Study of properties of pure and nanoparticle doped Cholesteric liquid crystal

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ABSTRACT

This paper examines the effect of silver nanoparticles on optical behavior and acoustical parameters of Cholesteryl Pelargonate. The ultrasonic attenuation and relaxation time is evaluated by measuring velocity of sound passing through samples at 1MHz with an ultrasonic interferometer at various temperatures. The wavelength dependence of birefringence of Cholesteric liquid crystal (CLC) and its nanocomposites is determined with hollow prism method at room temperature. The phase transition temperatures and clearing temperatures are determined with an optical polarising microscope. In order to understand their molecular dynamics and optical transmission capabilities, the acoustical parameters were measured. A small weight percent of silver nanoparticles has significantly increased the ultrasonic attenuation, relaxation time and birefringence of CLC material. The ultrasonic attenuation and relaxation time of nanoparticle doped cholesteric liquid crystals decreases with the increase in the concentration of nanoparticles in it. The blue phase temperature range of CLC material is broadened with the dispersion of silver nanoparticles.

Keywords: birefringence, cholesteric liquid crystal, hollow prism, nanoparticle, refractive indices, ultrasonic interferometer, ultrasonic attenuation, relaxation time

1. INTRODUCTION

Liquid crystal states are intermediate in structure and symmetry between the crystalline state and amorphous liquid state. A cholesteric liquid crystal is a thermotropic liquid crystal with a helical structure. Due to the helical structure, CLC possesses distinct physical and optical properties, which play an important role in practical applications. The physical and optical properties of liquid crystals are sensitive to external perturbation. They show modulation with the application of an external electric field, magnetic field, and addition to dopant impurities. The physical properties of liquid crystal materials are greatly affected by the strength of intermolecular forces. The study of ultrasonic waves and thermo-acoustical parameters provides information regarding the nature and strength of forces existing between the molecules, Liquid crystal materials are optically anisotropic and have variable refractive indices in different directions. Optical anisotropy or birefringence is the term used to describe the difference between refractive indices (RIs) of ordinary and extraordinary light beams. The molecular parameters of liquid crystal material constant, order parameter, molecular polarizability, average refractive index, and optical dispersion are connected to the anisotropy of their optical properties. Understanding internal molecular forces, molecular order, and orientation orders in the LC is aided by measuring the RI at different temperatures and wavelengths[1]. The birefringence of LC materials depends on both temperature and wavelength. These characteristics are required for the application of CLCs in displays and optical devices. Optical anisotropy is the most basic and important property that can be enhanced in liquid crystal mixtures for applications in thin-film technology, optical fibers, and display devices[2-4].

Ultrasonic waves, when propagating through material, displace fundamental particles and chain segments about their mean position, creating a series of rarefactions and compressions in the material and changing the modulus of elasticity. As the wave propagates, it suffers various types of losses and it results in its intensity. The variation of sound energy through the sample thus provides information about the molecular interaction existing in the material, durability and mechanical strength.The ultrasonic study of material is based on the velocity of sound and ultrasonic attenuation. The acoustic velocity is measured by measuring the velocity of sound traveling through the sample with an ultrasonic interferometer. The relaxation time and ultrasonic attenuation are determined with the value of the velocity of sound. The acoustical parameters are evaluated for the characterisation of the samples [5-6].

Recently, composite materials fabricated from nanoparticles (NPs) doped liquid crystals have attracted scientific and technological attention. The connected analysis has shown that dispersion of low concentration of nanoparticles in LC has considerably enhanced the optical and physical properties of liquid crystals and therefore the ensuing nanocomposites exhibit new electro-optical and thermodynamic properties. Jeng, Shie-Chang, et al (2007),Pathak, G., et al. (2018), Pandey, Abhay S., et al.(2011),Singh, U. B., et al.(2013). Mandal, Pradip Kr, et al. (2012),[7-11] have reported improved switching characteristics and reduced spontaneous polarization of ferroelectric liquid crystal mixture LAHS 9 when doped with silver nanoparticles. Mishra, Mukesh, et al. (2015)[12] have reported a decrease in the clearing temperature of nanocomposite systems as compared to the pure liquid crystal. Mani, Santosh, et al. (2020) [13] reported enhancement in dielectric and acoustical properties when a ferroelectric Nano powder of Barium Titanate ($BaTiO_3$) was dispersed in a cholesteric liquid crystal. Liquid crystals (LCs) are extensively used in a variety of optical devices because of the optical anisotropy of refractive indices. The desired birefringence of liquid crystal mixtures for various technological applications can be obtained by the proper selection and concentration of the dopants. Researchers have reported an increase in the birefringence of liquid crystal solutions by the addition of nanoparticles. Li, Xiaoping, et al. (2013) [14] have proposed a theoretical approach to enhance the birefringence of liquid crystals by dispersing metallic nanoparticles. Vardanyan, et al. (2011) [4] proposed enhanced optical birefringence in nematic nanocomposites dispersed with gold nanoparticles. High birefringence liquid crystals have many applications both in display devices as well as in non-display devices such as phase modulators, photonic devices, and beam steering effects in liquid crystals [6,15].

In this paper, the effect of the addition of silver nanoparticles (Ag NPs) on the acoustic and optical properties of Cholesteric Pelargonate with varying temperatures has been reported.

2. MATERIALS AND METHODS

The Cholesteryl Pelargonate (purity 97%) and silver nanoparticles (size less than 100 nm) were procured from Sigma Aldrich and were used as received without any further treatment. In our research work, the nanocomposites of cholesteric liquid crystals were prepared by adding a small weight percentage of silver nanoparticles (1%wt, 3%wt, and 5%wt) in the Cholesteryl Pelargonate. Silver nanoparticles were dissolved in ethanol and were ultra-sonicated for about an hour to obtain homogeneous dispersion. The slow evaporation of the solvent (C_2H_5OH) resulted in the formation of desired nanocomposites. A homogeneous solution of CLC and nanocomposites is obtained by dissolving the CLC and NPs in Toluene (T). The samples prepared for the various characteristics are labelled as follows.

S1: T + CP

S2: S1+1%wt Ag NPs

S3: S1+3%wt Ag NPs

S4: S1+5%wt Ag NPs

An ultrasonic interferometer with a constant temperature water bath was used to measure the ultrasonic velocities of the samples by varying the temperature from room temperature to clearing temperature of the samples. The measurement of ultrasonic velocity was done at a constant frequency of 1MHz. The acoustic velocity is used to obtain the viscosity of the samples. The acoustical parameters, ultrasonic attenuation, and relaxation time were evaluated using theoretical formulae at various temperatures [5].The refractive indices of cholesteric liquid crystal and nanocomposites dissolved in toluene were measured for three wavelengths and at room temperature with the hollow prism method correctly up to four decimal places. In Hollow prism method, the angle of minimum deviation method is used to obtain the refractive indices of the samples. Birefringence is obtained as the difference between the refractive indices of extraordinary and ordinary rays [2]. The morphological identification and the phase transition temperatures of the cholesteric liquid crystal nanocomposites were recorded with an optical polarising microscope equipped with a hot stage, infrared temperature sensor, and camera. The acoustical parameters and phase transition temperatures (PTTs) of nanoparticle-doped CLC are compared with that of the pure CLC [13].The surface tension and viscosity of the samples are calculated theoretically with statistical approach using the acoustic velocity measured with ultrasonic interferometer [6].

3. RESULTS AND DISCUSSION

The variation of ultrasonic attenuation and relaxation time of the samples with temperature is shown in Figures 1 and 2 respectively.

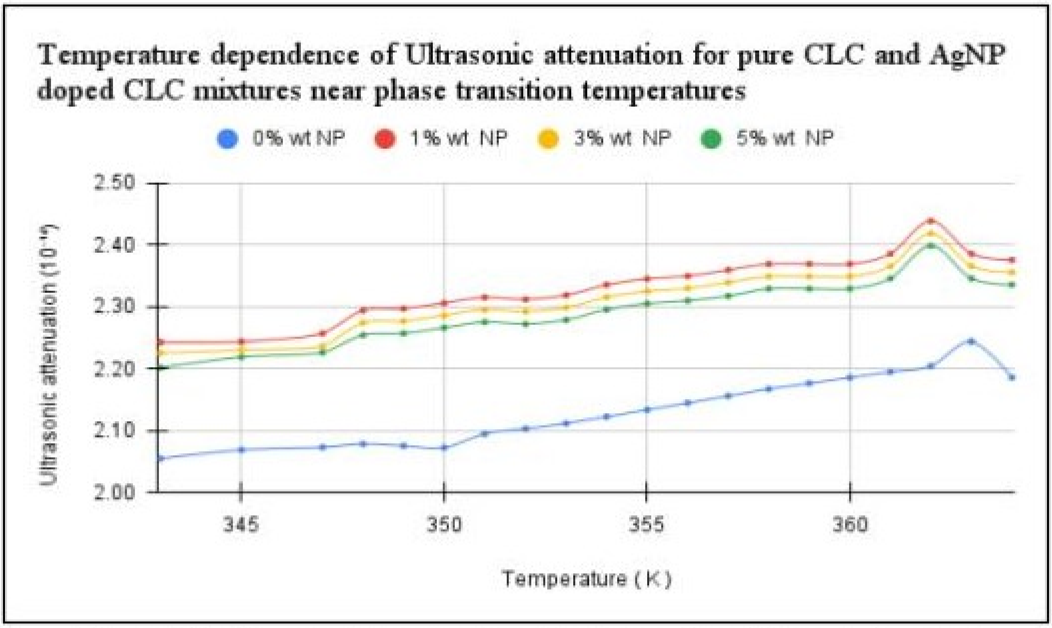

Figure 1. Variation of ultrasonic attenuation of samples with temperature and concentration of silver nanoparticles in CP

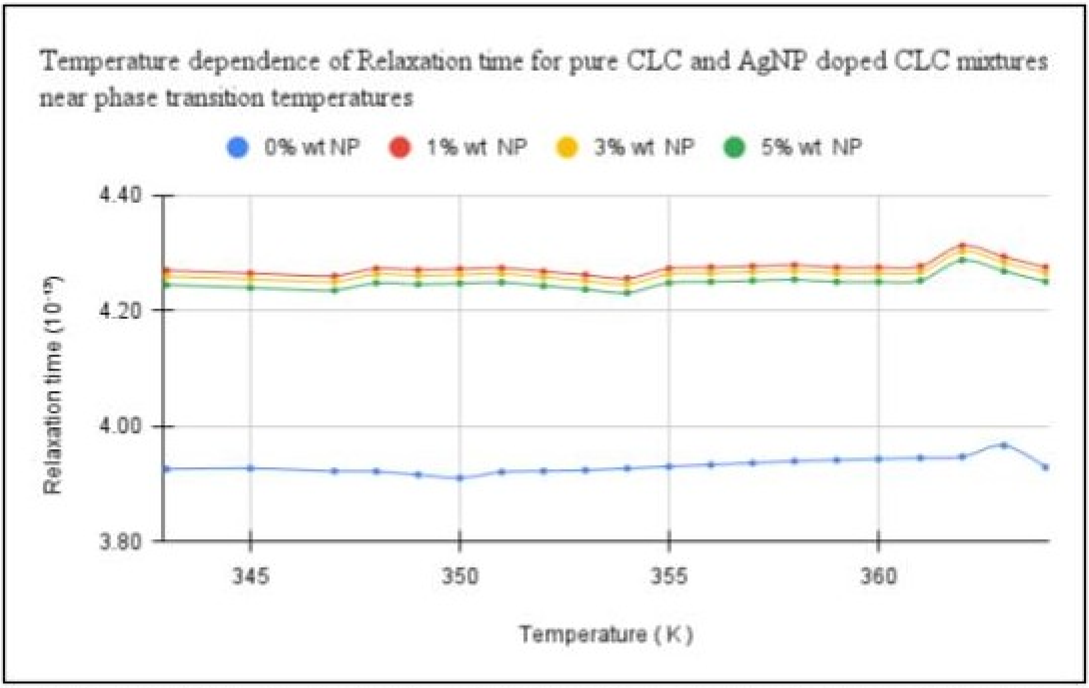

Figure 2 Variation of Relaxation time of samples with temperature and concentration of silver nanoparticles in CP

The experimental data shows that the addition of a small amount of nanoparticles in CLC has increased the ultrasonic attenuation and relaxation time in the system. The ultrasonic waves through LC mixtures alter the orientation of molecules in solutions, which alters the intensity of transmitted signal. The addition of nanoparticles alters the elastic properties of liquid crystal material, which results in an increase in ultrasonic attenuation and relaxation time. The percentage increase in the ultrasonic attenuation and relaxation time for 1wt %, 3wt %, and 5wt % Ag nanoparticle doped liquid crystal samples at room temperature are 7.78, 7.48 6.38, and

8.17, 8.07, and 7.70 respectively. The increase in the ultrasonic attenuation of liquid crystal nanocomposite is considerably due to the scattering losses of the structurally heterogeneous system .The increase in the relaxation time may be due to the dipole orientations of LC molecules due to the addition of silver NPs in pure Cholesteryl Pelargonate [16].

The phase transition temperatures of CLC and nanocomposites obtained with an Optical polarising microscope are mentioned in Table 1. The birefringence and average refractive indices of various samples are given in Table 2. The textures of sample S3 during the heating and cooling cycle is shown in Figure 3.

Table 1: Phase Transition Temperatures of LC samples (in Kelvin)

	CP	CP+1%wtAgNP	CP+3%wtAgNP	CP+5%wtAgNP
Heating cycle	347.2, 350.5,352, 365.4	347.2, 350.9,352.5, 362.2	347.8, 350.8, 352.5, 360.6	347.9,350.9,352.5, 360
Cooling cycle	363, 353, 349	360.8, 353.4,352.3, 350	359.2, 353.5, 352, 350.3	359,353.5,352,350.3

Table 2 Refractive indices, average refractive index, and birefringence of nanoparticle doped liquid crystal solutions

Wavelength	$n_{\parallel}$	$n_{\perp}$	Δn	<n>
T+0.1g CP				
440 nm	1.5398	1.5247	0.0151	1.5297
540 nm	1.5300	1.5072	0.0228	1.5148
580 nm	1.5296	1.5041	0.0255	1.5126
T+0.1g CP+1%wt Ag NP				
440 nm	1.5424	1.5263	0.0161	1.5317
540 nm	1.5332	1.5076	0.0256	1.5161
580 nm	1.5314	1.5044	0.0271	1.5134
T+0.1g CP+3%wt Ag NP				
440 nm	1.5368	1.5204	0.0164	1.5259
540 nm	1.5281	1.5027	0.0253	1.5112
580 nm	1.5258	1.4997	0.0261	1.5084
T+0.1g CP+5%wt Ag NP				
440 nm	1.5372	1.5186	0.0186	1.5248
540 nm	1.5274	1.5016	0.0258	1.5102
580 nm	1.5259	1.4983	0.0276	1.5075

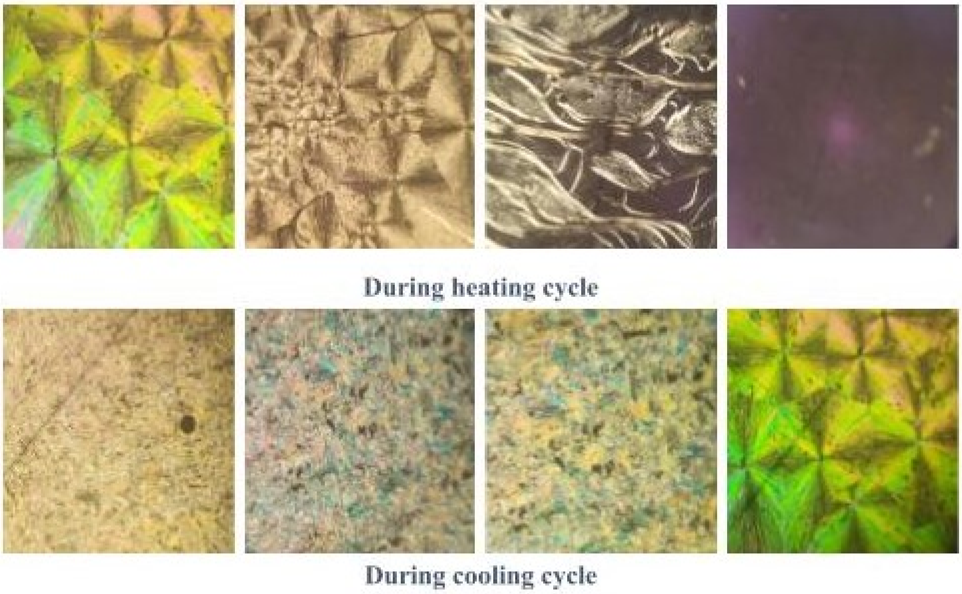

Figure 3. Texture of sample 1wt% of Ag NP in CP

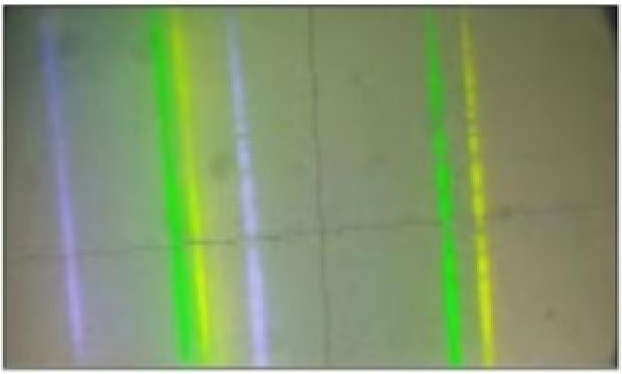

Fig. 4 Optical anisotropy of sample T+0.1gCP

The analysis of the texture of samples indicates that the dispersion of small quantities of silver nanoparticles in CP maintains the phases of pure cholesteric liquid crystal with a decrease in clearing temperature. When the temperature is increased, all samples exhibit a fixed sequence of various phases: Crystalline-Smectic-Cholesteric--Isotropic. On cooling the samples, the sequence of phases seen were: Isotropic, cholesteric, blue phases, smectic, and crystalline. It was observed that the range of the blue phase of the CLC nanocomposite during the cooling cycle is widened up to 45C. The melting point is nearly the same for each sample of about 74 C and there is a decrease in the clearing temperature of the nanocomposite. The percentage increase in the birefringence is more for sample CP+5wt%AgNP and is 22.7%, 13.25%, and 8.25% for blue, green, and yellow colors respectively. The range of the blue phase is widened up to room temperature for nanocomposites of CLC during the cooling cycle. The interaction between the CLC molecules and nanoparticles has increased the Birefringence, Relaxation time, and Ultrasonic attenuation significantly. The addition of a small amount of NP in CLC has increased the orientation order of LC molecules which resulted in a decrease in the clearing temperature. The enhanced birefringence of the CLC materials doped with nanoparticles is due to the improved alignment in the CLC matric.

Equations :

The various equations used to obtain the acoustical parameters in SI units are given below[17]**.**

1) Relaxation time (τ)

$$\tau = \frac{4\eta}{3\rho v^2} \qquad [1]$$

2) Ultrasonic attenuation (α/f^2)

$$\frac{\alpha}{f^2}=\frac{8\pi^2}{\rho v^3} \qquad [2]$$

3) Viscosity (η)

$$\frac{\eta}{S}=\frac{16}{15}\sqrt{\frac{M}{RT}} \qquad [3]$$

4) Surface tension (S)

$$v=\left(\frac{S}{6.3 \times 10^{-4} \times \rho}\right)^{\frac{2}{3}} \qquad [4]$$

where η is the viscosity
v is the velocity of sound=λ f=2df
λ is the wavelength of acoustic wave
f is the frequency of acoustic wave
d is the distance between adjacent maxima or minima anode current
S is the surface tension
M is the molecular mass
T is the temperature in kelvin
R is the universal gas constant
ρ is the density of LC solution

4. CONCLUSION

Optical studies show decrease in clearing temperature of liquid crystal nanocomposites as compared to pure Cholesteric liquid crystal. Addition of nanoparticles shows enhancement in birefringence, relaxation time, and ultrasonic attenuation of pure Cholesteric liquid crystal. Blue phase range for samples doped with small wt% of Ag nanoparticles in CLC solution is widened from 85C to 45C during cooling cycle. Enhancement of parameters has been explained based on molecular interaction between liquid crystal molecules and nanoparticles. Refractive indices of ordinary and extraordinary rays decrease with increase in wavelength of light and are in accordance with Cauchy’s empirical formula.

Analysis shows that dispersion of low concentration of nanoparticles in CLC has considerably enhanced properties of LCs and resulting nanocomposites exhibit new electro-optical and thermodynamic properties that may provide new dimensions in development of optical devices, photonic materials and electronic devices. High birefringence liquid crystals have applications both in display as well as in non-display devices such as phase modulators, photonic devices, and beam steering effects in liquid crystals. Acoustical study of liquid crystals finds applications in ultrasound imaging, characterisation of material, and liquid crystal displays. Wide temperature range of blue phase generated in cooling cycle of nanoparticle doped cholesteric liquid crystals may be utilised to produce flexible blue phase sheet with potential applications in flexible reflecting displays, lasers, and sensors. Technique of doping CLC with small quantity of suitable NPs can be used to modify material properties. Modified characteristics of CLC play important role in designing new materials and optical fibre technology.

5. REFERENCES

1. Singh, Shri. Liquid crystals: fundamentals. World Scientific, 2002.
2. Kanwar, Anita, and Priya S. Yadav. "Experimental Verification of Vuks Equation Using a Hollow Prism Refractometer." Journal of Atomic and Molecular Physics 2012 (2012).
3. Chandel, V. S., R. Manohar, and J. P. Shukla. "Refractive indices, order parameter and density study of BKS/B07 nematic liquid crystal." Analele Universitatii in Bucuresti Chime 20 (2011): 155-163.
4. Vardanyan, Karen Kolya, Ethan Daniel Palazzo, and Robert Dominic Walton. "Nematic nanocomposites with enhanced optical birefringence." Liquid Crystals 38.6 (2011): 709-715.

5. Rita, Gharde, and G. Bhave Manisha. "Ultrasonic Study of Polymer Dispersed Liquid Crystal." International Symposium on Ultrasonics. Vol. 22. No. 24. 2015.
6. Singh, Jatinder Pal, and Rajesh Sharma. "Viscosity variation of Cholesteryl oleyl carbonate at various temperatures with Acoustic parameters." IOSR Journal of Applied Physics 3 (2013): 88-91.
7. Jeng, Shie-Chang, et al. ``Nanoparticles-induced vertical alignment in liquid crystal cell." Applied physics letters 91.6 (2007): 061112.
8. Pathak, G., et al. "Analysis of birefringence property of three different nematic liquid crystals dispersed with TiO2 nanoparticles." Opto-Electronics Review 26.1 (2018): 11-18.
9. Pandey, Abhay S., et al. ``Enhancement of the display parameters of 4′-pentyl-4-cyanobiphenyl due to the dispersion of functionalized gold nanoparticles." Liquid Crystals 38.1 (2011): 115-120.
10. Singh, U. B., et al. "Influence of low concentration silver nanoparticles on the electrical and electro-optical parameters of nematic liquid crystals." Liquid Crystals 40.6 (2013): 774-782.
11. Mandal, Pradip Kr, et al. "Sub-hertz relaxation process in chiral smectic mixtures doped with silver nanoparticles." Applied Physics Letters 100.7 (2012): 073112.
12. Mishra, Mukesh, et al. "Electrical and electro-optical parameters of 4′-octyl-4-cyanobiphenyl nematic liquid crystal dispersed with gold and silver nanoparticles." Liquid Crystals 42.11 (2015): 1580-1590.
13. Mani, Santosh, et al. ``Effect of Ferroelectric Nanopowder on Electrical and Acoustical Properties of Cholesteric Liquid Crystal." Non-Metallic Material Science 2.1 (2020).
14. Li, Xiaoping, et al. "Enhanced birefringence for metallic nanoparticle doped liquid crystals." Optics Communications 286 (2013): 224-227.
15. Anita Kanwar, Gupta Sureshchandra J ``Study of PDCLC materials using Fabry Perot Scattering technique” (Journal of optics, Jan-March- 2007, Vol. 36, No. 1, Pages 31-37).
16. Manisha, Bhave, and Radha Srinivasan. "Effect of ferroelectric nanopowder on intermolecular free length of cholesteric liquid crystal." Materials Today: Proceedings 3.10 (2016): 3939-3944.
17. Kulkarni, S. S., and U. V. Khadke. "Effect of solvents on the ultrasonic velocity and acoustic parameters of polyvinylidene fluoride solutions." Indian Journal of Materials Science 2016 (2016).