ELECTRICAL FIELD INDUCED PROPERTIES OF NEMATIC LIQUID CRYSTAL/COPOLYMER PARTICLES COMPOSITE

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Au fost sintetizate particule de copolimeri alternanți divinilbenzen – anhidrida maleică. Dimensiunile lor au fost determinate prin microscopie electronică şi sunt de ordinul 1-2 μm. Aceste particule au fost amestecate prin agitare magnetică şi ultrasonare cu cristal lichid nematic în concentrație de 5% masic (polimer/cristal lichid) şi au fost introduse în celule convenționale de sticlă acoperită cu strat conductor (ITO). Au fost studiate caracteristicile curent-tensiune şi timpii de comutare electro-optică.

Particles of the type divinylbenzene - maleic anhydride alternated copolymers have been synthesized. Their dimensions were determined by electron microscopy and are in the range 1-2 μm. These particles were mixed by stirring and ultrasound with nematic liquid crystals ZLI 1221(Merck), in a concentration of 5% wt. (polymer/LC) and filled in conventional sandwich cells formed by ITO covered glass. Current-voltage characteristics and switching times have been studied.

Keywords: Liquid crystals, switching times, optical transmission, current-voltage characteristics.

1. Introduction

In recent years there have been many studies regarding the design of new liquid crystals and improved liquid crystals composite [1], [2]. In liquid crystal dispersions, particles form internal interfaces with large specific surface, making possible to stabilize different director configurations [3], [4]. Because small domains with different director configurations are formed, the system liquid crystal – guest particles shows strong light scattering. By applying electric or magnetic fields[5], the liquid crystal molecules reorient and the scattering state can be switched to the transparent one.

The general problem of colloidal systems is the particle tendency of forming clusters, their uniform dispersion being difficult even for very small concentrations of particles. In the recent years much attention has been paid to the particles/liquid crystals composites due to their applications in optoelectronics.

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Bistable operation of small formation of agglomerated nanosized silica spheres has been demonstrated (called filled nematics)[6] and micron sized polymer spheres dispersed in liquid crystals named Polymer Ball Type Polymer Dispersed Liquid Crystal have been studied[7].

In this paper we examined the electrical and optical properties of the liquid crystal ZLI 1221 (Merck) pure and in a composite system obtained by introducing synthesized polymer particles in this liquid crystal.

2. Experimental

2.1. Synthesis of polymer particles

The synthesis was performed as described in [8]: maleic anhydride (4g) and divinylbenzene (4g) were mixed with methylethyl ketone (4ml), heptane (60ml) and a reactive surfactant- $NPEO_4$ -nonyl phenol ethoxylated with 4 moles ethylene. Azobisisobutyronitrile (0.2g) was used as initiator. These mixtures have been stirred for 4 hours, at 70 °C**.** NPO_4 is a surfactant with a terminal functional group hydroxyl (OH) that can react with maleic anhydride (MA) in the copolymer. Thus we insured the attachment of some chains with phenyl group on the copolymer particle. These lateral groups insure a better compatibility between the copolymer particle and the LC and an increased stability [9], [10].

2.2. Sample preparation

The copolymer particles have been mixed with the liquid crystal ZLI 1221, provided by Merck, in a proportion of 5% wt. The liquid crystal ZLI1221 is a mixture of phenylcyclohexanes, biphenylcyclohexane, and phenylcyclohexane esters with the phase transition temperatures K-N: -11 °C, N-I: 90°C (K-crystalline, N- nematic and I- Isotrop) and has positive anisotropy of the dielectric permittivity $\Delta\varepsilon > 0$.

The composite system was filled in a cell of conventional sandwich type, consisting of two ITO covered glass plates separated by Millar spacers of 12μm thickness.

2.3. Scanning Electron Microscopy image acquisition

The morphology of the obtained particles was examined by scanning electron microscopy (SEM) with a FEI QUANTA 200 instrument, using low vacuum working mode and 15kV accelerating voltage.

2.4. Current-voltage characteristics.

The *I(V)* measurements were made by using a Keithley 2400 electrometer, a temperature-controlled hot stage Mettler-Toledo 3200 series and an adequated homemade software.

2.5. Electro-optical measurements

The experimental setup used for measuring the transmitted light intensity and the switching time is presented in fig.1. It consists of a 2mW linearly polarized He-Ne laser with a divergence of 1,2 mrad, Transistor-Transistor Logic (TTL) signal generating stage, an amplifying stage, a photodiode detector and a Tektronix TDS 210 oscilloscope. The laser beam is incident on the sample placed between the two crossed polarizers.

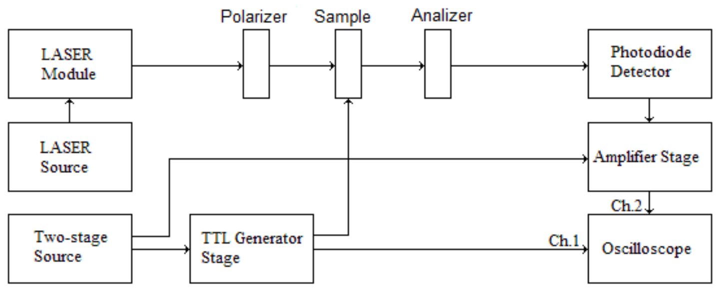


Fig.1. Experimental setup for the measurement of the switching times.

The output signal is collected by the photodiode detector and amplified through the amplifying stage before being visualized on the oscilloscope. The sample is subjected to the TTL signal offered by the generator stage of the amplifier. This signal can also be viewed on the oscilloscope in order to make necessary adjustments throughout the experiment.

3. Results and Discussions

3.1. Scanning Electron Microscopy.

In fig. 2 is presented the SEM image for the synthesized particles D12. The particles are well defined, with dimensions of 1-2 μm and have a rather uniform distribution.

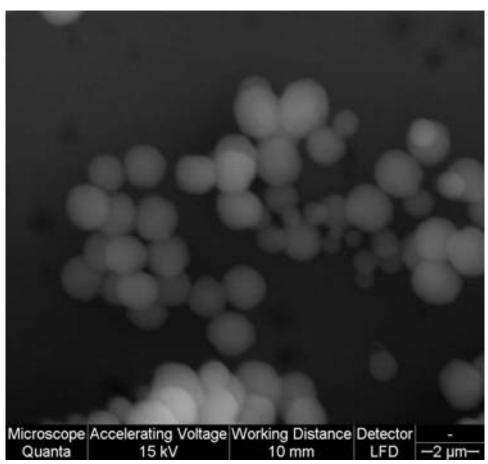
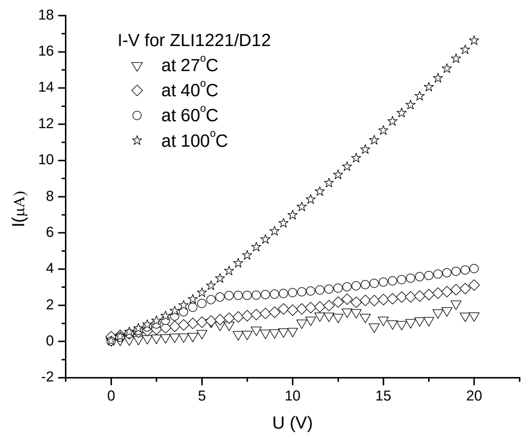


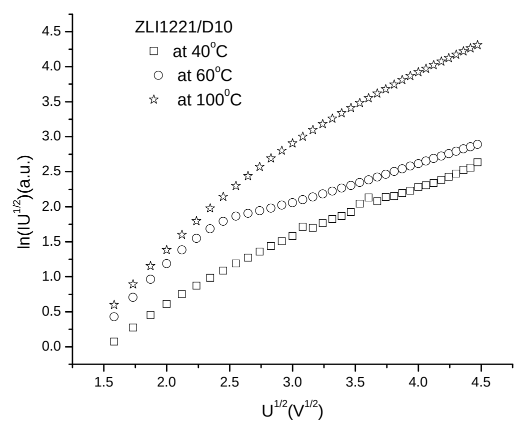
Fig.2. SEM image for the synthesized particles D12.

3.2. Current-voltage characteristics.

In fig. 3a are presented the I-V curves for the composite sample ZLI1221/D10, in the nematic phase, at 27°C, 40°C and 60°C and in the isotropic phase, at 100°C. From these curves we can see that at lower temperatures the behavior might be Ohmic. The linearization of the I-V curves is presented in fig. 3b as the graphs $\ln\left(I\sqrt{U}\right)= f(\sqrt{U})$. At 60°C and at 100°C, we may notice that the curves have two distinct zones, with a threshold (corresponding to an applied electric field ($\approx 5\cdot 10^5 V/m$). We may consider a Schottky conduction mechanism for the lower applied voltages and a Poole-Frenkel conduction mechanism for higher voltages[11-17].



a)



b)

Fig. 3. a) Current-voltage characteristics and b) $\ln\left(I\sqrt{U}\right)= f(\sqrt{U})$ representation for the composite sample liquid crystal/copolymer particles ZLI1221/D12, in a 12 μm thickness cell.

In fig. 4 are presented the optical transmission curves for the liquid crystal ZLI 1221 and for the composite sample ZLI1221/D12, for d.c. control voltage. As it is known[18], [19], the transmitted light intensity depends on the birefringence $\Delta n(U,T,\lambda)$ of the liquid crystal, where U is the applied voltage, T is the temperature and λ the wavelength. If the polarization direction of the incident light forms an angle θ with the director of the liquid crystal, phase retardation appears, due to the different propagation velocities of the ordinary and extraordinary waves in the liquid crystal.

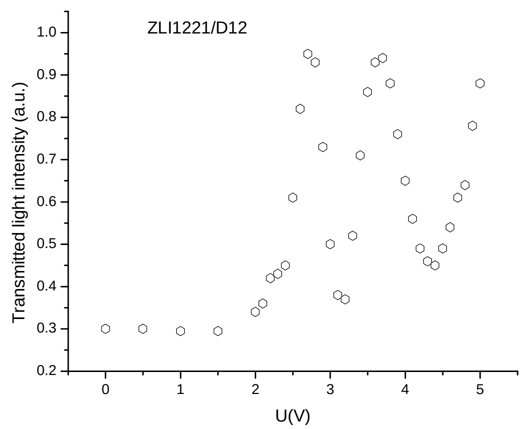


Fig.4. Transmitted light intensity versus d.c. applied voltage for the composite ZLI1221/D12 measured between crossed polarizers.

The phase retardation is given by the relation:

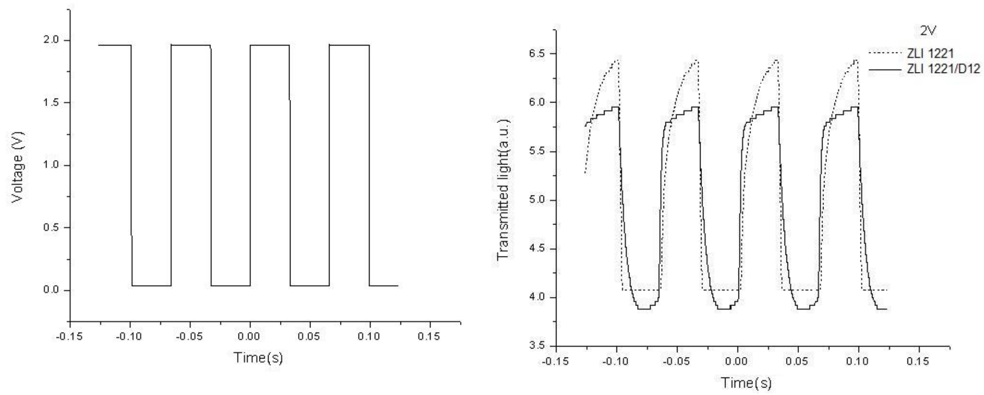
$$\delta(U,T,\lambda) = \frac{2\pi d}{\lambda} \cdot \Delta n(U,T,\lambda) \tag{1}$$

where d is the thickness of the liquid crystal cell. For a liquid crystal sample placed between crossed polarizers, the transmitted light intensity, $T_\perp$ is[18,19]:

$$T_\perp = \sin^2 2\theta \cdot \sin^2\left(\frac{\delta}{2}\right) \tag{2}$$

For monochromatic incident light, at constant temperature, the optical transmission will depend on the applied voltage, as observed in Fig. 4.

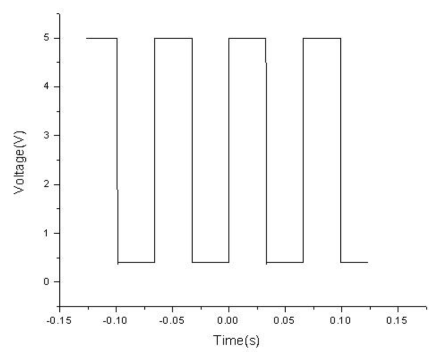
In fig. 5 are presented the 2V control voltage rectangular signals and corresponding detected transmitted light intensity for the liquid crystal ZLI 1221 and composite ZLI 1221/ D12.



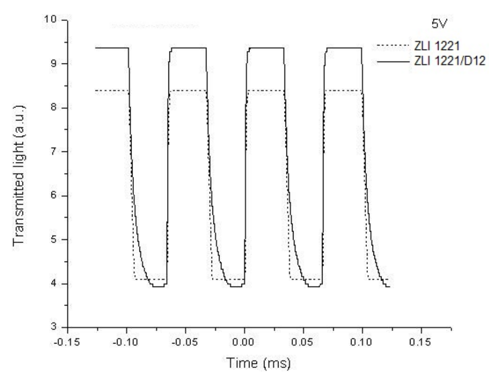
a) b)

Fig. 5. Control voltage signal of 2V a) and corresponding detected transmitted light intensity b) for the liquid crystal ZLI 1221 (dashed line) and composite ZLI 1221/ D12 (continuous line).

In fig. 6 are presented the 5V control voltage rectangular signals and corresponding detected transmitted light intensity for the liquid crystal ZLI 1221 and composite ZLI 1221/ D12.



a)



b)

Fig. 6. Control voltage signal of 2V a) and corresponding detected transmitted light intensity b) for the liquid crystal ZLI 1221 (dashed line) and composite ZLI 1221/ D12 (continuous line).

A better preservation for the shape of the signal is observed for the composite sample ZLI1221/D10 for the control signal of 2V (fig. 5b) and a higher transmitted signal for the composite sample at a 5V control signal (fig. 6b), as compared to the liquid crystal. The switching time is defined as the time between the moment when the optical transmission reaches 10% of the maximum value and the moment when the optical transmission reaches 90% of the maximum value. The obtained switching time values are presented in Table 1. The higher fall times obtained for the composite sample are probably due to the anchoring effects of the liquid crystal on the copolymer particles.

Table 1.

Rise time and fall time for the studied samples.

	Rise Time (ms)	Fall Time (ms)	Rise Time (ms)	Fall Time (ms)
Applied Voltage	2V		5V	
ZLI 1221	21	1	1	1
ZLI 1221/D12	2	15	2	18

4. Conclusions

We have synthesized polymer particles of the type alternated copolymers divinylbenzene (DVB)- maleic anhydride (MA). Composite samples of these particles and nematic liquid crystals ZLI 1221(Merck), in a concentration of 5% wt.(polymer/LC) have been prepared. We have studied the current-voltage characteristics, and the electro-optical properties of these samples as compared to the nematic liquid crystal. For a rectangular control signal, in some voltage ranges a better preservation of the shape of the control signal was obtained and a better contrast ratio.

Acknowledgements

The authors thank the Romanian Ministry of Education and Research UEFISCSU (Executive Agency for Higher Education and Research Funding), project ID_123 for funding this study and the Merck company for providing the liquid crystal.

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