

Antiferroelectric liquid crystal/carbon nano tube duo for achieving modified electro-optical properties; aiming at display applications

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ABSTRACT

Antiferroelectric liquid crystals are considered as smarter materials for display technologies owing to their faster response time over conventional nematics. However there is large scope for modifications of its physical properties. In the present study multi-walled carbon nanotubes (MWCNT) are dispersed in a high tilted antiferroelectric liquid crystal composed of rod like molecules. The effects of nano-dispersion on electro-optical and dielectric properties of the host are studied in details. The time for switching between dark and bright states and the rotational viscosity are reduced and spontaneous polarization is enhanced considerably by minute addition of MWCNTs. The high tilt angle of the molecules necessary for obtaining good dark state in displays has not changed after dispersion of nanotubes. The strong interaction of the aromatic cores of the rod like liquid crystal molecules with the honey-comb pattern of the CNT walls is considered responsible behind such improvements of physical properties of the host. Copyright © 2016 VBRI Press.

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Introduction

Carbon nanotubes (CNT) are cylindrical nanostructured allotrope of carbon with extraordinary electrical and mechanical properties. They are one dimensional material with high degree of anisotropy and can be thought of rolled graphene sheets in tubular morphology or a structure consisting of several such tubes arranged concentrically. To realize their practical application the primary challenge is to achieve perfectly aligned CNTs over large areas. Lynch et al. adopted a simple yet non-trivial method of aligning CNTs by dispersing them in an anisotropic liquid crystalline medium [1]. Liquid crystal (LC) is a thermodynamically stable state of matter which exists between three-dimensionally ordered crystal and completely disordered liquid while possessing physical property of both. This dual nature enables it to form a flowing ordered structure controllable by an external stimulus which is the key factor of its huge applications in display technology. When CNT-dispersed LC system is subjected to an external field, whether electric or magnetic, the LC molecules reorient along the electric field and in-turn also re-align CNTs with them. The key feature behind their compatibility is highly anisotropic nature of both liquid crystal molecules and CNTs. Nematic liquid crystal (NLC) which have fluid like arrangement of constituent molecules with their long axis oriented parallel to each other have been extensively used for this purpose. In addition to the LC-induced alignment of CNTs, the

composite system has drawn great interest in the recent years because of the outstanding interactions of CNTs with aromatic mesogenic units of NLCs [2-8] and significant modification of physical properties of the host. It has been observed that a minute addition of CNT greatly reduce the threshold voltage and residual DC of the host [5-8]. CNT-NLC composites yielded significant improvement in the response time for optical controlled birefringence (OCB) cells [9]. The dynamical behavior of CNTs in NLC medium and consecutive appearance of single and double four lobe textures is studied under both vertical and inplane field [10-12].

Recently comprehensive studies have been done with other forms of liquid crystals such as ferroelectric liquid crystals (FLC). In ferroelectric liquid crystals the molecules are arranged in layers and they are tilted with respect to the layer normal. The direction of tilt is opposite in adjacent layers in case of antiferroelectric liquid crystals. The ferroelectric or antiferroelectric phases exhibit polar ordering if the rod-like molecules are chiral. A fluid with overall polar order is considered to be highly appreciable for display applications owing to the fast response of the molecules. Ferroelectric liquid crystals (smectic C*) composed of rod shaped molecules are the first example of such fluid-like phase with polar ordering [13]. Recently nano-dispersion studies have been done using ferroelectric liquid crystals (FLC) as the host medium [14-20]. The response time is found to reduce considerably by addition of multi-walled carbon nanotubes (MWCNTs) in the FLC

medium and the fastness of response is attributed to the decrease in rotational viscosity and increase in anchoring strength [20]. Srivastava *et al.* presented a switchable gratings based on chiral single walled CNT doped FLC where the diffraction efficiency of the highly doped system was significantly increased [15]. Photoluminescence intensity and dielectric properties of ferroelectric liquid crystals are modified by functionalized MWCNTs [21]. The alignment of single-walled CNTs in a FLC medium is investigated through scanning electron microscope and their interactions are studied through Raman spectroscopy, FTIR etc. the studies revealed that SWCNTs can be well aligned by smectic liquid crystals [22].

Antiferroelectric liquid crystal (AFLC) (SmC_A^*) which is a sub phase of SmC^* has even faster response time, wide viewing angle, full grey scale compatibility and easy DC compensation. However till now their commercial applications have not been successful because of lack of good alignment which causes the static light leakage and poor contrast ratio. The dark state problem of AFLC was solved when materials with tilt angle $\sim 45^\circ$ (orthoconic antiferroelectric liquid crystal (OAFLC)) were proposed [23-24]. Till then several research groups have investigated such OAFLC materials in details [25-26]. However these OAFLC materials often possess very short helical pitch and high rotational viscosity etc. which in turn causes various technological problems like high driver costs and long switching times etc. Most convenient non-synthetic way to address this problem is dispersion of nanomaterials in AFLC host.

The motivation of this present study is to modify physical properties of an orthoconic AFLC by dispersing a very small amount of multi walled CNTs in it, thus facilitating its application in displays. Previously many studies have been done by dispersing CNTs in nematic and ferroelectric liquid crystals. Here for the first time CNTs are dispersed in an antiferroelectric liquid crystal to improve its dielectric and electro-optical properties significantly. The response time for switching between bright and dark states and rotational viscosity have been observed to decrease in the CNT doped OAFLC cell while spontaneous polarization increases remarkably. Also LC induced orientation of CNTs has been achieved as observed from optical micrographs. The study helps to understand the interaction of CNTs with surrounding anisotropic medium possessing antiferroelectric ordering.

Experimental

The material used is a single component fluorinated liquid crystal with high tilt angle $\sim 45^\circ$ in the antiferroelectric phase. Above the AF phase it possesses a ferroelectric (SmC^*) and de-Vries type SmA phase [27]. The phase sequence and molecular structure are shown in Fig. 1(a). The synthesis and detailed study of phases are reported earlier [28-29]. Multi-walled carbon nanotube is obtained commercially from CheapTubes.com. The Transmission Electron Microscopy image shows well-graphitized multi-walled nanotubes (Fig. 1(b)). The diameters of the nanotubes are $\sim 10\text{nm}$ while the lengths are several micrometers. Small amount of MWCNT sample was blended with the OAFLC such that the concentration of MWCNT in OAFLC is 0.07 % and the product was

dissolved in chloroform. The solution was then sonicated thoroughly for 50 minutes for preparing homogeneous mixture as well as to break the long MWCNTs to small nanotubes. Finally the chloroform was evaporated by heating. The resulting MWCNT-OAFLC mixture was filled into a planar aligned cell (EHC, Japan) of thickness $4\mu\text{m}$ via capillary action at the isotropic temperature of the OAFLC. The temperature of the cell was controlled by a Mettler FP52 hot stage attached to a FP5 temperature controller. Optical textures were observed using Leica DMLP polarizing microscope. The mesogenic behavior of the host and the nano dispersion system was investigated by dielectric spectroscopy and electro-optical studies. Dielectric data are recorded by the HP4192A Impedance Analyzer. Electro-optic measurements were done using HP33120A signal generator, F10A voltage amplifier, DL1620 oscilloscope, a photo detector with pre amplifier (FLC electronics). The electrical and optical response times were measured using a square wave of frequency 10Hz. The magnitude of the spontaneous polarization was determined from the current reversal peak of a triangular wave.

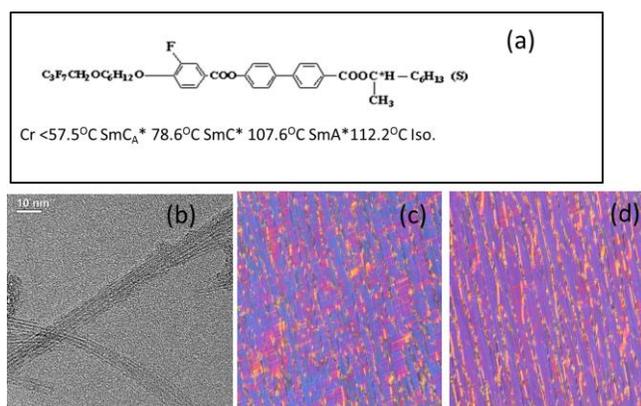


Fig. 1. (a) Chemical formula of the molecule of host liquid crystal and its phase sequence, (b) TEM image of MWCNTs showing concentric graphitic sheets, (c) texture of pure OAFLC and (d) OAFLC/CNT composite at 60°C .

Results and discussion

Polarizing optical microscopy

The textures observed using polarizing optical microscopy confirmed that a minute addition of CNTs did not perturb the molecular distribution of the AFLC sample significantly. The textures in both systems are essentially the same and no CNT aggregates were found (Fig. 1(c-d)). Strongly rubbed planar cells yielded good alignment of CNTs along with the AFLC molecules. The phase transition temperatures are found almost invariant in the AFLC/CNT cell by optical observation and further confirmed by dielectric spectroscopy.

Dielectric spectroscopy

Dielectric spectroscopy is an effective technique to reveal the complex molecular dynamics. The complex dielectric permittivity can be written as $\epsilon = \epsilon' + i\epsilon''$, where ϵ' and ϵ'' are real and imaginary part of permittivity respectively. Since the dielectric loss spectra of the sample have a

comparatively high dc loss at the low-frequency side and they are also asymmetric, the frequency dependence of the complex dielectric permittivity can be better described by the superposition of Havriliak-Negami fit function and a conductivity contribution. The characteristic dielectric parameters such as dielectric strength and relaxation frequency were extracted after fitting the dielectric data in the following extended Havriliak-Negami function:

$$\varepsilon'' = \frac{\sigma_0}{\varepsilon_0} \cdot \frac{1}{\omega^s} + \sum_{k=1}^N \text{Im} \left\{ \frac{\Delta\varepsilon_k}{[1 + (i\omega\tau_k)^{\alpha_k}]^{\beta_k}} \right\} \quad (1)$$

where, $\Delta\varepsilon_k$ is the dielectric strength and τ_k is relaxation time of each individual process k involved in dielectric relaxation, ε_0 is the vacuum permittivity (8.854 pF/m) σ_0 is the conduction parameter and ω is the angular frequency.

(SmC_A^*), ferroelectric (SmC^*) and paraelectric (SmA) in both pure and AFLC/CNT systems (Fig. 2(a)). The pure fluorinated material shows an additional ferrielectric phase (SmC_γ) in between SmC_A^* and SmC^* during heating in a 10 μm cell [29]. However this phase has not appeared in 4 μm cell since it is extremely sensitive to cell thickness, aligning material etc. The dielectric strength ($\Delta\varepsilon$) and relaxation frequencies of both cells as a function of temperature are plotted in Fig. 2 (b-e). Two relaxation modes are obtained in SmC_A phase in pure sample. The low frequency mode ($\sim 1\text{kHz}$) is high in dielectric strength similar to the goldstone mode in ferroelectric phase (Fig. 3a). This appears due to coexistence of both ferroelectric and antiferroelectric order in SmCA^* phase and this particular mode is called hereditary goldstone-like mode [29]. Another relaxation appears near 1MHz frequency range and can be ascribed to collective reorientation of molecules around their short axes. In the SmC^* and SmA^* phase of pure compound usual goldstone and soft mode are

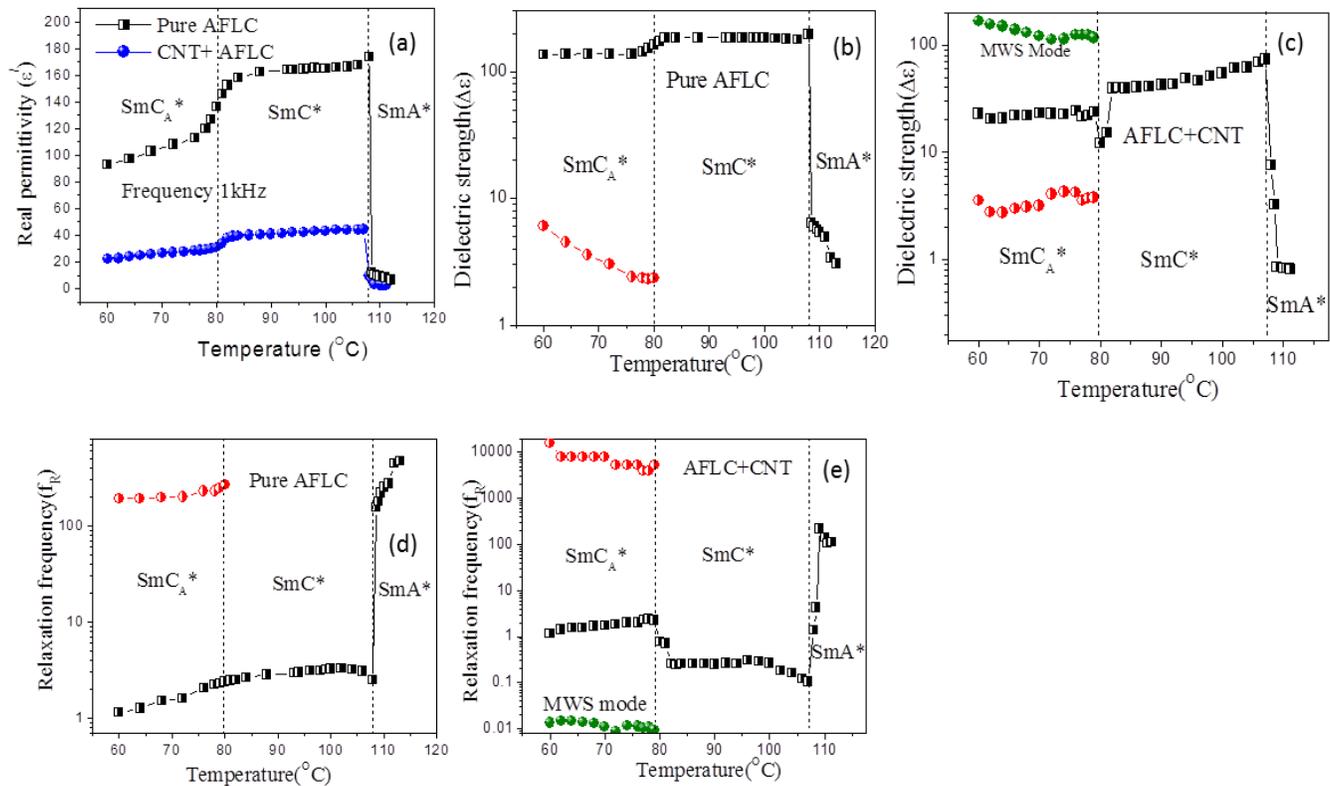


Fig. 2. (a) Temperature dependence of real part of permittivity (ε') in pure and doped system, (b) Dielectric strength ($\Delta\varepsilon$) vs. temperature of pure and (c) AFLC/CNT composite; (d) Relaxation frequency vs. temperature of pure and (e) AFLC/CNT composite.

The exponents α and β are empirical fit parameters, which describes a symmetric and non-symmetric broadening, respectively, of the relaxation peaks. The first term on the right-hand side of Eq. (1) describes the motion of free charge carriers in the sample. The exponent s determines the nonlinearity of the dc conductivity arising from charge accumulation at the interfacial layers. In the case of an Ohmic behavior ($s=1$), σ_0 is the Ohmic conductivity of the smectic material.

The temperature dependence of real part of permittivity reveals three distinct LC phases viz. antiferroelectric

observed respectively. In CNT doped system similar modes are observed with relatively lower dielectric strength and higher relaxation frequency. Another high strength mode at very low frequency (10 Hz) appears in the AFLC/CNT system (Fig. 2 (c) & (e)). The origin of this mode is charge accumulation at the interface of the LC medium and nanotubes as well as the cell surfaces. This mode typically appears in the nanomaterials doped LC and is called the Maxwell-Wagner-Sillars (MWS) mode [30].

Electro-optical studies

The electro-optical studies reveal faster switching dynamics in AFLC/CNT system. The dependence of electrical response time (τ_{el}) on applied electric field (E) in the antiferroelectric phase (at 60°C) of the liquid crystal for both systems is shown in **Fig. 4**. The response of the AFLC/CNT cell is almost 40% faster than the pure system

The electric field dependence of the rotational viscosity as obtained from equation (2) shows significant reduction in the doped system (**Fig. 3 (e)**). Such reduction in rotational viscosity is attributed to the fact that free ions are trapped by the dispersed CNTs resulting reduction in the internal friction.

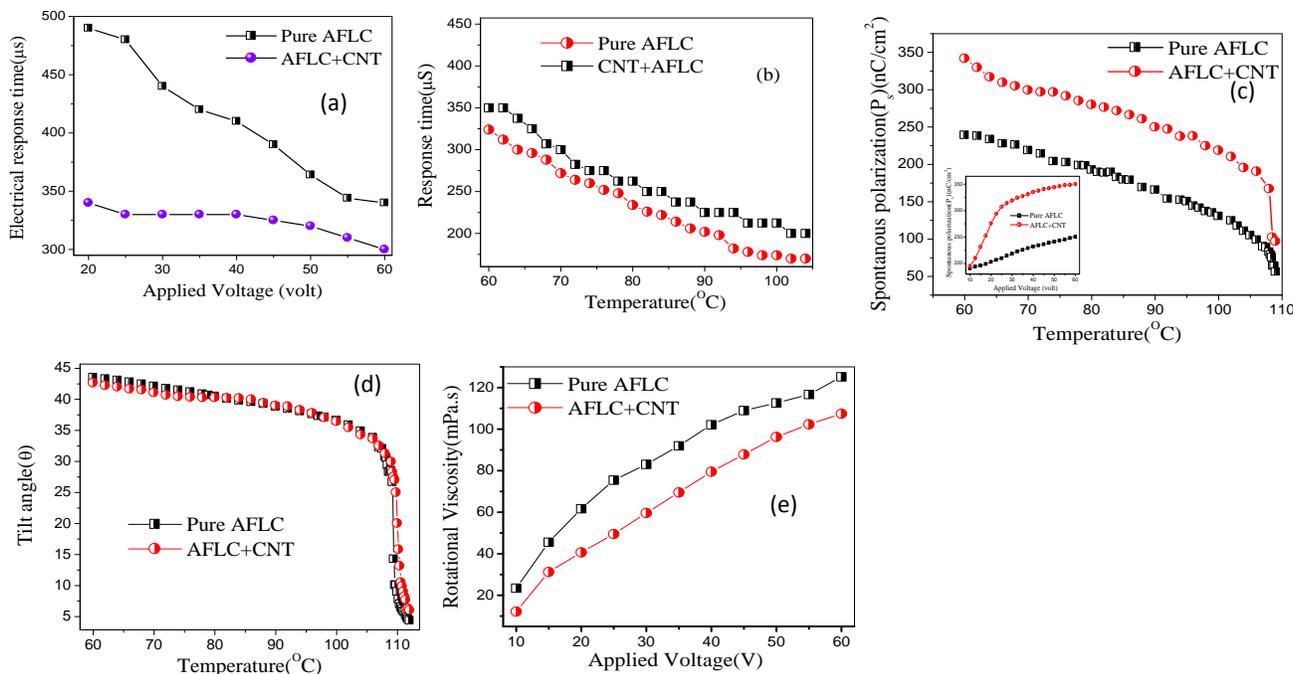


Fig. 3. (a) Dependence of response time of pure and doped sample with applied electric field in the antiferroelectric phase (60°C), (b) response time vs. temperature, applying a square wave voltage (70V_{pp}, 10Hz), (c) temperature dependence of spontaneous polarization (P_s) (Inset: voltage dependence of P_s) (d) tilt angle (θ) vs. temperature; (e) rotational viscosity vs. applied voltage in antiferroelectric phase (60°C).

at low voltages ($\sim 10V_{pp}$) (**Fig. 3(a)**). The large aspect ratio of CNTs and the π - π surface electron density causes a strong electrostatic interaction between the CNTs and the surrounding LC medium. This gives rise to a strong internal electric field which facilitates the reorientation of the LC molecules under applied field and thus reduces the response time. Temperature dependence of response time is shown in **Fig. 3(b)**.

Spontaneous polarization is enhanced in AFLC/CNT composite system (**Fig. 3 (c)**). It is well known that the aromatic cores of the LC molecules favor stabilizing themselves on the honeycomb pattern of the CNTs due to the strong anchoring of π - π electron stacking. Owing to this strong interaction, the LC layers adjacent to CNT wall have enhanced Smectic C_A arrangement which is reflected by the increase in P_s **Fig. 4 [31]**.

The measurements of tilt angle however did not show any significant change after doping (**Fig. 3(d)**) which is good from the application point of view since the sample maintains its orthoconic nature even after doping with CNTs.

The rotational viscosity is related to the response time (τ_{el}) spontaneous polarization (P_s) and applied electric field (E) as follows:

$$\eta = \tau_{el} P_s E \quad (2)$$

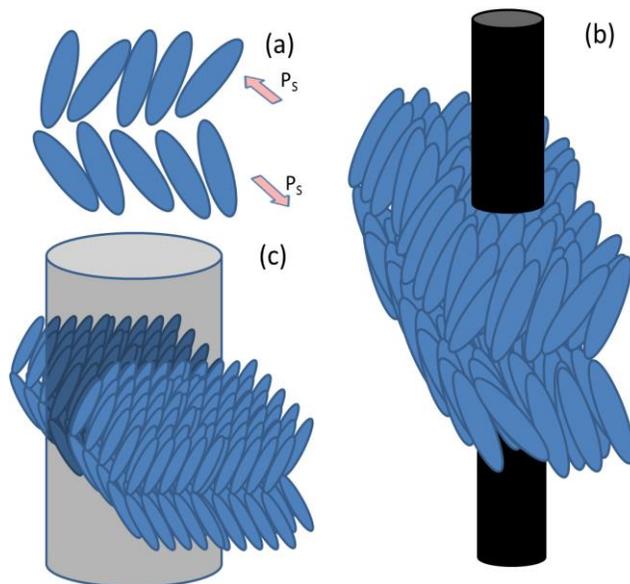


Fig. 4. Schematic diagrams: (a) natural molecular arrangement of SmC_A phase, (b) confinement of CNTs in SmC_A phase, (c) enhanced antiferroelectric ordering of the LC molecules around CNT owing to π - π interaction of the aromatic cores of the liquid crystal molecules with the CNT walls. Blue ellipsoids are liquid crystals and black cylinder represents the CNT.

