

Possible enhancement of physical properties of nematic liquid crystals by doping of conducting polymer nanofibres

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We report on the preparation and physical characterization of the colloidal suspension of conducting polyaniline (PANI) nanofibres and a nematic liquid crystal (5CB). The ac electrical conductivity anisotropy increases significantly and the rotational viscosity decreases with increasing wt. % of PANI nanofibres, while other physical properties such as birefringence, dielectric anisotropy, splay, and bend elastic constants are changed moderately. The high conductivity anisotropy of liquid crystal nano-composites is very useful for magnetically steered liquid crystal-nanofibre switch. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824030>]

Nanoparticle doped liquid crystals (LCs) have drawn a lot of attention over the last decade. There are many fundamental studies on the LC nano-composites, typical examples are aerosil,¹ metal nanoparticles,^{2–5} and carbon nanotubes (CNTs)^{6–8} dispersed liquid crystals. In many of these LC nano-composites, it has been reported that the physical and electrooptical properties are enhanced which improves the liquid crystal display performances.^{9,10} So far there is only one report on the dispersion of conducting nanofibres in liquid crystal,¹¹ in which substantial decreases in the threshold voltage were reported. Apart from the high conductivity, these fibres are very useful for various applications such as in flexible electronic devices and antistatic coatings.^{12,13} In the bulk or in the dispersed state in liquids, these nanofibres are, in general, not orientationally ordered. There are also some reports that elongated nanoparticles such as CNTs,^{14–16} gold nano-rods,³ and self-assembled chains of quantum dots¹⁷ are weakly coupled with the orientational order of the nematic liquid crystals. However, detailed physical characterization of these nano-composites is rare. In this paper, we report on the measurement of physical properties in dilute dispersion of conducting nanofibres of polyaniline (PANI) doped in a nematic liquid crystal. Our results indicate that the long axes of the nanofibres are oriented along the liquid crystal director (the average alignment direction of the molecules) as a result the ac conductivity along the director has increased significantly than the perpendicular direction, while the birefringence, dielectric anisotropy, and elastic constants are moderately modified. The increase of conductivity along the director is expected to come from the electronic conduction of the nanofibres.

In the present work, the experimental cells were made of two indium tin oxide (ITO) coated glass plates with circularly patterned electrodes. The plates were spin coated with polyimide (AL-1254) and cured at 180 °C for 1 h and rubbed antiparallely for planar or homogeneous alignment of the sample. For homeotropic alignment, ITO plates were spin coated with polyimide (JALS-204) and cured at 200 °C for

1 h. The perpendicular and parallel components of the static dielectric constant and conductivity were measured in a planar and homeotropic cells, respectively, using an impedance analyser (Novocontrol, Alpha-A) at a voltage below the Freedericksz' threshold voltage. The birefringence, elastic constants, and rotational viscosity are measured following the procedure reported in our previous studies.^{18–21} The structure of the polymer and the method of preparation of nanofibres are presented briefly in the supplementary materials.²² A typical field emission scanning electron microscope (FE-SEM) image of the nanofibres is shown in Fig. 1(a). The nanofibres are solid and mostly straight. The length of the nanofibre varies from 1.5 to 11 μm, while the diameter of the fibre varies from 100 to 250 nm.²² We used 4-n-pentyl-4'-cyanobiphenyl (5CB) liquid crystal. It has the following phase transitions Cr. 22 °C N 35 °C Iso. The colloidal dispersion of PANI in 5CB was prepared by using chloroform as a

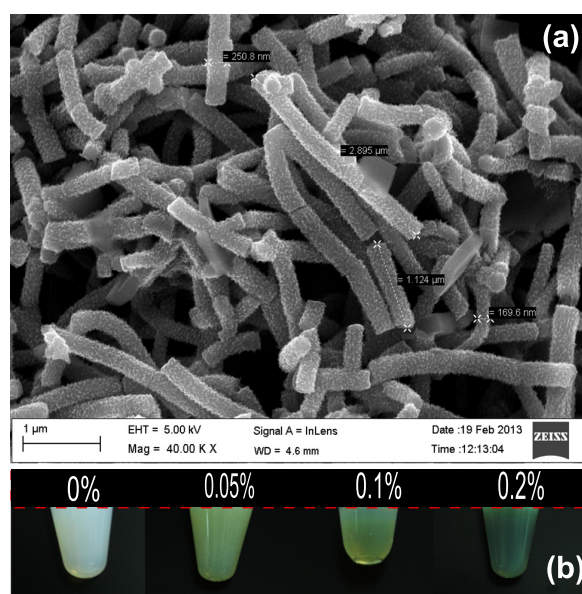


FIG. 1. (a) FE-SEM image of the conducting nanofibres (without liquid crystal). (b) Liquid crystal nano-composites (5CB-PANI) at various wt. % of PANI nanofibres.

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solvent. The mixtures were sonicated for 30 min and the solvent was evaporated slowly (12 h) using a vacuum oven. The picture of bulk samples at various concentrations of nanofibres (PANI) is shown in Fig. 1(b). The dispersions are stable, homogeneous, and becoming darker as the concentration is increased. We found from the optical microscope observation that beyond 0.2 wt. %, the nanofibres tend to agglomerate and defect free uniform alignment of liquid crystal director cannot be obtained. Hence, we restricted measurements within 0.2 wt. % of PANI nanofibres.

We measured the dielectric properties of the composites as a function of frequency in the nematic phase. The real and imaginary parts of the dielectric constant (ϵ' and ϵ'') as a function of frequency in the range of 10^{-3} – 10^6 Hz for the pure 5CB and sample with 0.1 wt. % PANI nanofibres are shown in Fig. 2. It is noted that both the dielectric properties are enhanced in the doped samples compared to the pristine sample especially at low frequency range and the frequency for the ionic relaxation has increased slightly. There are different mechanisms for dielectric response and the electrical conduction in organic and polymeric materials.^{23,24} The dielectric spectra in the low frequency range (10^{-3} – 10 Hz) describe the near electrode processes such as electric double layer and formation of space charge polarization.^{25–29} In the present data, the dielectric relaxation due to double layer (10^{-3} – 10^{-1} Hz) and space charge polarisation (10^{-1} – 10 Hz) are seen clearly in both the planar and homeotropic cells. Nematic liquid crystal exhibits finite conductivity due to the ionic impurities that depends on the density of ions, temperature, and the frequency of the applied field. Usually, the ionic conductivity along the director is different than the perpendicular direction and liquid crystal exhibits finite conductivity anisotropy $\Delta\sigma$ ($=\sigma_{\parallel}-\sigma_{\perp}$), where the subscripts refer to the direction in relation to the director. Since PANI has a large conductivity, we estimated the ac conductivity of composites by measuring the imaginary component of the dielectric constant. The ac conductivity (σ) is calculated using the relation, $\sigma_{\parallel,\perp}(f) = 2\pi f\epsilon_o\epsilon''_{\parallel,\perp}$, where ϵ_o is

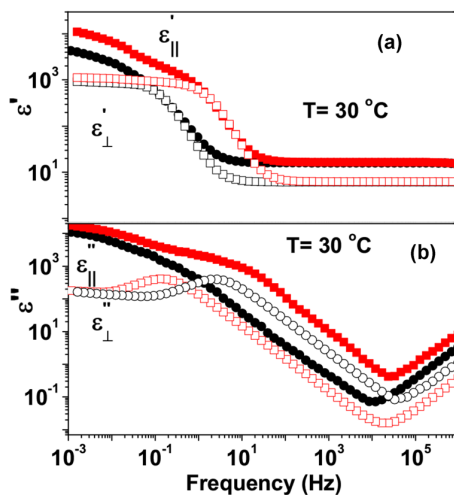


FIG. 2. Variation of (a) real and (b) imaginary parts of the dielectric constant (ϵ' and ϵ'') as a function of frequency. The solid and open symbols correspond to data in homeotropic and planar cells, respectively. The black and red colors represent data for pure 5CB and sample with 0.1 wt. % of PANI nanofibres.

the permittivity of the free space and f is the frequency of the ac voltage. In order to bring out the effect of PANI nanofibres on the estimated ac conductivity, we carried out temperature dependent measurement of the same at a fixed frequency (100 Hz), which is in the non-relaxation frequency range and reasonable away from the frequency range of space charge and electric double layer effects. In all the dielectric measurements, the applied voltage was chosen 0.2 V. This voltage is much lower than the Fredericksz threshold voltage (0.62 V at 31 °C) that causes elastic distortion. In Fig. 3(a), we show the variation of conductivity in homeotropic (σ_{\parallel}) and planar (σ_{\perp}) cells at various concentrations of PANI nanofibres. Some important features are noted in Fig. 3(a). The nematic-isotropic phase transition temperature (T_{NI}) slightly decreases with increasing concentration of PANI and the conductivity anisotropy vanishes above T_{NI} . At a fixed temperature, the estimated ac conductivity anisotropy ($\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$) increases with the increasing wt. % of PANI nanofibres. The temperature dependent slope of the ac conductivity in both the cells increases with the PANI nanofibre concentration. This clearly indicates that the estimated conductivity in the nano-composites is contributed by electron conduction. In Fig. 3(b), we plot the variation of ac conductivity in both the cells as a function of concentration of PANI nanofibres. It is

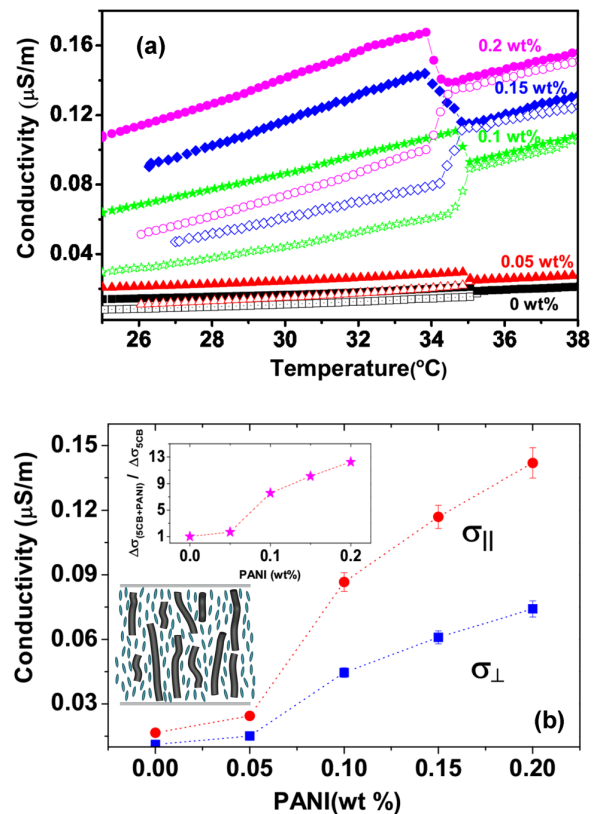


FIG. 3. (a) Temperature variation of estimated conductivity in homeotropic (σ_{\parallel}) and planar (σ_{\perp}) cells at a frequency 100 Hz and voltage 0.2 V. The solid and open symbols correspond to data in homeotropic and planar cells, respectively. (b) Variation of estimated conductivity in both the cells with the concentration of PANI. (Inset) Variation of the relative enhancement, $\Delta\sigma_{5CB+PANI}/\Delta\sigma_{5CB}$ with the wt. % of PANI nanofibres at 30 °C. The dotted lines serve only as a guide to the eye and no curve fitting has been performed. Schematic representation of the alignment of the nanofibres in the nematic liquid crystal.

TABLE I. Concentration dependent physical properties of the nano-composites. Except γ_1 (measured at 27 °C) all are measured at 31 °C.

PANI (wt. %)	0	0.05	0.1	0.2
$\Delta n (= n_e - n_o)$	0.147	0.149	0.144	0.148
$\Delta\epsilon (= \epsilon_{ } - \epsilon_{\perp})$	9.6	9.7	10.1	10.5
K_{11} (pN)	3.7	3.6	3.7	3.8
K_{33} (pN)	5.1	5.3	5.4	5.6
γ_1 (mPa s)	70	64	57	53

noticed that both $\sigma_{||}$ and σ_{\perp} increase with the concentration of PANI but the relative rate in $\sigma_{||}$ is much larger than that in σ_{\perp} . To show the relative magnitude of enhancement, we plot the variation of $\Delta\sigma_{(5CB+PANI)}/\Delta\sigma_{5CB}$ as a function of wt. % of PANI nanofibres in the inset of Fig. 3(b). It is found that the ratio increases rapidly, for example, at 0.2 wt. %, $\Delta\sigma_{(5CB+PANI)}/\Delta\sigma_{5CB} \simeq 12$. Such a large enhancement of conductivity anisotropy clearly indicates that the nanofibres are oriented along the liquid crystal director and the enhancement of ac conductivity is due to the electronic conduction of the nanofibres. A schematic representation of the orientation of PANI nanofibres in liquid crystal is also shown in the inset of Fig. 3(b). The estimated conductivity in pure 5CB liquid crystal in the frequency range of 1-10³ Hz is due to the presence of impurity ions in the sample and the anisotropy in the conductivity is related to the anisotropy in diffusion of ions, i.e., the ions can move easily along the director than the perpendicular direction. Usually, the adsorbed molecules of the liquid crystals form a Helmholtz layer which prevents or limits the charge transfer between the electrode and the ions. The highly resistive electric double layers also prevent charge transfer. The pronounced enhancement of $\sigma_{||}$ in our composites can be explained due to the charge transfer through the electrode double layers in which the nanofibres shunt the resistive double electric layer. Hence, nanofibres provide a medium for electron transfer between the ions and electrode. Similar near electrode process was reported in case of liquid crystal doped with multi-wall carbon nanotubes (MWCNTs).³⁰

In order to observe the effects of PANI nanofibres on the other physical properties, we measured birefringence ($\Delta n = n_e - n_o$), dielectric anisotropy ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$) and splay, bend elastic constants (K_{11} and K_{33}), and rotational viscosity (γ_1). The brief description about the method of the measurements is presented in the supplementary materials.²² In Table I, we show the variation of these physical properties with the concentration of PANI nanofibres at a fixed temperature for four samples. It is observed that Δn and K_{11} remain almost constant. Other properties such as $\Delta\epsilon$ and K_{33} appear to show a small ($\simeq 10\%$) but systematic increase with the increasing concentration of PANI nanofibres. However, it is hard to conclude about their dependence on the concentration unless composites with higher concentration of PANI can be made. Interestingly, we also find that the rotational viscosity decreases with increasing concentration of PANI nanofibres. For instance, at 27 °C, γ_1 for pure 5CB is about 70 mPa s and reduces to 53 mPa s in the nano-composite (0.2 wt. %) and this reduction is about 24%. The phenomena could be related to the decrease of T_{NI} with increasing

concentration of PANI in the sense that the easier the anisotropic particles can rotate, the less the amount of thermal energy is required to heat the system up to the isotropic liquid state. However, further studies are needed in this direction to fully understand the origin of decrease of rotational viscosity of the nano-composites. More details study towards the composites with higher concentration and their physical properties will be reported elsewhere.

In conclusion, we prepared colloidal suspension of nanofibres of conducting polymers (PANI) in 5CB liquid crystal and measured various physical properties. The nanofibres are oriented along the liquid crystal director and as a result the ac conductivity anisotropy has increased significantly due to the contribution from the electronic conductivity along the long axes of the nanofibres. The rotational viscosity tends to decrease while birefringence, dielectric anisotropy, both splay and bend elastic constants do not change significantly with the concentration of PANI nanofibres. As we have mentioned that in 5CB uniform dispersion of nanofibres was not possible beyond 0.2 wt. % nevertheless we anticipate that the conductivity anisotropy in the LC-nano-composites can further be increased in high concentration by appropriate choice of liquid crystals. These high conductivity anisotropies of liquid crystal nano-composites are useful for various applications such as magnetically steered liquid crystal-nanotube switch,³¹ in which the conductivity can be switched from low to high value by external magnetic fields.

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