Nanocomposites and nanomaterials

Impact of diamond nanoparticles on electrical conductivity of nematic liquid crystals: ion capturing and ion releasing effects

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The last few decades have been marked by intensive study of colloidal systems based on thermotropic liquid crystals (LCs) and nanoparticles (NPs). The great interest to such systems is mainly due to the possibility of radical changes of physicochemical properties of LC layers, being a core component of modern liquid crystal devices. Various sorts of nanoobjects such as magnetic, ferroelectric, dielectric, semiconducting and metal NPs of various size, shape and surface modification have been considered as fillers for LCs. One of the most interesting classes of the fillers is formed by carbonaceous materials including such unique objects as carbon nanotubes (CNTs), graphite plates and diamond NPs. Previously we studied comprehensively the suspensions of CNTs in nematic LCs. With increasing concentration of CNTs in these composites we observed several stages of structural evolution accompanied by conductivity growing and two stages of electrical percolation [1].

In the present work, we pay attention to different filler, nanoparticles of diamond (DNPs), which is different allotrope of carbon. While multiwalled CNTs based on sp^2 hybridized carbon have a quasi-metallic conductivity, DNPs consisting of sp^3 hybridized carbon are non-conductive. The purpose of this research was to clarify impact of these particles on dielectric properties of LC host and compare it with the effect of CNTs. We used spherical DNPs from Aldrich with a diameter ≤ 10 nm. Along with DNPs we involved in this research other fillers such as hydrophilic, A300, and hydrophobic, R812, aerosil from Degussa, which is a pyrogenic silica dioxide with an averaged particle size of 10 nm, and a powder of carbon nitride (C_3N_4) with the particle size of the order of 1000 nm. These NPs were dispersed in nematic LCs with relatively high (10^{-7} S/m) and relatively low (10^{-9}-10^{-8} S/m) electrical conductivity, 5CB (from Chemical Reagents Plant, Kharkiv, Ukraine) and ZLI4792 and E7 (from Merck), respectively. The NP concentration was varied from 0 to 5 wt. %. The suspension was placed in sandwich type LC cells with a thickness of 20 μm. The dielectric measurements were performed by oscilloscopic method. The sample conductivity

σ was determined from the dielectric spectrum $\varepsilon''(f)$, using the formula $\sigma = 2\pi f \varepsilon_0 \varepsilon''$. This estimation was made at frequency f=1 kHz, which corresponded to linear part of double logarithmic plot of $\varepsilon''(f)$ curves.

Fig. 1a shows electrical conductivity σ versus DNP concentration curves for the composites based on different nematic LCs. It can be seen that adding of NPs to LCs with low conductivity (ZLI4792 and E7) results in increasing of conductivity followed by saturation of this process. Notably, no percolation behavior for the $\sigma(c)$ curves was observed. In strong contrast to this, adding of DNP to LC 5CB with deliberately high conductivity results in drastic reduction of conductivity, which reaches two orders of magnitude at $C>1.5$ wt. %. Fig. 1b additionally shows that such ionic purification effect is not observed for any other particles involved in our research.
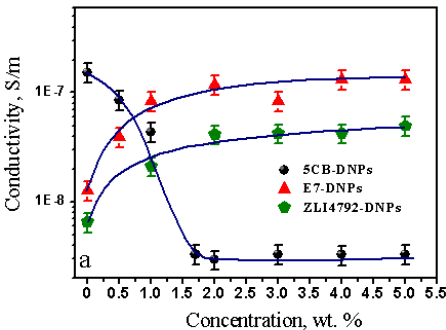

Fig.1. Plots of electrical conductivity σ for series 5CB-DNPs, E7-DNPs, ZLI4792-DNPs composites (a) as a function of DNPs loading and 5CB-NPs (b) versus different of NPs loading: DNPs, modified NPs of SiO_2 (R812), non-modified NPs of SiO_2 (A300) and micro-particles of C_3N_4.

We believe that the effect of NPs on the conductivity of LC depends on the ratio of adsorption and desorption processes of ions on/from the NPs. If LC is depleted in ions, the process of the releasing ions from the particles considerably prevails that leads to increasing of conductivity. However, as the concentration of particles increases, the LC is substantially enriched in ions and the processes of capture and release of ions by the particles are counterbalanced. This is manifested in the saturation of the $\sigma(c)$ curve. On the contrary, if LC is enriched in ions, the ion capturing process significantly prevails that explains the ion purification effect. High capturing ability of ions by DNPs we explain by clusters of water formed on the surface of these particles which cause strong surface polarization.
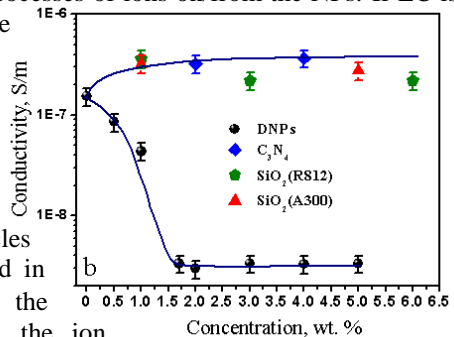
1. *Tomylko S., Yaroshchuk O., Lebovka N.* Two-step electrical percolation in nematic liquid crystals filled with multiwalled carbon nanotubes // Phys. Rev. E–2015.-92, N 1.-P. 012502: 1-8.