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A Synergistic Effect in Nematic Liquid Crystal with Nanotube and Magnetite

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Abstract

From the standpoint of the synergistic effect, the results on the influence of nanotubes and magnetite (separately and in combination) on the electrical properties of nematic liquid crystal with different geometric parameters – from 0.5 to tens of micrometers – are considered. Mechanisms of synergistic effect for such objects are offered.

1 Introduction

Displays based on liquid crystals (LC) are currently the most competitive and widespread in the modern electronic products market. In addition, scientific research shows the prospect of using liquid crystals in other than the displays, electronics industries. For such purposes, the functional properties of the LC are expanded by introducing various types of nanoparticles.

Nanoparticles of various type are used to extend functionality of LC. The most important of them are carbon nanotubes (CNT) [1]–[3]. It was shown that CNT dispersed in LC can essentially affect the concentration and spatial distribution of charges and thereby determine the electrooptical response of the CNT+LC composite [4, 5]. Besides, the analysis of the concentration dependence of the electric conductivity has shown that it can be described being based on the percolation theory [1, 3, 6].

One should note that CNT alone cannot always provide the desired parameters of CNT+LC composite. For example, sensitivity to a magnetic field is provided by addition of magnetite [7, 8]. A question arises: is it possible, knowing how each type of the nanoparticles affects the LC properties, to predict the combined action of nanoparticles of both types on the LC properties? A similar problem for homogeneous LC was studied in our earlier paper [9]. It was shown that simultaneous introduction of 0.02 wt.% CNT and 0.02 wt.% magnetite nanoparticles (MN) into

a liquid crystal results in the increase of conductivity by factor of nearly 20, while each of the components taken separately increases the LC conductivity not more than twice. This result confirms that it is difficult to predict the effect of combined action of even two nanoparticle types on the LC parameters being based on the separate effect of each impurity.

One of the mechanisms that can explain the synergistic effect of nanoparticles on the LC conductivity revealed in our earlier study [9] can be formation of complexes of nanoparticles. In this case, the process efficiency should be essentially affected by size effect (the LC volume), which can be achieved by dispersion of the LC molecules in a polymer matrix (PDLC cells). Such problem was considered in our earlier study [10]. The studies of the PDLC cells with the nematic droplet size of 8–10 μm (micro-PDLC) have shown that at such spatial scale the non-additive effect of carbon nanotubes and magnetite on the composite conductivity is smaller, though still essential.

The features of the synergistic effect of carbon nanotubes and magnetite on the conductivity of nematic liquid crystal for nano-PDLC (the average diameter of nematic droplets was of the order of 0.8 μm) was considered by us in [11]. It has been shown that in the case of nano-PDLC, the summary action of nanotubes and magnetite on the conductivity is less than that of each nanoparticle separately. The clear dependence obtained of the synergistic effects on geometrical scales requires their analysis from the standpoint of the only possible effect.

Therefore, the aim of this work was to analyze previously obtained data from the positions of synergistic effect [12]. Since we studied objects with different geometric parameters: homogeneous liquid crystals (tens of micrometers), micro-PDLC (8–10 μm), and nano-PDLC (about 0.8 μm), this allowed us to consider the manifestation of the synergistic effect on different scales. An analysis of a small number of publications on the manifestation of the synergistic effect in liquid crystals [13]–[16] showed that such a task had not been considered before.

2 Film morphology

The analysis of PDLC film morphology has shown that, for the chosen homogenizing technique, the size of the LC inclusions in PDLC under investigation did not exceed 1 μm and on the average was 500 nm [17]. It is by an order of magnitude lower than the droplet size for the PDLC in our earlier study [10]. Hence, one can consider the samples obtained to be nano-PDLC. Such conclusion is also confirmed by the optical characteristics of the samples under investigation. The micro-PDLC samples studied in Ref. [10] strongly scattered light in the visible spectral range and were non-transparent, while nano-PDLC samples of the same thickness transmitted light and were of orange colour.

Besides, the analysis of the SEM images showed that, similarly to the case of micro-PDLC, the morphology of nano-PDLC does not essentially change depending on the nanoparticle type and, as we have shown earlier in the work [12], on the nanoparticle shape for MN as well. No quantitative estimation of the nanoparticle diameter could be made as it was done in [10], since the edges of the LC inclusions were close to their diameter. From the earlier studies of PDLC it is known

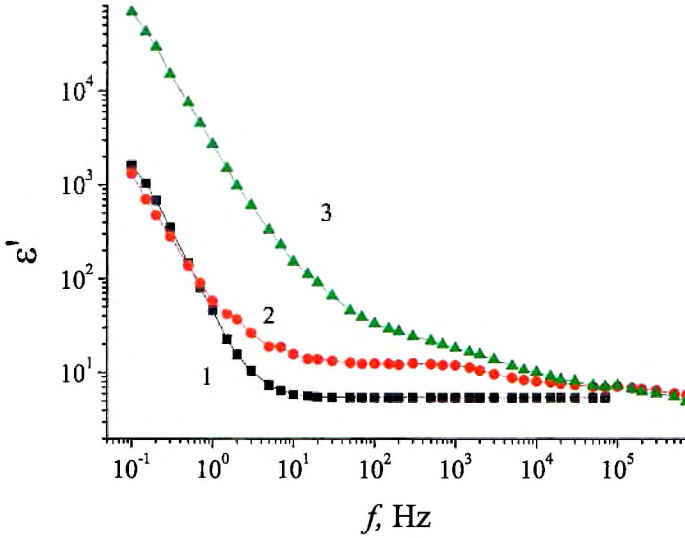


Figure 1: Frequency dependencies of the real part ϵ' of complex dielectric permittivity at 293 K for planarly oriented 6CHBT (1), micro-PDLC (2), and nano-PDLC (3)

that after the phase separation in the course of the PLDC sample preparation, the clear boundary between the LC and the polymer is not observed [18]. There always exists an intermediate layer consisting (at the molecular level) the mixture of monomers of the polymer and LC molecules. The thickness of such layer is near $1 \mu\text{m}$ what is comparable with the LC droplet size in the case of nano-PDLC.

3 Frequency dependencies of dielectric permittivity and electric conductivity for the homogeneous LC, micro- and nano-PDLC

Discussing the reasons for the non-additive effect of the nanoparticles on the LC conductivity at various spatial scale, one should analyze how the dielectric permittivity and conductivity spectra of micro- and nano-PDLC without nanoparticles change with respect to the similar spectra of pure homogeneous LC.

The spectra of dielectric permittivity ϵ' planarly oriented 6CHBT LC, micro- and nano-PDLC are shown in Fig. 1. A slight difference between the ϵ' spectra of 6CHBT LC and micro-PDLC as well as essential changes of the dielectric spectrum in the case of nano-PDLC are clear observed. This is especially noticeable for the frequency range $f < 10^3$ Hz.

It was shown earlier that high values of the dielectric permittivity at low frequencies are related to the effect of near-electrode processes [18]. Hence, one can assume that the role of the near-electrode processes for nano-PDLC is much more essential than that for the homogeneous LC and micro-PDLC. The slight difference

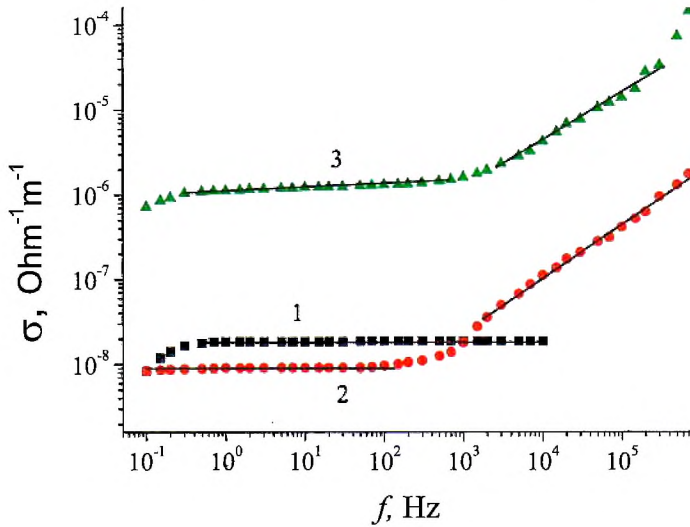


Figure 2: Frequency dependencies of electrical conductivity at 293 K for planarly oriented 6CHBT LC (1), micro-PDLC (2), and nano-PDLC (3)

between the ϵ' dielectric spectra of 6CHBT LC and micro-PDLC can be caused by the fact that in the case of micro-PDLC the LC droplet size was comparable to the PDLC film thickness [10]. In some areas of the micro-PDLC, the LC droplet size even exceeded the film thickness. This area of the micro-PDLC can be treated as “an hole” in the film filled with LC. Precisely such areas of the micro-PDLC can define the dielectric properties at low frequencies. Due to this fact, the difference in the dielectric spectra of LC and micro-PDLC, especially at low frequencies, is not essential.

As it follows from the analysis of the SEM images, for nano-PDLC the areas with “holes” are not observed. Therefore, this can be one of the reasons for the essential difference between the dielectric spectra of 6CHBT LC and the micro-PDLC with respect to that of nano-PDLC. However, solely the difference in the micro-PDLC and nano-PDLC morphology cannot be the main reason for the difference in the dielectric spectra. As it was shown earlier [18], the conductivity value σ essentially affects the near-electrode peculiarities of dielectric media, in particular LC. Hence, it is important to compare the conductivities of planarly oriented 6CHBT LC and the micro-PDLC with that of nano-PDLC (Fig. 2).

Similarly to the case of ϵ' , a slight difference between the conductivities of the planarly oriented 6CHBT LC and the micro-PDLC reveals for the frequency range $f < 10^3$ Hz, becomes essential for $f > 10^3$ Hz (Fig. 2). As it was noted in our earlier study [10], the main reason for this phenomena is the difference in the conductivity types for LC and micro-PDLC. For LC, what is typical for the most of dielectric liquids, the main type of conductivity is ionic conductivity that is independent of frequency. The micro-PDLC includes, besides LC, a polymer matrix,

for which the main conductivity type is electronic one. Taking into account the fact that the polymeric matrix has no distinct spatial order, it can be considered as a disordered system. Therefore, the electronic conductivity can be treated as hopping and, most likely, as conductivity through an inhomogeneous system with a variable hopping length. In such case, the micro-PDLC conductivity can be described as follows:

$$\sigma = \sigma_i + a \cdot f^s, \quad (1)$$

where σ_i is the ionic conductivity component through LC, a is a dimension factor, s is the index of power. The second term in Eq. (1) corresponds to the electronic component of conductivity through the polymer which is the main component of conductivity at the frequencies $f > 10^3$ Hz. As it follows from Fig. 2 (curve 3), for the frequencies $f < 10^3$ Hz the nano-PDLC conductivity is by two orders of magnitude higher than that of the micro-PDLC. Besides, in this frequency range, contrary to micro-PDLC, the conductivity is frequency-dependent. This is an evidence for the fact that “purely” ionic conductivity is not observed for nano-PDLC. In this case, in contrast to Eq. (1) the nano-PDLC conductivity can be described as

$$\sigma = b \cdot f^m + a \cdot f^s, \quad (2)$$

where b is a dimension factor describing the “disordered” ionic conductivity, m is the index of power for this conductivity. We introduced the term “disordered” ionic conductivity in order to separate purely electronic conductivity from the ionic conductivity present in some areas of PDLC separated by other areas (polymer) where the charge transfer occurs solely due to electron transfer.

As it follows from Fig. 2, the m value in Eq. (2) is essential lower than the s value, which makes it possible to separate these two conductivity processes. We should also note that the s value for nano-PDLC is lower than that for micro-PDLC.

4 Effect of magnetite and carbon nanotubes (separate and combined) on the dielectric permittivity and electric permittivity of nano-PDLC.

Figure 3 illustrates frequency dependencies of the dielectric conductivity of nano-PDLC+MN, nano-PDLC+CNT, and nano-PDLC+MN+CNT with 0.2 wt.% concentration of each impurity [13].

Changes caused by the nanoparticle effect are shown to be essentially stronger than the experimental error not only with respect to the matrix, but also with respect to the separate and combined effect of each nanoparticle type (Fig. 3). The strongest variation of the ϵ' value almost in the whole spectral range was caused by the separate effect of CNT (Fig. 3, curve 2). At the same time, at the simultaneous introduction of MN and CNT into nano-PDLC (curve 3) the spectral dependence of the dielectric permittivity becomes almost the same as at the separate effect of MN. Hence, the non-additive effect of nanoparticles on the nano-PDLC properties is revealed in a different way than for micro-PDLC (for micro-PDLC the dielectric

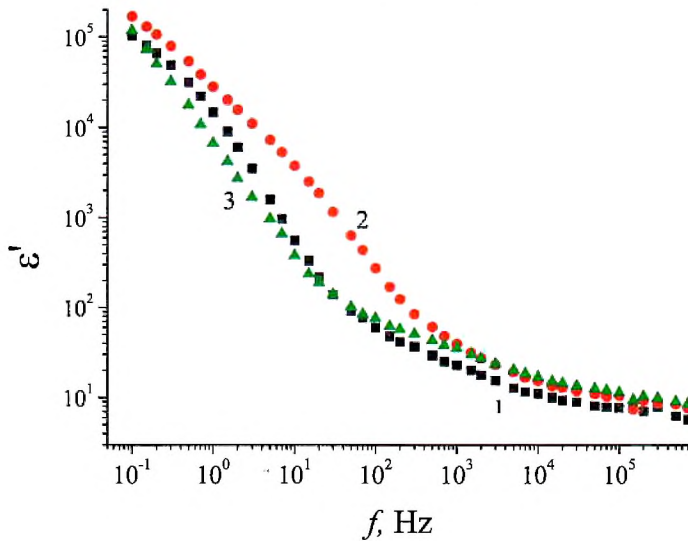


Figure 3: Frequency dependencies of the real part ε' of complex dielectric permittivity at 293 K for nano-PDLC with 0.2 wt.% MN (1), nano-PDLC with 0.2 wt.% CNT (2), and nano-PDLC with 0.2 wt.% MN and 0.2 wt.% CNT (3)

permittivity variation at the simultaneous introduction of MN and CNT is much stronger than at the separate introduction of each nanoparticle [10]).

The studies of electric permittivity reveal a much stronger difference between the nano-PDLC+MN, nano-PDLC+CNT, and nano-PDLC+MN+CNT properties (Fig. 4) than for the dielectric permittivity. Comparison of the frequency dependencies in Fig. 3 and Fig. 4 shows that the character of the nanoparticle effect on the nano-PDLC conductivity correlates with their effect on the dielectric permittivity ε' . Moreover, the frequency dependence of the nano-PDLC+CNT conductivity (curve 2 in Fig. 4) is much more different from those for nano-PDLC+MN (curve 1 in Fig. 4) and nano-PDLC+MN+CNT (curve 3 in Fig. 4) ones. Similarly to the case of the dielectric permittivity, the frequency dependence of the nano-PDLC+MN conductivity almost coincides with that of the nano-PDLC+MN+CNT conductivity. Besides, one should note a distinct difference of the frequency dependencies of the conductivity for the pure nano-PDLC (curve 3 in Fig. 2) from that for the nano-PDLC with nanoparticles (Fig. 4). It should be noted that none of the graphs shown in Fig. 4 can clearly distinguish a plot with a power dependence of conductivity on the frequency (straight line in double logarithmic coordinates). One of the main reasons for the observed effect can be superimposition of processes with the “disordered” ionic conductivity and purely electronic conductivity due to the effect of nanoparticles.

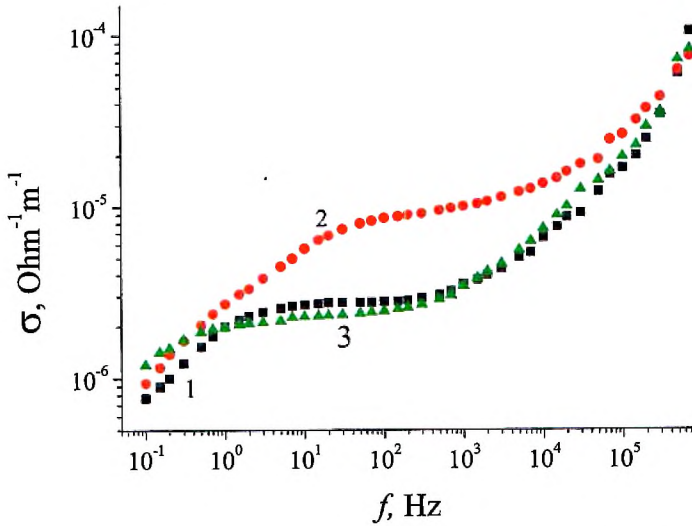


Figure 4: Frequency dependencies of electrical conductivity at 293 K for nano-PDLC with 0.2 wt.% MN (1), nano-PDLC with 0.2 wt.% CNT (2), and nano-PDLC with 0.2 wt.% MN and planarly oriented 0.2 wt.% CNT (3)

5 Synergistic effect of magnetite, carbon nanotubes (separately and in combination) on the conductivity of homogeneous LC, micro- and nano-PDLC

It follows from Fig. 4 that the frequency dependence of conductivity for nano-PDLC+MN+CNT is close to that for the nano-PDLC+MN and considerably differs from that for nano-PDLC+CNT. In order to characterize the difference between the conductivity of samples with two types of nanoparticles and the conductivity of samples with one type of nanoparticles the synergistic coefficient was introduced. To calculate this coefficient, we used the expression:

$$k_s = \frac{\sigma_{12}}{\sigma_1 + \sigma_2}, \quad (3)$$

where σ_{12} is the conductivity value for the nano-PDLC with simultaneously introduced MN and CNT, while σ_1 and σ_2 are the conductivity values when the nanoparticles of each type are introduced separately.

The frequency dependencies of the k_s value for the nano-PDLC at three different nanoparticle concentrations 0.01 wt.% (1) 0.1 wt.% and 0.2 wt.% (3) are shown in Fig. 5.

Analysis of the results illustrated by Fig. 5 shows that for all the nanoparticle concentrations under study, the conductivity of the nano-PDLC with two types of nanoparticles is lower than the summary conductivity of nano-PDLC with nanoparticles of each nanoparticle separately (the k_s value for all the concentrations under study is less than unity). This feature crucially differs the action

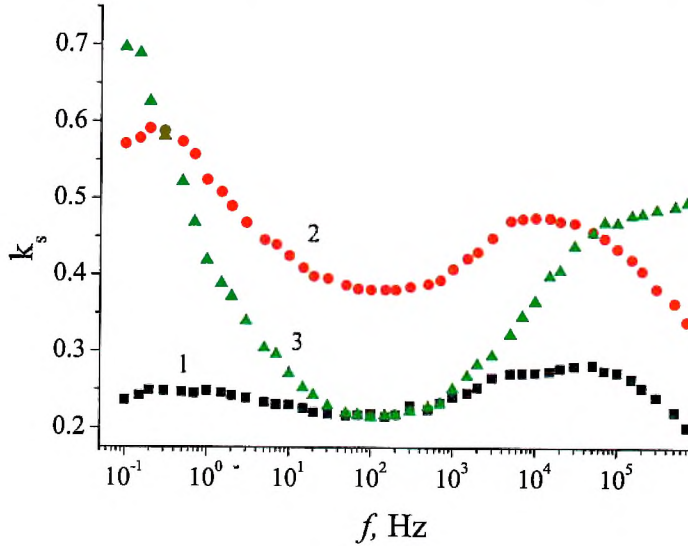


Figure 5: Frequency dependencies of the k_s value at 293 K for nano-PDLC at different concentration of nanoparticles: 0.01 wt.% (1), 0.1 wt.% (2) and 0.2 wt.% (3)

of nanoparticles on the nano-PDLC conductivity from the action of the same type of nanoparticles on the conductivity of homogeneous LC and micro-PDLC. planarly oriented The frequency dependencies of the k_s value relative to effect of MN and CNT separately and combined for the homogeneous planarly oriented LC and micro-PDLC plotted on the basis on the data of our works [9, 10] are shown in Fig. 6.

It follows from the comparison of Figs. 5 and 6 that, contrary to the k_s value for nano-PDLC, the k_s value when MN and CNT are introduced (separately and in combination) into the homogeneous planarly oriented LC and micro-PDLC is greater than unity in the whole spectral range. To explain this effect, we analyze the results shown in Fig. 6. It follows that as a whole (except the lowest frequencies), the k_s value for the homogeneous planarly oriented LC is higher than that for micro-PDLC. Hence, the main reason for increasing the k_s value should be related with the processes in LC. It is seen from Fig. 6 (curve 1), the frequency dependence of the k_s value for LC with introduced MN and CNT (separately and in combination) has at least three maxima. We consider that the main mechanism responsible for the synergistic effect is formation of complexes of nanoparticles, which result in new (with respect to the existing ones) charge carriers (ions). In this case, it is logical to compare the frequencies of the maximum in Fig. 6 (curve 1) with the Maxwell relaxation times arising due to the perturbation of the charge density in LC.

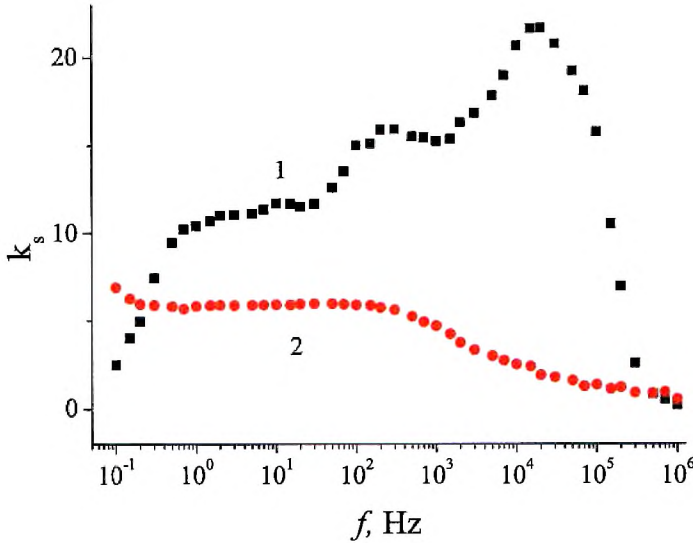


Figure 6: Frequency dependencies of the k_s value at 293 K for the case of MN and CNT being introduced (separately and in combination) into homogeneous planarly oriented LC (1) and micro-PDLC (2)

The Maxwell relaxation time is as follows:

$$\tau_M = \frac{\varepsilon\varepsilon_0}{\sigma}, \quad (4)$$

where ε_0 is the vacuum permittivity. The presence of three relaxation times can be explained by the fact that in the case of introduction of two types of nanoparticles into homogeneous LC, areas with different conductivity values can arise. This can be related to the geometric factor taking into account that the CNT length (1000 nm) essentially exceeds the MN diameter (5 nm) and the conductivity through CNT is much greater than that of LC conductivity.

From the data of our work [9][9] it is known that the conductivity of a homogeneous LC with MN or CNT separately is $1.3 \cdot 10^{-9}$ S/m, while for LC with the combination of MN and CNT it is equal to $2.0 \cdot 10^{-8}$ S/m. The τ_M values calculated according to Eq. (4) are $3.4 \cdot 10^{-2}$ and $2.7 \cdot 10^{-3}$ s, respectively. The frequencies, inverse to these values, will be 30 Hz and 370 Hz, respectively. These values are rather close to the frequencies corresponding to the two first maximum of the k_s value in the curve 1, Fig. 6. The presence of the maximum at the frequency $2 \cdot 10^4$ Hz in this curve can be explained by the relaxation of charge due to CNT by electron exchange between ions and CNT.

In the case of micro-PDLC (Fig. 6, curve 2), for the frequencies $f < 10^3$ Hz the k_s value (except for the lowest frequencies) is more than twice smaller than that for homogeneous LC. This can be explained by the fact that relaxation processes in the close volume of nematic droplets occurs in a different way compared to a homogeneous medium.

An essential difference between curves 1 and 2 in Fig. 6 is sharp decrease of the k_s value for micro-PDLC at the frequencies $f > 10^3$ Hz. The main reason for the high k_s values is relaxation and exchange of charges in the liquid. As noted above, in the micro-PDLC case for the frequencies $f > 10^3$ Hz the charge transfer occurs mostly due to electron transfer through polymer. In this case, the processes caused by the charge exchange between the LC ions and nanoparticles will not play an essential role.

Exactly the decrease of the k_s value for micro-PDLC at the frequencies $f > 10^3$ Hz enables one to explain why for nano-PDLC the k_s value is less than unity. This is caused by the fact that (as noted above), in nano-PDLC, the ionic conductivity in its “pure” form is not revealed. Therefore, there are no corresponding mechanisms which could lead to increasing the k_s value. With electron charge transfer, it will be essential to have the morphology of PDLC films for the presence of deep levels of electron capture. Analysis of the effect of the type and concentration of nanoparticles (within the interval under investigation) has shown that the nano-PDLC morphology does not reveal any essential changes due to the nanoparticles. Therefore, the main mechanism resulting in the low k_s values in the case of nano-PDLC can be the formation of deep levels of capture of charge carriers exactly by the nanoparticles of two types.

Within the proposed mechanism explaining the reason for the low k_s values in the case of nano-PDLC, we find it useful to analyze the frequency dependencies of k_s for nano-PDLC at various nanoparticle concentrations (Fig. 5). It is seen that on the average (within the whole frequency range) the lowest k_s value is observed for the samples with the lowest (within the range under study) nanoparticle concentration (0.01 wt.%). One can suppose that within the framework of the adopted mechanism explaining the reasons the fact $k_s < 1$ in nano-PDLC, exactly at such nanoparticle concentrations the deep electron capture levels due to the complexes of two different-type nanoparticles most efficiently affect the charge-carrier transfer. This effect should be maximal within the time close to the τ_M value what is entirely confirmed by the data shown in Fig. 5. Independent of the nanoparticle concentration, the minimum of the k_s value is observed at the frequencies, the inverse values to those are close to the τ_M value.

When increasing the charge-carrier concentration, besides the electron capture centers, additional channels of their transfer through polymer can arise. This can be the reason for increasing the k_s value with the nanoparticle concentration.

6 Conclusions

It has been shown that in the frequency dependence of k_s synergistic coefficient relative to action of magnetite nanoparticles and nanotubes (separately and in combination), three maxima can be distinguished. The frequencies of these maxima correlate with the inverse Maxwell relaxation times estimated from the conductivities of samples with each nanoparticle type separately and the conductivity in the simultaneous presence of the two nanoparticle type. This is one of the important factors confirming that the main mechanism of the synergistic effect of MN and CNT on the conductivity of LC is the formation of nanoparticle

complexes which result in the formation of additional (with respect to the existing ones) charge carriers.

For the micro-PDLC the synergistic coefficient at the frequencies $f < 10^3$ Hz on the average is shown to be half of the one for the homogeneous LC, while for the frequencies $f > 10^3$ Hz it sharply decreases. The reason for decreasing the synergistic coefficient at the frequencies $f > 10^3$ Hz is the fact that the main mechanism of the charge transfer in this frequency range is electronic conductivity through polymer. This result is another confirmation for the fact that the main mechanism when the synergistic coefficient is greater than unity is the formation of complexes of nanoparticles of different type exactly in the LC.

Acknowledgement

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References

- [1] N. Lebovka, T. Dadakova, L. Lysetskiy, O. Melezhyk, G. Puchkovska, T. Gavrilko, J. Baran, M. Drozd, *J. Mol. Struct.* **877**, 135 (2008).
- [2] S.-Y Lu, L.-C. Chien, *Digest of Technical Papers – SID International Symposium 39*, 1853 (2008).
- [3] W. Lee, Ch.-Yu Wang, Yu-Ch. Shih, *Appl. Phys. Lett.* **85**, 513 (2004).
- [4] A. Koval'chuk, L. Dolgov, O. Yaroshchuk, *Quantum Electronics & Optoelectronics* **11**, 337 (2008).
- [5] C-Y. Huang, C-Y Hu, H-C.Pan, K-Y. Lo, *Jpn. J. Appl. Phys.* **44**, 8077 (2005).
- [6] A.I. Goncharuk, N.I. Lebovka, L.N. Lisetski, S.S.Minenko, *J. Phys. D: Appl. Phys.* **42**, 165411 (2009).
- [7] P. Kopčanský, N. Tomašovičová, M. Koneracká, V. Závišová, M. Timko, A. Džarová, A. Šprincová, N. Éber, K. Fodor-Csorba, T. Tóth-Katona, A. Vajda, J. Jadzyn, *Phys. Rev. E* **78**, 011702 (2008).
- [8] N. Tomašovičová, P. Kopčanský, M. Koneracká, L. Tomčo, V. Závišová, M. Timko, N. Éber, K. Fodor-Csorba, T. Tóth-Katona, A. Vajda, J. Jadzyn, *J. Phys.-Condens. Mat.* **20**, 204123 (2008).
- [9] P. Kopčanský, O.V. Kovalchuk, N. Tomašovičová et al., The 13th Small Triangle Meeting on Theoretical Physics. Institute of Experimental Physics, Kosice, Slovakia, 72–79 (2012).
- [10] P. Kopčanský, M. Timko, Z. Mitrova, V. Zavisova, M. Koneracka, N. Tomašovičova, L. Tomčo, O.V. Kovalchuk, V.M. Bykov, T.M. Kovalchuk, *Semiconductor Physics, Quantum Electronics and Optoelectronics* **16** (4), 374–378 (2013).

- [11] I.P. Studenyak, P. Kopčanský, M. Timko, Z. Mitroova and O.V. Kovalchuk, *Liquid Crystals* **44**, 11, planarly oriented 1709–1716 (2017).
- [12] H. Haken, *Synergetics. An introduction*, Springer-Verlag, 385 pp.
- [13] J.A. King, R.A. Hauser, A.N. Tomson, I.M. Wescoat, J.M. Keith, *Journal of Composite Materials* **42**, 1, 91–107 (2008).
- [14] N. Dair, S. Javadian, *J. Appl. Phys.* **123**, 115103 (2018).
- [15] A. Honglawan, D.S. Kim, D.A. Beller, D.K. Yoon, M.A. Gharbi, K.J. Stebe, R.D. Kamienc, Sh. Yang *Soft Matter* **11**, 7367–7375 (2015).
- [16] L.-P. Zhang, Sh.-H. Tang, Ch.-E Mo, Ch. Wang, Y.-P. Huang, Z.-Sh. Liu *European Polymer Journal* **98**, 226–236 (2018).
- [17] P. Kopcansky, M. Timko, Z. Mitrova, V. Zavisova, M. Koneracka, N. Tomasovicova, L. Tomco, O.V. Kovalchuk, V.M. Bykov, T.M. Kovalchuk, A.I. Lad, *Semiconductor Physics, Quantum Electronics and Optoelectronics* **16**, 253–258 (2013).
- [18] H. Stark, *Physics Reports* **351**, 387–474. (2001).
- [19] A.V. Koval'chuk, *J. Phys.: Condensed Matter* **13**, 10333 (2001).