Orientational order parameter of liquid crystalline nanocomposites by Newton’s rings and image analysis methods

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Liquid crystalline nanocomposites are prepared by dispersing TiO$_2$, ZnO, Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles separately in 4-Cyano 4'-Propoxy-1, 1'-Biphenyl (3O-CB) liquid crystal in a 1:100 ratio. The characteristic textures exhibited are captured at different liquid crystalline phases by using POM. The phase transition temperatures are measured by both polarizing optical microscope (POM) and differential scanning calorimeter (DSC). The optical textures are analyzed by using MATLAB software to compute birefringence and order parameter of samples. The birefringence and order parameter also measured by conventional Newton’s rings technique, the results are discussed.

Keywords: liquid crystals, nanocomposites, optical textures, phase transition temperatures, birefringence, order parameter.

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1. Introduction

Liquid crystal technology has a major effect on many areas of science and technology. Applications of this kind of materials are being discovered and continued to provide effective solution to many different problems. For modern industrial application, wide temperature range of liquid crystal phase, high optical and dielectric anisotropy and fast switching time are required. By composing liquid crystalline mixtures or using guest materials in host liquid crystals are two basic methods for obtaining liquid crystals with enhanced properties. Metal oxide nanoparticles are novel type of guest materials. Doping nanomaterials in liquid crystals enhances the properties of liquid crystals. Different types of metal oxide nanoparticles are used to achieve this purpose [1].

Incorporation of metal oxide nanoparticles into liquid crystals makes it easier to obtain better display parameter profiles [3]. The metal oxide nanoparticles embedded in liquid crystal bases have attracted much interest not only in the field of magnetic recording media but also in the area of medical care. The medical applications, which include radio frequency, hyperthermia, photo magnetic and magnetic resonance imaging, cancer therapy, sensors and high frequency applications, were reported [4–7].

In the present work, an effort has been made to study the effect of metal oxide nanoparticles on the orientation order parameter of 4-Cyano 4’-Propoxy-1, 1’-Biphenyl liquid crystal by image analysis and Newton’s ring techniques. There are several techniques for studying the temperature dependence of liquid crystal properties [8–11]. But they involve technical difficulties in measuring required parameters.

In this paper, we have explored image analysis-computer program technique to find orientation order parameter of liquid crystalline nanocomposites. In the image analysis technique, textures of liquid crystal samples are captured from crystal to isotropic phase by using POM. The changes in textural feature as a function of temperature are useful to compute thermo-optical properties of liquid crystals. By this technique, it is possible to extract as much information as possible from the textural image by means of applying computational algorithms on image data or intensity values. MATLAB software [12, 13] is used for the analysis of liquid crystal textures and to estimate the orientational order parameter.
2. Materials and methods

In this present work 4-Cyano 4’-Propoxy-1, 1’-Biphenyl liquid crystal was purchased from TCI, Ltd. and ZnO, TiO$_2$, Fe$_3$O$_4$ and Fe$_2$O$_3$ nanoparticles were obtained from VTU-PG centre, Muddenahalli, Chikkaballapura District, Bengaluru, India. Liquid crystalline nanocomposites are prepared using sonication method and its composition names are given in the Table 1. Textural features are studied using POM to confirm its liquid crystalline behavior. Then the transition temperature is measured with DSC studies for reliable information. Optical parameters like birefringence and order parameters of such nanocomposites are studied using conventional newton’s ring method as well as computational methods using MATLAB program.

3. Results and discussions

3.1. Polarizing optical microscope

The liquid crystalline nanocomposites are characterized by different liquid crystalline phases due to the changes in local molecular order with temperature [14]. The characterization of these mesophases will provide very important information on the pattern and textures of LCs. The transition temperatures and optical textures observed by polarizing optical microscope is shown in Figs. 1–5. As a representative case, the schlieren texture of nematic phase from isotropic phase is observed at 61.5 $^\circ$C then it is grown to curved brushes texture observed at 54 $^\circ$C and finally at 47.5 $^\circ$C the crystalline texture is formed which is not transparent hence look dark, all this textures are represented in the set of Fig. 1.

![Fig. 1. POM Textures of sample S$_1$: Isotropic – Nematic Transition Phase @ 61.5 $^\circ$C (a); Nematic Phase @ 54 $^\circ$C (b); Solid Phase @ 47.5 $^\circ$C (c)](image)

Dispersion of nanoparticles with liquid crystal influenced the textural features of the sample at different phases with respect to temperature and nanomaterial is observed in POM textures. The surface to volume ratio of sample liquid crystal increases due to surface restructuring by nanoparticle dispersion. This phenomenon of molecular restructuring varies as a function of temperature and nanoparticle composition. It is observed that orientational order of liquid crystal molecules are further strengthened heavily at isotropic to nematic phase and strengthened less at

<table>
<thead>
<tr>
<th>S$_1$. No.</th>
<th>Liquid crystalline compound (100 mg)</th>
<th>Metal oxide nanoparticles (1 mg)</th>
<th>Liquid crystalline nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Cyano 4’-Propoxy-1, 1’-Biphenyl (C$<em>{16}$H$</em>{15}$NO)</td>
<td>—</td>
<td>S$_1$</td>
</tr>
<tr>
<td>2</td>
<td>4-Cyano 4’-Propoxy-1, 1’-Biphenyl (C$<em>{16}$H$</em>{15}$NO)</td>
<td>ZnO</td>
<td>S$_{11}$</td>
</tr>
<tr>
<td>3</td>
<td>4-Cyano 4’-Propoxy-1, 1’-Biphenyl (C$<em>{16}$H$</em>{15}$NO)</td>
<td>TiO$_2$</td>
<td>S$_{12}$</td>
</tr>
<tr>
<td>4</td>
<td>4-Cyano 4’-Propoxy-1, 1’-Biphenyl (C$<em>{16}$H$</em>{15}$NO)</td>
<td>Fe$_3$O$_4$</td>
<td>S$_{13}$</td>
</tr>
<tr>
<td>5</td>
<td>4-Cyano 4’-Propoxy-1, 1’-Biphenyl (C$<em>{16}$H$</em>{15}$NO)</td>
<td>Fe$_2$O$_3$</td>
<td>S$_{14}$</td>
</tr>
</tbody>
</table>
crystalline phase by the nanoparticles with shifting transition temperature. This is because possibility of increasing its surface area and decreasing its volume. It is also observed that molecular weight of nanoparticles plays vital role in restructuring liquid crystal molecules. The observation of POM shows that restructuring of molecules leads to defective textural images at various instances.

Phase transition temperatures observed for liquid crystalline nanocomposites using POM and DSC shows that they are reduced due to the dispersion of nanoparticles. The nanoparticles ZnO, TiO$_2$, Fe$_3$O$_4$ and Fe$_2$O$_3$ influences the liquid crystal and reduces the transition temperature by 1 °C, 1 °C, 1 °C and 2 °C respectively.

Fig. 2. POM Textures of sample S$_{11}$: Isotropic – Nematic Transition Phase @ 60.5 °C (a); Nematic Phase @ 56.5 °C (b); Solid Phase @ 46 °C (c)

Fig. 3. POM Textures of sample S$_{12}$: Isotropic – Nematic Transition Phase @ 60.5 °C (a); Nematic Phase @ 56.5 °C (b); Solid Phase @ 46 °C (c)

Fig. 4. POM Textures of sample S$_{13}$: Isotropic – Nematic Transition Phase @ 59.5 °C (a); Nematic Phase @ 54 °C (b); Solid Phase @ 50 °C (c)
3.2. Differential scanning calorimeter (DSC) studies

The thermal analysis by DSC study provides data regarding the temperatures and heat capacity of different phases. DSC study reveals presence of phase transition in materials by detecting the enthalpy change associated with each phase transition. DSC study is used in conjunction with optical polarizing microscopy to determine the mesophase types exhibited by the materials. The different thermograms of liquid crystalline nanocomposites are recorded from DSC as shown in Figs. 6, 7.

The phase transition temperatures obtained by POM and DSC are tabulated for pure and nanocomposites liquid crystals at different phases in Table 2. The samples show isotropic, nematic and crystalline phases. The phases of samples are confirmed with the help of POM images obtained and corresponding transition temperatures are considered with the help of DSC values. The temperatures are measured in degree centigrade ($^\circ$C). The enthalpy jump at various phase is noted in the given table with in units of Joules per gram (J/g).

3.3. Birefringence studies by Newton’s rings method

The experimental setup consists of plano-convex lens of small radius of curvature (13 mm) and plane glass plate which is being placed in hot stage connected to specially designed microcontroller based temperature and image capturing device. The LC sample is introduced between the glass plate and lens and set the polarizer and the analyzer in the crossed position. The hot stage along with LC sample mount is placed on the microscope stage and then adjust hot stage axis to coincide with the microscopic axis. Set the reflector of the microscope to pass the light through LC sample until the clear Newton’s rings are formed on the monitor. These rings are formed due to the interference of ordinary and extra ordinary rays after passing through the analyzer. The diameter of various rings was measured. The experimental setup is shown in the Fig. 8 and ring pattern in Fig. 9.
The optical path difference between e-ray (extra ordinary ray) and o-ray (ordinary ray) is given by $y$, $\delta n$ which corresponds to ring number $k$ and wavelength $\lambda$ for a bright fringe is given by:

$$\delta n = \frac{k\lambda}{y}, \quad (1)$$

$$y = \frac{x^2}{2R}. \quad (2)$$

From equations (1) and (2):

$$\delta n = \frac{(2R\lambda)k}{x^2}. \quad (3)$$

Since $2R\lambda = c$, cell constant for the given wavelength of light:

$$\delta n = \frac{ck}{x^2}. \quad (4)$$

where $x$ is the radius of the ring and $R$ – the radius of curvature of the lens used.
\[ \delta n \] can be measured with great accuracy by finding the slope of the straight line drawn between \( r^2 \) versus the ring number \( k \) and shown in Figs. 10–12. We can obtain the same result by considering the dark rings also. The schematic diagram is shown in Fig. 13.

**Fig. 8.** Experimental setup to measure birefringence (Newtons rings method)

**Fig. 9.** Newtons Rings observed in samples \( S_1 \) at temperatures 59 \(^\circ\)C

**Fig. 10.** The square of radius of ring Vs ring number at various temperature of sample \( S_1 \)

**Fig. 11.** The square of radius of ring Vs ring number at various temperature of sample \( S_{11} \) (a) & \( S_{12} \) (b)
As the temperature decreases, birefringence $\delta n$ increases. The method adopted for the estimation of orientational order parameter from $\delta n$ given by Kuczynski et al. as follows where $\Delta n$ is birefringence at crystalline phase and is obtained by linear regression method shown in Figs. 14–16 [15, 16]:

$$S = \frac{\delta n}{\Delta n}. \tag{5}$$
3.4. Birefringence and order parameter by image analysis

Phase transitions are characterized by abrupt changes, discontinuities, breaking of symmetry and strong fluctuations of the molecules in a compound. The identification of transition temperatures is essential to study the physical properties of the LC materials. The transition also indicates the transformation from an ordered phase to relatively disordered phase and Vice versa as the temperatures are raised or cooled [17, 18].

The behavior of light with respect to temperature is known as the thermo-optical parameters. Optical birefringence and order parameters are the important thermo-optical parameters. Image analysis is the extraction of meaningful information from images (Textures) by applying computational techniques and algorithms to image data. Image analysis technique compute the statistics and measurement based on grey level intensities of the image pixels. In the present work, optical birefringence and order parameter are computed from the optical textures of samples as a function of temperatures by image analysis technique.

The birefringence of the liquid crystals was measured as a function of temperature by substituting the thickness \(d\) of liquid crystalline sample layer and wavelength of color in the following equation to calculate birefringence [8]:

\[
I = I_0 \sin^2 \left( \frac{\pi d \delta n}{\lambda} \right),
\]

where \(d\) is thickness of liquid crystal layer, \(I_0\) is the intensity of light observed when there is no sample (Liquid crystal layer) between light source and lens, \(I\) is the Intensity of light observed when there is sample (Liquid crystal layer).
The temperature dependent birefringence values of the samples are used to calculate the order parameter using Kuczynski equation given below [16, 19]:

\[ S = \frac{\delta n}{\Delta n} \]  

(7)

where \( \Delta n \) is birefringence at crystalline state and is obtained by linear regression method using Newton’s rings experiment.

In the image analysis technique, optical textures, thickness of the liquid crystal layer \((d)\) and birefringence in perfect order \((\Delta n)\) are given as input to obtain birefringence and order parameter. The birefringence and order parameter evaluated at different liquid crystalline phases by image analysis and Newton’s rings methods are represented in Tables 3–7. The order parameter values are found to be same using both methods. The order parameter found to decrease with increase of temperature. The temperature variation of order parameter is depicted in Fig. 17.

**TABLE 3.** Birefringence and order parameter of sample \(S_1\) by Newton’s ring and image processing methods at various phases

<table>
<thead>
<tr>
<th>(\Delta n = 0.35)</th>
<th>(\beta = 0.24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp ( (^{\circ}C))</td>
<td>(T) ( (K))</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>61.5</td>
<td>334.5</td>
</tr>
<tr>
<td>54</td>
<td>327</td>
</tr>
<tr>
<td>47.5</td>
<td>320.5</td>
</tr>
</tbody>
</table>

**TABLE 4.** Birefringence and order parameter of sample \(S_{11}\) by Newton’s ring and image processing methods at various phases

<table>
<thead>
<tr>
<th>(\Delta n = 0.391)</th>
<th>(\beta = 0.186)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp ( (^{\circ}C))</td>
<td>(T) ( (K))</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>60.5</td>
<td>333.5</td>
</tr>
<tr>
<td>56.5</td>
<td>329.5</td>
</tr>
<tr>
<td>46</td>
<td>319</td>
</tr>
</tbody>
</table>

From our investigation it is observed that order parameter increases due to the dispersion of metal oxide nanoparticles in 4-Cyano 4’-Propoxy-1, 1’-Biphenyl liquid crystal. The percentage of increase of order parameter in nematic phase is 1.27 % to 4.5 %, 7.13 % to 15.81 %, 19.93 % to 23.1 % and 18.51 % to 19.03 % due the dispersion of ZnO, TiO\(_2\), Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\) nanoparticles respectively.
Table 5. Birefringence and order parameter of sample S12 by Newton’s ring and image processing methods at various phases

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$T$ (K)</th>
<th>Phase Variance</th>
<th>Newton’s ring method</th>
<th>Image processing method</th>
<th>Thickness of sample layer ($d$ in meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta n$</td>
<td>$S = \frac{\delta n}{\Delta n}$</td>
<td>$\delta n$</td>
</tr>
<tr>
<td>60.5</td>
<td>333.5</td>
<td>I–N</td>
<td>0.15611</td>
<td>0.449885</td>
<td>1.30E-06</td>
</tr>
<tr>
<td>56.5</td>
<td>329.5</td>
<td>N</td>
<td>0.20503</td>
<td>0.590865</td>
<td>1.05E-06</td>
</tr>
<tr>
<td>46</td>
<td>319</td>
<td>Cr</td>
<td>—</td>
<td>—</td>
<td>0.79E-6</td>
</tr>
</tbody>
</table>

Table 6. Birefringence and order parameter of sample S13 Newton’s ring and image processing methods at various phases

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$T$ (K)</th>
<th>Phase Variance</th>
<th>Newton’s ring method</th>
<th>Image processing method</th>
<th>Thickness of sample layer ($d$ in meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta n$</td>
<td>$S = \frac{\delta n}{\Delta n}$</td>
<td>$\delta n$</td>
</tr>
<tr>
<td>59.5</td>
<td>332.5</td>
<td>I–N</td>
<td>0.15548</td>
<td>0.479877</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>54</td>
<td>327</td>
<td>N</td>
<td>0.22365</td>
<td>0.690278</td>
<td>9.70E-07</td>
</tr>
<tr>
<td>50</td>
<td>323</td>
<td>Cr</td>
<td>—</td>
<td>—</td>
<td>0.788E-6</td>
</tr>
</tbody>
</table>

Table 7. Birefringence and order parameter of sample S14 by Newton’s ring and image processing methods at various phases

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$T$ (K)</th>
<th>Phase Variance</th>
<th>Newton’s ring method</th>
<th>Image processing method</th>
<th>Thickness of sample layer ($d$ in meter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta n$</td>
<td>$S = \frac{\delta n}{\Delta n}$</td>
<td>$\delta n$</td>
</tr>
<tr>
<td>60</td>
<td>333</td>
<td>I–N</td>
<td>0.141953</td>
<td>0.431468</td>
<td>1.1E-06</td>
</tr>
<tr>
<td>52</td>
<td>325</td>
<td>N</td>
<td>0.221508</td>
<td>0.673277</td>
<td>1.02E-06</td>
</tr>
<tr>
<td>49.5</td>
<td>322.5</td>
<td>Cr</td>
<td>—</td>
<td>—</td>
<td>0.78E-6</td>
</tr>
</tbody>
</table>
Fig. 17. Order parameter with respect to temperature by Newton’s rings method and Image analysis method in samples $S_1$, $S_{11}$, $S_{12}$, $S_{13}$ and $S_{14}$.
4. Conclusion

The advantage of the image analysis method is that it is simple, less complex, efficient and reliable in this type of studies, unlike other techniques, there is no need to arrange different experimental setup except to arrange POM. By conventional techniques, the order parameter can be estimated in the nematic and smectic phases only; however, in the image analysis method, the order parameter can be evaluated in the crystalline phase in addition to the nematic and smectic phases. By the image analysis technique, the order parameter can be estimated in all liquid crystalline phases such as nematic, smectic and crystalline phases, whereas in Newton’s rings method it can be evaluated only in nematic, smectic phases. Due to the dispersion of Nano particles, the birefringence anisotropy increases. Therefore, the view angle increases and this can be most advantageous in liquid crystal display devices, to produce large panel LC displays with good depth.

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