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Colloid–liquid-crystal composites: An unusual soft solid

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Mixing model colloidal particles with a thermotropic nematic liquid crystal results in a soft solid with significant storage modulus ($G' \sim 10^3 - 10^5$ Pa). The soft solid comprises a network of particle aggregates, formed by the exclusion of particles from emergent nematic domains as the mixture is cooled below the isotropic-nematic transition. The unusually high storage modulus of the colloid–liquid-crystal composites may be due to the local frustration of nematic order within the particle aggregates. The birefringent soft solid is potentially important as a switchable electro-optical material that can be readily handled and processed.

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Mixing two individually well-known ingredients is an established route to novel materials. Thus, alloys of ''hard'' materials have been produced for more than two millennia [1]. More recently, the investigation of mixtures has also proved fruitful in soft condensed matter: colloids, polymers, and surfactants, with polymer blends being a particularly well-developed area. For both ''hard'' and ''soft'' matter, exploitable mixtures are often metastable states formed by the incomplete demixing of thermodynamically incompatible parent components. Here we report a soft solid formed by mixing a well-characterized model colloid, sterically-stabilized polymethylmethacrylate (PMMA), with a well-characterized thermotropic nematic liquid crystal, 4-*n*-pentyl-4′-cyanobiphenyl (5CB). A suspension of hard spheres at ~10% is an easily pourable liquid, as is 5CB in its nematic phase; the mixture at room temperature, however, is a birefringent waxy solid with significant storage modulus ($G' \sim 10^3 - 10^5$ Pa).

Mixtures of colloids and liquid crystals have been the subject of many studies recently. On the one hand, much attention has been devoted to how a single particle affects ordering and induces defects in various mesophases, and the resulting (anisotropic) forces between two particles in such media [2–7]. On the other hand, attempts have been made to disperse finite concentrations of particles in liquid crystals. Often, most of the particles are expelled, since ordering on their surfaces disrupts the bulk order of the mesophase. Most previous studies overcome this by choosing a *lyotropic* over a *thermotropic* liquid crystal as the dispersion medium [8,9], the much smaller elastic constants in the former reducing the energy cost of adding particles. The elastic properties of such a system in the nematic phase were studied by Raghunathan *et al.* [9] by aligning the samples in a magnetic field. For particle concentrations up to 2 wt % they observed no change in the elastic constants; however, above this concentration they were unable to align the samples. The authors suggest that this ''might be an indication of a drastic change in the elastic properties of the medium above this concentration.'' Very recently, Zapotocky *et al.* [10] have reported that colloidal dispersions (particle volume fraction $\phi \sim 0.3\%$) in a *thermotropic* cholesteric liquid crystal stabilized ''oily streak'' defects and increased the low-frequency storage moduli by a factor of two or three times relative to the pure cholesteric phase. These authors state that ''colloidal particles dispersed in a nematic [liquid crystal] have no effect on the bulk rheological properties, at least at small volume fractions.'' Our experiments focus on the unexplored concentrated regime and show that higher volume fractions of particles in a thermotropic nematic liquid crystal can have dramatic rheological effects.

The particles we used were nearly monodisperse PMMA spheres sterically stabilized with chemically grafted poly-12-hydroxystearic acid, radius $a = 250$ nm, initially dispersed in cis-decalin at approximately 30% volume fraction. Thus suspended, these particles behave as nearly perfect hard spheres [11]. We evaporated off the solvent to provide dry particles, which were then redispersed in liquid crystal 5CB at $44 \pm 2\,^\circ$C by sonicating and slowly tumbling in an oven. At this temperature, pure 5CB is in its isotropic phase (isotropic-nematic transition temperature $T_{\mathrm{IN}} \approx 35\,^\circ$C). Particle–liquid-crystal composites with particle volume fractions $2\% \leq \phi \leq 20\%$ were prepared. In all cases, when the mixture was cooled from $\sim 44\,^\circ$C to room temperature ($25\,^\circ$C), a waxy solid resulted (Fig. 1). The mixtures became fluid again on reheating to temperatures $T > 35\,^\circ$C.

To gain insight into the structure of this soft solid we

FIG. 1. A slice of the colloid–liquid-crystal composite, particle volume fraction $\phi = 20\%$. At room temperature it is sufficiently rigid to slice with a knife and engrave. It is shown resting on a paper clip to illustrate sample dimensions.

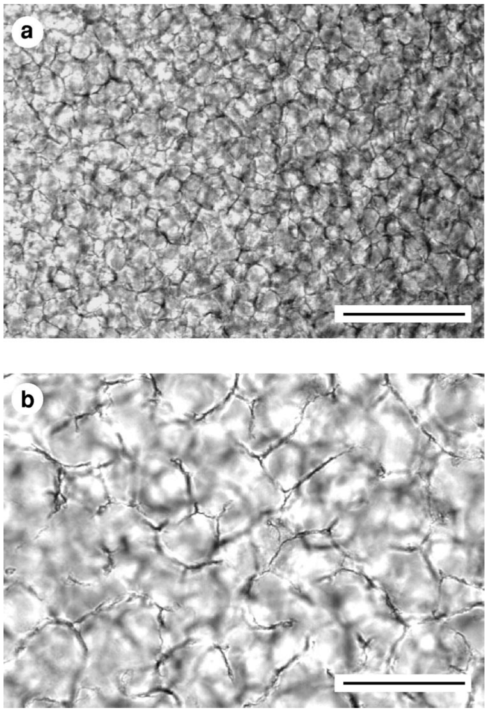

FIG. 2. Micrographs of the typical particle structure, an aggregate network, in the colloid–liquid-crystal composite. The particle structure is viewed by heating the sample above T_{IN}, removing the obscuring birefringent texture. Particle volume fraction (a) $\phi=5\%$, (b) $\phi=2\%$. The initial cooling rate for both samples was $10\,^{\circ}\mathrm{C\,min}^{-1}$. The scale bar is 100 μm.

performed bright-field microscopic observations of composites contained within 0.4 mm thick flat capillaries. In each case, the sample was initially at 45 °C. At this temperature, all samples appeared homogeneous, showing no particle aggregates above 1 μm (the resolution limit of the microscope used). Samples were then cooled at a fixed rate to 25 °C. In all cases the isotropic-nematic transition was clearly marked by the sudden appearance of a birefringent texture which coarsened over a small temperature interval ($\approx 1\,^{\circ}\mathrm{C}$), after which there was no further change in appearance. Below T_{IN}, the birefringent texture of the liquid crystal obscured the particles from view. However, heating the sample above T_{IN} removed the birefringence, leaving the underlying particle structure intact and observable for up to a minute. Figures 2(a) and 2(b) show the typical particle structure, an aggregate network, for composites of $\phi=5\%$ and 2%, respectively. Very recently, this aggregated particle network was observed in the *nematic* phase of the liquid crystal using confocal microscopy [12]. In general, the details of the structure observed depend on the cooling rate as well as the particle volume fraction. Extensive microscopic observations suggest the sample morphology is determined by the phase transition kinetics of the liquid crystal, as shown schematically in Figs. 3(a) to 3(c). Growing nematic droplets expel particles, because the homeotropic alignment of the molecules at the particle surface [13] leads to defects and long-range director distortions (which are energetically unfavorable). These expelled particles become trapped between droplets of pure nematic liquid, forming an interconnected network of particles.

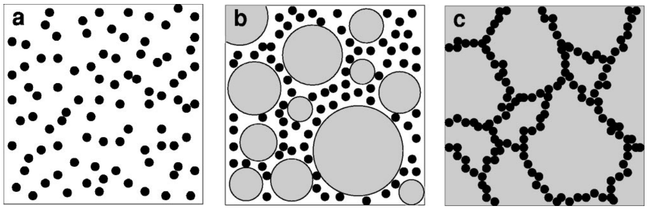

FIG. 3. Stages in the formation of the composite morphology, shown schematically, based on optical microscopy observations. (a) The isotropic dispersion: the colloidal particles (black circles) are dispersed homogeneously in the isotropic phase of 5CB (white). (b) The kinetic mechanism by which the particle network is formed: at the isotropic-nematic transition the colloidal particles are expelled from the emergent nematic droplets (grey regions). The mixture therefore separates into pure (particle-free) nematic domains separated by (particle-rich) isotropic regions. The nematic domains continue to grow until the network morphology is fully developed. The final result, (c), is therefore largely determined by the phase transition kinetics of the liquid crystal.

To quantify the mechanical properties of the composite we performed small-amplitude oscillatory viscoelastic measurements at 1 Hz, strain amplitude 2%, and a constant cooling rate of $3.5\,^{\circ}\mathrm{C\,min}^{-1}$. The storage and loss moduli (G' and G'') as a function of sample temperature T for a $\phi=5\%$ composite are shown in Fig. 4. Close to the pure 5CB isotropic-nematic transition temperature ($T_{\mathrm{IN}}\approx 35\,^{\circ}\mathrm{C}$) we observe a sudden increase in G' by four orders of magnitude to $>10^{2}$ Pa. The storage modulus continues to increase gradually with further cooling to $\sim 10^{3}$ Pa. Qualitatively similar behavior is observed for composites at other particle volume fractions, with the low temperature G' an increasing function of ϕ, reaching $\sim 10^{5}$ Pa for the $\phi=20\%$ composite.

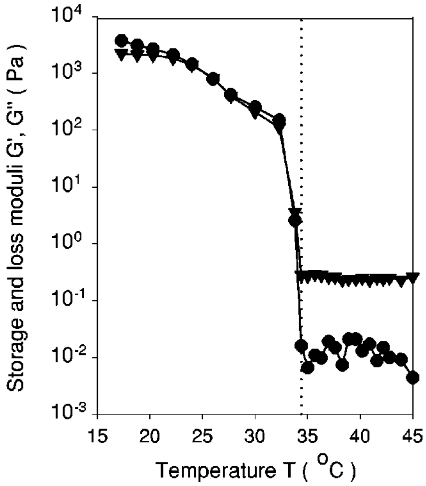

FIG. 4. Oscillatory viscoelastic measurements (1 Hz, amplitude 2%) for a composite of particle volume fraction $\phi=5\%$, as the sample is cooled from the isotropic to the nematic phase (at $3.5\,^{\circ}\mathrm{C\,min}^{-1}$). A transition from a fluid to a viscoelastic solid is evident from the dramatic increase of both the storage modulus G' (solid circles) and the loss modulus G'' (solid triangles). The temperature at which this transition occurs is close to the isotropic-nematic transition temperature of the pure liquid crystal material ($T_{\mathrm{IN}}\approx 35\,^{\circ}\mathrm{C}$, dotted line). The nematic to crystal transition occurs at about 24 °C in the pure material but, in practice, requires significant undercooling and does not affect our observations.

Strong particle interactions are necessary to form such a soft solid. First we may inquire about any intrinsic attraction between the particles, irrespective of the degree of order in the solvent (e.g., van der Waals force). Such forces are obviously present, as indicated by steady-shear viscosity measurements on the isotropic composites ($T=45\,^{\circ}\mathrm{C}$), which were significantly higher than those for hard-sphere suspensions. However, they must be negligible compared to the interactions required to form the nematic soft solid, as microscopic observation of a suspension of particles ($\phi=10\%$) in the isotropic liquid crystal ($T=45\,^{\circ}\mathrm{C}$) showed no significant particle aggregation over 24 h, and the Brownian motion of the particles was evident. On reheating a newly formed colloid–liquid-crystal composite from the nematic into the isotropic phase, the aggregates sediment and break up, most of the particles redisperse, and the mixture becomes fluid again, i.e., the process is essentially reversible.

A more likely source of strong attraction is that arising from the disturbance of the ordering in the nematic phase by the particle surfaces. A simple estimate for the elastic modulus can be made on the basis of previous investigations on dilute suspensions. Pairs of particles in a nematic host interact (anisotropically) in order to minimize elastic distortion energy of the director field, resulting in an effective attraction between the particles [5–7]. This energy is of order $U\sim Ka$, where K is a typical Frank elastic constant for a thermotropic liquid crystal ($\sim 10^{-11}\ \mathrm{J\,m^{-1}}$) and a is the particle radius ($\sim 1\ \mu\mathrm{m}$), resulting in interaction energies of $\sim 1000k_{\mathrm{B}}T$. From the interaction energy U an estimate of the elastic modulus is given by $G'\sim\phi U/a^3\sim\phi K/a^2$ which, for $\phi=5\%$, $a=250$ nm and $K=10^{-11}\ \mathrm{J\,m^{-1}}$, gives $G'\sim 10$ Pa, an underestimate by two orders of magnitude compared to the experimental result.

A different physical picture seems necessary to understand the mechanical properties of colloid–liquid-crystal composites. The following speculative description based on competing molecular interactions is promising. Specifically, the particle-rich regions provide a complex, confining geometry within which nematic order is severely frustrated (assuming homeotropic anchoring is preserved). The gaps between close-packed particles (only several tens of nanometers across) thus contain locally melted isotropic material (Fig. 5). This is analogous to the core of a disclination in a nematic liquid crystal. The estimate of corresponding energy density is well known and given by K/ξ^2 [14], where ξ is the nematic coherence length (typically $\gtrsim 10$ nm). The elastic modulus is obtained from the product of this energy density and the total volume fraction of melted material ($\sim 0.3\phi$, i.e., the volume fraction of the gaps between the close-packed particles). This gives $G'=1500$ Pa for $\phi=5\%$ and $G'=6000$ Pa for $\phi=20\%$, substantially closer to the experimental values. This argument needs to be developed to explain why the energy cost of melting the nematic is less than that incurred by overcoming the homeotropic anchoring at the particle surface. This may be related to the depression of the isotropic-nematic transition temperature in highly confined geometries [15] and a mechanism of particle aggregation by phase separation. In any event, we stress that the storage modulus of this composite is anomalously high, and cannot easily be deduced from the known properties of the parent components.

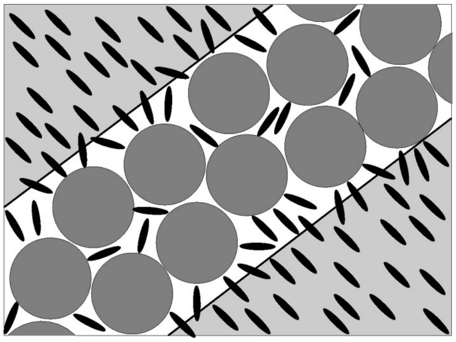

FIG. 5. Schematic representation of the proposed molecular order within particle aggregates (large spheres are particles, small dark rods are liquid crystal molecules). The equilibrium state of the bulk liquid crystal is nematic (light grey regions). The gaps between close-packed particles contain locally melted isotropic material (white region), analogous to the core of a disclination in a nematic liquid crystal.

To conclude, we have shown that mixing colloidal particles with a thermotropic nematic liquid crystal results in a soft solid with an unexpectedly high storage modulus. This exotic composite comprises an interconnected network of particle aggregates, formed by the exclusion of particles from emergent nematic droplets as the mixture is cooled below the isotropic-nematic transition. The unusually high storage modulus of the colloid–liquid-crystal composites may be due to the local frustration of nematic order within the particle aggregates. Finally, we note that the colloid–liquid-crystal composite is a switchable electro-optical material. Preliminary experiments have shown that thin ($\approx 10\ \mu\mathrm{m}$) PMMA-5CB composites can be aligned with moderate voltages ($\gtrsim 3$ V), with the particle network not substantially perturbed by the switching. Since the colloid–liquid-crystal composites are soft solids at room temperature, they may be simply cut and moulded as required, potentially giving them significant advantages in handling and processing over conventional liquid crystalline materials.

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