U.P.B. Sci. Bull., Series A, Vol. 86, Iss. 2, 2024 ISSN 1223-7027

OPTICAL PROPERTIES OF NEMATIC LIQUID CRYSTALS WITH MULTIWALL CARBON NANOTUBES

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A simple method to determine a liquid crystal composite's birefringence is used to quantify the influence of multiwalled carbon nanotubes (MWCNT) on the optical properties of the host. Experimental light intensity versus applied voltage data for five different samples containing 5CB nematic and multiwalled nanotubes with mass fractions of 0.61% 0.36%, 0.22% and 0.097% were recorded and analyzed. The results show a constant decrease of the birefringence independently of the clustering effect appearing in samples containing more than 0,5% mass fraction of MWCNTs.

Keywords: nanomaterials, carbon nanotubes, birefringence, liquid crystals

1. Introduction

Commonly known as 5CB, 4-Cyano-4'-pentylbiphenyl is a nematic liquid crystal with the chemical formula C18H19N. It was first synthesized by George William Gray, Ken Harrison, and J.A. Nash at the University of Hull in 1972 and at the time it was the first member of the cyanobiphenyls.[1][2] The 5CB molecule is 20 Å long with a phase transition from crystalline to nematic phase at 22.5 °C and from a nematic to isotropic state at 35.0 °C. Although it is not suitable for LCD due to its low transition temperature to isotropic and its narrow nematic phase range, it is still one of the most used nematic in fundamental research. It is one of the reference materials for positive dielectric anisotropy material and with the largest amount of physical data available.

Carbon nanotubes are tubular structures made of rolled graphene sheets. As many nanoparticles, they are studied in order to be used and inserted in other materials to improve their electrical [3-5] or biological [6] properties but also as doping agents for advanced materials in opto-electronic and magneto-optic devices [7-12]. Yet, for a proper use, they must be studied at microscopic level as single particles, not as bulks where they exhibit a totally different behavior. Many

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studies in the LC field are focused on the nanoparticles theoretical and experimental analysis, on composite synthesizing and possible applications in electro-optic domain [11-18]. When the focus is on the nanotube host, new discoveries and interesting applications may rise with consistent impact on electronic devices [14-16]. It is also the case of this manuscript where the impact of MWCNT on optical birefringence of thermotropic nematic is analyzed. The method proposed in previous papers [14-15] is used to determine the birefringence from simple emergent intensity versus applied voltage plots. The results for pristine 5CB are as indicated in most of the scientific reports while for the samples containing carbon nanotubes a significant decrease of the birefringence is observed. An interesting thing about the optical properties of the composites is the birefringence uniform with the increase of the mass fraction of nanotubes even when the fraction is high enough to induce the clustering effect as indicated in other papers[16- 25].

2. **Experimental set-up and method**

The method used to determine the birefringence of a liquid crystal composite is presented in reference [15]. This is a simple method which allow us to calculate the phase difference from the intensity versus applied voltage plots. Briefly, it can be described like this:

When a laser beam is crossing a homogenous aligned LC sample, the phase difference between the ordinary and extraordinary rays can be written as:

$$\delta = \frac{2\pi d \Delta n}{\lambda} \cos^2 \theta \tag{1}$$

where d is the cell thickness, Δn is the sample birefringence, λ is the wavelength of the incident beam and θ is the pretilt angle of the molecules on the substrate.

If the pretilt angle is less than 5° we can assume that

$$\delta = \frac{2\pi d \Delta n}{\lambda} \tag{2}$$

When the sample is placed between two parallel polarizers with the axis making a 45° with the nematic director (*Fig.1*), the emergent intensity is:

$$I_{\parallel} = \exp(-\alpha d) \cos^2 \frac{\delta}{2} \tag{3}$$

Where α is the absorption coefficient of the sample.

A similar equation can be written when crossed polarizers are used, both of them making a 45° with the nematic director:

$$I_{\perp} = \exp(-\alpha d) \sin^2 \frac{\delta}{2} \tag{4}$$

From Eq. 3 and Eq.4, we can easily obtain the path difference as:

$$|\delta| = N\pi + 2\arctan\sqrt{\frac{I_\perp}{I_\parallel}} \text{ for N = 0, 2, 4.....} \quad (5)$$

and

$$|\delta| = (N+1)\pi - 2\arctan\sqrt{\frac{I_\perp}{I_\parallel}} \text{ for N = 1, 3, 5....} \quad (6)$$

The equation can be applied for materials with positive or negative birefringence but the method provides a residual uncertainty of $N\pi$ which, fortunately, can be solved for liquid crystals.

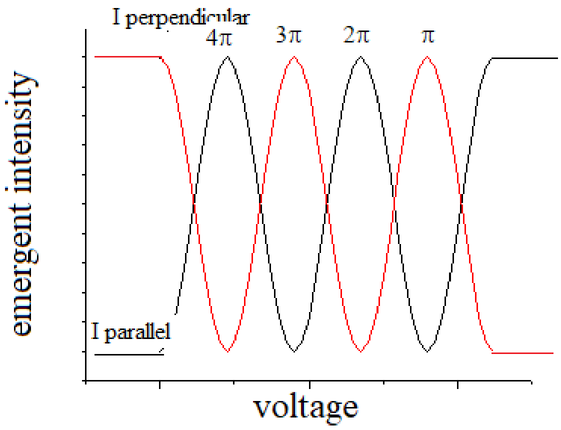
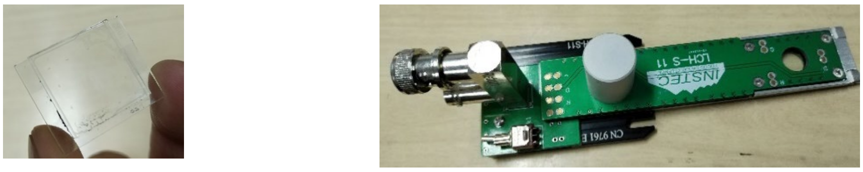


Figure 2: Emergent intensity versus applied voltage for an LC sample between crossed polarizers (red line) and parallel polarizers (black line)

A typical intensity versus voltage plot for liquid crystals is given in *Fig.2*. The first maximum of the intensity in crossed polarizers configuration (I perpendicular) and the first minimum of the emergent intensity in parallel polarizers configuration (I parallel) from the highest voltage correspond to a phase difference of π. Thus, by counting the minima and maxima for each configuration intensity we can determine the corresponding N for each applied voltage, determine the phase difference from Eq.5 or Eq.6 and calculate the birefringence from Eq.2

3. Results and discussion

The purpose of our work is to observe the influence of low concentration of multi-walled carbon nanotubes (MWCNT) on the 5CB liquid crystal birefringence. For the sample preparation we used powder multiwalled carbon nanotubes from Merck having 6 to 8 wall tubes with an average diameter of 10 nm and the length of 4 micrometers. The tubes were dispersed in toluene and sonicated for several hours to break the clusters from the powder. The toluene dispersion was mixed with 5CB nematic and left in vacuum roof till the complete evaporation leading to a 0.61% mass fraction of MWCNT in 5CB. The mixture was diluted leading to other three concentrations: 0.36%, 0.22% and 0.097%. Instec SG100A150uG180 planar cells with the gap d = 15 µm, an active region S= 1cm^2 and pretilt angle of 1^o up to 3^o were filled with the mixtures (*Fig.3*).



a) b)

Fig. 3:a) Planar cell filled with a 0,61% MWCNT in 5CB, b) Sample holder for LC-cells

Each sample was placed into a cell holder (*Fig.3b*) on which the voltage can be applied. We used and alternatic voltage at 1kHz increasing from 0 to 5 V.
The holder was inserted in the hot stage of a Mettler Toledo thermostatic device and placed between crossed polarizers (*Fig.4*). Thus, a 24 Celsius degree temperature of the sample was set and maintained during the measurements. A 632.8 nm HeNe laser was used as light source for the microscope.

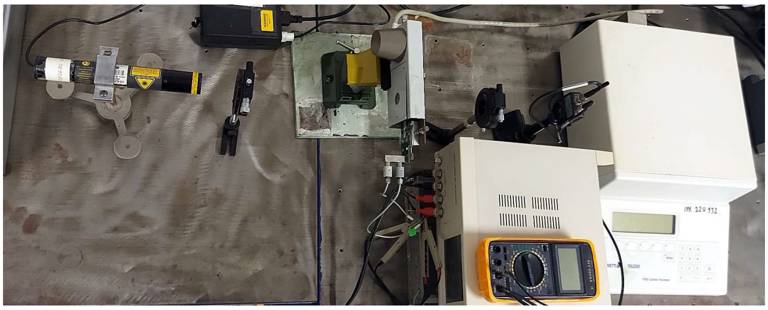
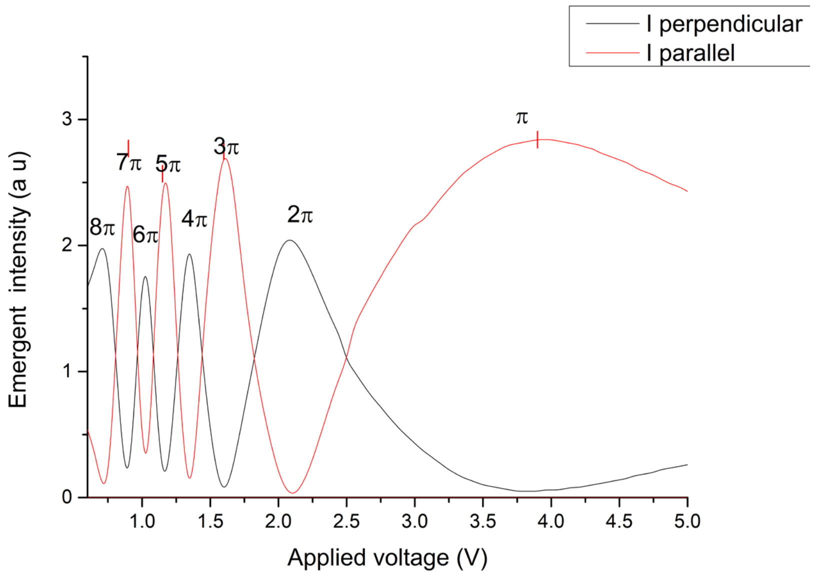


Fig. 4: Experimental set-up for the birefringence measurement.

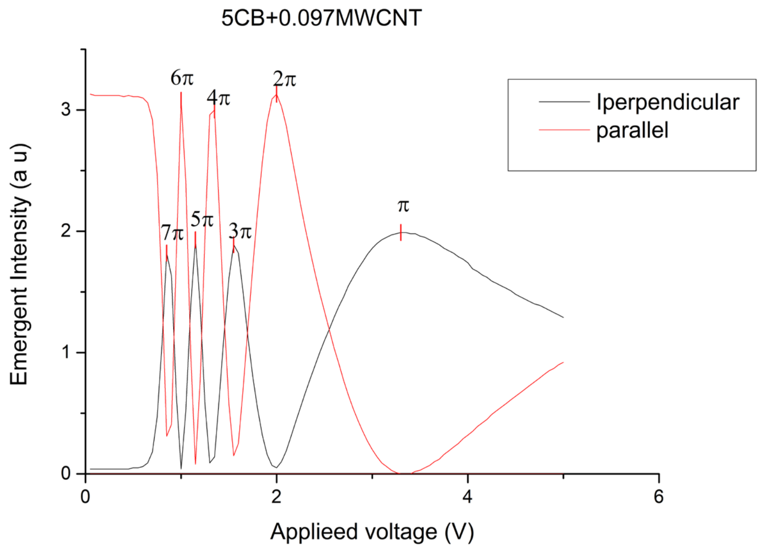
A photovoltaic cell is placed behind the sample to observe the emergent light intensity. Using a power source, an electric field was applied to the sample by gradually increasing the voltage from 0 to 5 V.

4. Results and discussion

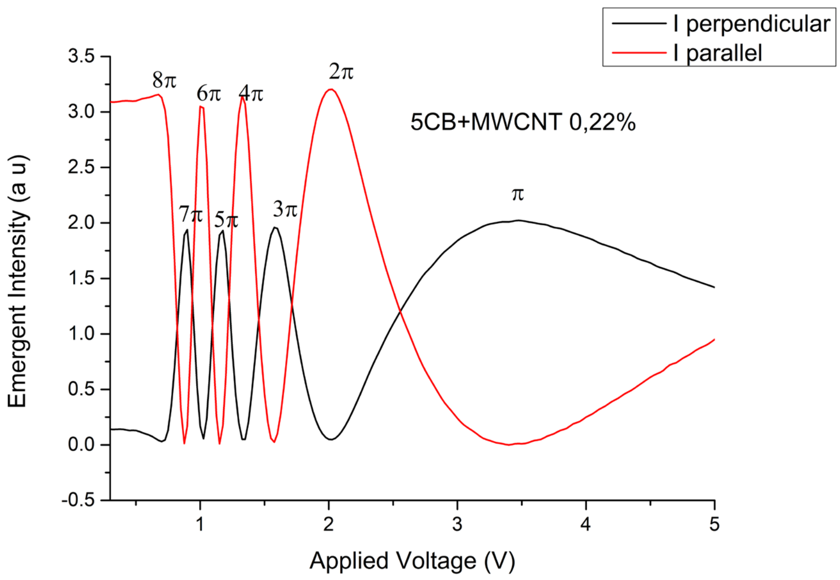
Intensity versus applied voltage records were made for each sample at a constant temperature of 24 Celsius degrees leading to a set of plots similar to the one given in *Fig.1* as presented in *Fig.5*. For each sample the number of maxima and minima was set and the phase difference was calculated at different voltages.



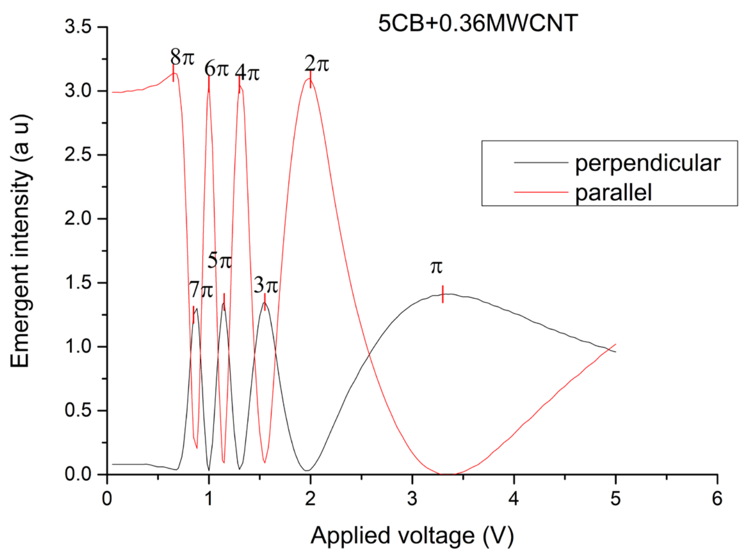
a)



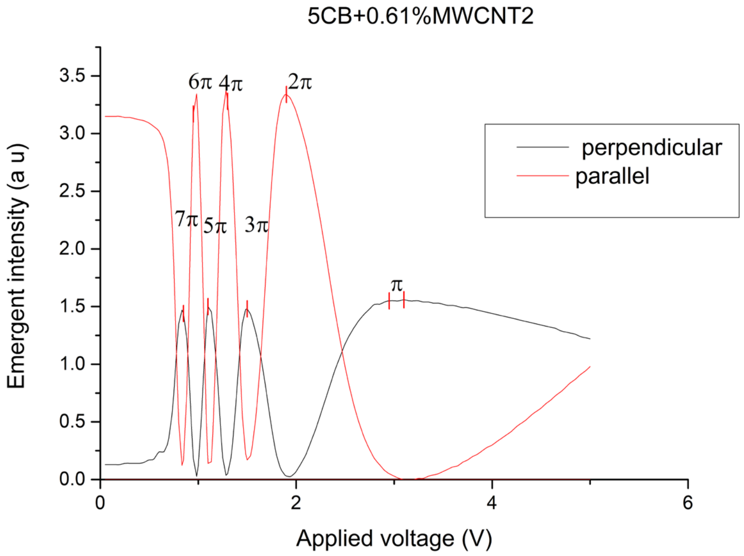
b)


I perpendicular
I parallel
5CB+MWCNT 0,22%
8π
6π
4π
2π
7π
5π
3π
π
Emergent Intensity (a u)
Applied Voltage (V)

c)


5CB+0.36MWCNT
perpendicular
parallel
8π
6π
4π
2π
5π
7π
3π
π
Emergent intensity (a u)
Applied voltage (V)

d)



e)

Fig. 5: Intensity versus applied voltage plots a) for pristine 5Cb , b) 5CB + 0.091%MWCNTc) 5CB + 0.22%MWCNT, d) 5CB+0.36%MWCNT, e) 5CB+0.61%MWCNT

For each sample, the birefringence was calculated at different voltages indicating a considerable influence of carbon nanotubes on the optical properties of liquid crystal as it can be observed in *Fig.7.*

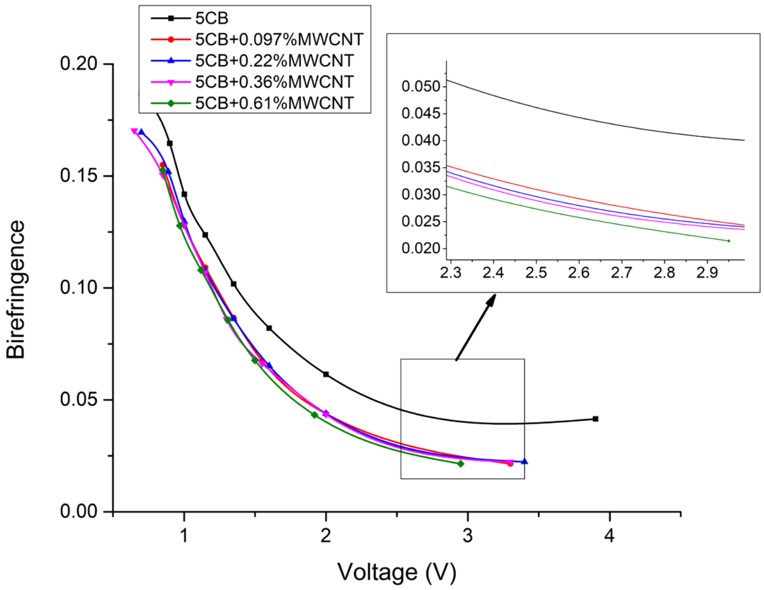


Fig. 6: The voltage dependence of birefringence for 5CB and for its composites at different mass fractions.

We can notice that the carbon nanotubes containing samples present a lower birefringence compared to pristine 5CB not only for the Freedericksz transition limit but also for higher voltages. Besides, the birefringence's decrease for MWCNT containing samples is steeper than pristine 5CB. This can be explained by the nematic molecules reorientation on the nanotube's surface which can affect the field influence. Several papers [20-25] indicate a parallel alignment of molecules to the nanotubes surface and some of them [23,24] provide a detailed discussion on how the anchoring forces that keep the molecules attached to the surface can reduce the external field effect on the molecules and, thus, the effect on optical properties. An interesting aspect here is the uniform evolution of the system even for high nanotubes concentration as presented in the inset of *Fig. 6*.

5. Conclusions

The birefringence of 5CB liquid crystals with multiwalled carbon nanotubes at different concentrations 0.61%, 0.36%, 0.22% and 0.097% at an environmental temperature of 24°C was determined by experimental method using the technique presented in [15]. The results indicated not only a decrease of the sample birefringence at the limit of the Freedericksz transition but also a faster decrease for higher voltages when compared to pristine 5CB as a natural indicator of molecular reorientation induced by liquid crystal - carbon nanotubes interaction.

Acknowledgment:

The research was funded by the grant Advanced Infrastructure for Nuclear Photonics research experiments at ELI-NP / ELI-INFRA through the national research and development program PNCDI IV / 5.9.1 ELI-RO: ELI-NP infrastructure development projects

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