Nanocomposites and nanomaterials

Two-stage percolation of carbon nanotubes in nematic liquid crystal

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Doping liquid crystals (LCs) by nanoparticles (NPs) has been intensively studied in recent times as a method of improving their electro-optical, dielectric, magnetic, and mechanical properties. Among a huge variety of nano-objects, carbon nanotubes (CNT) differ by a large anisotropy of shape and effective interaction with LC molecules. In view of this, special attention is paid to these NPs as a filler for LCs.

In a vast majority of works devoted to these composites LC is doped by a trace amount (about 10^{-3} wt.%) of CNTs to avoid their essential aggregation. At the same time, increasing of CNTs concentration leads to a number of exciting features such as percolation phenomena and accompanying memory effect [1]. The percolation features are caused by aggregation of CNTs and association of such aggregates in a continuous three-dimensional network. Formation of this network at some critical concentration $c=c_c$ sharply changes mechanical, dielectric and electro-optical properties of the composites. In typical LC cells with a thickness of 5-50 µm, critical concentration of conductivity percolation is very low, $c_c < 10^{-2}$ wt. %. This is because the aggregates of even several nanotubes with a typical length of 5-20 µm are able to short-circuit the cell that leads to percolation behavior of conductivity.

In the present work we demonstrate that additional percolation process takes place at significantly higher concentration of CNTs. We have succeeded to find such a process by changing filling method of LC-CNT composite in the cells. When usually the suspension is filled by capillary method, we applied another approach connected with compression and crushing of the droplet of the composite between two substrates.

Concentration dependencies of conductivity for these two filling methods are shown in Fig. 1. It can be seen that concentration curve for the capillary filling series (curve 1) sharply increases and saturates at about c=0.1 wt.%. According to inset of this Figure, this curve obeys a percolation power law $\sigma=(c-c_c)^p$ with $c_c \rightarrow 0$.



Figure 1. Conductivity versus CNT concentration curves for the layers of 5CB-CNT suspensions with a thickness of 250 μ m. Curves 1 and 2 correspond to capillary filling and pressing suspension between two substrates, respectively. The curves are measured at room temperature. The insets present the same curves in double logarithmic scale.

The curve measured for the drop crushing series (curve 2 in Fig. 1) is more complex. Initial part of this curve is quite similar to the curve 1. However, after the first increase started at $c_{c1}\approx 0$ this curve shows second increase beginning at $c_{c2}\approx 0.8$ wt. %. These results allow us to draw the following two conclusions. (1)The capillary filling method does not work well at c>0.5 wt. %. This is evidently caused by the fact that bulky aggregates of CNTs are partially filtered out at the entrance to a cell. This does not allow to observe second percolation process. (2) In turn, in case of drop crush filling, all CNTs remain in a cell independently of concentration. This allowed us to reach higher concentrations of CNTs and thus observe second percolation process. We believe that the second percolation is caused by steric hindrance in growing of aggregates. This leads to denser packing of CNTs in aggregates and denser CNT network.

[1] L. Dolgov, S. Tomylko, O. Koval'chuk, N. Lebovka and O. Yaroshchuk, Liquid crystal dispersions of carbon nanotubes: dielectric, electro-optical and structural peculiarities. In book "Carbon nanotubes", Jose Mauricio Marulanda (Ed.), INTECH (2010).