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Liquid Crystal Dispersions of Carbon Nanotubes Assisted by Organically Modified Laponite Platelets

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Outline

1. Introduction: liquid crystal-carbon nanotubes (LC-CNT) composites.
2. The problem of dispersion of CNT in LC and the methods of its solution.
3. Materials and methods.
4. Liquid crystal-carbon nanotubes dispersions assisted by clay particles.
5. Results and discussion:

   - Microstructure of LC-CNT and LC-CNT-LapO composites, comparison.
   - Dielectric studies.
   - Electro-optical studies.
6. Conclusions

Liquid crystal-carbon nanotubes (LC-CNT) composites

High aspect ratio and strong interaction with LC molecules ($E_{LC\text{-}CNT}$ ~2 eV)

→

CNTs are ideal fillers for LCs

→

LC is ideal host for CNTs allowing ones to obtain orientationally ordered ensembles of CNTs with readily controllable ordering axis

↔

→

The doping of LC by NTs allows reducing of the response time and driving voltage, suppressing of the parasitic back flow and image sticking typical for LC cells

Problem

But

Giant aspect ratio and high flexibility, integral interaction energy of CNTs
is high due to a great length (~1-10 mkm) of CNTs

→

CNTs bundle and cluster together in disordered agglomerates, so that their anisotropic properties are weakened

Methods of improvement of dispergation of CNT in LC

Physical

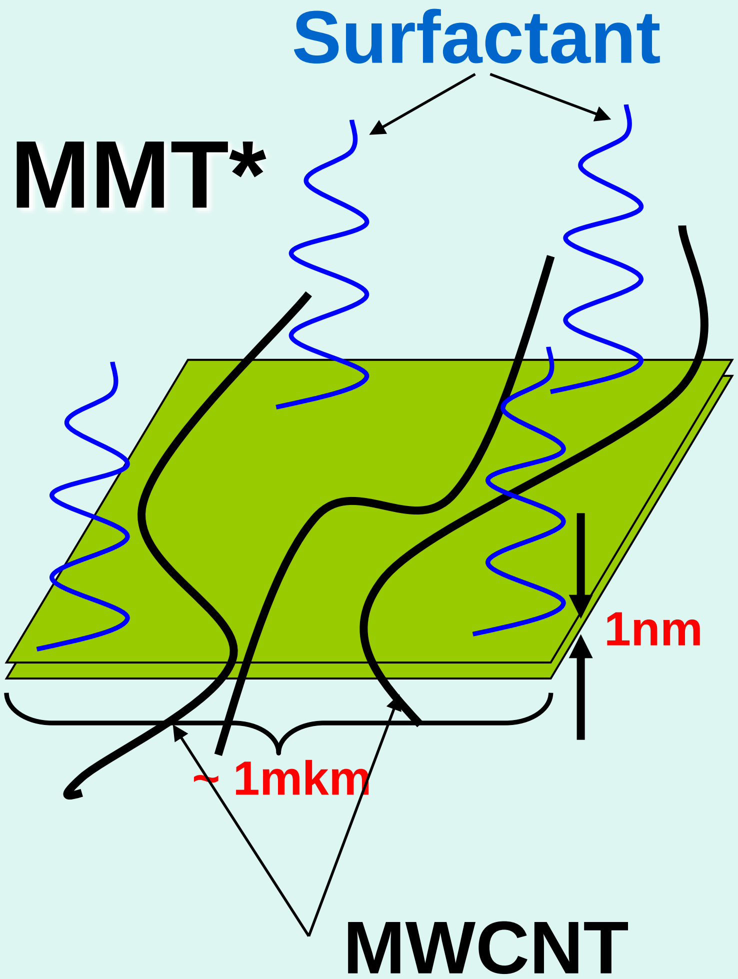
Electro-hydrodynamic dispergation of CNT and their debundling in high electric field[1]

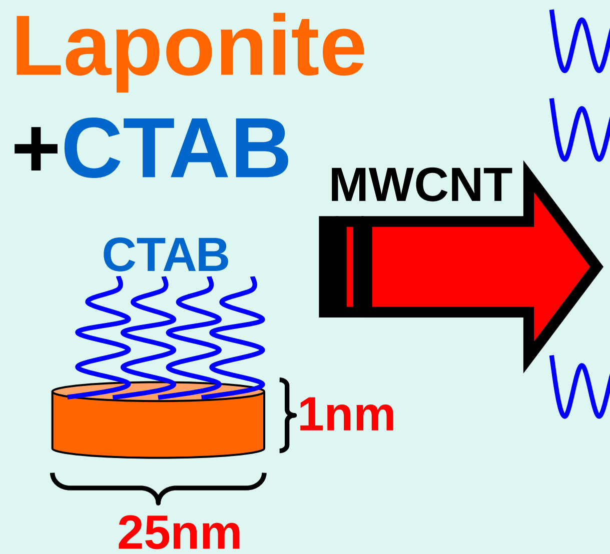
Chemical

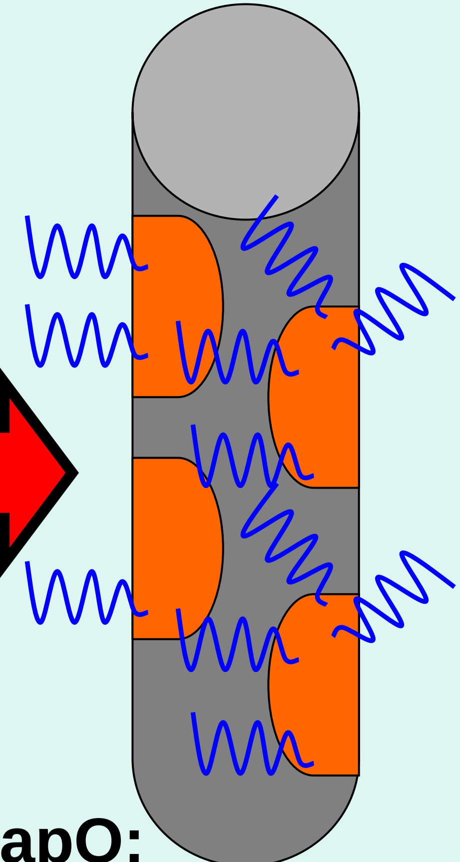
Attaching of various fragments to CNTs via covalent bonding, π-π interaction, *etc.*[2]

1. Tie W., Yang G.H., Bhattacharyya S.S., Lee Y.H. & Lee, S.H. Electric-field-induced dispersion of multiwalled carbon nanotubes in nematic liquid crystal. *Journal of Physical Chemistry C* **115**, 21652-21658 (2011).
2. M. Kuhnast, C. Tschierske and J. Lagerwall, Tailor-designed polyphilic promotors for stabilizing dispersions of carbon nanotubes in liquid crystals. *Chem. Commun.*, **46**, 6989–6991 (2010).

Montmorillonite (MMT) and LapO







<u>Advantages of LapO:</u>

-reproducibility of synthesis

-smaller size

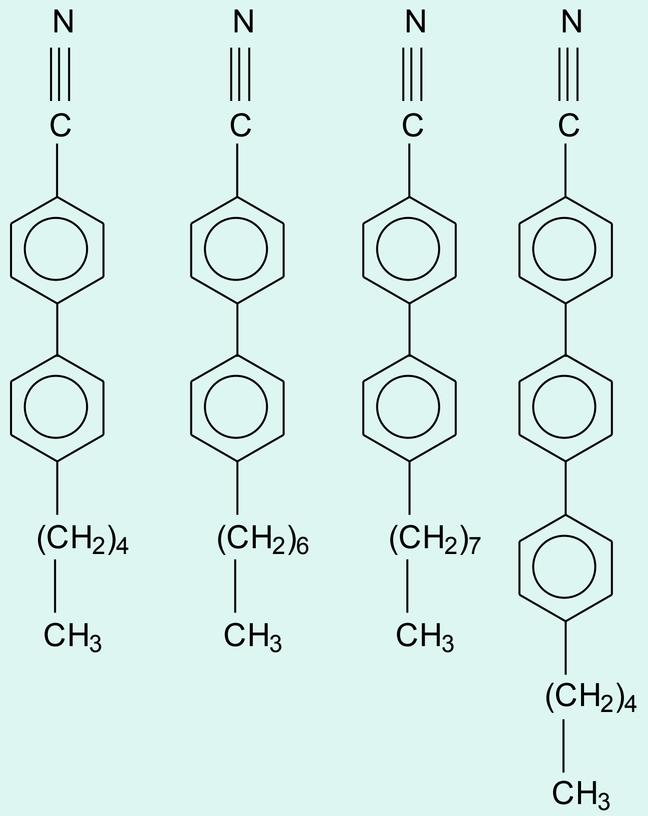
* Lebovka N.I., Lysenkov E.A., Goncharuk A.I., Gomza Yu.P., Klepko V.V., Boiko Yu.P., “Phase behaviour, microstructure, and percolation of poly(ethylene glycol) filled by multiwalled carbon nanotubes and organophilic montmorillonite”, *Journal of Composite Materials*, **45**, 2555–2566 (2011)

Materials and methods

Materials

Nematic liquid crystal mixture E7 (Merck, Germany)

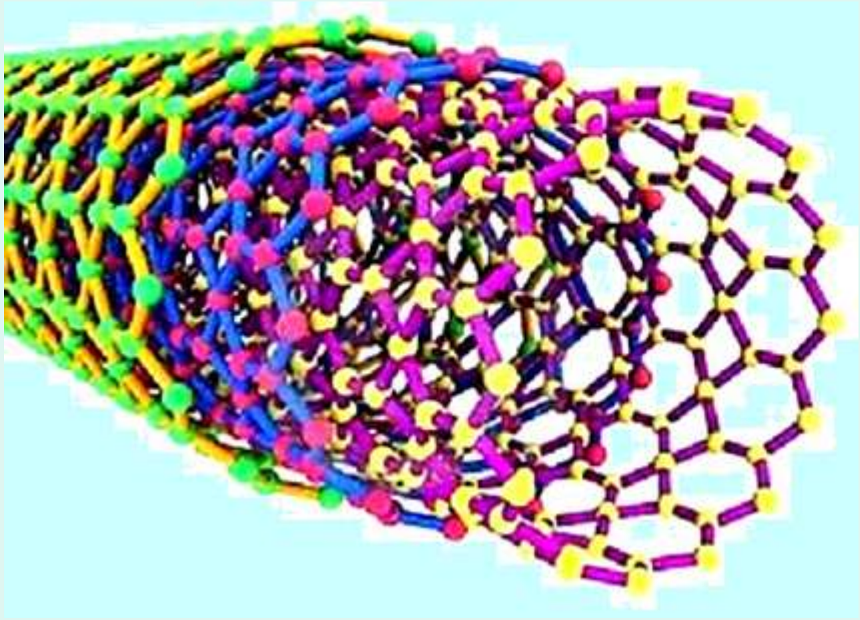
5 CB	7 CB	80 CB	5 CT
51%	25%	16%	8%



Characteristic	Value
T_{C-N}, C	-40
T_{N-I}, C	58
ρ, g/cm^3	1
$\varepsilon_\perp$	5,2
ε_{II}	19
Δε	13,8
n^o	1,522
n^e	1,746
Δn	0,224
U_{th}	1,41

Materials

Multiwalled carbon nanotubes (MWCNTs)
TM Spetsmash Ltd., Kyiv, Ukraine



Parameters of MWCNT*

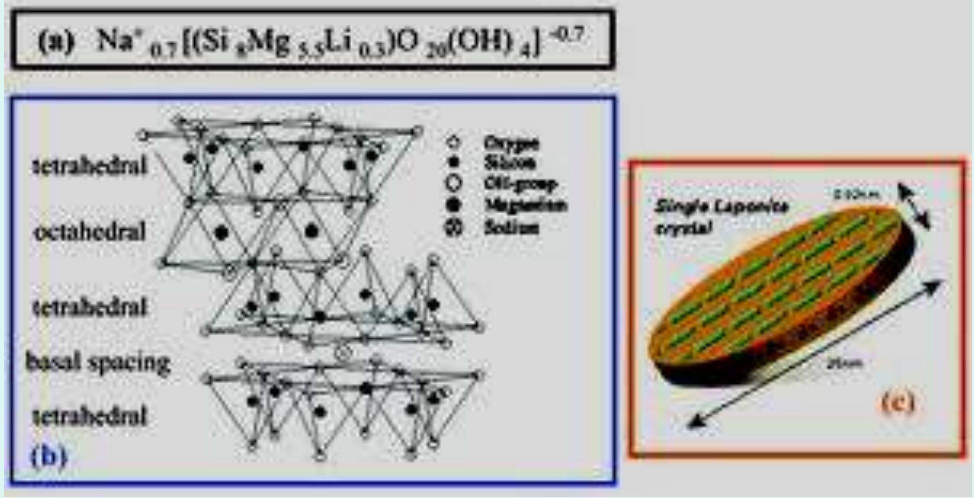
Characteristic	Value
S_n	130 ± 5 m^2/g
σ_p	10 $S{\cdot}cm^{-1}$
d_n	20 – 40 nm
L_n	5 -10 μm

*Lisetski, L.N. *et al.* Microstructure and incubation processes in composite liquid crystalline material (5CB) filled with multi walled carbon nanotubes. *Materialwissenschaft und Werkstofftechnik* **42**, 5-14 (2011).

Materials

Organo-modified Laponite sample (LapO)

Rockwood Additives Ltd., UK



(a) chemical formula; (b) structure, symmetry; (c) single Laponite crystal

\+ CTAB[$C_{16}H_{33}$-$N(CH_3)_3Br$](1 wt. %) Fluka, Germany

Parameters of LapO*

Characteristic	Value
S_L	**370 m²/g**
ρ_L	**2530 kg/m³**
h_L	**1 nm**
d_L	**25 – 30 nm**

*Zebrowski, J., Prasad, V., Zhang, W., Walker, L.M. & Weitz, D.A. Shake-gels: shear-induced gelation of laponite ???PEO mixtures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **213**, 189-197 (2003)

Preparation of suspensions

1. Sonication of the mixture :

Series
E7-CNT (0.025-0.5 wt. %)

+ LapO (0.1 wt. %)

10 min. UZDN-2T ultrasonic disperser

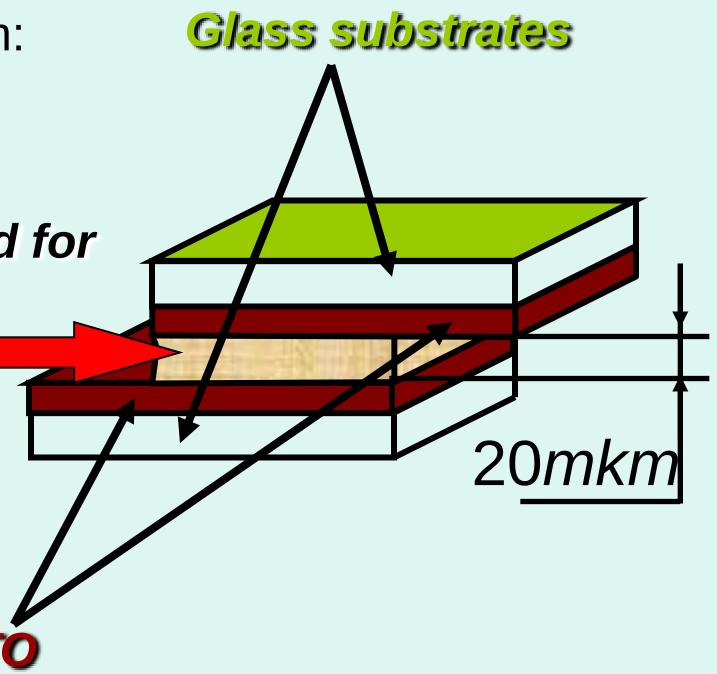
Series E7-CNT (0.025-0.5 wt. %)-LapO (0.1 wt.%)

2. Loading into the measurement cells 20mkm:

Mixture: E7-CNT (0.025-0.5 wt.%)-LapO(0.1 wt.%)

Incubated for 24 hours

2 min. UZDN-2T



Methods. Microstructure of cells

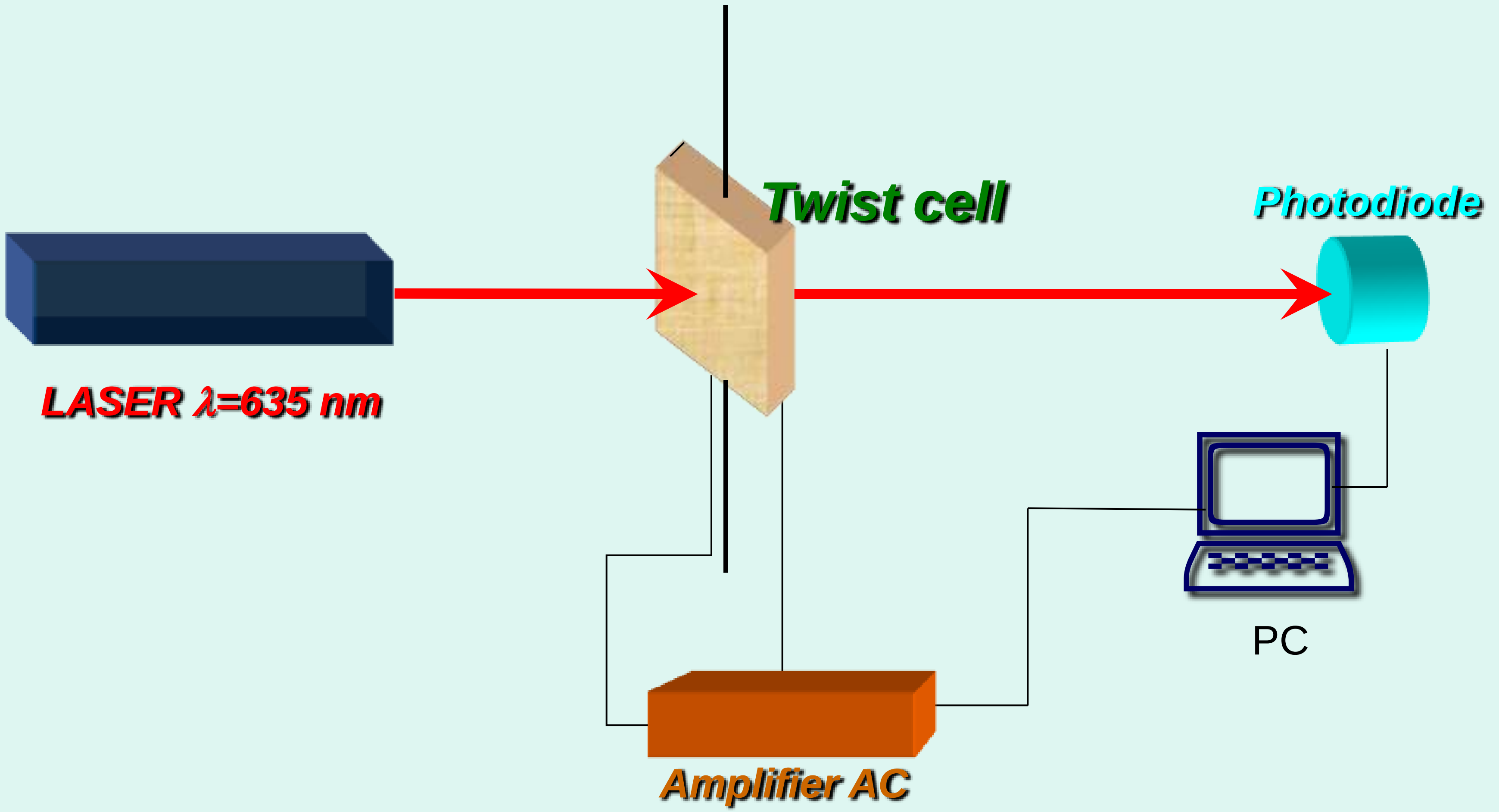
Optical polarization microscope
“Polam L-213M”

X100

Crossed polarizer and analyzer

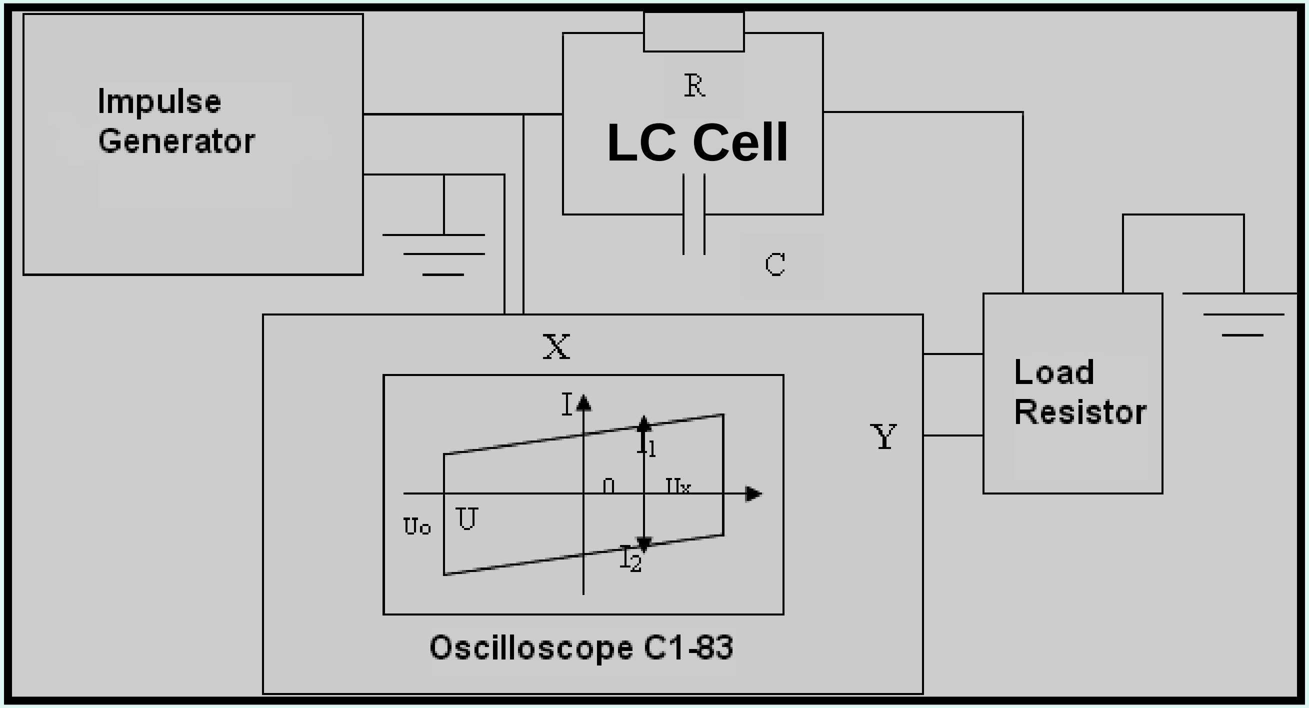
Deduced analyzer

Electro-optical measurements



Scheme of electro-optical measurements

Dielectric measurements



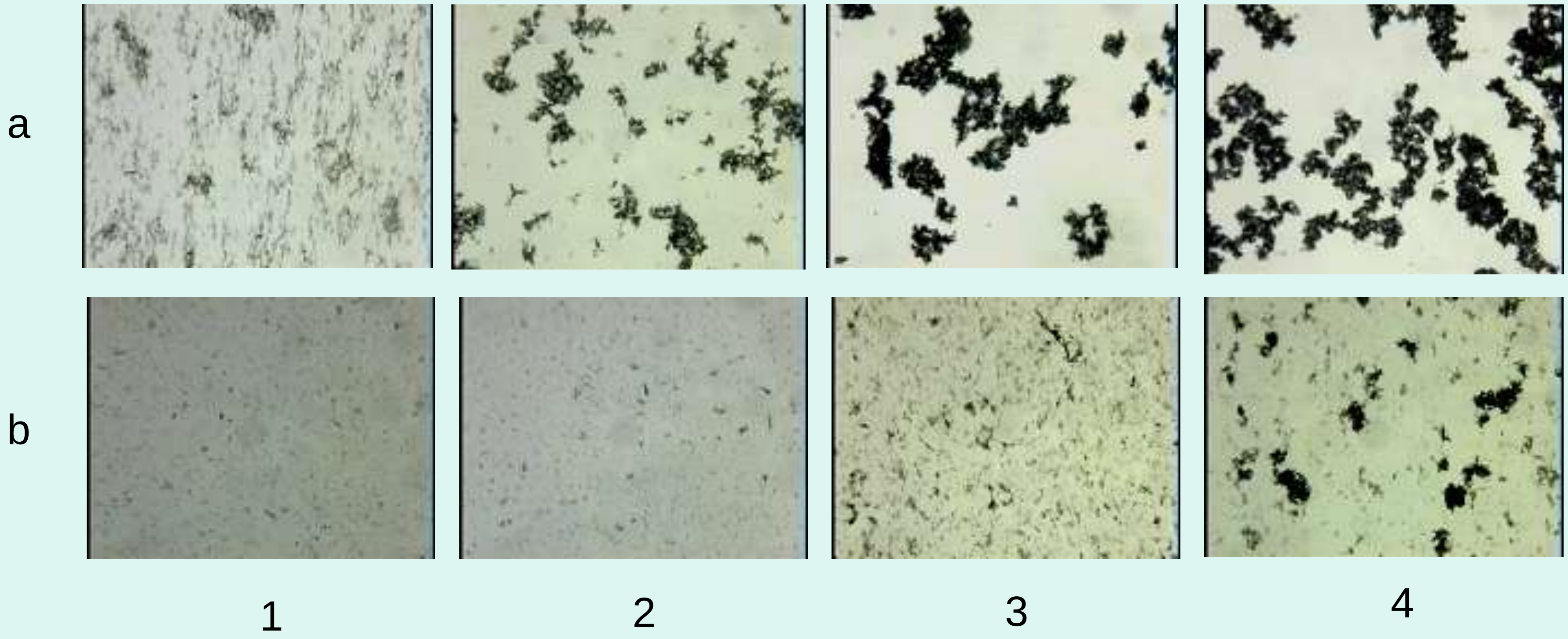
Scheme of dielectric measurements*

Dielectric constants ε' and ε'' were determined in a wide frequency range 10^{-1}-10^{6} Hz by measuring the resistance and capacitance of the composite layer using the osciloscopic method. The value of ε'' was used to calculate the conductivity.

*A.V. Koval'chuk, Low-frequency dielectric relaxation at the tunnel charge transfer across the liquid/electrode interface // *Functional Materials* 8(4), p. 690-693 (2001).

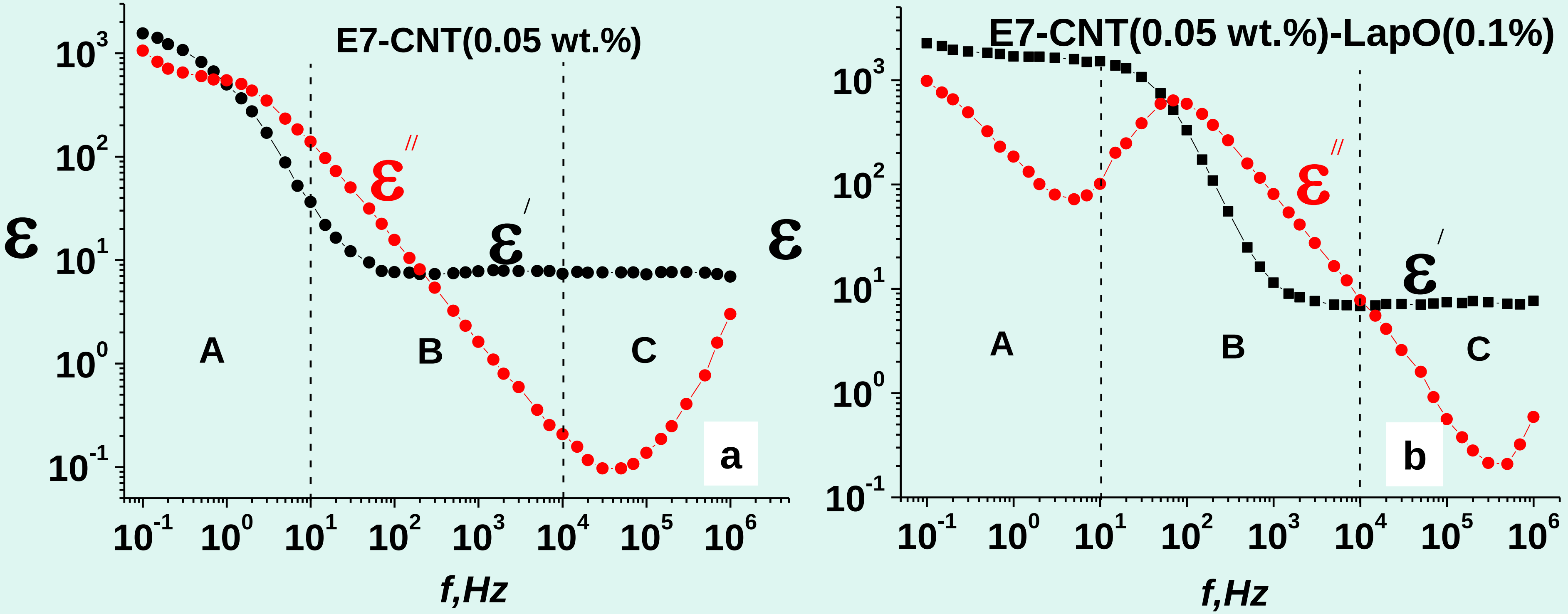
Results

Microstructure of composites



Microsopic pictures of (a) E7-CNT and (b) E7-CNT-LapO (0.1 wt.%) suspensions. Concentration of CNTs is 0.025, 0.05, 0.1, and 0.3 wt.% in case 1, 2, 3 and 4, respectively.

Dielectric spectra

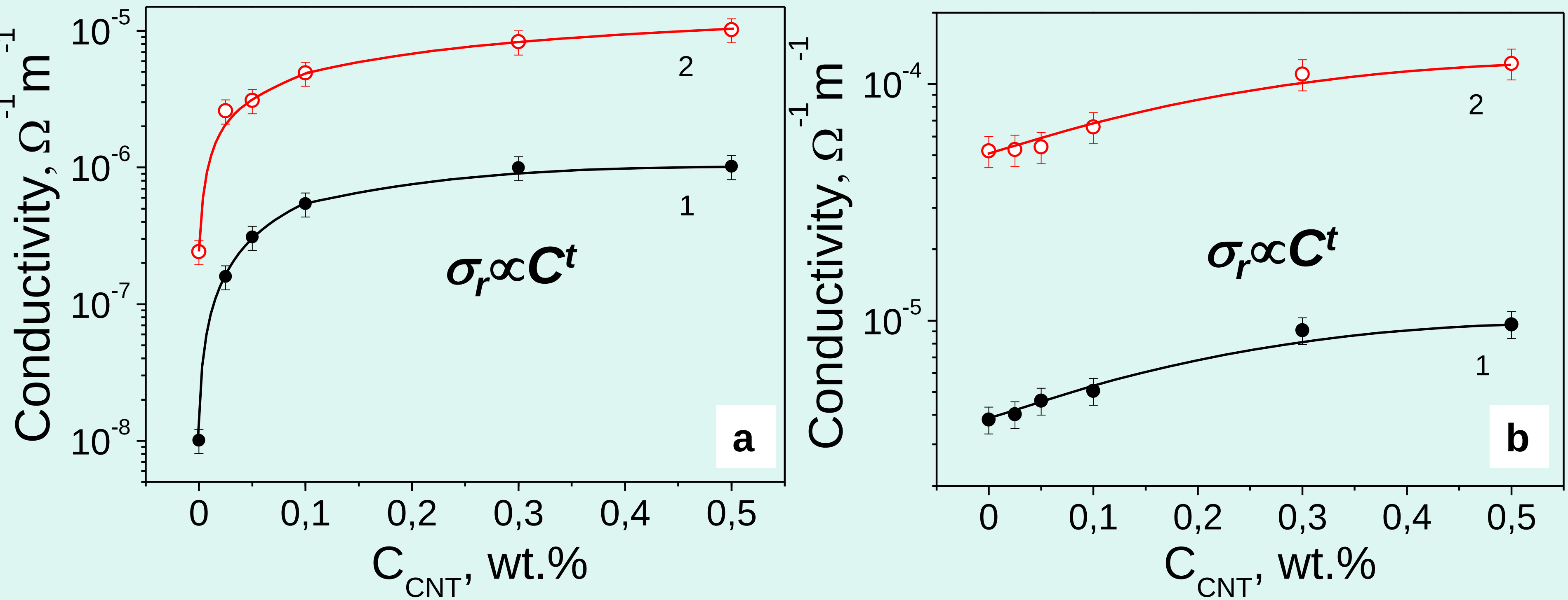


Permittivity components ε′ and ε″ as functions of the frequency of testing electric field *f* for E7-CNT(0.05 wt.%) (a) and E7-CNT(0.05 wt.%) -LapO(0.1 wt.%) (b) at 20C (nematic phase).

A: The low-frequency range: ($10^{-1} < f < 10$ Hz)
B: The moderate frequency range: ($10 < f < 10^4$ Hz)
C: The high-frequency range: ($10^4 < f < 10^6$ Hz)

f=10-10[4] Hz

Electrical conductivity

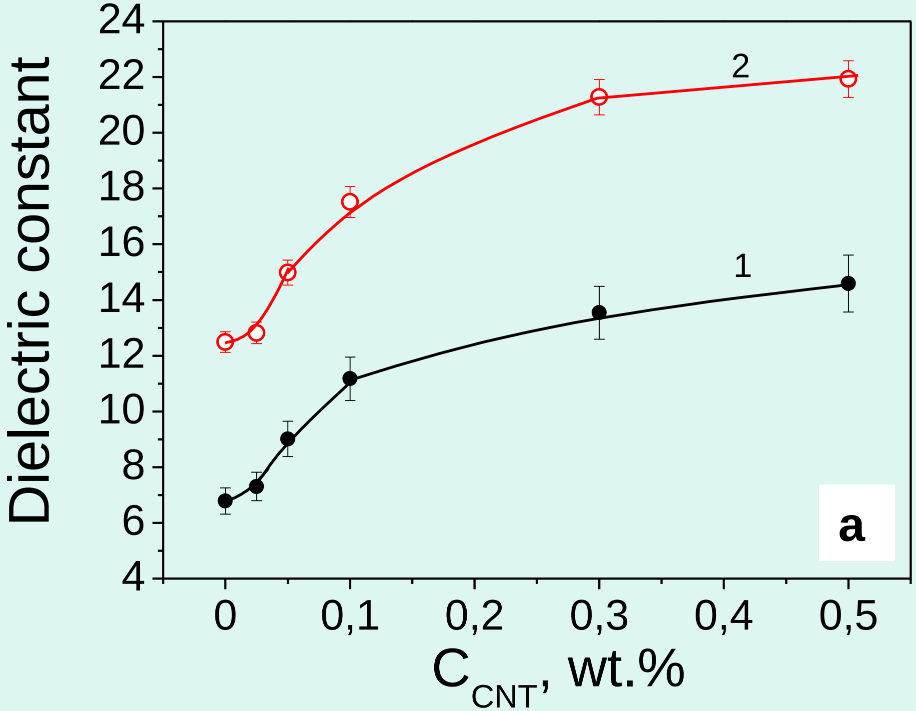


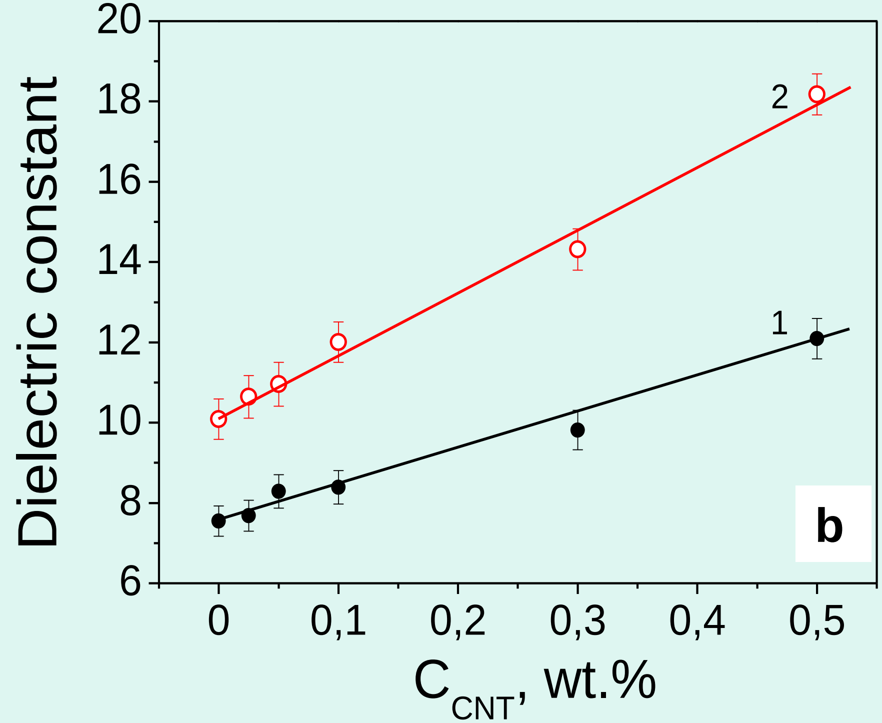
E7-CNT: t = 0.63 ± 0.08 (T = 20C) and 0.48 ± 0.03 (T = 80C)
E7-CNT-LapO: t = 0.32 ± 0.04, T = 20C and at 80C.

Electrical conductivity **σ** versus concentration of CNTs, *C*, in the samples (a) E7-CNT and (b) E7-CNT-Lap0 (0.1%) at two different temperatures: *T*=20 C (nematic phase) curve 1 and *T*=80C (isotropic phase) curve 2.

f=10-10[4] *Hz*

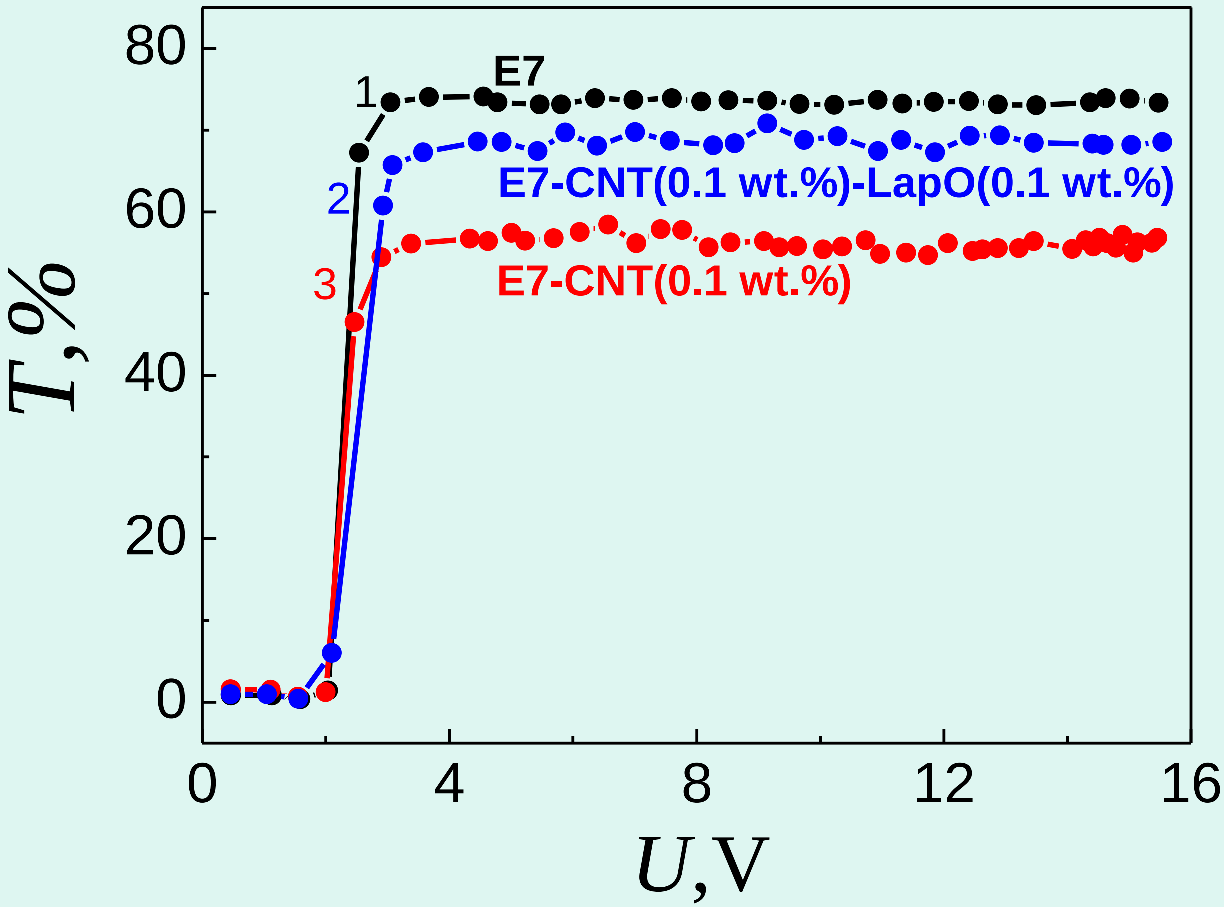
Dielectric permittivity





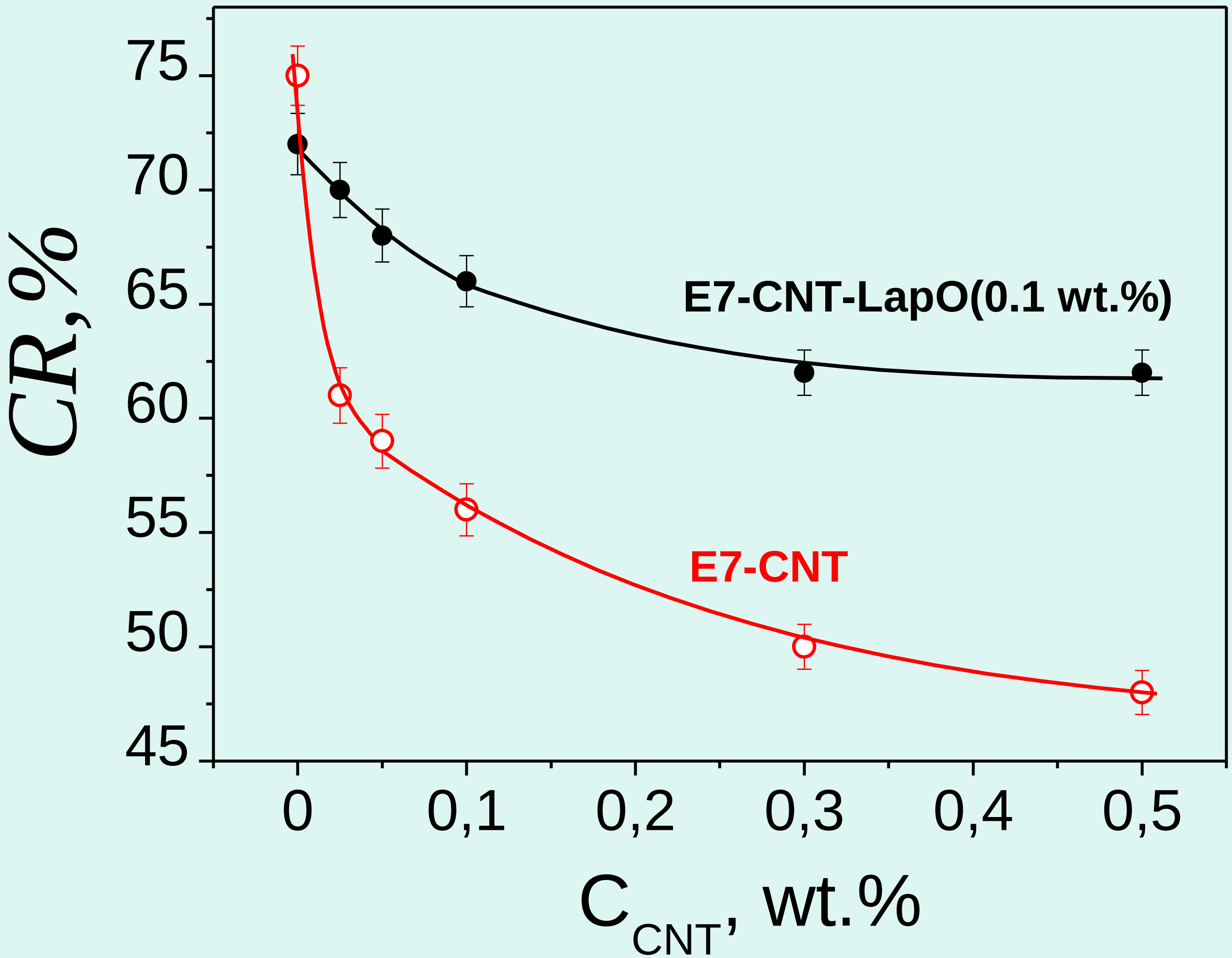
Dielectric permittivity ***ε*** versus concentration of CNTs, *C*, in the samples (a) E7-CNT and (b) E7-CNT-Lap0 (0.1%) at two different temperatures: *T*=20 C (nematic phase) curve 1 and *T*=80C (isotropic phase) curve 2.

Results of electro-optical measurements



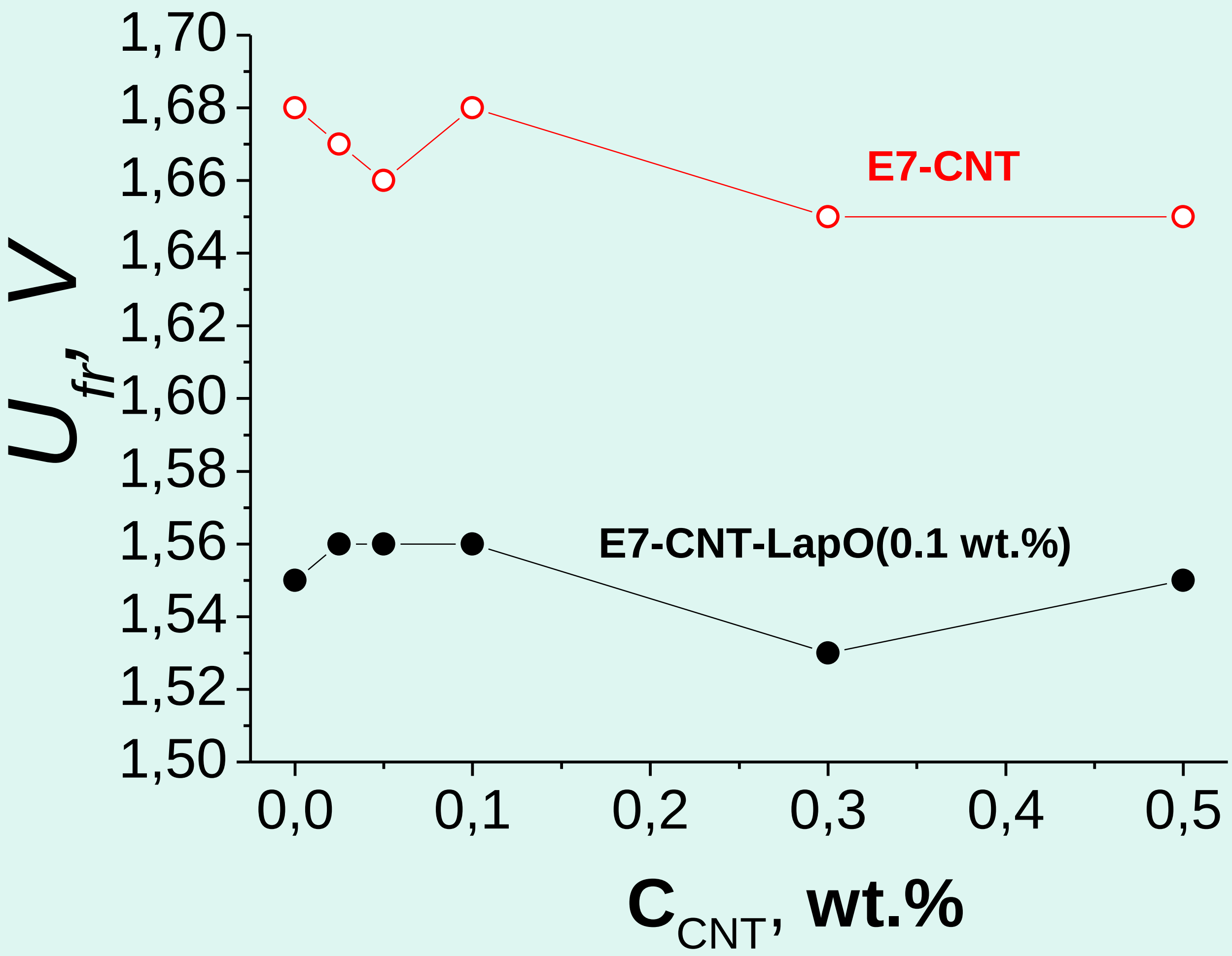
Transmittance T_r versus applied voltage U for E7, E7-CNTs (0.1 %) and E7-CNTs (0.1 %)-LapO (0.1%). The temperature was 20C (nematic phase).

Results of electro-optical measurements



Contrast ratio *CR* (%) versus concentration of CNTs C_{CNT} in the absence and in the presence of LapO (0.1 wt. %) at 20C (nematic phase). The contrast ratio *CR* (%) was calculated as a ratio of the brightest and darkest parts of the image.

Results of electro-optical measurements



Freedericks threshold voltage (U_{th}) versus concentration of CNTs C_{CNT} in the absence and in the presence of LapO (0.1 wt. %) at 20C (nematic phase).

Conclusions

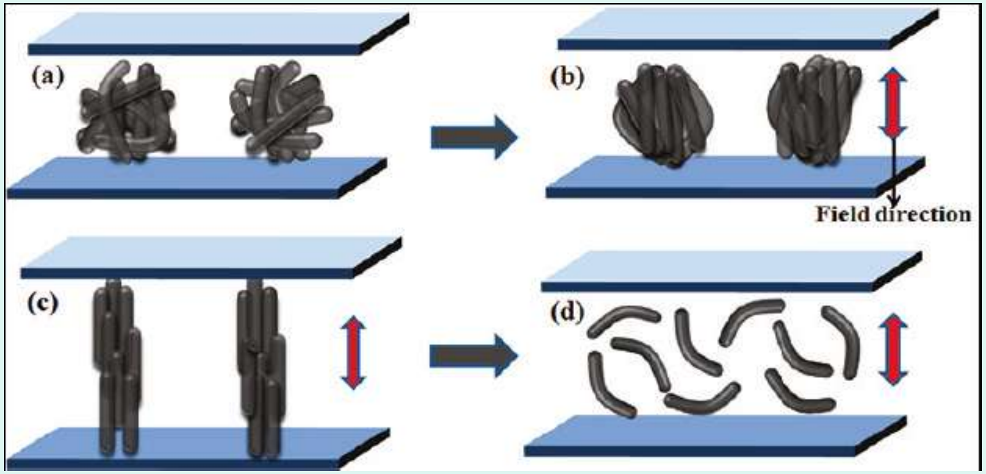
Thus, the obtained results allow us to draw the following conclusions:

Adding a small amount of nanoplatelets LapO radically improves dispersion CNT in the liquid crystal;

Weak aggregation of NT and insulating effect of plates on CNT, in turn, leads to the absence of classical percolation of conductivity, as well as to improvement of electro-optical characteristics of the samples, namely, reduction of Fredericks threshold and significant growth of contrast ratio.

The model is suggested, which assumes that nanoplatelets of LapO wrap up nanotubes preventing them to effectively aggregate. In addition, this weakens charge transfer from one nanotube to another.

Electro-hydrodynamic dispergation of CNT



Schematic diagram showing dispersing behavior of CNT cluster in the cell in the presence of applied AC field. (a) Field off state, (b) CNT was reoriented with field direction, (c) individual CNTs could be extracted out from bundle or CNT cluster, and (d) dispersion of the CNT cluster.