EFFECT OF MULTI-WALLED CARBON NANOTUBE CONCENTRATION ON NEMATIC LIQUID CRYSTAL

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Abstract: Liquid crystals (LCs) owing to their distinctive molecular shape and long-range orientational order, represent an interesting novel route to many important technological uses. They have been widely studied in various research fields, considering the ease in controlling the orientation of their molecules in desired direction using different factors, for instance, surface anchoring. Further, inclusion of dopants in LC produces perturbation in the alignment of molecules and eventually disturbing the orientation. Consequently, it is important to understand the interactions between liquid crystalline molecules and the added dopant. Out of the mostly used dopants, carbon nanotubes (CNTs) well integrate in LCs and have shown interesting effects on their properties. The present study reveals the effect of heavy doping of multi-walled carbon nanotube (MWCNTS) on the nematic liquid crystal \(N-(4\text{-methoxybenzylidene})-4\text{-butylaniline} \) (MBBA).

Index Terms- Liquid crystals, Multi-walled Carbon Nanotubes, MBBA

I. INTRODUCTION

Liquid crystal (LC) an intermediate phase between crystalline solid and amorphous liquid is composed of anisotropic molecular units. They exhibit several intriguing features and have been used in display devices, drug delivery, laser technology, biosensors, etc [1-11]. Various types of defects naturally grow in its phases, and can be observed under the microscope as defect textures. Liquid crystalline defects can also be induced via device construction, dopant addition etc. [12-20]. In a perfectly pure LC; physical, optical and electrical properties get deteriorated or completely diminished due to the presence of defects [13,14]. However, at the same time, appearance of some specific defects after the addition of dopant, can help in modifying certain properties like enhancement in optical transparency, laser damage threshold etc. [15-19].

The simplest of LC phase is Nematic Liquid Crystal (NLC), whose direction of average orientation is described by the director \(\hat{n}\). Since the orientations of NLCs are director dependent, it is sensitive to external fields, temperature, presence of dopants, etc. Whenever a dopant is added, it brings change in the director \(\hat{n}\) and hence disrupts the molecular orientation in LC. Also, NLCs properties, for instance, optical, dielectric properties etc. depends on the orientation and shape of the LC molecule [21-22]. Thus, it is important to investigate the changes caused by the dopant in the orientation of LC molecules. Different characterization techniques have been used, for instance, Raman spectroscopy, UV-Vis spectroscopy, FTIR spectroscopy, etc to study the LC systems. Out of these, Raman spectroscopy has been frequently utilized to investigate the orientation and motion of segments of LC molecules [23-28]. The measurements and analysis of peak positions, intensity and width in Raman spectra yields information regarding rotational, vibrational energy and average orientation of liquid crystalline molecule [28-30].

Raman spectroscopy has also been used to understand the effect of presence of dopant (Ag nanoparticles, carbon fibres, MnTiO\(_3\) nanoparticles, carbon nanotubes etc.) in the host LC material [31-38]. Recently, enhancement of peak intensity in Raman spectra has been reported for the LC molecule confined in a nano-cell with Ag nanorod film deposited on the substrate [34]. Fan et al, reported that the intensity of Raman peak depends strongly on the orientation of CdS nanowire [31]. Also, the doping concentration of nanoparticles plays an important role on the properties of NLC [32]. In present work, we investigate Raman spectra, FTIR spectra and UV-Vis Spectra of a LC doped system in the presence of dopant. In previous works, LC doped systems were studied at lower concentration of nanoparticles. Herein, relatively higher concentration of dopant (2% and 5% by weight) was used to understand the effect of their presence on the LC doped system. Along with Raman spectroscopy, the doped system was also observed using an optical microscope.
In present work, to study the effect of dopant on NLC, widely used NLC, N-(4-methoxybenzylidene)-4-butylaniline (MBBA) was synthesised. Its molecular structure is shown in Figure 1. It has negative dielectric anisotropy. In the nematic phase, its molecules align locally such that they possess an average orientation ‘n’. For the synthesis of MBBA, 4-Butylaniline (purity >97.0%) and p-Anisaldehyde (purity >99.0%) obtained from TCI Chemicals, were used without further purifications via method given in literature [39]. The synthesized material was then heavily doped with 2% and 5% w/w concentration of Multi-Walled Carbon Nanotubes (MWCNTs), obtained from AVANSA Technology & Services. The doped samples were made by simple mixing MWCNTs in pure MBBA which leads to the formation of MWCNT aggregates. No special care was taken during the doping process.

To study the optical textures of samples, cells were made from optically transparent indium tin oxide (ITO)-coated glass substrates (sheet resistance of ~10Ω). The substrates were coated with 10% solution of polyvinyl alcohol (PVA), followed by baking them at 90°C for an hour. The coated substrates were assembled in planar configuration with uniform thickness of 100 μm maintained with the help of mylar spacers. Pristine and MWCNT doped MBBA samples were heated over isotropic temperature to facilitate capillary action in order to fill the prepared cells.

To investigate the molecular structure of MBBA, 1H-NMR and 13C-NMR spectra were recorded on NMR Spectrometer JEOL operating on 400 MHz. UV-Vis absorption spectra of the pure and doped materials were recorded using Shimadzu-1800 spectrophotometer in the wavelength region of 200-800 nm. The analysis of functional groups in the synthesized MBBA and doped MBBA was done by recording FTIR spectra recorded on a Perkin Elmer FTIR with a resolution of 0.5 cm⁻¹ over a spectral range of 500-4000 cm⁻¹ at room temperature. No treatment was applied to the samples prior to this spectrum reading. Raman spectra was taken in the spectral range from 500 to 3000 cm⁻¹ with laser 532 nm DPSS Laser (Laser Quantum gem 50 mw) from Princeton Instruments Acton Spectra Pro 2500i. The optical textures of pure and doped sample cells were investigated using image analysis system consisting of a MAGNUX MLX PLUS microscope fitted with MAGCAM MU2A camera and a custom-built heating cum hot stage.

III. RESULTS AND DISCUSSION

In the present work, the doped systems have been investigated by Raman spectroscopy, UV-Visible spectroscopy, FTIR and Image Analysis System. The synthesized MBBA was characterized using different analytical techniques including NMR, FTIR, Raman and UV-Vis spectroscopy.

The optical textures of pure and doped MBBA are given in Figure 2. Figure 2 (a,b,c) represents the optical micrograph of crystalline phase of pure MBBA, 2% w/w and 5% w/w concentration of MWCNT in MBBA, respectively. With increase in temperature, nematic phase of pure, 2% and 5% MWCNT doped MBBA appeared in sample at 22°C, 20°C and 19°C respectively as represented in Figure 2 (d,e,f). In doped samples, MWCNTs form agglomerates in the host MBBA owing to Van der Waals force acting between the nanotubes. The MWCNT aggregates can be clearly seen as dark patches in the host material as represented in optical micrographs of 2% and 5% doped sample Figure 2 (b,c,e,f,h,i). With further increase in temperature nematic phase was followed by the appearance of isotropic phase for pure, 2% and 5% MWCNT doped MBBA at 38°C, 34°C and 23 °C, as shown in Figure 2 (g,h,i).

The 1H NMR (CDCl3, TMS) spectrum of the synthesized MBBA is shown in Fig.3a. The non-equivalent protons of MBBA were labelled from a-j used in structure assignment as shown in Fig 3a. The spectrum showed two pairs of doublet at δ 7.81-7.85 and δ 6.94-7.25 assigned to two para substituted benzene rings with different substituents at para position (b, c, e, f). The deshielded proton (d) of -CH=N bond (imine group) was observed as a singlet at δ 8.38. The methoxy group protons (-OCH3) were detected at δ 3.82 (singlet). The para-substituted butyl group displayed four different signals due to the presence of four types of non-equivalent protons in the chain. The three -CH2 groups (g, h, i) were observed as triplet (δ 2.62), quintet (δ 1.60), sextet (δ 1.335), respectively, and –CH3 group protons were detected at δ 0.93 (triplet) [40-41].
Figure 2: Optical photographs of pure MBBA (a,d,g), 2% w/w concentration of MWCNT doped MBBA (b,e,h) and 5% w/w concentration of MWCNT doped MBBA (c,f,i). The figure represents the crystalline phase (a,b,c), nematic phase (d,e,f) and isotropic phase (g,h,i) of Pure MBBA, 2% and 5% MWCNT doped MBBA samples respectively. The micrographs represent a region of 400 μm in height and 720 μm in width.

Figure 3a: $^1$H NMR spectrum of the synthesized MBBA
The proton-decoupled $^{13}$C NMR (CDCl$_3$, TMS) of the synthesized MBBA is presented in Fig. 3b. The non-equivalent carbons of MBBA were labelled for structure assignment as shown in Fig 3b. The aromatic carbons directly bonded to oxygen and nitrogen ($4'$, 1, respectively) were relatively deshielded and recorded at $\delta$ 162.21 and $\delta$ 159.01, respectively. The aromatic carbon bonded to butyl group (4) and the aromatic carbon bonded to imine group via carbon (7') were detected at $\delta$ 149.98 and $\delta$ 129.93, respectively. The other aromatic ring carbons were observed at $\delta$ 130.90 (2'), $\delta$ 129.18 (3), $\delta$ 120.57 (2) and $\delta$ 114.26 (3'). The chemical environment of imine carbon (7') was deshielded owing to the presence of nitrogen and benzene ring and its chemical shift was observed at $\delta$ 140.57. The methoxy group carbon ($\alpha'$) was recorded at $\delta$ 55.51 and the carbons belonging to three methylene groups of the butyl substituent were observed at $\delta$ 33.82 ($\alpha$), $\delta$ 35.28 ($\beta$), $\delta$ 22.46 ($\gamma$) along with a methyl group at $\delta$ 14.08 ($\delta$) [42].

The recorded UV-Visible absorbance spectra of MBBA and MWCNT doped MBBA are shown in Figure 4. Pure MBBA shows high absorption in UV region, therefore substantial dilution using a suitable solvent is necessary for recording the spectrum. The UV spectrum of MBBA exhibited two absorption bands around 215 nm and 300 nm. The peak around 215 nm corresponded to $\pi-\pi^*$ transition of C=N bond and the other one around 300 nm was related to n-$\pi^*$ transition of the same bond. The absorption spectra of the doped MBBA indicate only a change in intensity without any positional shift in comparison to the pure MBBA. It indicated that the doping with MWCNT does not cause any significant change in the electronic environment that the MBBA molecule inhabits [43].
The FTIR spectra of the synthesized MBBA, 2% and 5% w/w concentration MWCNT doped MBBA samples are shown in Fig. 5. The spectra displayed an absorption peak at 3001 cm$^{-1}$ corresponding to $\equiv$C-H stretching vibration of the aromatic ring. The absorption peaks between 2955-2855 cm$^{-1}$ were related to the aliphatic asymmetric and symmetric C-H stretching. The well-defined peaks of the samples at 1625 cm$^{-1}$ were related to the stretching vibration of imine ($\equiv$C=N) bond in combination with the out-of-plane distortion vibration of the benzene ring attached to the imine bond. The absorption peaks at 1598 cm$^{-1}$, 1511 cm$^{-1}$ and 1460 cm$^{-1}$ were attributed to carbon-carbon stretching vibrations in the aromatic ring. The absorption peak corresponding to $\equiv$C-O stretching vibrations was observed between 1374-1249 cm$^{-1}$. The in-plane C-H bending of aromatic ring was observed in the region between 1162-1031 cm$^{-1}$. The absorption peaks in the region of 975-603 cm$^{-1}$ reflected the substitution pattern of the aromatic ring and represented the out-of-plane bending vibrations of para substituted benzene ring attached to the imine group and the methoxy ($-$OCH$_3$) group. The introduction of dopant did not cause any obvious change in peak positions and peak intensities of MBBA. The vibrational and rotational states of MBBA remained unaffected with doping and did not affect the FTIR spectrum.

The inset shows the peak positions corresponds to C-N stretching mode.

The Raman spectra observed for MWCNT, MBBA, 2% and 5% MWCNT doped MBBA samples are shown in Figure 6. The two bands at 1333 cm$^{-1}$ and 1576 cm$^{-1}$ in the spectrum of MWCNT were assigned as D-band representing vibrations of the $sp^3$ hybridized carbon atoms in CNTs wall and G-band corresponding to the $sp^2$ hybridized carbon atoms, respectively. In the Raman spectrum of MBBA, the 1624 cm$^{-1}$ band was allocated to the $\equiv$C=N stretching vibration coupled to the benzene ring vibrations. The 1595 cm$^{-1}$ and 1575 cm$^{-1}$ bands were assigned to the benzene ring vibrations parallel to the molecular long axis of MBBA. The band at 1502 cm$^{-1}$ was corresponding to C-N stretching mode for pure and 5% doped sample. For 2% MWCNT doped MBBA, a band shift corresponding to C-N stretching mode was observed from 1502 cm$^{-1}$ to 1498 cm$^{-1}$. The 1165 and 1193 cm$^{-1}$ bands were interpreted as CH$_3$ and CH$_2$ deformation modes. Most of the bands mentioned here in the Raman spectrum of MBBA were found to be in common with its FTIR spectrum [44,45].
From Raman spectra [Figure 6], it was observed that the bands appeared at the same wave-number regions for pure, 2% and 5% MWCNT doped MBBA systems. This illustrates that, the presence of nanotubes does not cause any disturbance to the polarization of various functional groups present in MBBA and does not change intermolecular parts of the MBBA molecule. However, the only peak shift observed was in case of 2% MWCNT doped MBBA for C-N stretching mode at 1498 cm\(^{-1}\) band from 1502 cm\(^{-1}\). Also, peak width at band 1498 cm\(^{-1}\) increased and intensity decreased with respect to pure and 5% MWCNT MBBA. The decrease in the Raman intensity at 1498 cm\(^{-1}\) is attributed to the decrease in the conjugation of phenyl ring with -C=N group. Thus, the stretching frequency of the C-N bond decreases.

The variation in Raman intensity is closely related to the orientational phenomena in LC molecules and thus change in alignment direction of the director vector [29,44] as Raman scattered intensity is proportional to order parameter of liquid crystals. Also, Raman intensities increases with the presence of dopants [38]. In the observed Raman spectra [figure 6], same has been observed i.e., Raman intensities of 2% and 5% doped samples are more than the pure MBBA. This represents that the order parameter of MWCNT doped MBBA samples is more than the pure MBBA. However, it was observed that, the Raman band intensities of 2% MWCNT doped MBBA were relatively more than the pure and 5% MWCNT doped MBBA, this shows that, the order parameter of 2% doped MBBA is more than 5% doped MBBA. This result is attributed to fact that, the Raman intensities of an isotropic state is minimum. In our 5% doped samples, heavy concentration of CNTs act as local heater resulting in decreasing the Nematic-isotropic phase transition as illustrated by the optical micrographs (isotropic phase at 38˚C for pure MBBA [Figure 2(g)]; isotropic phase of 2% MWCNT doped MBBA at 34˚C [Figure (h)]; isotropic phase of 5% doped MBBA at 23˚C[Figure 2(i)]), thus bringing the 5% doped sample near to isotropic phase, resulting in decreasing the order in the system and hence decrease in Raman band intensities.

IV. CONCLUSION

Since, the presence of dopant affects the LC properties, different w/w% of dopant has been used in the study to investigate the dopant concentration on LC system. The UV-Visible results shows that the doping with MWCNT does not cause any significant change in the electronic environment of the MBBA molecule. Also, the vibrational and rotational states of MBBA remained unaffected with doping and did not affect the FTIR spectrum. Raman spectra shows that, the presence of nanotubes has no effect on the polarisation of the various functional groups present in MBBA, nor does it change the intermolecular parts of the MBBA molecule. However, the only peak shift observed was in case of 2% MWCNT doped MBBA for C-N stretching mode at 1498 cm\(^{-1}\) band from 1502 cm\(^{-1}\). Also, peak width at band 1498 cm\(^{-1}\) increased and intensity decreased with respect to pure and 5% MWCNT MBBA. This shows that the order parameter of 2% doped sample is more than the 5% doped sample. Thus, the order parameter of the system is dependent on the amount of the dopant added into the host material.

REFERENCES


