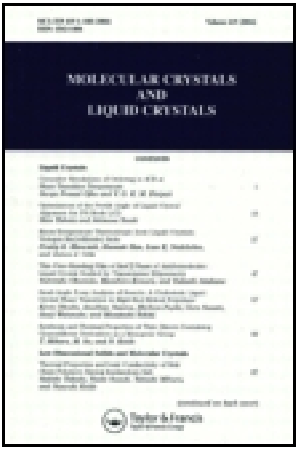

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Mechanical Properties of Thermo-Reversible Colloid Liquid Crystal Composites

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Mechanical Properties of Thermo-Reversible Colloid Liquid Crystal Composites

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The mechanical properties of concentrated dispersions of sterically-stabilised colloidal particles in nematic hosts are explored using a combination of optical microscopy and viscoelastic shear measurements. Starting from an initially homogeneous dispersion in an isotropic host, it is found that the kinetics of the isotropic-nematic transition lead to the formation of a percolated particle network that imparts surprising mechanical rigidity to the resulting colloid/liquid crystal composite. Specifically, the viscoelastic storage modulus G' is observed to rise by approximately 5 orders of magnitude within a few degrees of the bulk isotropic-nematic transition temperature. Using 4–4'pentyl cyano-biphenyl as the solvent, the composite at room temperature is a self-supporting soft solid over a wide range of particle concentrations. The particle microstructure depends sensitively on thermal treatment and particle concentration and it is found that faster cooling enhances the visoelastic moduli of the composite. Also, several classes of network topology have been identified. In all cases studied to date, the particles can be redispsersed upon heating the solvent through the nematic-isotropic transition. The formation of the composite is therefore thermally reversible. A rigorous theory to account for the observed mechanical properties is not currently available.

Keywords: Colloids; Microstructure; Rheology; Cellular Solids

1. Introduction

There is an increasing level of interest in classes of materials comprising colloidal dispersions in liquid crystalline hosts[1,2,3]. This has resulted from potential promise in technological applications as well as in fundamental theoretical challenges inherent in these systems. In the early and simplest cases, attention was focussed on the ultra-dilute case where particle concentrations were so low that multiple particle effects were negligible and the properties of interest could be determined from a single particle in an otherwise perfect nematogen. In this case,

the bulk properties of the liquid crystal are unaffected and the only issue concerns the nature of the director distortions induced by the particle. This has now been investigated in detail by several authors who have reported analytical forms for the director field in the vicinity of the particle as a function of anchoring strength. The main results from these studies suggest the existence of two intuitively reasonable limiting regimes of anchoring strength *W*. In the weak anchoring limit, the particle only slightly perturbs the nematic director profile from equilibrium and introduces no topological defects. A simple analytical expression for the director profile in this regime has been found to give the director angle β (at a distance r from the particle and at spherical polar angle, θ, in terms of the particle radius (R) anchoring strength (W) and average elastic constant (K), The expression is [1]

$$\beta(r) = \frac{1}{4}\left(\frac{WR}{K}\right)\left(\frac{R}{r}\right)^3 \sin 2\theta$$

In the strong anchoring regime the director profile is strongly perturbed close to the particle and rigid anchoring introduces a topological discontinuity between the spherically-symmetric near-surface director and the uniformly-aligned far-field profile. There remains some uncertainty as to the most energetically favorable director structure in the strong anchoring regime but there are two leading candidates. One of which is the "Saturn Ring" defect illustrated in Figure 1 (a) and the other is the more complex dipolar structure with an associated monopolar defect[2].

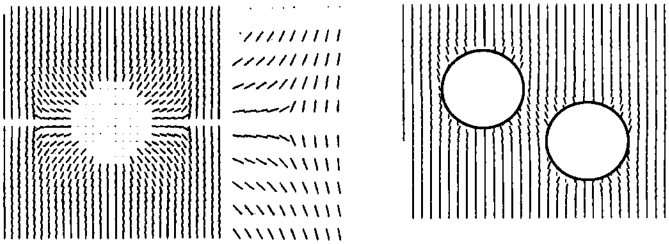

Fig 1. The Saturn-ring director distribution surrounding a single colloidal particle in the strong anchoring regime (a). A magnified view of the director distribution near the radially symmetric disclination ring is shown to the right. In (b) a schematic illustration of inter-particle interactions mediated by the director field distortions is shown.

More recently, attention has shifted toward the more concentrated regime[4,5] in which high volume fractions of colloidal particles are suspended in mesogenic hosts. In such a situation, interparticle interactions mediated by director strain fields are non-negligible and influence many important bulk properties Fig 1(b). For example, colloidal dispersions have been recently shown to stabilize defects in cholesteric hosts and to lead to an increase in the low-frequency storage moduli[4]. The most extreme examples of these effects have been demonstrated in dense dispersions of spherical PMMA particles in nematogens where the particles adopt complex percolated network structures at the isotropic nematic transition which endows the material with unexpected mechanical strength [5]. The purpose of the present paper is to review current understanding concerning Colloid Liquid Crystal Composites (CLCC) and to present new results on the way their properties can be controlled. In a companion paper[7], the electro-optical properties of CLCCs will be explored with a view to assessing their potential promise for liquid crystal display applications[7].

2. Experimental

The colloidal particles used in these experiments are all made from polymethyl methacrylate with a particle radius of between 190 and 250 nm and approximately 7% polydispersity[4]. A layer of poly-12-hydroxysteric acid (12PHSA) is chemically grafted onto the particle surface to sterically inhibit aggregation.

Preparation of a colloid liquid crystal composite begins with a stock of colloidal particles initially dispersed in a standard non-mesogenic solvent such as cis-decalin. The particles are then dried and redispersed (using a heated magnetic stirrer or tumbling apparatus) into a liquid crystal forming host initially heated above the clearing point. Light scattering results have confirmed that the particles remain well dispersed in the isotropic phase of 5CB indefinitely.

3. Microstructure and viscoelastic response

At high particle concentrations, cooling across the isotropic nematic transition temperature the transforms the sample from an isotropic liquid to a strong viscoelastic solid that is self supporting and sufficiently rigid to be engraved (2(a), inset). Small amplitude viscoelastic shear measurements indicate that the the storage modulus undergoes an increase of several orders of magnitude near the isotropic-nematic transition(2b). This increase is a strong function of both particle concentration and cooling rate but storage moduli in excess of 10^5 Pa have been observed.

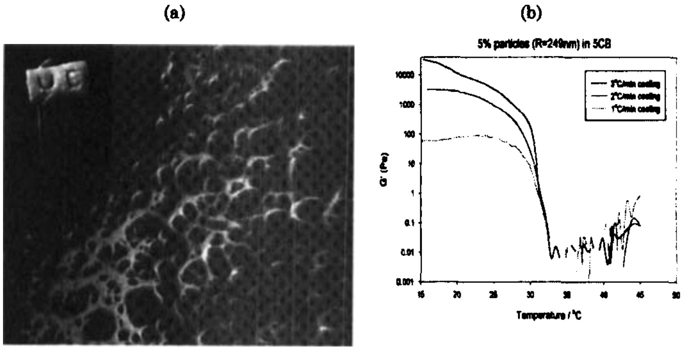

Fig 2. In (a) a laser scanning confocal microscope image of a dense (10%) composite is shown illustrating the complex network microstructure. The inset of the figure shows an image of a self-supporting composite that has been engraved. The viscoelastic storage modulus vs temperature for a 5% composite is shown as a function of temperature at several cooling rates (b). 5CB is used as the host material.

The effect of cooling rate on the viscoelastic properties of CLCC materials is found to be very strong as shown in Fig 2(b) for a 5% sample. In general it is found that slow cooling results in a mechanically weaker composite with very strong composites forming at high cooling rates(2b). The strongest composites also show an unexpected additional increase in the storage modulus further into the stability field of the nematic. Qualitatively different behavior is seen for weaker composites for which no discernible temperature dependence is seen below the nematic transition temperature. The majority of all results on CLCC materials have been obtained using 5CB as the host material. However, we have made preliminary studies to demonstrate that the formation of the CLCC cellular network microstructure can be formed in other mesogenic hosts including cholesteric and smectogenic solvents. Self supporting CLCC samples were formed in these cases using analogous preparation methods though there is at present no quantitative rheological data available.

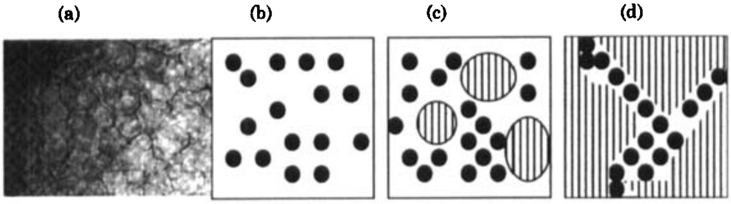

Fig 3. Schematic illustration of the evolution of the general CLCC cellular network microstructure formed via a microphase separation mechanism. An optical micrograph showing the cellular microstructure obtained from bright field microscopy is shown in (a). Stage I (b) shows the initial *isotropic dispersion*, *Stage II (c) shows the expulsion of the particles from* emerging nematic droplets. Stage III (d)

Optically, all CLCC samples are more opaque than is the pure particle-free liquid crystal. This is expected because of the enhanced light scattering due to the particle-induced domain structure. However, optical microscopy reveals that even concentrated CLCC specimens preserve the underlying birefringence of the liquid crystal hosts and are therefore potentially optically switchable. A survey of electro-optical response of CLCC materials will be presented in the companion paper.

3. Models

We first consider the evolution of the network microstructure. A schematic illustration of the formation of the CLCC microstructure is shown in Fig 3 and depicts structural evolution proceeding in three stages. The experimentally-observed microstructure is shown in (a). Schematically, Stage I (b) is the homogeneous dispersion within which the colloidal particles are distributed throughout the isotropic solvent. Light scattering studies confirm that the particles are not aggregated and show well-defined single-particle diffusion. Upon approaching the nematic phase from above, emergent nematic domains begin to expel the colloidal particles into the remaining isotropic regions. This is Stage II (c). *This occurs because the director distortion (elastic free energy) within the nematic* domains can be minimized by expulsion of the particles. This is a type of microphase separation that leads to a structure in which the particles are driven into ever smaller isotropic interfaces between nematic domains until the final network structure is fully developed. This is identified as Stage III and is shown in Fig 3(d)

A model for the anomalous elastic properties of these composites is not yet fully developed though the basis for such a model has been proposed by Anderson et al [6]. They consider in some detail the phase separation mechanism and propose that the origin of the mechanical rigidity lies in the high effective surface tension of the interfaces.

4. Conclusions

The mechanical and microstructural properties of an unusual class of heterogeneous soft condensed matter - colloid liquid crystal composites – have been described with a view to exploring in qualitative terms their dependence on process parameters. A strong sensitivity of elastic modulus to cooling rate has been revealed at fixed volume fraction but it remains to explore the limits of the mechanical strength and to relate this to physical models.

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References

[1] E.M. Terentjev Phys. Rev. E, **51**, 1330 (1995).

[2] P. Poulin, H. Stark, T.C. Lubensky and D.A. Weitz, Science, **275**, 1770, (1997).

[3] R. Ruhwandl and E.M. Terentjev Phys. Rev. E, **55**, 2958, (1997).

[4] M. Zapotocky, L. Ramos, P. Poulin, T.C. Lubensky and D.A. Weitz Science, **283**, 209, (1999).

[5] SP. Meeker, W.C.K. Poon, J. Crain and E.M. Terentjev, Phys. Rev. E, *Rapid Communications*, **61**, R6083, (2000).

[6] V.J. Anderson, E. M Terentjev S.P. Meeker, W.C.K. Poon and J. Crain, European Journal of Physics. (in press).

[7] H. Nakamura, S.P. Meeker, W.Poon, W. Hossack, Y. Taira and J. Crain,.