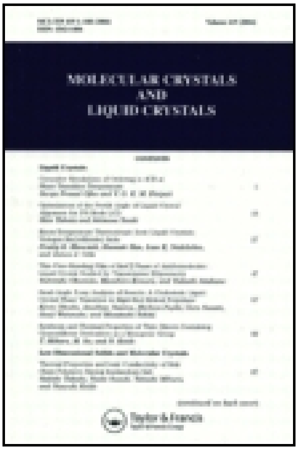

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Studies of Nano-Particle Doped Liquid Crystal Mixtures

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Liquid crystals (LCs) are rod-shaped molecules which can diffuse freely like liquid and orient themselves under the influence of electric field with the long axis of molecules pointing in the same direction. Carbon nanotubes and bucky balls are ideal LC dopants because of their strength, conductivity, flexibility and novel electrical characteristics. LCs doped with C60 show enhancement of the director axis reorientation and enhancement of its nonlinear optical properties. Refractivity of LCs can also be altered by doping nanoparticles and/or nanotubes. In this paper, the effect of the presence of nanoparticles/nao-tubes on the phase transition temperatures of the LCs and the classification of the mesophases so formed are investigated by us with the help of the textures studied under the polarizing microscope. The phase transition temperatures as well as the heats of transition of the doped LCs using various techniques are also presented.

Keywords: doped LCs; phase transition temperatures; polarizing microscope

1. INTRODUCTION

Liquid Crystals (LCs) are made up of strongly anisotropic molecules either elongated (calamatic molecule) or disc like (discotic molecule). In most cases the central part of mesogenic molecule is rigid (phenyl group) and the outer parts are flexible (say aliphatic chain). By supplying

The authors sincerely thank M/s. Merck Ltd., Japan for providing us free samples of NLC TL205 and also to Cheap Tubes, USA for free samples of MWCNT.

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energy; the orientation of the long axis of the molecule in the layer, the interpenetration of layers and distances between them can be altered.

With the discovery of carbon nanotubes in the year 1991 by Iijima many new avenues of research have opened up. Nano is a prefix that means one-billionth of something. A carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer and length up to few micrometers. This results in an essentially one-dimensional nanostructure. Typical carbon nanotubes are classified as armchair, chiral and zigzag. [e.g., zig-zag (n, 0); armchair (n, n); and chiral (n, m)]. Nanotubes can also be described as single-walled (SWNT – like a single graphene sheet, rolled up or MWNT-like a bunch of SWNT stacked one inside of another.

The properties of a substance greatly change at nanoscale. All conventional materials in principle can be obtained with a nanoscale dimension. Nanoparticles range from inorganic to organic and crystalline to amorphous particles. The above can be found as single particles, powders or liquid dispersions up to fullerenes. We used Zinc oxide nanoparticles in the present work. ZnO is group II–VI semiconductor, it has a wide range of properties and hence the applications. The properties including range of conductivity from metallic to insulating, high transparency, room temperature ferromagnetism, piezoelectricity etc. mainly depend on doping other unique merits for which it is widely studied are following: Wide band gap of 3.37 eV (applications in the area of electronics, optoelectronics), biodegradable and possibly biocompatible material (suitable for medical and biological applications). Piezoelectric and pyroelectric properties (useful for fabricating electromechanical coupled devices.)

In the present work mixtures of (1) Nematic Liquid Crystal (NLC) TL205 with Zinc Oxide (ZnO) nanoparticles and (2) TL205 with Multiwalled Carbon Nanotubes (MWCNT) in varied concentrations are studied using three different techniques. The addition of these nanomaterials alters the crystalline alignment of the LCs and changes the optical properties. Just as some materials react to an electrical current these doped LCs react to light. The axis of refraction of the doped LCs changes when exposed to light. The study of the index of refraction is of prime importance for understanding the fascinating optical properties of the liquid crystals. The colorful textures seen when observing a liquid crystal sample under polarized light microscopy result from the dependence of the speed of light on the wavelength and on the direction of the plane of polarization relative to the director [6].

1.2. Sample Details/Preparation

In this paper we have used:

1. Nematic Liquid Crystal TL205 (halogenated bi- and tri-phenyls with aliphatic tails of lengths up to two to five carbons.) [Merck] It has a great temperature stability (the range is from 78°C–91°C).
2. Zinc Oxide nanoparticles – [Nanoamor, (Texas)] of size 20 nm (99.5%), particle morphology nearly spherical, crystallographic structure hexagonal, SSA – 50 m^2/g
   It has antibacterial, antifungal, anti-corrosive properties. The catalytic and UV filteringproperties make it useful in wide areas. Another reason for using ZnO is that it is a wide band gap (3.37 eV) semiconductor that displays luminescent properties in the near ultra violet and visible regions.
3. MWCNT – Prepared by C-CVD technique, 10–20 nm Outer Diameter, length 10–30 micrometers [Cheap Tubes-USA].

In order to dope TL205 with nanotubes/nanoparticles, we first soaked it in choloroform/acetone then allowed it dry for more than 24 hrs. This is then sonicated for 10 minutes and added to TL205 This combination is then stirred using magnetic stirring method in order to achieve homogeneous dispersion.

2. EXPERIMENTAL DETAILS

A liquid crystal phase has distinct texture and Optical Polarizing Microscopy (OPM) is the most preferred technique for phase identification of liquid crystal sample. In a polarizing microscope there are two polarizing filters. The polarizer is situated below the specimen stage usually with its permitted vibration direction fixed in the east west direction although this usually can be rotated through 360°. The analyzer usually aligned in north south direction but again can be rotated through 360°. So in general both analyzer and polarizer are in the optical path and they are perpendicular to each other in other words they are said to be crossed and dark field of view is present in the eyepiece. Insertion of isotropic material does not change this because polarization of light is unchanged as it travels through isotropic material; whereas LCs normally appear bright when viewed between crossed polarizer as the polarized light makes an angle other than 0° & 90° with the director of the liquid crystal.

DTA (Differential Thermal Analysis) is a technique which is used to measure the temperature and heat flows associated with transitions in material as a function of time and temperature. Such measurement provides qualitative and quantitative information about physical and chemical changes that involve endothermic and exothermic processes or changes in heat capacity. It is generally use to corroborate the results obtained from other techniques.

Abbe Refractometer

The Refractive Index (R.I) of the material is studied using Abbe Refractometer. The operation of this instrument is based on total internal reflection (Accuracy up to Four decimal digits). The ordinary or extraordinary ray can be selected using a polarization filter in front of the eyepiece of the instrument and total reflection will occur only if the R.I to be measured is less than the R.I of the glass prism of the refractometer.

3. RESULT AND DISCUSSION

Properties of nanoparticles in itself are very unpredictable for following factors:

- Material properties can be change and become tunable by size of the constituent substance.
- Chemical reactivity of nanoscale materials greatly different from macroscopic form.
- surface of the particle starts to dominate at nanoscale as surface to volume ratio become high.
- All quantum phenomenon like tunneling effects are possible at this scale.

In spite of all the above sensitive factors we tried to incorporate nanoparticles and MWCNT in NLC with varied concentration in order to study the behavior of system as a whole. The variation observed in clearing point temperature and refractive index plot are discuss below.

I) MWCNT

1. Clearing Point temperature for TL205 + MWCNT mixture varies in the range of 85°C to 90.6°C for the concentrations at 0.5%, 1, 1.5, 2.5, 3%. A discontinuity is observed at the concentration of 2% for which the clearing temperature is 78°C (Fig. 1).
2. Refractive index of the sample steadily increases from 1.5128–1.5140 over the conc of 0.5% to 3% of MWCNT (Fig. 2).
3. The combined graph of the observations of clearing point temperature vs R.I were also studied for the same concentrations. This graph shows that the R.I in the range of 1.512–1.514 corresponds to the clearing point temperature range of 78°C to 91°C (Fig. 3).

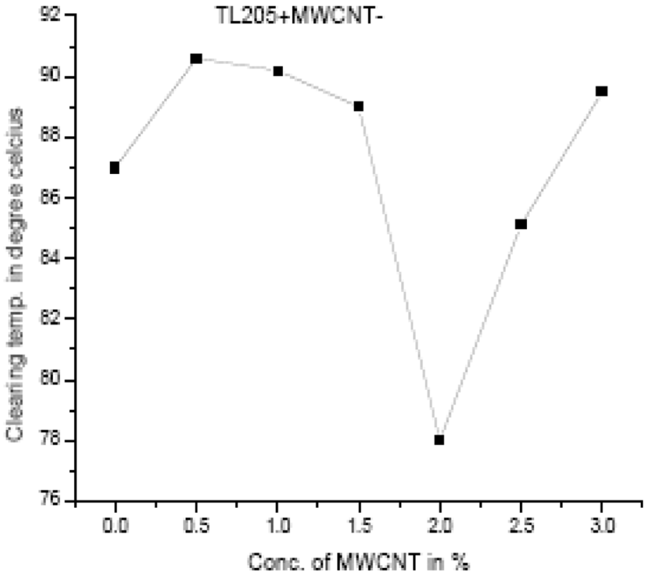

FIGURE 1 Graph of Clearing point temperature Vs % concentrations of MWCNT in TL205.

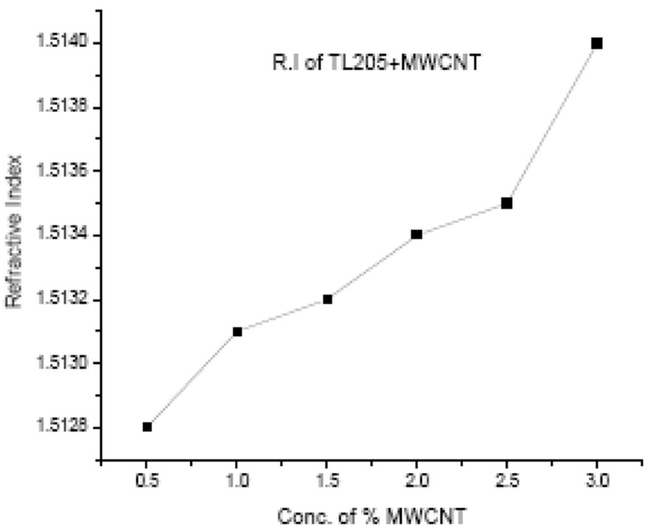

FIGURE 2 Graph of Refractive index Vs % concentrations of MWCNT in TL205.

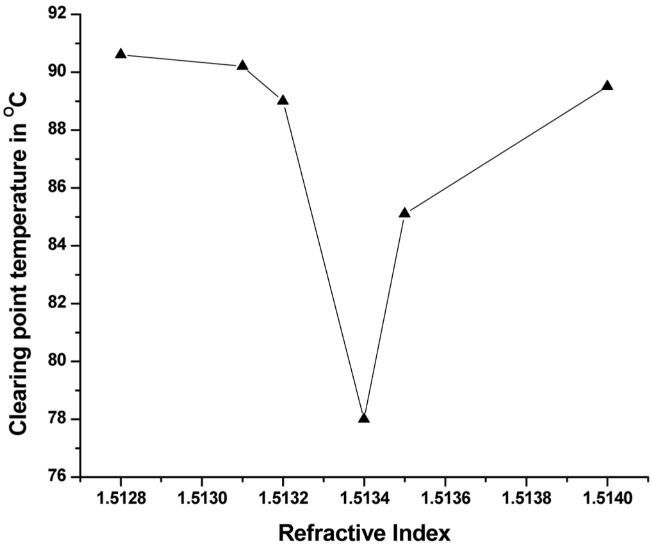

FIGURE 3 Combine graph of Clearing point temperature Vs Refractive Index for doped MWCNT samples.

For the 2% concentration of MWCNT, the clearing temperature point is at 78°C whereas for the rest of the concentration it lies between 85°C to 91°C. Hence we get a sufficient temperature range from 78°C to 91°C with negligible change (0.001) in the refractive index of the sample.

II) Zno

1. Clearing point temperature over a concentration of ZnO from 3% to 50 % lies in the range of 80°C to 88°C (Fig. 4).

   Clearing point is between 86.5°C to 88.3°C for the following ZnO nanoparticles Concentrations – [3% and 20% to 40%] whereas the clearing point for 0% and 10 to15% is between 79°C and 81.4°C.
2. The R.I of this sample is in the range of 1.5100 to 1.5135 with the difference of 0.0035 for different concentrations over the region of 3% to 50%. (Fig. 5).

   It is also found that the R.I remains constant at 1.5135 for 3%, 10%, 15% of ZnO nanoparticle. However the clearing point for the same concentrations varies from 79°C–88°C.

   These clearing point temperatures have been verified using DTA.

The LC molecule is composed of a head part with polarity, a rigid part with hexagonal rings and a tail part with alkyl groups. When CNTs are added in LC medium a vast molecular library can be formed by different

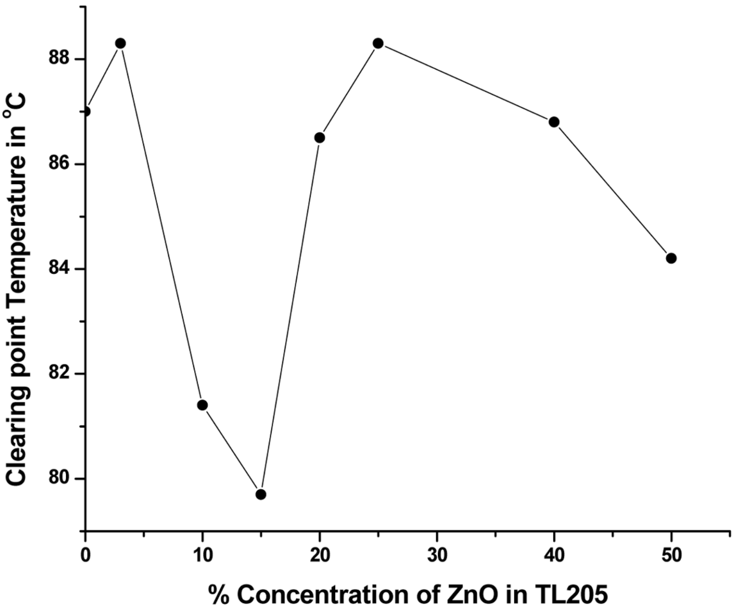

FIGURE 4 Graph of Clearing point temperature Vs % concentration of ZnO in TL205.

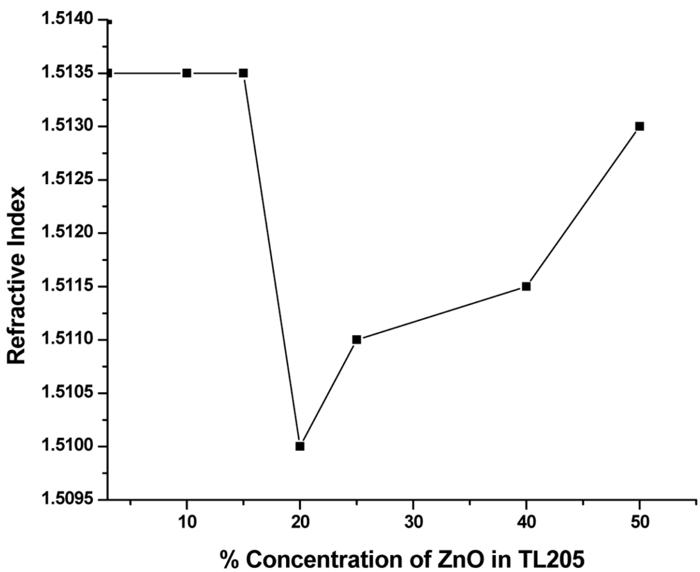

FIGURE 5 Graph of Refractive index Vs % concentration of ZnO in TL205.

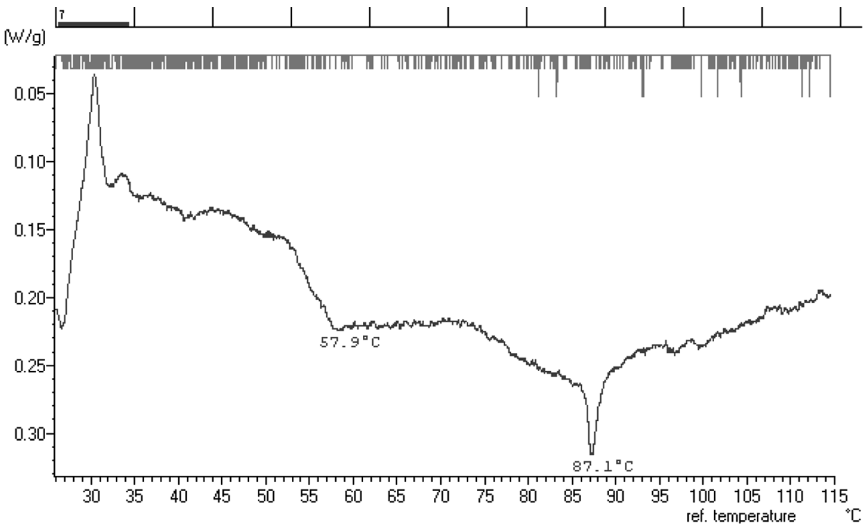

FIGURE 6 Thermogram of TL205 + 40% ZnO.

functional groups at the head part and a number of rings that seemingly induce anchoring on the CNT walls via ∏ stacking interaction [12]. which alters binding energy required to overcome the CNT-LC bonding. The variation causes is out of the bonding of the two which may be either from side walls or head part of LC molecule therefore has overall affect on the clearing point temperature of the system.

The variation observed in R.I could be because of the nanoparticle orientation with respect to LC molecule. This is one of the decisive factor in determining the R.I as scattering phenomenon is mainly depend on the mutual orientation, the more they are in align with respect to each other less scattering and hence lesser value of Refractive Index.

Some of the textures observed using Optical Polarizing Microscopy are reproduced below.

Similarly the DTA curve corresponding to 40% of ZnO is shown below (Fig. 6). The clearing point temperature obtained so is in good agreement with the value obtained from OPM as shown in Figure 4.

4. CONCLUSION

So in materials where strong chemical bonding is present delocalization of valance electrons can be extensive. The extent of delocalization can vary with the size of the system. This is yet another structural effect due to the addition of MWCNT and ZnO. The change in the R.I

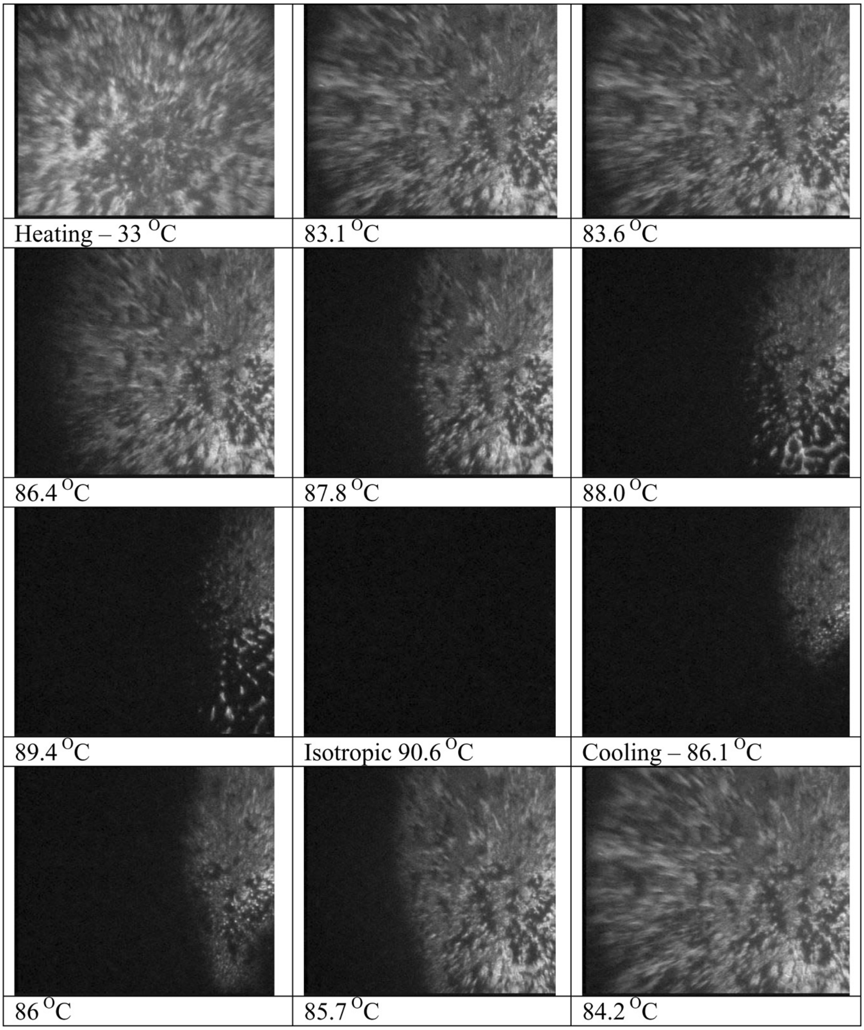

FIGURE 7 PMS images of [(TL205) + 40% of ZnO nanopracticles] at various temprature.

and clearing point temperature owe to Structural effects arising out of nanoconfinement also the surface effect dominates nanomaterials as compared to bulk effects. The possibility of agglomeration of nanoparticles with it's increasing percentage concentration can not be completely denied. The inclusion of MWCNT in TL205 has alter the binding energy required to overcome the CNT-LC bonding. The variation causes is out of the bonding of the two which may be either from side walls or head part of LC molecule Therefore has over all affect on the clearing point temperature of the system.

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