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Thermodynamical and optical properties of liquid crystal nanocomposites

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Abstract
We have prepared the composites of a room temperature Liquid Crystals (LCs) and Nano-Particles (NPs) and investigated their thermodynamical and optical properties. Effect of doping of Nps on various thermodynamical and display parameters on host LCs are studied.

Keywords: Thermodynamics, soft-matter, electro-optic, transition

Introduction
Liquid crystals are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a crystalline solid. For instance, liquid crystals (LCs) may flow like a liquid, but have the molecules in the liquid arranged and/or oriented in a crystal-like way [1-2]. The LCs posse's different phases which are call *mesophases*. There are many different types of LC phases, which can be distinguished based on their different physical properties (such as birefringence, dielectric). The various LC phases can be characterized by the type of ordering that is present. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientational order (whether molecules are mostly pointing in the same direction), and moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). LCs can be divided into thermotropic and lyotropic LCs. Thermotropic LCs exhibit a phase transition into the LC phase as temperature is changed and most thermotropic LCs will have an isotropic phase at high temperature whereas lyotropic LCs exhibit phase transitions as a function of concentration of the mesogen in a solvent (typically water) as well as temperature [3-5].
One of the most common LC phase in thermotropic LCs is the nematic, where the molecules have long-range orientational order, but they have no positional order. Nematic Liquid crystal (NLCs) emerges as a smart fluid for dispersion of nano structures (viz. nanoparticles, nanotubes, and quantum-dots) because of its anisotropic physical properties and elastic mediated interaction between medium and foreign objects which is promising for self - assembly of nanostructures. In addition, the nano-structures could share their intrinsic properties with the NLCs matrix due to the surface anchoring of NLCs. Hence dispersed nano-structures in NLCs could alter the properties of composites which are useful in device application. Because of this extra-ordinary property, NLCs-nanostructures composites emerge a multi-disciplinary field of research and attracted great attention of scientist from soft matter and nano-science [6-11].
In this paper we have investigated the following properties of nanoparticles dispersed liquid crystalline materials.
(i) Thermodynamical properties
(ii) Optical properties

Methodology
Following procedures are adopted to disperse the nanoparticles in liquid crystals and to carry out the most relevant physical parameters of Liquid Crystals-Nanoparticles (LC-NPs) composites.
1. To achieve high quality dispersion, NPs will be first added to organic solvents or a low concentration surfactant solution and then submitted to high power sonication. Further this solution will be added to LC to get different weight ratio composites. Mixture will be sonicated again to get uniform distribution of NPs in LC.

The other organic solvents will be removed from the mixture by evaporation.
2. The other route to get high quality dispersion will be approached by covalently functionalize the NPs according to molecular structure of LC host to make them chemically compatible.
3. Thermodynamical study of LC-NPs composites will be made on Differential Scanning Calorimeter (DSC) and the peak transition temperatures, the onset temperatures and transition enthalpies will be determined.
4. Optical textures of different composites will be monitored by using the polarizing microscope equipped with a programmable temperature controller of Instec model-HCS302 (proposed) with a temperature accuracy of ±0.1 ºC.

Thermodynamical Studies

Thermodynamical studies of the pure LC and composites have been carried out with the help of Differential Scanning Calorimeter (DSC) NETZCSH analysis software has been used to acquire and analyse the data by a programmable computer. Transition temperatures and corresponding enthalpies of various mesophases have been determined with accuracy of 0.1 °C. The temperature of the sample has been scanned at the rate of 1 K/min to 20 K/min in the heating and cooling cycles. The transition temperatures in heating and cooling cycles are found to be different due to temperature hysteresis. Hence actual transition temperature has been determined by extrapolating peak transition temperature at 0 K/min which is same in heating and cooling cycle.

Preparation of LCs Cells

Liquid crystals cells have been prepared in the form of parallel-plate capacitor by using Indium Tin Oxide (ITO) and gold-coated glass plates of dimension 3 ×4cm. The sheet resistance of used ITO plates are ~20 Ω and gold plates are less than 1.0-1.5Ω. The chemical treatment has been done for LCs alignment which is discussed below.

Planar alignment

To get parallel alignment of the samples molecules, the conducting surface of the glass plates (ITO Coated) are thoroughly cleaned with isopropyl and dried. Then the plate is dipped in silane solution (0.2% solution of phenyl-trichlorosilane in toluene) for about 10 minutes and then rinsed thoroughly in isopropyl alcohol. A film coating of polyamide nylon is now deposited on glass plate. To deposit a few hundred-angstrom thick layer of nylon polymer, a 0.5% (weight to volume) solution of nylon prepared in 60% m-cresol and 40% methanol (volume to volume) solution is used. Excess solvent is removed by heating the glass plates in oven at 130 °C for one hour. Both glass plates are rubbed unidirectionally by cotton in order to obtain planar orientation of the molecules samples sandwiched between two plates. Two Teflon strip spacers of suitable thickness (5-50 µm) are kept along the length side of the plates are closed while both breadth sides are open. Material filled in cell by capillary action at about 10 °C above transition to isotropic phase. Then it is cooled very slowly to get planar orientation.

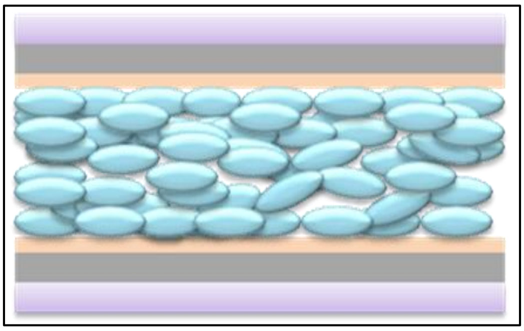

Fig 1: Planar alignment

Preparation of liquid crystals–nanoparticles composites:

We have taken small wt% of NPs like (0.01 & 0.02) and dissolved in chloroform for uniform dispersion. Now, we weighted liquid crystal host material and adding them. The composites are stirred in the isotropic phase of LCs by using a magnetic vibrator to get homogeneous dispersions.

Temperature Controller

For temperature dependence texture, dielectric and switching studies a hot and cold stage made by Instec Inco, USA has been used.

Optical Studies

Optical textures of different phases of LC-NPs have been studied on a binocular polarizing microscope of CENSICO and still photographs as well as video were recorded on the computer with the help of Aver TV software.

Fig 2(a): Optical Study Setup: Polarized Light Microscope (PM) coupled with digital Camera made by CENSICO (India).

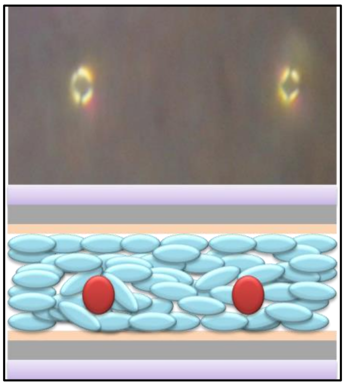

Fig 2(b): Optical Textures of different LC-NPs composites systems.

Thermodynamical and Electro-Optical properties of Nematic Liquid Crystalline Material with Gold Nanoparticles

Results and discussion

A typical plot of heat flow (mW/mg) with temperature (°C) for pure, 0.01% and 0.02% GNPs composites has been shown in Fig. 3 in the heating and cooling cycles at the scan rate of 5.0°C/min. Thermodynamical study suggest that clearing temperature i.e. nematic to isotropic transition temperature (T_{NI}) is slightly increased due to the dispersion of GNPs. According to Gorkunov and Osipov theory this is due to the anisotropic behaviour of GNPs clusters.

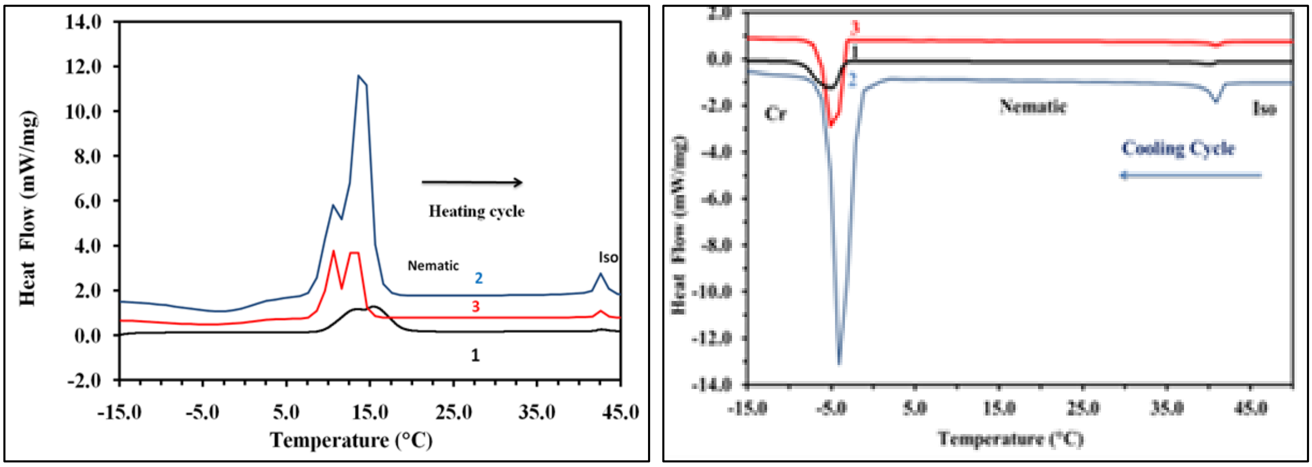

Fig 3: DSC thermograms for the heating and cooling cycles at the scan rate of 5.0 K/min for pure (curve 1) and 0.01 wt % (curve 2) and 0.02wt % (curve 3) GNPs dispersed LC.

Conclusions

- The inclusion of small amount of GNPs in the nematic matrix slightly increases nematic-isotropic transition.
- It decreases threshold voltage required for switching of molecules from planar (bright state) to homeotropic (dark state) configuration.
- The nematic ordering of host medium increased due to dispersion of GNPs which causes increasing the value of dielectric anisotropy for composite systems.

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