Experimental investigations on weakly polar liquid crystal–aerosil composites

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Abstract

We have carried out differential scanning calorimetric and dielectric studies on composites of hydrophilic aerosil with a liquid crystal that does not possess a terminal polar group. While the shift in the nematic–isotropic transition temperature is in agreement with the general behaviour observed for such composites, the dielectric studies show, contrary to the commonly observed feature, that there is a systematic increase in the relaxation frequency associated with the rotation of the molecules around their short axis, as the aerosil concentration in the composite is increased.

1. Introduction

Investigations on liquid crystals confined in restricted geometries have been attracting significant attention in the past few years [1]. The voids in the confining matrix could be highly regular as in the case of membranes like Anopore and Nuclepore, or an irregular network like in the case of aerogels. The geometrically enforced disorder observed in these situations can also be realized by including or 'filling' certain particles into the liquid crystal (LC). A popular choice for the particle has been aerosil: silica spheres of $\sim$7 nm diameter whose surfaces are decorated to achieve hydrophilic or hydrophobic interactions [2–10]. The choice arises from the fact that by simply varying the concentration of such aerosil inclusions the random disorder can be controlled and fine tuned. The fragile hydrogen bond network that results from the interactions between the particles permits the disorder to be created *in situ*, allowing the study of the role of the quenched randomness on various phase transitions in LC materials. Calorimetric [4, 5, 7, 11] and x-ray scattering [12] measurements have been extensively used to investigate LC–aerosil systems, particularly employing the homologues of the alkyl cyanobiphenyl family. An important finding that has come out of these studies is that depending on the concentration or density of silica particles (denoted ρ_a) two distinct regimes can be observed: at densities lower than a critical value ($\sim$0.1 g cm^{-3}) the system behaves as a soft gel with sharp phase transitions whereas at higher concentrations the transitions are smeared out.

Dielectric studies on the LC–aerosil systems have been either on materials having a strongly polar terminal (the dipole moment pointing essentially along the long axis of the molecule) group to investigate the isotropic–nematic (Iso–N) transition [10, 13–15] or on the smectic A–smectic C [16] transition in chiral materials. There has been only one report of work on a weakly polar compound [17]. The strong interplay between the nature of the molecule and the surface interactions and the resulting influence on the physical properties of liquid crystals is quite well known. The studies by Sinha *et al* [17] showed that the polar nature of the molecule does alter the dielectric properties of the medium in aerosil–LC systems also. In this paper we report the results of an investigation on a molecule that does not possess a strong polar group along the long axis of the molecule but has a sufficiently strong dipole moment along the lateral axis. Incidentally, this compound exhibits the 'dual frequency characteristic', i.e., there is a crossover in the sign of the dielectric anisotropy above a certain crossover frequency; the sign is positive below this frequency and negative above it. In a later section, we will discuss the advantage of using such a material for the intended studies.

2. Experimental details

The molecular structure of the liquid crystalline compound used for the investigation is given below.
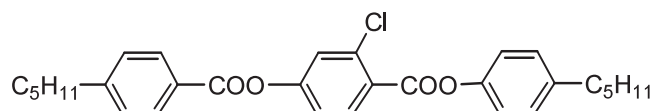
This compound (PCPBB for short) exhibits an Iso–N transition at 121.8 °C and the N phase can be supercooled to 0 °C. At low frequencies PCPBB has a positive dielectric anisotropy $\Delta\varepsilon$, defined as $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ stand for the dielectric constants along and perpendicular to the director respectively. It belongs to the class of materials termed as dual frequency materials exhibiting a crossover in the sign of the anisotropy at a certain frequency.

For these investigations we used hydrophilic aerosil particles (Aerosil 300) with a diameter of ~7 nm obtained from Degussa Corporation[1]. Before the preparation of the mixtures, the aerosil particles were degassed and dried at a temperature of ~200 °C for 4 h. Mixtures of aerosil and PCPBB were prepared by a simple physical mixing process. Since the quantity of the sample required was quite small (~15 mg), the possibility of inhomogeneous mixing was drastically reduced. To prove the efficacy of the method one set of mixtures was also done by the generally employed solvent procedure [4], and as will be shown later the results are invariant with respect to the physical mixing method. The properly weighed aerosil and LC materials were physically stirred while maintaining the temperature of the system at ~10 °C above the clearing point (i.e., the nematic–isotropic transition point). Aerosil mixtures are usually characterized in terms of the aerosil density defined as $\rho_a = m_a/V_{LC}$, where m_a is the mass of aerosil and V_{LC} is the volume of the liquid crystal. Since the density of the LC is $\cong 1$ g cm^{-3}, ρ_a can be written as just m_a/m_{LC}. Investigations have been carried out on mixtures with $\rho_a = 0.01, 0.06, 0.11$ and 0.18 g cm^{-3} (we drop the units hereafter) as well as on pure PCPBB. A visual observation made during the preparation of these mixtures may be mentioned here. Whereas the mixtures with $\rho_a = 0.06, 0.11$ and 0.18 were quite viscous, the $\rho_a = 0.01$ mixture was as fluid as the pure sample, indicating occurrence of gelation in the former mixtures.

Differential scanning calorimetric measurements were done with a Perkin Elmer DSC (DSC7) and the dielectric measurements with an impedance analyser (HP 4194A/4284A). For

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[1] The aerosil samples were kindly given to us by Mr Vikas Rane of d-hindia Ltd, Mumbai.
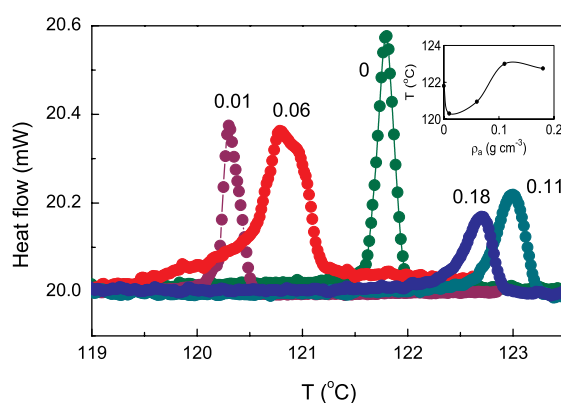
Figure 1. DSC scans obtained in the heating mode in the vicinity of the nematic–isotropic transition for the bulk and different LC+aerosil composites. The concentration of the aerosil in terms of ρ_a, the density of the aerosil, is indicated above each profile. The non-monotonic variation of the transition temperature, taken to be the value at the peak, is seen in the inset.

(This figure is in colour only in the electronic version)

the dielectric measurements the samples were contained between two ITO-coated glass plates. Such plates were used to enable visual observation of the quality of alignment of the sample. But the usage of such plates puts a limit on the maximum probing frequency of <1 MHz. However, the very low sheet resistivity ($\sim$10 $\Omega/\square$) of the plates (from Delta-Technologies) used here combined with the fact that the material is a dual frequency compound (thus having quite a low frequency value for the director relaxation frequency) enabled us to perform a proper dielectric relaxation measurement. Since for the mixtures with higher ρ_a values the viscosity was quite high, we could not use the standard capillary filling method to fill the sample into a pre-fabricated cell. Therefore we adapted the following method. The sample was placed on one plate and the other plate was kept on top of it with the two plates being separated by Mylar spacers ($\sim$0.125 mm thickness) located outside the electrically active area of the cell. The plates were held together by a UV curable epoxy put on the sides of the two plates and cured using a low-power UV source. A mask prevented the radiation from falling on the sample while the epoxy was cured. This procedure resulted in a highly reproducible method for the measurements except that the thickness could not be accurately measured and consequently the absolute value of the dielectric constant could not be calculated.

3. Results and discussion

3.1. Differential scanning calorimetric measurements

Figure 1 shows the DSC scans taking in the heating mode at a rate of 1 °C min^{-1} for pure PCPBB as well as for the different aerosil mixtures. Pure PCPBB and the mixtures with $\rho_a = 0.11$ and 0.18 show single peak profiles, although the peaks are broader for the mixtures. In contrast, the mixture $\rho_a = 0.06$ shows what appears to be a two-peak profile. It may in fact be noticed that a shoulder is observed on the lower temperature side of the peak for the $\rho_a = 0.01$ mixture. Similar features have been reported in high-resolution AC calorimetric experiments on 8CB+aerosil and 8OCB+aerosil systems (see e.g., [7]). The reports identify a critical ρ_a ($\leqslant$0.1) below which the mixtures are termed soft gels and above it stiff gels. The broadening of the two-phase coexistence for the weakly first-order Iso–N transition has been anticipated

for higher concentrations of aerosil and are explained to be due to quenched random disorder created by the aerosil network. The double-peak profile obtained for $\rho_a = 0.06$ appears to be a common feature found in other LC–aerosil systems with similar aerosil concentrations. Recently, Caggioni *et al* [18] have performed high-resolution calorimetric, light scattering and microscopy measurements, and based on the experimental data propose that in the LC–aerosil systems the nematic order develops from the isotropic phase through a two-step process. They also argue that a double peak in the calorimetry data is due to a crossover from a random-dilution regime to a random-field regime present at lower temperatures. Our data for $\rho_a = 0.06$ could in fact be fitted to a double-peak profile with the two peak temperatures being separated by 0.2 K, a value which is in the same range as that obtained by Caggioni *et al* [18], and supports the argument that such a profile is perhaps a generic feature of first-order transitions with weak quenched disorder. The inset to figure 1 gives the dependence of T_{NI} on the concentration of aerosil. The non-monotonic behaviour with T_{NI} decreasing for lower values of ρ_a, and then increasing to exhibit a broad maximum at higher concentration levels, are qualitative features, which now have become the hallmark of the LC–aerosil systems. (Non-monotonic behaviour is observed for the nematic–smectic A transition also; see [4].) Of course, the specific ρ_a values at which these features are observed and the corresponding shifts in the transition temperatures are material (liquid-crystalline) dependent. For example, the initial minimum obtained in the soft-gel regime is $\sim$1 K for 8CB+aerosil, 1.5 K for 8OCB+aerosil as well as for the PCPBB+aerosil system studied here. The value at which such a minimum is seen occurs at $\rho_a \sim 0.05$, 0.1 and 0.01 for the three materials respectively. The thermal behaviour of the LC–aerosil systems has been analysed in terms of different theoretical models [4, 18, 19]. In the pinned-boundary-layer (PBL) model [4] the orientational anchoring at the surface of the aerosil particle is assumed to be strong resulting in the LC molecules at the boundary layer being quenched and not participating in the phase transformation process; the rest of the LC molecules behave as the pure bulk material. In the random-field (RF) model [4] the quenched LC is distributed randomly, causing a lowering of the average order parameter. A model based on the surface-induced order (SIO) considers the isotropic phase as a paranematic phase [19]. Each of these models predicts a different type of expression for the shift in the transition temperature as a function of the aerosil density. The PBL model does not predict any shift in T_{NI} with the aerosil density. According to the RF model, the shift in T_{NI} depends on the radius of curvature of the elastic distortions. But this has been proved to result in too large a shift with increasing ρ_a value. When the SIO is taken into account the theory seems to predict the behaviour seen at least in the low aerosil concentration regime. Even the model by Caggioni *et al* [18] which considers a crossover from a random-dilution regime to a random-field regime also does not fully reproduce the experimentally observed trend. Thus none of the existing models have satisfactorily reproduced the experimentally observed non-monotonic dependence of T_{NI} on the aerosil concentration.

3.2. Dielectric measurements

To possibly orient the LC molecules for these studies a magnetic field of 1.4 T magnitude was employed. The relative directions of the magnetic field and the probing electric field defined the geometry of the measurement. Whereas the magnetic field was very effective to realize very good quality aligned samples in the case of pure PCPBB, the same could not be confirmed for the aerosil mixtures, despite a possible memory effect [13, 20] by which the sample would retain the orientation even after the orienting field is removed. This feature in conjunction with the problem of determining the cell constant as mentioned earlier prevented us from getting the absolute values of the dielectric constant. Therefore we present the data in terms of the
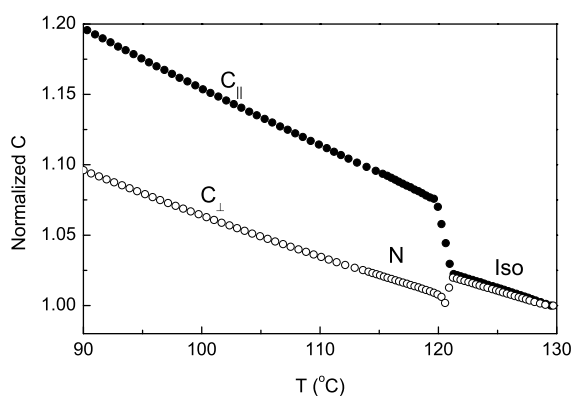
Figure 2. Temperature dependence of the sample capacitance at 10 kHz for the $\rho_a = 0.06$ mixture measured parallel ($C_\parallel$) and perpendicular ($C_\perp$) to the magnetic field direction, showing that the composite still retains the positive dielectric anisotropy of the host PCPBB compound.
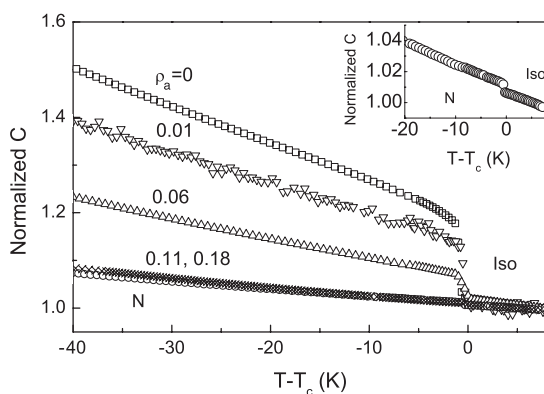

Figure 3. Thermal variation of the sample capacitance $C_\parallel$ normalized to the value in the isotropic phase for the bulk (squares) and $\rho_a = 0.01$ (inverted triangles), 0.06 (upward triangles), 0.11 (circles) and 0.18 (crosses) mixtures. The data for $\rho_a = 0.11$ are shown on an enlarged scale in the inset. (T_c stands for the transition temperature in each case.)

measured capacitance rather than the dielectric permittivity of the sample. The temperature dependence of the capacitance values measured with the probing directions parallel ($C_\parallel$) and perpendicular ($C_\perp$) to the magnetic field direction for the $\rho_a = 0.06$ mixture and normalized with respect to the value in the isotropic phase is shown in figure 2. The data show that on entering the nematic phase from the isotropic phase $C_\parallel$ increases and $C_\perp$ decreases, indicating that the mixture retains the positive dielectric anisotropy of the parent PCPBB compound. This was true of all the mixtures studied here. (For the higher concentrations of the mixtures the value of $C_\parallel$ realized while cooling the sample from the isotropic phase in the presence of the magnetic field was slightly higher than that which could be obtained by turning the field on after the sample was in the nematic phase. This could be perhaps due to the memory effect, mentioned earlier.) The thermal variation of $C_\parallel$ for different concentrations of aerosil is shown in figure 3. To facilitate comparison we have shown the data as a ratio of the measured capacitance to that in the isotropic phase and in terms of the reduced temperature $T - T_c$. Note that the transition can be seen clearly for all the mixtures. With increasing ρ_a the value in
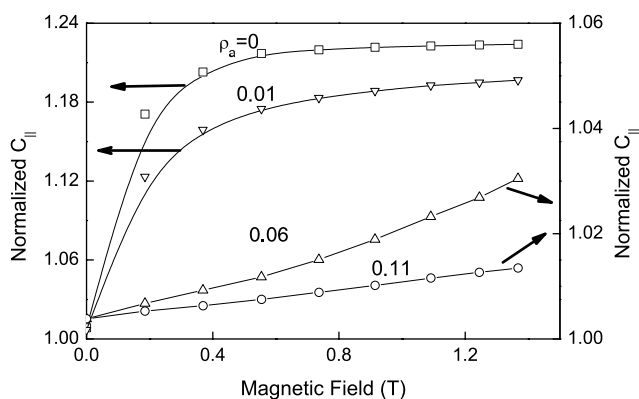
Figure 4. Variation of the normalized capacitance $C_\parallel$ as a function of the applied magnetic field for the bulk (squares) and $\rho_a = 0.01$ (inverted triangles), 0.06 (upward triangles) and 0.11 (circles) mixtures. Note that the scales are different for the former two and latter two materials.

the nematic phase decreases drastically, so much so that for $\rho_a = 0.11$ and 0.18 the change is hardly noticeable (see the inset of figure 3). In order to find out whether the reduction in the normalized capacitance in the nematic phase as ρ_a is increased is due to a reduction in the orientational order or an imperfect alignment, we have collected data for the pure PCPBB sample and three mixtures with $\rho_a = 0.01$, 0.06 and 0.11 (see figure 4). In the case of the pure compound and the 0.01 mixture the saturation of the capacitance value at higher magnetic fields is quite clear. For the higher ρ_a value mixtures, however, there is no saturation, and in fact, for the $\rho_a = 0.11$ mixture, there is hardly an increase in the value of the capacitance with increasing field. Thus it is clear that the reorienting capability of the magnetic field is reduced upon increase in the aerosil concentration. The field appears to be effective in the soft-gel regime, but not in the stiff-gel regime. Comparing the data for the pure sample and the two mixtures for which saturation in the capacitance value was seen for at least the highest value of the magnetic field applied, it is noticed that presence of aerosil *per se* leads to a decrease in the normalized value of capacitance. The normalization done with respect to the isotropic value takes care of the geometry as well as the change in the (isotropic) dielectric constant of the LC–aerosil medium. Thus the observed decrease in the nematic phase can perhaps be taken to be entirely due to the aerosil-driven diminution in the orientational order. Taking the difference in the values for the pure sample and the mixtures it is seen that there is a 12% reduction in the orientational order for the $\rho_a = 0.06$ mixture. A further point to be noted is that the behaviour of the $\rho_a = 0.06$ mixture is such that the threshold field for reorientation is large and also the path to saturation is gradual as against the sharp threshold curve for the bulk and $\rho_a = 0.01$ mixtures, suggesting an increase in the value of the splay and bend elastic constants.

Figure 5 shows the frequency spectra of the real (C') and imaginary (C'') parts of the complex capacitance in the parallel geometry for the bulk as well as for the $\rho_a = 0.11$ mixture at a temperature of $70\,^\circ$C. To extract the relaxation frequency the data was fitted to the Havriliak–Negami equation [21]

$$C^*(f) = C_\infty + \frac{\Delta C}{[1 + (\mathrm{i}f/f_R)^\alpha]^\beta}. \tag{1}$$

Here $C^*(f)$ is the complex capacitance at a frequency f, and C_∞ is associated with the dielectric strengths of all the high-frequency modes other than the one under consideration. ΔC
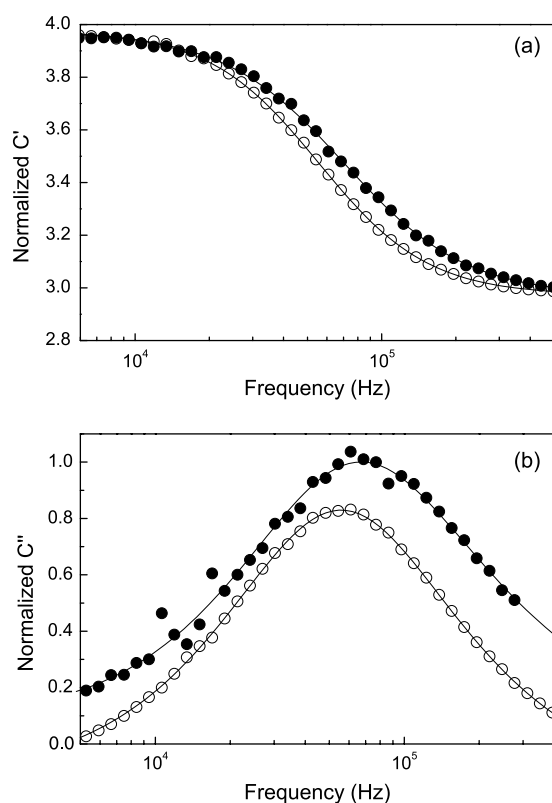
Figure 5. The frequency spectrum of the complex capacitance in the nematic phase at 70 °C shown as the (a) real part and (b) imaginary part for the bulk (open circles) and $\rho_a = 0.11$ mixture (filled circle). (In (b), for the sake of clarity the data for the mixture have been given an arbitrary shift in the vertical direction.) The solid lines represent the fit to equation (1). The increase in the frequency at which the maximum in C'' occurs (panel (b)) clearly indicates that the relaxation frequency is higher for the mixture.

is the difference between low-frequency and high-frequency capacitance values and f_R is the characteristic relaxation frequency. The parameters α and β describe the width and asymmetric broadening of the relaxation curve. To account for the DC conductivity contribution to the imaginary part of the capacitance, a term proportional to $1/f$ was added to the right-hand side of equation (1). For the bulk sample the α and β values were ≈ 1 over the entire temperature range of measurement. For the aerosil composites, $\alpha \approx 1$ but β was ~ 0.9, indicating that the presence of the aerosil network broadens the relaxation profile in an asymmetric fashion. The most important feature to be noted is that the value of the relaxation frequency, signified by the peak frequency in the C'' data, shifts to higher values for the aerosil mixture. The detailed temperature dependence of the relaxation frequency for the bulk and the aerosil composites (figure 6) shows that the qualitative feature noticed in figure 5 is indeed true: with increase in the aerosil density in the composite, there is a systematic increase in the relaxation frequency. (For the $\rho_a = 0.18$ mixture the dielectric strength was very low. Therefore it was difficult to get reliable values of the relaxation parameters for the mixture and hence we have not shown the data here.) Further, this feature holds good over the entire range of temperature investigated here. In 7CB–aerosil mixtures [13] such an increase was also seen, except that the increase in f_R for the aerosil mixture was only in the vicinity of the transition, whereas
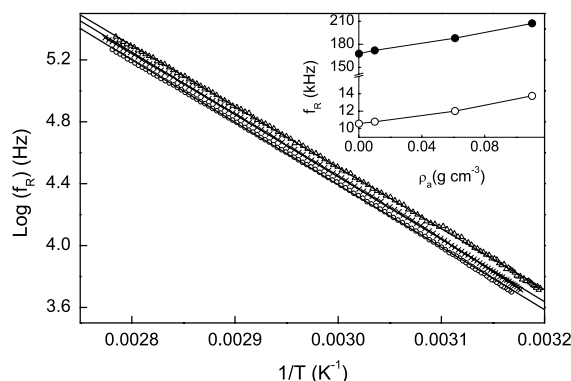
Figure 6. Temperature dependence of the relaxation frequency for the bulk (circles) and $\rho_a = 0.06$ (crosses) and 0.11 (triangles) mixtures. Notice that at any given temperature the mixtures have a higher relaxation frequency than the bulk and that the increase is higher for the mixture with higher aerosil concentration. The concentration dependence of the relaxation frequency is shown explicitly in the inset for two temperatures: 50 °C (open circles) and 70 °C (filled circles). The lines stand for the fit to the Arrhenius behaviour.

away from the transition the values seem to collapse to a single value for the pure compound as well as for the mixtures. The inset to figure 6 shows the f_R values as a function of the aerosil density at two fixed temperatures, namely 50 and 70 °C: the enhancement in f_R upon confinement in the aerosil network is linear with the aerosil concentration. For example, the relaxation process becomes faster by a factor of 4 at 50 °C and by a factor 5 at 70 °C. Notice, however, that in the semi-logarithmic plot shown in figure 6 both the bulk and the aerosil sample have a linear variation of f_R over the temperature range studied, indicating Arrhenius behaviour. Also to be seen is that the data sets seem to be parallel to each other. We fitted the temperature-dependent f_R data to a linear equation from the slope of which the activation energy value was determined. For the bulk and $\rho_a = 0.01$ and 0.06 mixtures we obtain the activation energy to be 34 kJ mol^{-1}, whereas for the $\rho_a = 0.11$ there was a slight lowering of the value to 33 kJ mol^{-1}. It may be remarked that the change in the relaxation frequency at a fixed reduced temperature of $T - T_c = 40$ K, the f_R value increases by 11% between the pure compound and the $\rho_a = 0.06$ mixture. This compares with the 12% decrease seen in the normalized capacitance value for these two materials, which, as mentioned in an earlier paragraph, can be associated with a lowering of the orientational order. Thus it appears that the increase in f_R for the aerosil mixture is largely due to such a reduction in the orientational order.

A doubt that has been expressed in the literature [4] about the physical mixing method of preparing the aerosil–LC composites is that it can lead to inhomogeneous preparations. To alleviate such doubts, at least in the low aerosil concentration regime investigated here, we have performed measurements on the $\rho_a = 0.11$ mixture prepared using the standard solution mixing method. For this purpose the weighed aerosil was added to the LC material dissolved in pure acetone. Then the mixture was sonicated for 1 h followed by evaporation of the solvent over a period of 15 h and finally kept under vacuum for 24 h while the temperature was maintained at 110 °C. Figure 7 shows the temperature-dependent relaxation frequency data obtained for the mixture prepared in this manner as well as the previously mentioned physical mixing method. The very good agreement between the two sets of data over the entire temperature range of measurement indicates that the physical mixing method can be employed to prepare the composites.
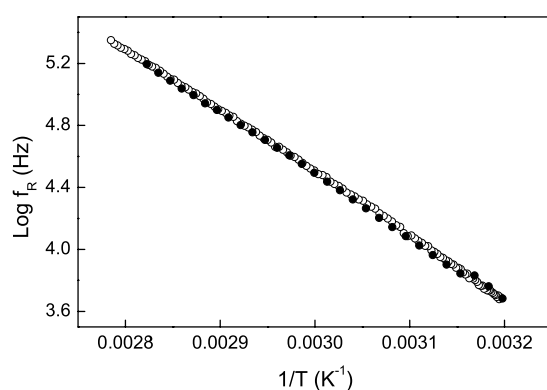
Figure 7. Plot to show the equivalence of the mixtures prepared by the physical mixing (open circles) and solution mixing (filled circles) methods.

These features, especially the increase in f_R with increasing aerosil concentration, are not generally observed for aerosil dispersion of nematic liquid crystals. But it must be borne in mind that most of the studies on aerosil dispersions have been carried out on cyanobiphenyls, i.e., molecules having a strong terminally polar compound (the dipole moment of the cyano group is 4.2 D). In the dielectric studies on such systems the magnitude of the relaxation frequency is impervious to the concentration of the aerosil particles. The temperature dependence of the process remains, however, Arrhenius-like in the case of non-chiral cyanobiphenyl. For the chiral isopentylcyanobiphenyl the bulk as well as the aerosil mixtures showed glass formation behaviour. The activation energy associated with the Arrhenius behaviour has been found to increase when the aerosil concentration is high. An exception to the negligible dependence of f_R on the aerosil concentration has been recently published in a weakly polar compound [17]. Between the bulk and one mixture with a high concentration ($\rho_a = 0.19$) of hydrophilic aerosil particles these researchers find that the relaxation time decreases (or f_R increases) by a factor of 3. In the current studies we observe that between the bulk and $\rho_a = 0.11$ mixture the f_R value increases by ~50%. Also to be noted is that the PCPBB molecule does not have a strongly polar terminal group. It has, of course, two ester groups and a chlorine atom in the meta position, all of which contribute to the dipole moment in the lateral direction. Now let us recall the scenario discussed by earlier authors (see, e.g., [18]) for the liquid crystal molecules and the aerosil dispersions. The high density of the silanol groups on the surface of the aerosil particles causes them to have a hydrophilic character. The particles can bind with one another by means of the intermolecular hydrogen bonds through the Si–O–H groups present at the surface. When the liquid crystal molecules and the aerosil particles coexist as dispersion then such a bonding leads to the formation of a random gel. If the interaction between the surface of the aerosil particles and the liquid crystalline molecules is significant then two contradictory influences can develop: the presence of the non-liquid crystalline aerosil particles reduces the orientational order in the liquid crystal medium and if the interface between the aerosil and the liquid crystal promotes is of the proper type then it could promote the orientational order at least at the surface. A consequent possible LC–material dependent scenario is that in molecules such as the cyanobiphenyls the strongly polar terminal cyano group would like to be normal to the silica surface and therefore the surface induced order would tend to minimize, at least in the soft-gel regime, the disorder due to the presence of foreign particles. Thus the director relaxation frequencies do not change with increasing aerosil concentration. On the other hand, in systems not possessing a strongly polar terminal group, the surface-induced order

could be significantly small and disorder due to the presence of the aerosil particles dominates the properties. The disorder reduces the magnitude of the orientational order parameter and therefore the director relaxation frequency increases, with the extent of the effect increasing with aerosil concentration. This explains the observation in the report by Sinha *et al* [17] as well the current studies that the relaxation frequency increases for a finite concentration of the aerosil when the LC molecule is of the non-polar type.

In summary, we have performed differential scanning calorimetric and dielectric studies on composites of a liquid crystal that does not possess a terminal polar group and hydrophilic aerosil. Contrary to the commonly observed feature, we find that there is a systematic increase in the relaxation frequency associated with the rotation of the molecules around their short axis, as the aerosil concentration in the composite is increased, which could entirely be due to the increased disorder.

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