NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2013, 4 (3), P. 425–429

COMPOSITES OF SINGLE WALLED CARBON NANOTUBES AND LIQUID CRYSTALS AS SWITCHABLE CONDUCTORS

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PACS 61.30.-v, 64.70.mj, 52.25.Mq, 77.84.Nh, 81.07.De

Realizing large anisotropic electrical conductivity in systems wherein the magnitude of the anisotropy can be switched and controlled by employing an external field such as magnetic, electrical or optical fields is of significant interest. The large electrical conductivities possible with carbon nanotubes (CNT) have been combined with the field-switchable orientation of liquid crystals (LC), although the stabilization of such composites is a difficult proposition. Recently we have performed measurements over reasonable lengths of time where the LC-CNT composites are stable without any serious segregation. Here, we describe the results of electrical conductivity, which establish that the LC-CNT composites have a bright future in applications using switchable electrical insulator-conductor devices, for example Mott insulator-conductor systems. The added advantage, as a result of LC use, is the phenomenal ease with which large scale devices can be fabricated. The present work also discusses possible methods for increasing the loading factor, which currently is quite low.

Keywords: carbon nanotube, liquid crystals.

1. Introduction

The research and development of nano materials in science and technology have received significant interest over the past decade [1–4]. From different dimensions, carbon nanotubes (CNT) and liquid crystals have established their own niches, owing to many interesting properties, and a few similarities. Composites of the two materials are expected to yield extraordinary properties, especially with the combination of switchability arising from liquid crystallanity, and the large mechanical and electrical anisotropy of CNTs. The anisotropy of the electric conductivity, being large along the tube axis and small perpendicular to it, has led to proposals of nano-tubes being used in the fabrication of electronic devices [5–8]. Carbon nanotubes occur in two general morphologies, single-wall (SWNT) and multi-wall nanotubes (MWNT), and are normally produced by the techniques of arc-discharge, chemical vapor deposition, or laser ablation [9–11]. For many applications, a uniform alignment of CNTs is essential, and in general, the ability to provide nanotubes in a predetermined direction is of great importance. Additionally, it is desirable to be able to manipulate this direction, for example, by the application of external fields, such as electric, magnetic, or mechanical. Liquid crystals (LC) are anisotropic fluids, located between the isotropic liquid and three-dimensional positionally ordered solid states [12]. Due to molecular self-assembly, LCs exhibit orientational order of e.g., rod-shaped molecules, resulting in anisotropic physical properties while maintaining flow properties in their least ordered structure — the nematic phase. The average direction of the long molecular axes called the director n, can easily be controlled by suitable surface treatment or external fields. The phenomenon of reorientation when achieved with an electric field, known as the Freedericksz transition [13], is exploited in all common LCD applications from cheap wrist watches to highly sophisticated laptop displays. Attempts have been made [14–20] to employ liquid crystals for imposing alignment on dispersed carbon nanotubes, and to use the Freedericksz transition to manipulate the alignment direction through elastic interactions with the liquid crystal director field. This approach makes it possible to dynamically and collectively change the orientation of nanotube assemblies, and thus, their direction of mechanical and especially electrical anisotropy.

2. Experimental

For the experiments, two liquid crystal compounds were chosen, one of which (labelled SPLC) is strongly polar, having a nematic (N) to isotropic (I) transition temperature (T_{NI}) at 35 ° C. The other liquid crystal (WPLC) is weakly polar and has a much higher T_{NI} at 123.8 ° C. Both compounds have a positive dielectric anisotropy $\Delta\varepsilon$ (= $\varepsilon_{\|}-\varepsilon_{\perp}$, where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ indicate the dielectric permittivity parallel and perpendicular to the nematic director). The CNT which were used were procured from Heji and had an average length of 500 nm and diameter of 2 nm. Several LC-CNT composites comprising low (<0.1wt%) CNT concentrations were prepared. However, we present here the results obtained for a representative mixture with 0.05wt% concentration. A novel method for preparing the mixture, similar to that previously described [19] was employed. The procedure used resulted in the prepared composites appearing slightly darker in color than pure LCs materials with no CNT sedimentation, a problem seen generally with LC-CNT mixtures. The samples were placed in prefabricated Indium Tin Oxide coated glass cells with an electrode dimension of 0.5 cm × 1 cm and a cell gap of 25 μm through capillary action in the nematic phase. The cell was then observed under a polarizing optical microscope in the crossed polarizer configuration to ascertain the uniform dispersion of CNT. For dielectric and conductivity measurements, the cell was kept inside a homemade heater and placed between the poles of an electromagnet with a maximum field of 1.6 T. The orientation of the cell normal being parallel or perpendicular to the maganetic field direction yields ($\sigma_{\|}$,$\varepsilon_{\|}$) or ($\sigma_{\perp}$,$\varepsilon_{\perp}$).The measurements were carried out using an impedance analyzer(HP 4294A) at five different frequencies spanning 100 Hz – 1 MHz.

3. Results and Discussion

Figures 1 (a) and (b) depict the temperature dependence of conductivity in $\|$ and $\perp$ directions for SPLC as well as WPLC along with their CNT-composites obtained, at a frequency of 1 kHz. The composites with both LC materials exhibited significant enhancement of the conductivity upon the addition of CNT. The magnitude of the enhancement is about 2 orders of magnitude for SPLC, whereas it is a further one order higher with the WPLC compound. The anisotropy in conductivity was retained in the composites. Furthermore, for the SPLC composite there was a 2.5-fold increase in the ratio $\sigma_a = \sigma_{\|}/\sigma_{\perp}$ with respect to that of the pure material. The WPLC case had the opposite behavior, with the ratio σa being roughly halved for the composite [For purposes of better comparison, the data in the isotropic phase obtained with the two orientations have been matched]. In fact, σa values less than 1 are known to be associated with the appearance of smectic ordering or 1-dimensional periodicity parallel to the director. Since it is clear from microscopic observation that the system remains in the nematic phase, this feature suggests that the additional ordering is only short range. Detailed measurements for mixtures with different concentrations as well studies such as XRD are being planned to understand the difference in the behavior between SPLC and WPLC composites.

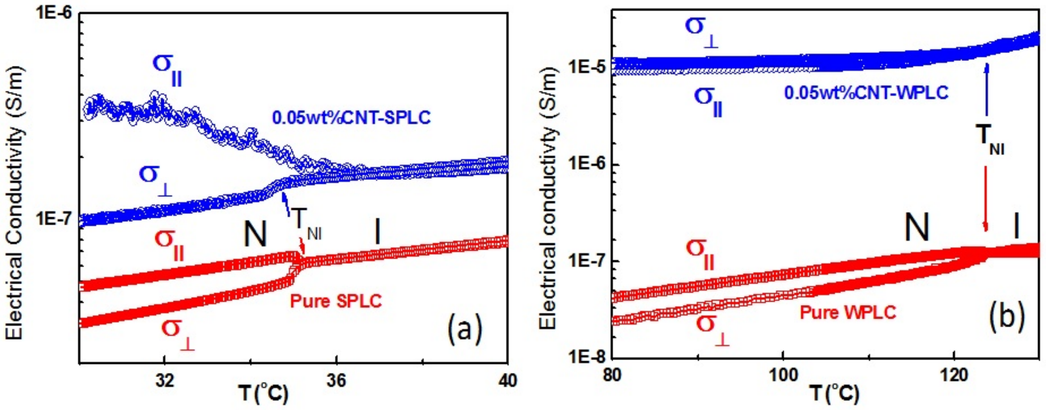

Fig. 1. Electrical conductivity at 1KHz as a function of temperature || and ⊥ to the nematic director for pure and composites of (a) SPLC and (b) WPLC materials

Figures 2(a) and (b) present the thermal behavior of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ for both pure compounds and their composites. In these cases the addition of CNT resulted in a significant increase in both $\varepsilon_{||}$ and $\varepsilon_{\perp}$ as well in the permittivity of the I phase. However, the magnitudes of increases were definitely dependent on the polar nature of the host material: for SPLC the increase for the isotropic permittivity was $\sim 25\%$, but for WPLC, the value was tripled. A possible reason for the amplified change in WPLC value could be connected with the low frequency dielectric relaxation that the pure WPLC exhibits. Further study of director relaxation dynamics is expected to shed more light on this feature.

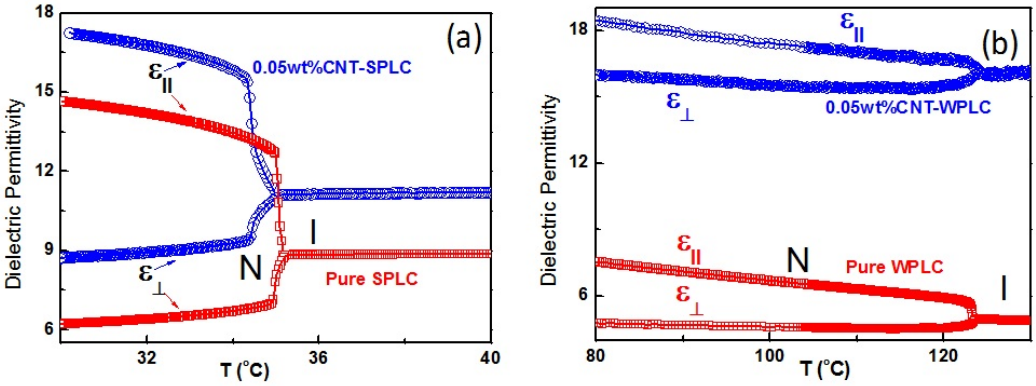

Fig. 2. Thermal variation of the dielectric permittivity at 1 KHz along (||) and perpendicular (⊥) to the director for pure and composites of (a) SPLC and (b) WPLC

Another interesting aspect observed is the temperature dependent permittivity behavior in the I phase of the strongly polar material. The pure material exhibits a concave shaped anomaly (CSA) that has been argued to be associated with the antiparallel arrangement of the molecules even in the I phase, but in the vicinity of T_{NI}. It is observed that the temperatures at which the anomaly has a maximum and the highest ε value obtained are larger for the SPLC composite than for the pure SPLC compound. We propose that this is a direct indication of the enhancement of the nematic-like short range order in the

I phase resulting from the presence of CNT particles. Since CSA is not seen for even the pure WPLC, it is not possible to compare the effects between the two types of composites.

Preliminary studies indicate that the composites of both types can be switched using an electric field, causing a reorientation of the nematic molecules. The notable changes in conductivity between the parallel and perpendicular directions for the SPLC composite makes it attractive for possible use in electrically-controlled conductivity altering devices. Development of systems in which the conductivity change is substantially higher than seen here would make the LC-CNT composites quite attractive.

4. Conclusions

We have reported anisotropic electrical conductivity and dielectric permittivity studies on two liquid crystals and their low concentration composites with SWCNT. The two liquid crystals are chosen such that one of them is strongly polar having its dipole moment parallel to the long axis of the molecule whereas the other one is weakly polar with its dipole in the transverse direction. Both conductivity and permittivity retained their anisotropic nature, even in the composites. More importantly, the conductivity exhibited a large increase, as much as 3 orders of magnitude, for the composite with the weakly polar material. The qualitative permittivity behavior was also quite different upon the inclusion of CNT. Along with the mentioned switchable electrical character, which imparts a field-modifiable conductivity value, these materials are quite promising for inclusion in future electronic devices.

Acknowledgments

The financial support by SERB, DST under the project No. SR/S2/CMP-0029/2011 is gratefully acknowledged.

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