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Thermotropic liquid crystals embedded in a high water gel system

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Abstract: An emulsion was formed when the thermotropic liquid crystal (LC) mixture E5 was added to an aqueous polyvinylalcohol (pva) solution and shaken. This emulsion was gelled by addition of an aqueous borax solution. The pva polymer functioned not only as the gelling agent but also appeared to act as a polymeric surfactant which stabilised the LC droplets. This high water gel-liquid crystal (HWG-LC) system contained nearly 80 wt % water and more LC wt % than polymer. The system was thermally reversible, undergoing a gel to sol transition upon heating to 70 °C and reforming a gel upon cooling. The HWG-LC showed electrooptical behaviour dependent upon a switched electric field when constrained between transparent electrodes. The pressure required to form a thin film between these electrodes induced a structural emulsion in the dispersion causing LC droplet disruption and the formation of an LC network in the gel.

Key words: Liquid crystal – emulsion – gel – polyvinylalcohol – electrooptic

Introduction

Low molecular weight liquid crystals (LC) dispersed in polymeric carrier materials (polymer-dispersed liquid crystals, PDLC) have been widely investigated in recent years. Two types of PDLC systems have been described. In some systems the LC molecules in the separate LC bulk have no preferred orientation [1, 2] in others the LC molecules have a preferred orientation in the LC bulk in the absence of an electric field [3–5]. In the latter case the preferred LC orientation is induced by the structure of the polymer used. Electric fields may influence the orientation of the LC in the droplets [1, 5].

The aim of this work was to examine the possibility of using a gel as carrier material for dispersed thermotropic LC. The gelation properties of gelatin in aqueous solutions have long been known [6]. More recently the gelation properties of gelatin have been exploited in low water systems in organic solvents [7]. Microemulsion-based organo gels can be formed by inclusions of gelatin in a w/o microemulsion [7–9]. Although the phase stability, structure and physical properties of gelatin-containing, AOT (sodium salt of bis(2-ethylhexyl sulphosuccinate) stabilised microemulsion-based organo-gels have been studied as a function of systems composition, these are complex multicomponent systems [10]. Less complex gelling systems have been described which contain fewer components. An example of such a system would be aqueous polyvinylalcohol (pva) which may be gelled by controlled addition of borax [11]. Gels are very sensitive systems, especially with respect to the concentration relationship between the components. In this paper, we address the issue of whether it is possible to embed guest molecules (in our case thermotropic LC) in a pva gel as a separate phase without destroying gelation behavior or the final gel structure.

Experimental methods

A high water gel with embedded liquid crystals (HWG-LC) was prepared from a solution containing 5 wt % (w/v) polyvinyl alcohol (pva) of molecular weight range 30 000–70 000 (Lalls) in double distilled water. The LC mixture E5/12/(Merck) was edded to this aqueous polymer solution to give a final ratio of 5 : 1 (w/w) of polymer solution to LC mixture. The resulting mixture was either shaken vigorously or homogenised using an OMNI 2000 mixer (Camlab). The pva/LC emulsion was gelled by addition of saturated aqueous borax solution to a final weight ratio of emulsion to borax solution of 6 : 1.

Structural investigations of the HWG-LC systems were carried out using a polarization microscope (Carl Zeiss Jena) and a scanning electron microscope SEM 501 B (Philips). The range of LC droplet size in the resulting emulsion and in the HWG-LC was determined using a polarization microscope.

The electrooptical behaviour the HWG-LC was investigated by mounting a sample between two transparent electrodes. The latter consisted of an In_2O_3 layer (750 Å) sputtered on a glass substrate. The gel layer thickness between the electrodes was 25 μm or 100 μm.

Results and discussion

The possibility of embedding LC in an aqueous high water content gel system was studied using a water/polyvinylalcohol/borax carrier system [11]. Initially, the emulsifying properties of solutions were investigated to determine whether stable emulsion could be formed with the pva acting as the surfactant. This decision was based on the observation that during the preparation of aqueous pva solution, stable foams were formed. This indicated that the pva molecules possessed surfactant-like properties. Sample emulsification studies were undertaken using mixtures of aqueous pva solutions and heptane (5 : 1 w/w) and stable emulsions were formed. In separate experiments, emulsions were prepared with aqueous pva solutions and LC mixture E5 (5 : 1 w/w). Again, stable emulsions were observed after mixing. There was no evidence of breakage of the emulsion to yield a separate organic phase after 3 weeks' storage. The LC droplet size was dependent upon the emulsifying power and was characterized by microscopy. Vigorous manual shaking produced droplets of diameter 40–300 μm, and homogenisation using the OMNI 2000 operating at 5000 r.p.m. produced droplets in the size range of 3–20 μm. No significant reduction in the droplet size was obtained by increasing the homogeniser speed to 30 000 r.p.m. Droplets of embedded LC can be seen clearly in the micrograph of the emulsion shown in Fig. 1. Furthermore, the polarisation optics used revealed that orientation of the LC in the droplets was variable.

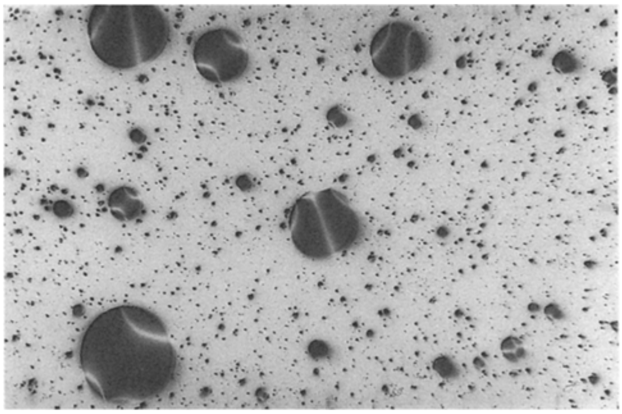

Fig. 1. Thermotropic liquid crystal droplets in a 5 wt % aqueous polyvinylalcohol solution under the polarization microscope. $T = 25\,^{\circ}C$. (Magnification 25 ×)

If 0.2 g of a saturated aqueous borax solution was added to 1 g of aqueous pva solution (5 % w/w) a transparent gel was quickly formed. The most important factor controlling gel formation was the pva concentration. If this concentration was too low (under 2.5 wt %) no gel was formed.

Similarly, the aqueous pva/LC emulsion can be gelled by addition of aqueous borax solution. Gelation was rapid in spite of the system containing a molar excess of LC. Visual examination of the gel showed it to be similar to that formed in the absence of LC. Scanning electron microscopy was used to investigate the structure of the liquid crystal/pva gel. Figure 2 shows clearly that the LC is embedded in droplet form in the gel. There are two possible explanations that could account for the formation of the stable LC emulsion in aqueous pva solution. In the first model, the pva does not adsorb on the interfacial layer but acts as a stabiliser that prevents creaming and coalescence of th droplets by increasing the viscosity of the aqueous continuous phase. In the second

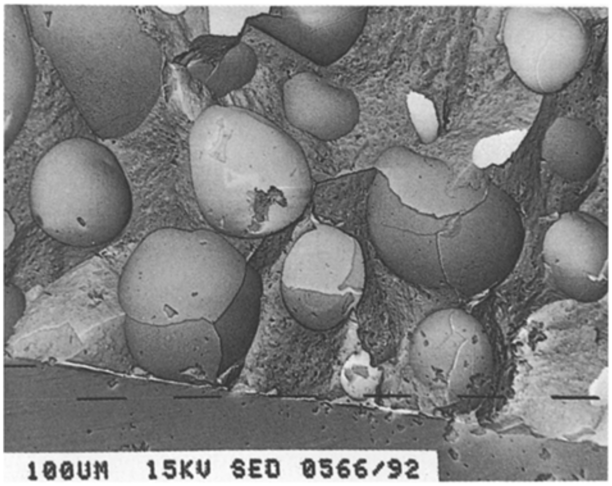

Fig. 2. Scanning electron micrographs of thermotropic liquid crystal droplets embedded in a polyvinylalcohol-water/borax-gel

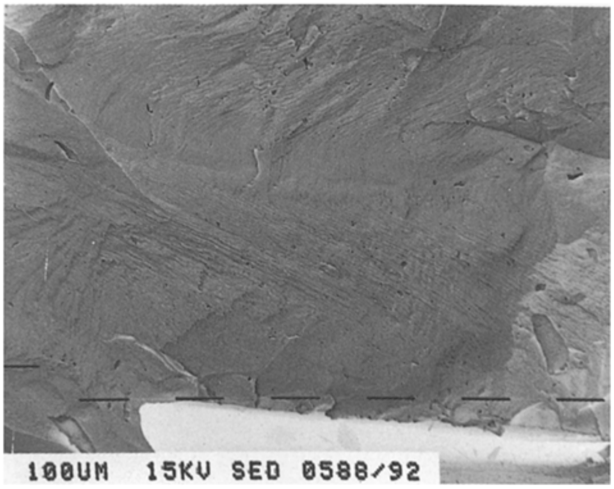

Fig. 3. A scanning electron micrograph a polyvinylalcohol-water/borax-gel (5 wt% pva)

model, the pva acts as a surfactant and is adsorbed onto the droplet surface. Electron microscopy provides evidence for the second model. As can be seen in Fig. 2, there is clear evidence of a shell-like structure that covers the surface of the droplet. It is interesting to consider whether the pva molecule chains adsorbed at the LC-water interface can take part in the gel formation.

The following experiment was performed to investigate this question. Two samples containing 1 g of pure 5 wt% aqueous pva solution were prepared, one of which contained 0.2 g of embedded LC. Both pva solutions were titrated with a borax solution. Gelation occurred in both solutions after addition of the same amount of borax solution. This indicated that a similar number concentration of hydroxyl groups, which form the complex with borax, was present in the sample irrespective of the presence or absence of LC. This supports a model where the aliphatic chains project towards the LC droplet surface and the hydroxyl groups are in contact with the aqueous continuous phase. This would suggest that a proportion of the hydroxyl groups of the adsorbed pva molecules could be involved in complex formation with the added borax ions and be intimately involved in the gelation process [11]. Figure 3 shows the pure pva/water-borax gel and confirms that the observed inclusions in the gel are LC containing droplets and not embedded air bubbles.

The thermal behaviour of the sample was investigated by heating at the rate of 1 °C per 3 min to a maximum temperature of 70 °C. Heating the sample to a temperature of 32.5 °C resulted in no visually determined change in the gel structure. Above this temperature the gel melted to produce a very viscous solution but this was not accompanied by any change in turbidity. At 50 °C, the clearing point [12] of this LC mixture (corresponding to a phase transition from nematic to isotropic for E5), no change was observed. A stable gel formed again when the sample was allowed to cool to room temperature and LC droplets were observed by microscopy. Thus, the gelation properties of the HWG-LC sample were thermally reversible.

Preliminary investigations of the electrooptical properties of the LC molecules embedded as a separate phase in the high water gel were also made using the polarization microscope. Samples between two transparent electrodes with a cell gap of 25 μm or 100 μm showed a scattering effect [1] dependent upon application of an electric field. The threshold voltage V_{th} [13] was nearly 40 V for a sample with a thickness layer of 25 μm and 95 V with a thickness layer of 100 μm. It was notable that the droplet structure of the separate LC phase in the HWG-LC sample between the transparent electrodes was destroyed by the

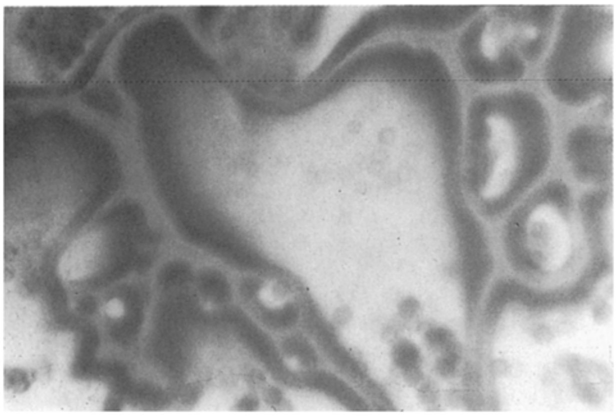

Fig. 4. A liquid crystal network in a polyvinylalcohol-water/borax-gel (sample under pressure) under the polarization microscope. $T = 25\,°C$. (Magnification 12.5 ×)

pressure exerted on the HWG-LC when the sample was mounted between the two transparent electrodes. The embedded droplet structure was lost and replaced by the formation of an LC network penetrating through the gel (Fig. 4). Observations by microscopy revealed that the LC network was widespread and distributed throughout the sample. The electrooptical properties of this system remained active for long periods. The sample could still be electrically switched after 9 weeks even when there was no provision made to seal the gel between the electrodes. This suggested that electrolysis was strongly inhibited in this sample.

Further studies of this system are underway including more detailed characterization of the electrical conductivity (see also [5]), the dependence of the electrooptical properties on the thickness of the HWG-LC and the refractive index measurements of the components.

Conclusion

A high water content (80 wt%) gelled system containing embedded LC has been described. The dispersed LC phase can be switched by application of an electric field and the systems shows good stability against electrolytic degradation.

These studies have been extended to investigate LC behaviour in other gelled systems. In preliminary studies we have identified the formation of a lamellar phase in a microemulsion-based gel which contained nearly equal volumes of oil and water.

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