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Dielectric anisotropy of nematic liquid crystals loaded with carbon nanotubes in a microwave range

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Abstract: Liquid crystals are attractive materials for microwave applications as tunable dielectrics due to low losses and high anisotropy of dielectric properties. In this paper we study the possibility of further enhancing their dielectric anisotropy by loading with highly polarizable and anisotropic rods - carbon nanotubes at various concentrations. The studies are performed using two different methods, one in the range 1-4 GHz and the other at 30 GHz. We report more than two times increase of microwave dielectric anisotropy in liquid crystals when loaded with 0.01%wt of carbon nanotubes which is a metastable suspension and 28% increase in an equilibrated suspension. The stability of the LC-CNT composites is discussed.

Introduction: Materials with large tunability of dielectric properties and low loss in the microwave region are required for the microwave engineering industry. Potential application areas are in telecommunications, remote sensing and global navigation systems. In comparison with the existing candidate materials such as ferroelectric ceramics, liquid crystals (LC) have drawn attention in recent years because of lower losses at microwave frequencies and comparatively high anisotropy.[1-3] LCs can be loaded with various types of nanoparticles for enhanced performance. Anisotropic particles make particularly interesting additives because they may align with the anisotropic host and further enhance its anisotropy. For example, the addition of 0.2% wt metallic micro tubules (0.5µm in diameter and 10 – 30µm length) to a liquid crystalline host increases the birefringence at 30GHz by 54%.[4]

Carbon nanotubes (CNT) are nanoparticles with perhaps the highest known shape anisotropy, with diameter of ~1nm and length ~1µm or more. They possess extremely high anisotropy of the physical parameters.[5] When dispersed in liquid crystal, CNTs can be ordered with a high order parameter, up to 0.9.[6] This ordering can be dynamically reconfigured with electric[6] or magnetic [7] fields. Loading with CNTs changes the low frequency electrical and dielectric properties of LCs.[8, 9] In the present work we employ carbon nanotubes (CNT) as an additive to LC in an attempt to increase the anisotropy at microwave frequencies.

Materials: Liquid crystal E7 (Merck) was loaded with single wall CNTs with an average diameter of 1nm and lengths of 1-1.2 µm (produced by HiPCo process, purified, by CNI). 0.01%wt CNTs were dispersed in the LC host in the nematic phase using ultrasonication at 20 kHz, 300W power delivered to the bath, for 5 h at 10–12^{o}C in an ultrasonicator from Diagenode (Bio-Ruptor). The 0.005%wt CNT suspension was prepared by dilution with pure E7 and further ultrasonication. Stable suspensions of CNT in LCs have a concentration of CNT of the order of 10^{-10} by weight.[10] However, we have obtained suspensions with higher loading that remained unchanged for at least 2 months. Such equilibrated suspensions were prepared by repeated ultrasonication of 0.01%wt suspension and centrifugation to remove the insoluble fraction.

The polarisation microscopy and nano particle tracking analysis (NTA)[10] of the CNT-loaded materials revealed that over 90%wt of the CNT were in large bundles (>1µm diameter), which have good alignment in the LC host. The suspensions were stable for the duration of a measurement. Thereafter, the non-equilibrated suspensions deteriorated slowly from day to day, and more rapidly when an electric field above 1V/µm was applied or the temperature was raised close to the transition into the isotropic phase.

The degradation was manifested by a dramatic increase in the loss and a decrease in the measured values of the dielectric anisotropy. A 0.01% CNT loaded LC cell short-circuited when fields above 1V/µm were applied, while 0.005% and equilibrated mixtures could withstand fields up to 2V/µm. The deterioration process due to voltage application was studied by microscopy in glass cells with transparent electrodes (Fig 1a). As voltage was applied to the cell, electrophoresis led to CNTs settling out on the electrodes. This led to a decrease of the loading and also to a loss of the planar LC alignment on the cell surface. The net effect was a decrease of the observable anisotropy. Multiple switching by magnetic field was used in the 30GHz study did not lead to the material deterioration. However, raising the temperature of the mixture lead to a fast CNT agglomeration. This observation may be explained by the following factors. A liquid crystalline host in the isotropic phase has much lower viscosity compared with the nematic phase (39 mm^2/s in nematic phase and ~1 mm^2/s in the isotropic phase for E7[11]). The reduced viscosity could promote CNT aggregation. In addition, CNTs are better aligned in the nematic phase. While aligned rod-shaped particles may not come in physical contact, the loss of alignment at the same concentration may result in the particles overlapping and forming agglomerates. Ultrasonication restores the mixtures to the initial state.

Experimental techniques: The dielectric properties of the mixtures at 1-4 GHz were studied by measuring the reflection coefficient of a capacitor at the end of transmission line.[3] An LC sample was sandwiched between a pair of parallel metal electrodes with polyimide coating to achieve planar alignment and 20µm spacers outside the electrode area ($\varepsilon_\perp$ measurement). An electric field up to 40V AC (1 kHz) is applied to the sample to switch it into homeotropic geometry ($\varepsilon_{||}$ measurement).

For the measurement of the dielectric properties at 30 GHz the resonant cavity perturbation method was used.[12] This method offers high precision for the extraction of both the permittivity and the dielectric loss. The LC inside the PTFE capillary was oriented parallel ($\varepsilon_{||}$) or perpendicular ($\varepsilon_\perp$) to the electric field in the resonator by a magnetic field (0.5 T). The temperature was controlled and the measurements were taken during heating. At each temperature, both LC orientations were measured in direct succession. After reorienting the magnetic field, a two minute waiting period was used to allow the system to stabilise and thus ensure complete reorientation of the LC and CNTs.

Results: The parallel component of the dielectric permittivity of mixtures loaded with carbon nanotubes increases compared with pure LC while the perpendicular component remains almost unchanged. 0.01%wt loading of CNTs leads to ~120% increase in dielectric anisotropy as compared with unloaded LC at 3GHz (Fig 1b) and ~165% increase in dielectric anisotropy (150% increase in birefringence) at 30GHz (Fig 2a). This is two times better than the results reported for metallic microtubules[4] at 20 times lower concentration. The larger anisotropies at 30GHz are in line with previous findings in pure LC.[2] In the 1-4GHz experiment, the LC orientation is controlled by an electric field. In order to avoid electrophoretic damage, we restricted the maximum value of the electric field with the consequence that full reorientation of the LC director may not have been achieved. The mixture with 0.005%wt CNT loading showed intermediate properties between the pure and the 0.01% loaded LC, with ~42% increase in dielectric anisotropy at 3GHz (Fig 1b) and ~47% increase in dielectric anisotropy at 30GHz compared to the unloaded LC (Fig 2a). The equilibrated LC-CNT mixture was studied in 1-4GHz frequency interval and exhibited increased anisotropy by 28% compared to the unloaded liquid crystal. The material could be repeatedly switched using fields up to 2V/µm, without observable electrophoretic damage.

Figures 1c and d show how the dielectric permittivity and loss values changed as the applied field was increased from zero to 0.5V/µm for pure and CNT loaded liquid crystal. Dielectric loss (ε'' or $\varepsilon''/\varepsilon' = \tan\delta$) increased in the CNT loaded materials (Figs 1d and 2b). The loss correlated with the CNT loading concentration. The perpendicular component of the dielectric loss, $\tan\delta_{\perp}$, was increased by 10-30%. The increase of the parallel loss component, $\tan\delta_{||}$, depended on the CNT concentration and was 2-5 times larger in the 0.01%wt loaded material, and 26% larger in the 0.005%wt loaded material. However, in the equilibrated LC-CNT material, the loss was virtually unchanged compared to the unloaded liquid crystal.

Conclusions: We have shown that the high frequency dielectric anisotropy $\Delta\varepsilon$ of nematic liquid crystals can be increased by loading with carbon nanotubes. This is a promising result for creating tunable dielectric materials that can be deployed in tunable microwave devices.

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Figure captions:

Figure 1 a) polarized microscopy: CNTs in LC are uniformly distributed and aligned (right side). Under the influence of electric field CNTs aggregate and deposit on the electrodes (left) b) $\Delta\varepsilon$ in 1-4GHz range, switching with 0.5V/µm; c, d) 3GHz, sweeping from $\varepsilon_{\perp}$ to $\varepsilon_{||}$ and from $\tan\delta_{\perp}$ to $\tan\delta_{||}$;

Figure 2 Pure and CNT loaded E7 at 30 GHz versus temperature, resonator method, switching with magnetic field. E7+0.005% (a star) was evaluated only at room temperature. a) Dielectric anisotropy; b) Loss tangent; unfilled markers represent $\tan\delta_{\perp}$, filled markers represent $\tan\delta_{||}$. E7+0.005% (a star) has virtually the same parallel and perpendicular loss;

Figure 1

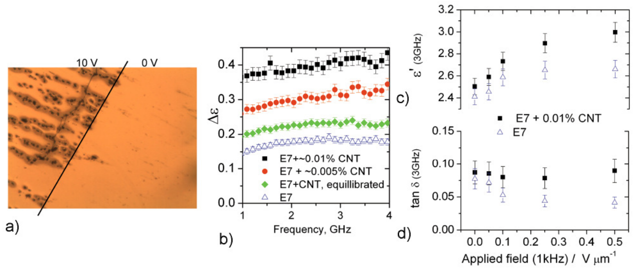

Figure 2