Morphology and dielectric properties of polymer dispersed liquid crystal with magnetic nanoparticles

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Abstract. It has been shown that introduction of magnetic nanoparticles (MN) of various shapes with the concentration 10^{-1} wt.% into polymer dispersed liquid crystal (PDLC) causes two effects: the size of liquid crystal droplets decreases, and the amount of the latter with through holes increases. MN increase the effective value of permittivity by more than one order within the frequency range $10^{-1} - 10^2$ Hz, as well as the electron and ion components of conductivity. MN reduce the exponent in the frequency dependence of the electron component of conductivity. The changes caused by the presence of the nanoparticles quantitatively depend on their shape.

Keywords: magnetic nanoparticle, polymer matrix, liquid crystal, permittivity, electron and ion components of conductivity.

1. Introduction

The large scale study of dispersions of nematic liquid crystal in a polymer matrix (PDLC) began after publications [1, 2], where it was shown that these systems can be used to create electro-optical devices of a new type [3].

Wide spread of these systems in display technology is limited by two important factors: the rather high (as compared to homogeneous systems) value of voltage, for example, for transition from a state with a strong light scattering into the transparent one, as well as more longer times of transition from one state to another (especially when the voltage is turned off). Therefore, the PDLCs are currently considered as promising materials for specific applications such as creation of window blinds controlled by electric field, fog simulators, UV protective glasses, etc. In all these

devices, the mechanism providing control of PDLC optical properties is of fundamental importance.

It is known [4] that, when electric field acts on PDLC, the electric field inside droplets of liquid crystal can be significantly lower than the external electric field due to effects of polarization. This fact principally leads to controlling voltages that are significant in their magnitude (tens and even hundreds of volts). Polarization effects can be ignored if using the magnetic field for controlling the electro-optical properties of PDLC. Due to relatively low anisotropy of the diamagnetic susceptibility of liquid crystal, magneto-optical effects in PDLC are possible in the case of sufficiently strong magnetic fields that can be practically realized only in a few research laboratories over the world.

The effect of magnetic field can be significantly enhanced by introducing the magnetic particles into PDLC. To have no influence on the light scattering,

these particles should possess dimensions that are shorter than the light wavelengths, and their concentration must be relatively low. It is clear that for these purposes the magnetic nanoparticles (MN) are best matched, and great success in their manufacturing technology was presently achieved.

The analysis of publications has showed that the effect of MN on the properties of homogeneous liquid crystal was extensively investigated [5-8], but only few data for MN influence on the properties of PDLC were obtained. In our opinion, the properties of PDLC with the MN will be to a large extent determined by the fact how the MN act on the structure and dielectric properties of this matrix. The purpose of this work was to investigate this influence.

2. Materials and methods

The samples of PDLCs have been prepared by the following method. Liquid crystal (6CHBT, i.e. 4-trans-4'-n-hexyl-cyclohexyl-isothiocyanatobenzene) of amount 0.05 ml was added to 5 ml with 10% polyvinyl alcohol (PVA). This mixture was stirred at 10,000 rpm for 1 min. A creamy white emulsion was obtained. It was let to degas and a thin bead was placed on a slide. After the water evaporation, we got a thin film.

This technique was also used for preparation of the PDLC films doped with various kinds of magnetic particles.

The sample thickness was 50 μm. The structure of the films was investigated by using the scanning electron microscope JSM-35 with the accelerating voltage 35 keV. To eliminate the effect of charging the surface, before the measurements a graphite film was deposited onto the surface of the PDLC film.

Dielectric measurements were performed using the oscilloscope method [9, 10] at the temperature close to 293 K. We applied to the sample the alternating voltage of a triangular shape with the amplitude value 0.25 V. The range of measuring signal frequency was within 10^{-1} to 10^6 Hz. The PDLC film was placed between two glass plates covered with a transparent layer of ITO. To improve the electrical contact, a small amount of 6CHBT was deposited onto the surface of electrodes.

3. Results and discussion

1. The morphology of the samples

Fig. 1 shows the morphology of the films PDLC (*a*), PDLC with spherical MN (*b*), and PDLC with rod-like MN (*c*). Our analysis of these data demonstrates that the MN act on the sizes of droplets of liquid crystal in the polymer matrix. In the case of PDLC films, the average LC droplet size was 5 to 8 μm (Fig. 1a). When introducing the MN, the average droplet size was decreased down to 3…5 μm for spherical MN and 4…6 μm for the rod-like MN. A decrease of the droplet sizes can be explained by an increase in the rigidity of
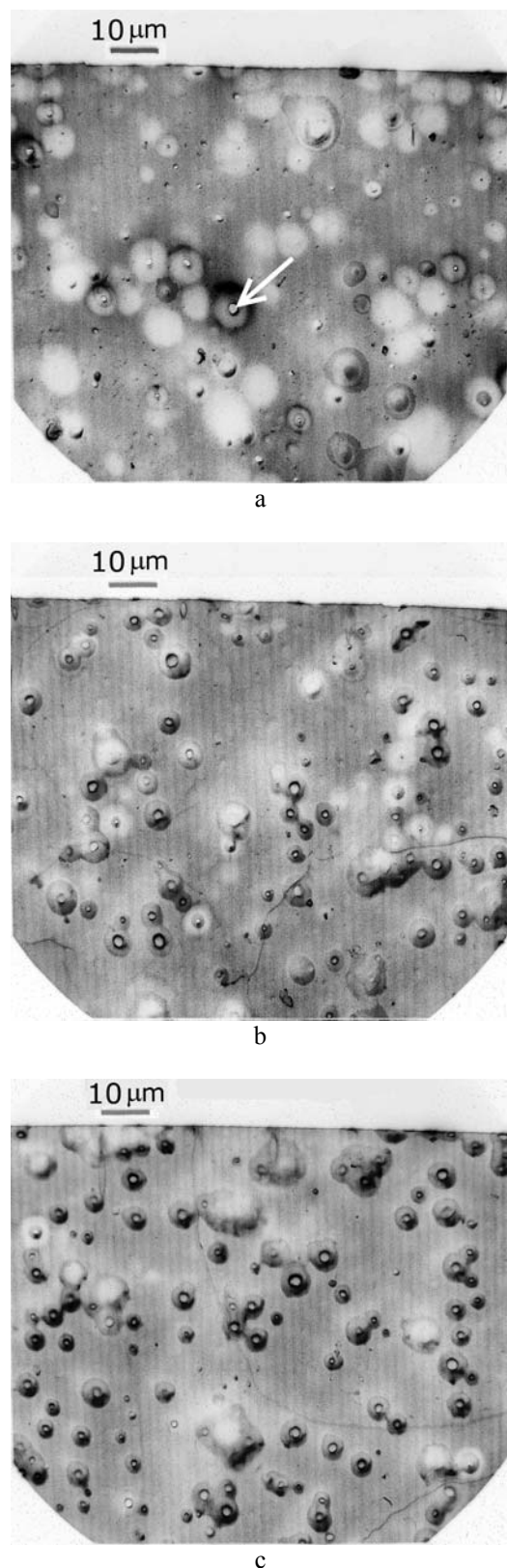

Fig. 1. Morphology of PDLC films: pure (*a*), with spherical MN (*b*) and with rod-like MN (*c*) obtained by using the scanning electron microscope JSM-35. The accelerating voltage was 35 keV. The arrow indicates the location where a hole was formed. These images are of the negative type.

the polymer film. In this case, MN act as rebar in concrete.

Beside reduction of droplet sizes, presence of MN leads to an increase in the number of droplets with through holes (black dots in the center of the droplets). It follows from Fig. 1 that this effect is most pronounced in the films with rod-like MN. The difference in the amount of droplets with through holes for the MN of different shape is understandable, because the rod-like MN change geometrical parameters of the polymer matrix more significantly than the spherical ones.

It should be noted that the concentration of spherical and rod-like MN was 10^{-1} wt.%. I.e., even a small amount of MN may considerably change both morphology and other properties of PDLC (as will be shown below).

2. Dielectric properties

Fig. 2 shows the frequency dependence of dielectric films PDLC (*1*), PDLC with spherical MN (*2*) and PDLC with rod-like MN (*3*). The data obtained suggest that the greatest difference between the samples in the ε' value is observed at the frequency $f < 10^2$ Hz. Within this frequency range, the very ε' value is sharply increased, too. As was shown in [11, 12], the sharp increase in the components of the permittivity (real and imaginary) is caused by redistribution of the electric field due to near-electrode processes. For non-uniform electric field, the ε' value can be considered as the effective one.

From the above analysis, we can conclude that the spherical and rod-like MN influence most significantly on the parameters of the near-electrode area. As seen from Fig. 2, the greatest difference in the ε' magnitude (more than one order) is observed for $f = 0.1$ Hz. For this frequency range, the influence of the near-electrode area is the most essential.

In [11, 12], it was shown that redistribution of the field in the near-electrode area is the most pronounced in liquids. Therefore, an analysis of Fig. 2 data demonstrates that the introduction of MN into PDLC leads to an increase in the amount of liquid crystal in the near-electrode area. Based on the analysis of morphology of these films, we concluded that significant increase in the number of holes in liquid crystal droplets in the presence of MN promotes this process. As follows from Fig. 1, for the case of rod-like MN the amount of liquid crystal droplets with holes is larger than that for PDLC with spherical MN. There is a complete correlation between the changes in the ε' value and the amount of droplets with through holes. I.e., the main reason for the change of dielectric properties of PDLC, when introducing the MN, is a change in the parameters of the near-electrode area.

A comparison of the ε' value for three types of the samples measured at frequencies $f > 10^2$ Hz shows that for these frequencies also a change in the ε' value is observed, but it is considerably smaller than the above

changes. The largest change in the ε' value for these frequencies is observed when $f > 10^5$ Hz and may be caused by the influence of MN on dipole polarization in LC droplets. This indicates that when phases are separated, as a result of polymerization, a part of MN goes into the polymer, but some of them remain in the LC droplets.

Fig. 3 shows the frequency dependence of conductivity for films of PDLC (*1*), PDLC with spherical MN (*2*) and PDLC with rod-like MN (*3*). It follows that this frequency range can be separated into three sections.
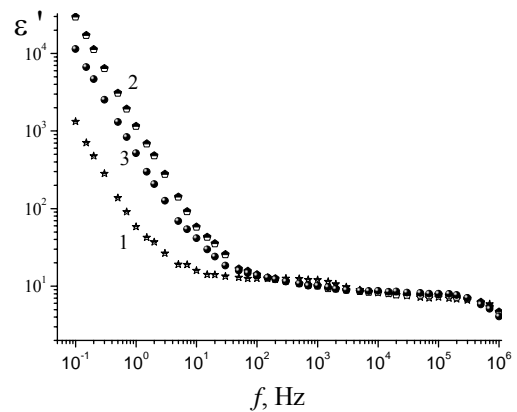
Fig. 2. Frequency dependence of the effective value of the permittivity for the PDLC films: pure (*1*), with spherical MN (*2*) and with rod-like MN (*3*). The film thickness is 50 μm. The amplitude value of the voltage of measured signal is 0.25 V. The temperature is 293 K.
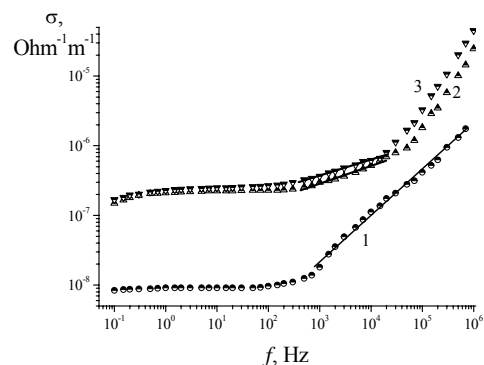
Fig. 3. Frequency dependence of the conductivity for the PDLC films: pure (*1*), with spherical MN (*2*) and with rod-like MN (*3*). Lines indicate the regions where the conductivity depends on the frequency in accord with a power law.

For frequencies $f < 10^2$ Hz, the conductivity is almost independent of frequency. Such behavior is characteristic for ion conductivity in LC. Since most of the LC droplets in the presence of spherical and rod-like MN have through holes, it promotes charge transfer due to ion motion. This is the main reason for the change of the ion component of conductivity σ_i. In addition, the presence of MN in the LC droplets leads to increase in the ion conductivity of the very LC.

Comparison of the σ_i value for the films of PDLC (*1*), PDLC with spherical MN (*2*) and PDLC with rod-like MN (*3*) (Fig. 3) shows that when introducing the MN into PDLC, the σ_i value is increased by more than one order. And in the case of rod-like MN, a change of σ_i is approximately 1.2 times higher than that in the case of spherical MN. This small difference in the magnitude of the ion component of conductivity does not give grounds to assert that the main reason for total increase is formation of through holes in the films. An increase in σ_i with introducing the MN is most likely caused by changes in the conductivity of the very LC, and the shape of nanoparticles has no special meaning in this case. The obtained experimental data do not allow to determine which of the mechanisms providing the change in the σ_i value is the main one. To solve this problem, additional experiments must be carried out. This is not an aim of this work and will be a subject of our further studies.

As follows from Fig. 3, at frequencies $f > \cdot 10^3$ Hz for all the samples, the conductivity depends on the frequency in accord with the power law

$$\sigma_e = \sigma_{DC} + A\omega^s, \qquad (1)$$

where σ_{DC} is the dc conductivity ($f = 0$), $\omega = 2\pi f$ – angular frequency, A – constant value for this process of changes in the conductivity, s – the exponent that characterizes mainly the transfer of charge carriers. The dependence (1) is characteristic for charge transfer in disordered solids, where the hopping process is inherent to charge carriers (mainly electrons) being in electric field and changing one stable state for another. It can be assumed that for PDLC films the conductivity that obeys relation (1) is caused by electron transfer in the polymer film.

As noted above, the most important parameter characterizing the charge transfer process (1) is the s value. Fig. 3 shows that for the PDLC films $s = 0.67 \pm 0.03$. For the PDLC with spherical MN $s = 0.26 \pm 0.03$, and for PDLC with rod-like MN $s = 0.23 \pm 0.03$. It enables one to conclude that the magnetic nanoparticles change the electrical properties not only of liquid crystal droplets, but the polymer (PVA), too.

It is seen from Fig. 3 that the MN effect on the electron conductivity in the polymer is less than on the ion component in LC. But the influence of the MN shape on conductivity changes is more clearly expressed in this case. In contrast to σ_i, the σ_e value for PDLC with rod-like MN is more than 1.8 times greater than that for PDLC with spherical MN.

If to compare the effect of MN on σ_i and σ_e values one can draw the following conclusions. At the presence of MN, the σ_i value increases 25 times, while the maximum change in σ_i (for $f = 10^6$ Hz) equals 15 for PDLC with rod-like MN. I.e., the presence of MN in PDLC has a greater effect on the magnitude of the ion component of conductivity than on the σ_e value. Since σ_i is caused by LC conductivity and σ_e – by conductivity of polymer, this comparison allows to suggest that, after separation of the phases, most of the MN is located in the LC droplets.

Within the total frequency range, the conductivity can be represented as a sum of the ion conductivity in LC σ_i (its value does not depend on the frequency) and the electron conductivity in polymer σ_e:

$$\sigma = \sigma_i + \sigma_{DC} + A\omega^s. \qquad (2)$$

By using the equation (2), one can describe the frequency dependence in the transition parts, too.

Conclusions

1. The presence of MN in PDLC films based on liquid crystal 6CHBT and polyvinyl alcohol leads to two effects: an increase in the amount of droplets with holes and decrease in droplet sizes. For PDLC films, the LC droplet size was 5 to 8 μm. When introducing MN into PDLC, the droplet size was decreased down to 3…5 μm for spherical MN and 4…6 μm for rod-like MN. The decrease in sizes of droplets can be explained by rigidity of the polymer film in the presence of MN. Due to MN introduction, effect of an increase of holes in the droplets is more essential than the effect of reducing their size.

2. With MN introduction into PDLC, the most significant changes in the effective value of the permittivity were observed for frequencies $f < 10^2$ Hz. These changes may be caused by an increase in the amount of liquid crystal in the near-electrode area due to formation of holes in LC droplets. This assumption is confirmed by the influence of the droplet shape on the ε' value and by correlation between the change in ε' and amount of holes in the LC droplets with different shapes of MN.

3. The conductivity of PDLC within the frequency range $10^{-1} - 10^6$ Hz has two components: the ion one σ_i caused by transfer of ions in LC and electron one σ_e caused by transfer of electrons inside polymer. The ion component of conductivity does not depend on frequency, and it is the main component for frequencies $f < 10^2$ Hz. The determining contribution of the electron component is observed for frequencies $f > \cdot 10^3$ Hz. This component of conductivity is characterized by the power dependence on the frequency.

4. The MN introduction into PDLC leads to an increase in the ion component of conductivity by a factor

of more than 25. The shape of the nanoparticles does not practically influence on the change in the value of conductivity (in the case of rod-like MN, the change of σ_i is approximately 1.2 times higher than that for spherical MN).

At the presence of MN, the maximum change in the electron component of conductivity is equal to 15. In this case, for the rod-like MN the change of σ_e value is 1.8 times larger than that for the spherical MN. The presence of MN in PDLC leads not only to a change in the conductivity value, but also to a decrease in the exponent for the dependence $\sigma_e(f)$ from 0.67 ± 0.03 for the PDLC to 0.26 ± 0.03 for the PDLC with spherical MN and 0.23 ± 0.03 for the PDLC with rod-like MN. The smaller change of the σ_e value than the σ_i value when introducing MN into PDLC may be caused by the fact that, when phases are separated, the most of MN passes to LC in the process of structure formation.

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