Comparative study of acoustic relaxation time of cholesteric liquid crystal and mixtures

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Abstract. The present study focuses on the relaxation processes in Cholesteric Liquid Crystal and mixtures. We have dispersed two different monomers in CLC to form Polymer dispersed liquid crystals (PDCLCs). PDLC films have a remarkable electro-optical behavior since they can be switched from highly light scattering state (OFF) to transparent state (ON) simply by application of an electric field. We have also doped ferroelectric nano – powder (NP) in CLC. The phase transitions occurred at temperatures lower than those exhibited by the mesogenic component before doping. The viscosity, ultrasonic velocity and density show variation with change in the material as well as temperature. The acoustic relaxation time and ultrasonic attenuation decrease with increase in temperature for CLC and CLC+NP. The parameters of PDCLC2 in comparison with PDCLC1 are more linear in isotropic and anisotropic regions. For PDCLC2 the values reach maximum value at the Cholesteric-isotropic transition.

Keywords: Cholesteric Liquid Crystal (CLC), Polymer Dispersed Liquid Crystals, Ferroelectric Nanopowder (NP), Acoustic Relaxation Time

1. Introduction
Liquid crystals (LCs) are matter in a state that has properties between those of conventional liquid and those of solid-crystal [1]. The molecules of Cholesteric Liquid crystals (CLC) are twisted along the director. The molecular alignment within a layer is parallel, but the alignment in adjacent layers is rotated. Thermotropic CLCs exhibit a phase transition into the liquid-crystal phase as temperature is changed. For enhancing the physical properties of the LC, a monomer or prepolymer or nanomaterial is dispersed in it and it requires a proper selection of the same. This depends upon various factors such as size, shape, preparation methods, surfactant concentration, and amount of doping materials [2-4]. Related work shows that the doping of Liquid crystal enhances physical as well as optical properties of the material which improves the thermal and mechanical stability of thermooptical devices [5-8]. Ultrasound corresponds to a mechanical wave propagating at frequencies above the range of human
hearing (conventionally 20 kHz). The mechanical perturbation provokes tiny disturbances of the medium particles from their resting position. These disturbances induce a displacement of these particles and are transmitted step by step to other parts of the medium. In particular the wave propagation depends on the intrinsic elastic properties of the medium as well as on its mass density. Ultrasonic testing (UT) has long been one of the most widely used and most effective methods of inspecting composite materials [9-11]. In the present paper, we have studied the relaxation processes in the CLC, CLC dispersed with nanoparticles (NP) and CLC dispersed with two different monomers.

2. List of Chemicals and sample preparation

The CLC in the present study, Cholesteryl Myristate is a thermotropic liquid crystal whose properties change with the change in temperature.

EGDMA -Monomer M1: EGDMA is dispersed in CLC by encapsulation method to form PDCLC1.

2EHA -Monomer M2: 2EHA is dispersed in CLC by encapsulation method to form PDCLC2.

The PCDLCs formed contained 10% of monomers with 90% of CLC.

Ferroelectric nano – powder of Barium titanate (BaTiO$_3$) -NP: Barium titanate (BaTiO$_3$) is dispersed in the CLC to form CLC + NP. The BaTiO$_3$ particles are slightly anisotropic and their size is less than100nm. NP was mixed with Oleic acid and Heptane in appropriate proportion by weight and then this mixture was doped with CLC by ultra-sonication method. The ultrasoundaton ensures homogeneous distribution of NP in CLC. The mixture was kept in vacuum for six hours for complete evaporation of heptane. The resulting sample contains the small concentration (~1%) of BaTiO$_3$ NP.

Samples: CLC, PDCLC1, PDCLC2, CLC+NP (these acronyms will be used throughout the paper).

3. Experimental Techniques

3.1. Measurement of velocity of an ultrasonic wave

Measurement of velocity of an ultrasonic wave is done using multifrequency interferometer by Mittal enterprises. The temperature range of this instrument is varied from room temperature to 200$^\circ$ C. The arrangement of oil bath and display is as shown in Fig.1. It is provided with digital micrometer to minimize error in the measurement.

![Figure 1. Ultrasonic Interferometer](image)

3.2. Measurement of Density

The conventional methods for measurement of density require very large quantities of sample which is very expensive; we have adopted a different method for measuring density so as to reduce cost of experimentation without compromising on accuracy of results. For density measurement, we used capillary method. The amount of 0.1gm pure CLC was mixed in 10ml of solvent and the height of the solution raised in the capillary tube (h) is measured using travelling microscope. Using the radius of the bore of the tube(r), the volume of the solution was determined at different temperatures. Similarly the mass at different temperatures is measured using analytical microbalance. The digital thermometer (Model 305) with K-type thermocouple as a temperature sensor is used for accurate temperature measurement. The mica-band heater (as shown in Figure 2) along with variac is used for changing the
temperature of the solution. The densities of the mixtures were also measured using the above mentioned procedure.

3.3. Measurement of Viscosity
The viscosity \( \eta \) was measured at constant shear rate of 1 1/s and as a function of different temperatures using equipment MCR 52 with measuring System PP25 by Anton Paar. (Gap=0.1mm)

3.4. Measurement of Phase Transition Temperatures
At phase transition temperatures (PTT) Liquid Crystals change their phase. PTTs are measured using Differential scanning calorimetry (DSC) technique. The PTTs using DSC are obtained from peaks in the DSC plots.

4. Formulae used in the present study

Ultrasonic velocity \( U = \frac{2 \times D \times F}{n-1} \), \hspace{1cm} (1)
Where: \( D \)=Distance of micrometer screw for ‘n’ rotations  
\( F \)=Frequency of the ultrasonic wave

Density \( \rho = \frac{\text{Mass}}{\text{Volume}} \) \hspace{1cm} (2)
Where: Volume= \( \pi r^2 h \);  
\( r \)= radius of capillary,  
\( h \)= height of liquid column in capillary

Ultrasonic Attenuation \( = \frac{8}{3} \pi r^2 \beta_a \eta \) \hspace{1cm} (3)
Acoustic Relaxation Time \( \tau = \frac{4}{3} \eta \beta_a \) \hspace{1cm} (4)

5. Results and Discussion
The thermotropic liquid crystals change their phase with change in temperature. The temperature at which it changes its phase is called phase transition temperature (PTT). The values of phase transition temperatures are given in table 1.
The values of the PTTs in Table 1 clearly indicate the change in the values of PTTs in the doped sample than the sample in the pure state. This has resulted because of the alteration in the pitch of the CLC. Also, CLC + NP show reduction of 14°C in the PTT. Due to spatial confinement and an interphase of adsorbed mesogen at the droplet boundaries, the mesophase transition for PD CLCs occurred at a lower temperature than CLC in pure state. The low concentration of NP in CLC host increases the orientational ordering of the liquid crystal resulting in lower phase transition temperatures.

The ultrasonic velocities, densities and viscosities for CLC and mixtures are measured beyond mesomorphic-isotropic transition with proper attention near Phase transitions. From the measured values, Ultrasonic Attenuation and Acoustic Relaxation Time at a given temperature are calculated using formulae 3 and 4 respectively. Both the ultrasonic parameters are measured for the CLC in the neat state as well as in the doped state.

Table 1: Phase Transition Temperatures

| Sample   | Heating PTT °C | ΔH J/g | Cooling PTT °C | ΔH J/g |
|----------|---------------|--------|----------------|--------|
| CLC      | 45.19         | -8.44  | 34.09          | 0.08   |
|          | 71.49         | -13.91 | 76.05          | 0.64   |
|          | 79.12         | -0.45  | 84.59          | -0.28  |
|          | 84.59         | -0.35  |                |        |
| CLC+NP   | 70.23         | -9.13  | 33.21          | 0.07   |
| PDCLC1   | 44.88         | -3.99  | 44.88          | -0.37  |
|          | 71.38         | -18.28 | 77.21          | 0.40   |
|          | 78.61         | -0.59  | 83.01          | 0.28   |
|          | 84.15         | -0.34  |                |        |
| PDCLC2   | 70.84         | -63.63 | 42.61          | -0.12  |
|          | 78.49         | -1.86  | 76.64          | 0.31   |
|          | 84.02         | -1.23  | 77.21          |        |

Figure 3. Viscosity vs Temperature (a) For CLC (b) For CLC+NP
Figure 4. Ultrasonic Attenuation vs Temperature (a) For CLC (b) For CLC+NP

Figure 5. Acoustic relaxation Time vs Temperature (a) For CLC (b) For CLC+NP

Figure 6. Acoustic relaxation Time vs Temperature (a) For PDCLC1 (b) For PDCLC2
From Figures 3 to 8 it is evident that viscous forces play a dominant role in the relaxation process.

Viscosity which is the measure of cohesiveness or rigidity present between the ions or ion-solvent or solution, contributes in a significant way to the absorption and is indicated in the measurements of acoustic attenuation and the relaxation time.

The Viscosity, Ultrasonic velocity and density show variation with change in the material as well as temperature. The viscosity values for the samples except CLC + NP at 30°C are of the order $10^{-9}$. In the temperature range of 55°C to 80°C, these values vary from $10^2$ to $10^5$. Hence for plotting the graph, the temperature range is restricted to 55°C to 80°C for all the samples except CLC+NP.

The viscosity, acoustic relaxation time and ultrasonic attenuation decrease with increase in temperature for CLC and CLC+NP. The parameters of PDCLC2 in comparison with PDCLC1 are more linear in isotropic and anisotropic regions. For PDCLC2 the values reach maximum value at the Cholesteric-isotropic transition.

As an ultrasonic wave propagates through a material, the energy of directed motion of material particles in an acoustic wave is transferred to internal degrees of freedom due to the recovery of thermodynamic equilibrium. As a result, the energy of a wave reduces as it spreads in the material. The speed of sound depends also on dissipative processes in the material. The energy exchange between vibrational and rotational degrees of freedom and the translational energy of directed motion, the excitation of motion of side macromolecule chains and of their individual segments of various lengths, are among the basic representative mechanisms of acoustic relaxation in Liquid Crystals. A relaxation process is usually characterized by acoustic relaxation time which is the time interval it takes for a parameter of the material which has experienced deviation from its thermodynamical equilibrium value to be equilibrated.

6. Conclusion

The present paper focuses on the relaxation process in CLC and mixtures. We observed that the viscous forces play important role in the relaxation process. Acoustic relaxation time which characterizes the process was found to be dependent on the material as well as temperature. Doping CLC with monomers or NP affects the molecular orientation in the sample which affects the relaxation process.

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