultrasonic stirring with aerosil concentration of 3 weight percentage. This suspension was placed between two glass plates covered with transparent electrodes. Suspension film thickness (d =

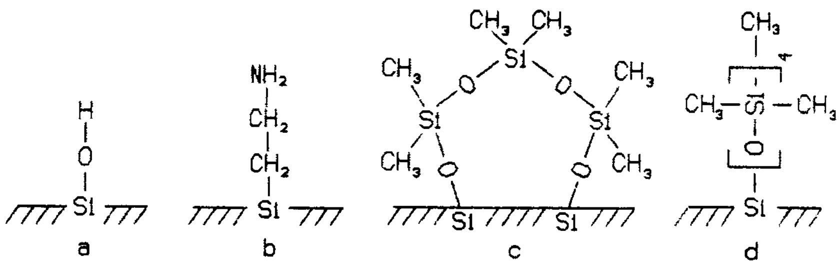

FIGURE 1 Molecular structures on the aerosil surface (according[9-11]): aerosil without modification (a) and aerosil modified with: b) MEA, c) OMTS, d) PMS.

20 μm) was given by teflon strips placed between substrates.

Dependencies of the cell light transmittance **T** on the applied voltage (voltage-contrast characteristics) as well as dependencies of the varying component of **T** on applied field frequency (frequency characteristics) were measured. The beam of He-Ne laser went perpendicularly through the cell partially diffusing on it. The photodiode **PD** was placed in the beam axis and measured the intensity of the transmitted beam in the spatial angle of 2°. Voltage impressed on cell electrodes caused the decrease in the cell light scattering with both constant and variable constituents of light transmittance. Voltage-contrast dependence was measured under the application of the voltage **U** = (0 ÷ 100) V at the frequency **f** = 1 kHz, while the frequency one -- under **U** = 10 V, **f** = (1 ÷ 10000) Hz.

2. Obtained results are shown in Fig.2. One can see that suspensions with non-modified aerosil manifest a high voltage of transmittance saturation $U_s \geq 120$ V, gradual contrast vs voltage dependence and a small contrast ratio. Feature peculiar to such a suspension is a rather essential voltage-contrast hysteresis, nature of which was discussed in.[6] It is associated with the destroying of a microscopic network of aerosil particles, which is formed due to

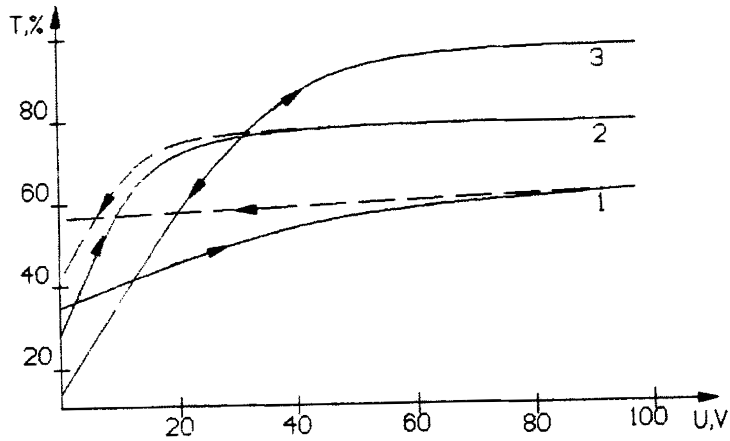

FIGURE 2 Voltage-contrast dependences of suspensions based on: non-modified (1), OMTS-modified (2) and PMS-modified (3) aerosil.

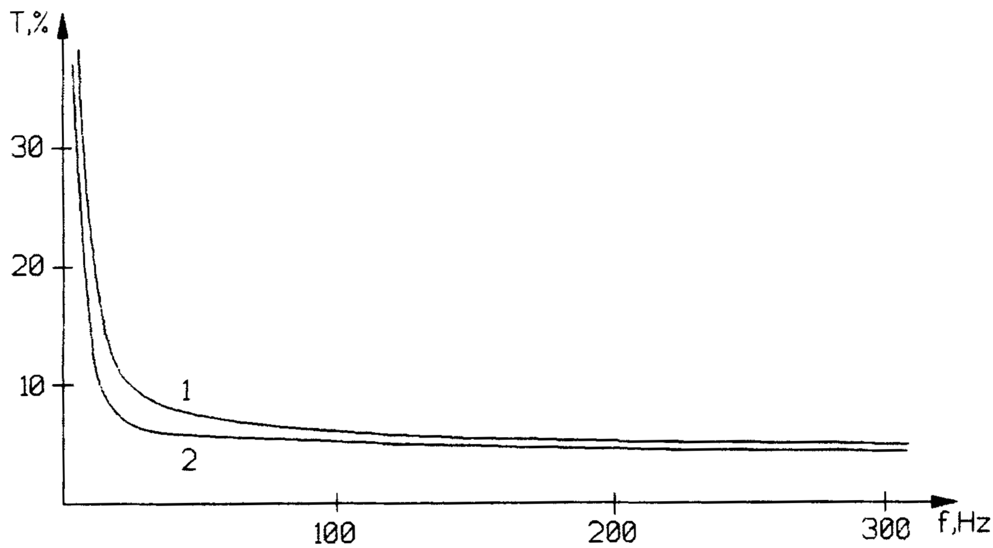

FIGURE 3 Frequency dependences of suspensions based on aerosil modified with: (1) OMTS, (2) PMS.

interparticle H-bonding, on the one hand and the formation of a newer one oriented in an electric field on the other.

Hydrophilization of the initial aerosil (MEA-modification) crucially affects a system behavior. It becomes unstable and easily separates out in applied field in two phases -- an almost pure nematic liquid crystal and a suspension of large particle aggregations well observed in an optical microscope. Such properties are obviously associated with a strong interparticle interaction due to the increased number of hydrogen bonds.[8] Phase separation leads to system electro-optical characteristics growing worse, with the negligible response to the field influence.

Hydrophobization of the particle surface leads vise versa to an improvement of characteristics of filled LC. Suspensions based on PMS- and OMTS-modified aerosil appeared to be stable with no visible aggregation. OH-groups substitution with siloxanes seemed to diminish greatly particle-particle interaction. Organosiloxane modification essentially improves voltage-contrast characteristics of the system: saturation voltage decreases, contrast ratio and steepness radically grow up. The contrast ratio increase being almost the same the steepness grows more after the modification with bridge-like siloxanes. Whereas the voltage-contrast hysteresis substantially decreases after the trial with linear siloxanes.

Frequency dependencies of hydrophobic aerosil based suspensions are shown on Fig.3. This behavior is slightly dependent on a steric structure of siloxane. Analogous features have not been measured for non-modified and hydrophilic aerosil because of an essential phase separation and system unhomogeneity. Two main reasons could be taken into account considering the influence of modification. The first one is the alteration of aerosil inerparticle interaction, i.e., the change of its coagulation. The second factor is the variation of interaction between LC-molecules and aerosil particles. Particle coagulation decrease after hydrophobic modification is well-known. Efficiency of such an influence for different agents is rather specific what makes general conclusions impractical. Frequency dependences $\Delta T(f)$ for both linear and bridge-like hydrophobic modificators are almost coinciding in our experiments. They are determined by system response times that are in turn dependent on the mean interparticle distance of aerosil. It is reasonably to suggest that the influence of steric structure of hydrophobic modificators upon suspension electro-optical behavior is rather small in our case.

Thus, the variation of interaction between LC-molecules and aerosil particles after modification appeared to be the main factor affecting suspension electro-optical features.

Steeper slope of the voltage-contrast curve and, respectively, lower saturation voltage for bridge-like modificator testify about the lower anchoring energy W of NLC with silica particles then that for the linear agent.

Let us estimate values of these energies assuming the complete silica particle dispersion and the equality of electric field energy to the LC elastic one under the saturating voltage $\mathbf{U}_S$:

$$\frac{1}{2}\cdot\varepsilon\cdot\varepsilon_0\cdot\frac{U_s}{d}\cong W\cdot n_p\cdot S_p \tag{1}$$

where $\mathbf{n_p}$ - particles concentration, $\mathbf{S_p}$ - area of a one particle surface, **d** - cell thickness. From the experiment conditions $\mathbf{n_p} \approx 10^{16}$ cm^{-3}, $\mathbf{S_p} \approx 1.2\times10^{-12}$ cm^2, **d**= 20 μm, $\mathbf{U_{s1}}$= 15 V (OMTS) and $\mathbf{U_{s2}}$= 50 V (PMS) receive $\mathbf{W_1} \approx 3\times10^{-4}$ erg/cm^2, $\mathbf{W_2} \approx 10^{-3}$ erg/cm^2 what is in excellent agreement with available data[12].

As it was shown, the conditions of the aerosil surface seem to influence greatly the electro-optical behavior of the system. It provides a possibility to control and improve effectively electro-optical characteristics of filled LC due to the chemical modification of aerosil surface. Aerosil modification with hydrophobic substances was established to improve the suspension features. The reasons for this are: i)a sylica particles trend to coagulate essentially decreased, ii) a decrease of the interaction energy between a LC and aerosil. Also electro-optical characteristics of suspensions were found to be influenced by a structure of a hydrophobic modificator. This dependence for the most part is caused by the influence of a surface fragment structure on the anchoring energy 'aerosil-LC' and this offers some expectations for future enrichment of such medium characteristics.

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