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LIQUID CRYSTAL CLAY COMPOSITES

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We report a successful method of sterically stabilising small, high aspect ratio clay platelets in a liquid crystalline host using a quaternary ammonium surfactant. Small Angle X-ray Scattering results for the dry powder 2HT-treated Laponite show that there is a monolayer of 2HT on the platelet surface. The data for the Laponite suspension in 5CB indicate free tumbling disks which do not aggregate in the nematic phase.

Keywords: clay; colloid; liquid crystal; platelet; X-ray scattering

INTRODUCTION

Recent work has focused on liquid crystal colloids where particles are suspended in a liquid crystalline solvent. Much of this research has concentrated on the behaviour of spherical particles, such as colloidal silica and polymer lattices of the size range 30 nm to several microns in diameter, dispersed in a liquid crystal [1–5]. Anisometric particles, such as rods and platelets, should give rise to different properties [6]. We look at small high aspect ratio platelets suspended in a thermotropic liquid crystal.

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EXPERIMENTAL

Materials

The thermotropic liquid crystal is 5CB (4-pentyl-4-cyanobiphenyl; K15 Merck BDH) with an isotropic-nematic transition temperature of 35.5°C. We have chosen this liquid crystal because it is a pure substance and the low transition temperature allows handling at room temperature. Laponite RD, a monodisperse synthetic hectorite clay made by Laporte Industries, was chosen as the platelet. The platelets have a diameter of 25 nm and a thickness of 1 nm. BET analysis gives a surface are of $350\,m^2g^{-1}$.

As a surface treatment a cationic surfactant, dimethyldioctadecyl ammonium bromide (2HT; Acros Chemicals), was chosen. This consists of a positively charged ammonium head group and two C_{18} alkyl chains. The cationic head group is attached to the Laponite via a cation exchange process with the sodium counter ions on the platelet surface.

Steric Stabilisation of Laponite

A good suspension of Laponite in water is essential prior to the addition of the surfactant stabilising layer. The dilute Laponite suspensions ($1\,gL^{-1}$) were freshly prepared and stirred vigorously for 24 hours prior to use. The cationic surfactant may be added to the suspension in a quantity slightly in excess of the cation exchange capacity to ensure good surface coverage (0.46 g). The cation exchange capacity (CEC) value for Laponite of 73 meq/100 g determined by Cione et al. [7] was used to calculate the number of available cation exchange sites on the clay surface. The 2HT is added in an 80:20 water/propanol solution.

The mixture was stirred for at least 4 hours after the addition of the 2HT to ensure good surface coverage and maximum delamination of the platelets. The suspension flocculated upon addition of the surfactant, the particles sedimented and the supernatant was removed and replaced with a clean wash solution (80:20 water/propanol). Particles were washed at least three times to remove salt and excess surfactant. The solvent was removed by rotary evaporation and the particles were subsequently dried under vacuum for 24 hours at 80°C. The temperature must not exceed 90°C as degradation of the surfactant may occur. Mechanical grinding with a pestle and mortar to form a fine powder removed large aggregated of dried particles. The fine powder was dried at 80°C under high vacuum at 40 mbar for at least 2 hours to remove all traces of solvent prior to suspension in the liquid crystal.

Suspensions

The particles were added to 5CB above the transition temperature, T_{NI}, and stirred vigorously for 30 minutes. The mixtures were transferred to a thermostatted ultrasonic bath and sonicated at 65°C for 4 to 6 hours until a good suspension was achieved. Immediately prior to dispersion, a number of bubbles appear at the surface of the mixture. It is unclear whether this is trapped gas from the stirring step, or the last traces of bound water close to the particle surface. Successful suspension was achieved when the mixture became translucent.

The suspension is stable for 24 hours, after this point colloidal phase separation occurs, however this phase separation may be easily reversed by heating to the isotropic phase and stirring. To ensure that the treatment necessary to result in suspension had not degraded the liquid crystal, the refractive indices of both pure 5CB and the 1% suspension were measured using an Abbe refractometer and compared. The results, given in the table below, clearly indicate that the liquid crystal has not degraded. Measurements of the transition temperature were recorded and show no change for the suspensions as compared to the pure 5CB. This test may be used as an indicator for the absence of solvents in the system.

X RAY SCATTERING

Small Angle X ray Scattering (SAXS) over a temperature range for, 25°C to 40°C was performed at the University of Bristol Physics Department. The diffraction measurements were made using copper Ka X-rays, from a sealed tube with other wavelengths removed using a nickel filter and a graphite monochromator. The diffraction pattern was detected using a multi-wire are a detector [8]. It was placed at 840 mm from the sample with an evacuated path so that a Q (scattering vector) range from 0.003 Å^{-1} to 0.5 Å^{-1} was covered. The sample to detector distance was calibrated using a silver behenate standard [9]. The samples were cooled from the isotropic phase in an ~ 0.5 T magnetic field. The scattering data were radially averaged.

TABLE 1 Refractive Index Measurements: Light Source was a Sodium Lamp and Measurements Were Taken at a Temperature of 21.5°C

$\lambda = 589.6$ nm T = 21.5°C	Pure 5CB	1%w./w. suspension
n_o	1.5330 ± 0.0004	1.5327 ± 0.0004
n_e	1.7234 ± 0.003	1.7257 ± 0.003

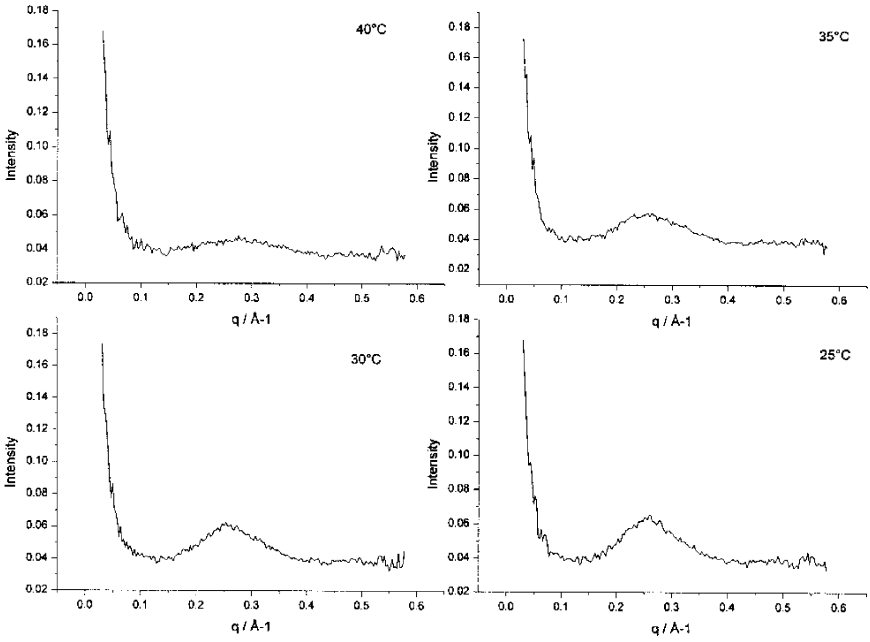

FIGURE 1 SAXS of Pure 5CB at temperatures of 40°C, 35°C, 30°C and 25°C. The peak at $q = 0.26\,Å^{-1}$ equivalent to $25\,Å^{-1}$ is typical for the dimer length of 5CB molecules.

As calibration, SAXS data was recorded for pure 5CB in the temperature range of 25°C to 40°C. The 5CB sample was aligned in the 0.5 T magnetic field and these data were used to correct for the background on subsequent data sets for the suspension. The radially averaged data show a clear peak at $q = 0.26\,Å^{-1}$ equivalent to 25 Å which is typical for the dimer length of 5CB. The single molecule length is 18.7 Å [10]. The peak is most prominent at 25°C and decreases with increasing temperatures, showing that long-range order is destroyed by increasing temperatures.

A sample of the dry powder of 2HT-treated Laponite shows a shoulder at $q = 0.27\ Å^{-1}$ which corresponds to a platelet separation of 24 Å. The inter-platelet separation is therefore 14 Å, slightly greater than the molecular length of the 2HT molecule, 12 Å [11]. This suggests that only a monolayer of 2HT is present on each platelet surface and these overlap almost completely with the 2HT molecules on the surface of the neighbouring platelet.

For a 5%w./w. suspension of 2HT-treated Laponite 5CB, the scattering date appear to be almost featureless. It does not show any temperature dependence. This strongly suggests that the sample is now so viscous that it

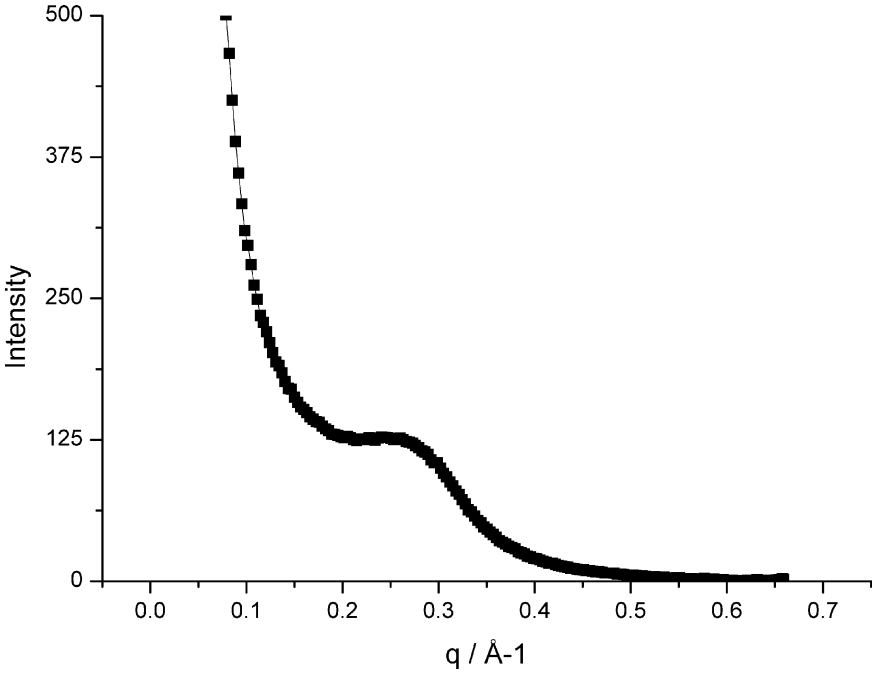

FIGURE 2 SAXS of Dry Powder 2HT treated Laponite. The peak a $q = 0.27\,Å^{-1}$ corresponds to a distance of 24 Å.

cannot be aligned by the magnetic filed. The smoothness and shape of the curve suggest that the platelets are well dispersed and free tumbling. However, a flattened section between $q = 0.14\,Å^{-1}$ and $q = 0.25\,Å^{-1}$ Shows that aggregates of a wide range of sizes also contribute to the scattering intensity.

We were not able to confirm the radius of 130 Å for Laponite. The Guinier Approximation, a widely used approximation for particle sizing [12], restricts the range of scattering wavevectors that may be used for size analysis to $0 < q < qR < 1$ where R is the radius of the platelet. Unfortunately there are insufficient data points at low q to determine the particle size, however further experiments at lower q may be used to analyse this further.

CONCLUSIONS

The translucence of the nematic phase suggests that nematic ordering of the platelets occurs. The platelets themselves are too small to scatter light

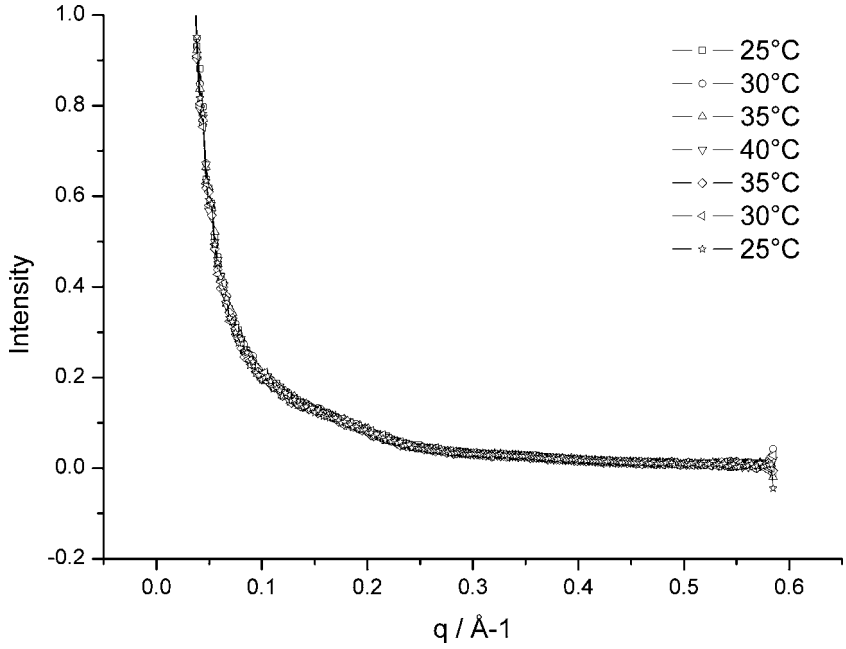

FIGURE 3 SAXS of 5%w./w. 2HT treated Laponite in 5CB over a temperature range.

in the visible range. The scattering signal from background corrected SAXS data proves that the clay particles are suspended in the liquid crystal in both the isotropic and nematic phases. There is no discernible difference between the scattering from the suspensions in the isotropic and nematic states indicating that no further aggregation upon cooling to the nematic phase. These suspensions are stable for up to 24 hours. This differentiates liquid crystal clay suspensions from suspensions of spheres in liquid crystals.

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