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Cholesteric materials with photonic band gap sensitive to shear deformation and mechanical sensors

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Shear deformation of highly viscous liquid crystals obtained as mixtures of high and low molar weight liquid crystals results in dramatic reversible changes of the selective reflection band and colour. The colour of the material changed instantaneously during the deformation; the time of its restoration increases with the viscosity of the polymer mixture. A qualitative model considering viscoelasticity of the liquid crystals is proposed to explain changes in the reflection spectra and microscopic observations of the texture.

Keywords: cholesteric; colour; deformation; shear; viscoelastic; deformation sensor

1. Introduction

In this article, highly viscous cholesteric liquid crystals (CLCs) displaying significant colour changes under shear deformation are described. In previous publications [1, 2] we focused on the mechanical properties of highly viscous CLCs confined between two silicone strips and studied the elongation of that system. Gigantic colour changes displayed during stretching of such a system were explained by contraction of the cholesteric helix in terms of a simple mechanical model.

The shear deformation applied to highly viscous CLC sandwiched between two glass plates leads to different structural changes in CLCs which can not be explained in terms of the model developed previously [2], as that model was suitable only for a particular geometry. Since highly viscous CLCs can be very sensitive to mechanical stress and will respond to it by altering their colour while retaining these alterations for a prolonged period of time, they are good candidates for novel colour changing mechanical sensors. The complex reflection properties of CLCs under different types of deformation were scarcely studied. A shear orientation effect has been observed at low viscosities but no selective reflection studies were made [3]. Periodic dark and bright bands often observed after shear cessation have been explained in terms of formation of a more nematic-like order [4] and in terms of storage of elastic energy by polymer chains [6]. The re-orientation of the cholesteric helix towards the direction of shear was observed in cholesterol nonanoate in case of a short helical pitch and the opposite orientation of helix in case of a long pitch [5]. The rheological behaviour of low molar mass CLC has also been studied [6] and explained in terms of a Maxwell model.

In our system, Wacker oligomer chains form rings with a number of monomer units between 5 and 8 (Figure 1(a)) and it is the ring structure that actually contributes to a very high melting point and the ability to vitrify (the same is true for other oligomers with cyclic polymer chains [7, 8]). Adding some low molar mass liquid crystals to Wacker polymers results in highly viscous CLCs [1, 2], which can be used to visualise mechanical stress on objects of complex shape, thus overcoming the major obstacle in stress visualisation in a variety of lyotropic systems [9] or in common CLCs, which is related to their low viscosity and the absence of memory about the previous deformation state. Indeed, in common liquid crystals the alteration of helical pitch quickly vanishes due to fast relaxation that is proportional to

$$\frac{\gamma P^2}{K} = 3 \times 10^{-3}\ \text{s},$$

where K is a typical elastic constant, γ is viscosity and P is helical pitch, with typical values corresponding to 10^{-11} N, 0.1 Pa s and 500 nm, respectively.

The other class of materials that responds reversibly to different types of deformation by changing their helical pitch and keeping these changes in the deformed state are cholesteric elastomers. The properties of different cholesteric elastomers have been studied and modelled (see, for example, [10–13]). Recent developments of elastomeric models and other cholesteric systems are reported elsewhere [14–16]. It is also worth noting that shear deformation may result

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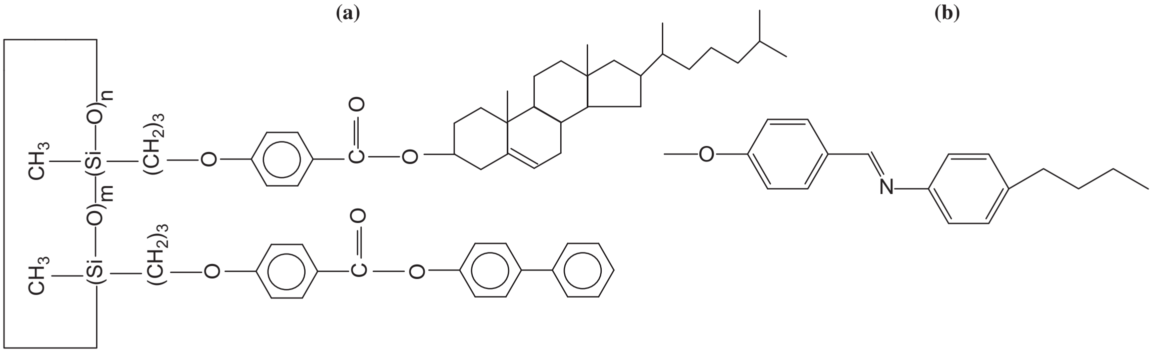

Figure 1. Chemical structure of the components of the mixture: (a) Wacker oligomer; and (b) MBBA.

in a development of peculiar orientation of liquid crystal [17].

In this paper we discuss novel highly viscous CLCs under shear stress leading to profound and peculiar colour changes, which are observed for the first time and are explained in terms of the qualitative model.

2. Results and discussion

The procedure used to obtain highly viscous CLCs was described previously [1, 2]. Here we merely mention that the procedure is based on dissolving the oligomers shown in Figure 1(a) in low molar mass liquid crystals, 4-methoxybenzylidene-4-butylaniline (MBBA), shown in Figure 1(b). Planar cholesteric film was placed between two glass plates with the appropriate treatment of the surface (rubbed with polyvinyl alcohol or polyacrylic acid). The separation between the glass plates was kept constant by placing some glass beads between them.

A schematic representation of the CLC placed between two glass plates and subject to shear deformation is given in Figure 2(a), where the light source and spectrometer used to collect reflection spectra are also shown. The lower glass stayed at rest, but the upper glass was able to move parallel to the lower one (Figure 2(b)). This movement was achieved either by the weight attached to the upper glass, or by punching it with an electromagnet to ensure repeatability of the experiments. The spectra of the sample and its deformation were recorded at the time of deformation in 30 ms intervals.

The mechanical properties of the mixture are quite different from the properties of the original compounds. In the range of MBBA concentration between 25% and 14%, the mixture displays highly visible viscoelastic behaviour; a small stretched piece of the material contracts back – if the material is put between two glass plates and the upper plate is shifted, the deformation is reversible. It becomes especially evident when an air bubble is trapped between glasses. Before applying shear deformation, the bubble is round; during the deformation it elongates and then relaxes back to its initial shape (Figure 3). This can actually serve as a measure of relative relaxation time. A typical relaxation time for the mixture consisting of 85% Wacker polymer and 15% MBBA is about 25 min and increases with decreasing concentration of MBBA. At lower concentrations (less than 5%) of low molar mass liquid crystal (MBBA), the mixture behaves as glass.

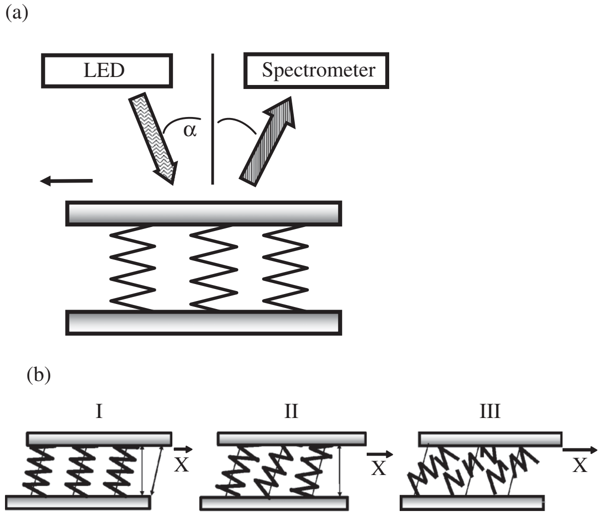

Figure 2. Experimental setup (a) and stages of sample deformation (b): stage I – elongation of helical pitch, stage II –distortion of the helical pitch and folding of cholesteric planes, stage III – breaking of planar cholesteric order.

The shift of the glass and shear deformation both induce significant colour changes and displace the spectral position of the selective reflection band (SRB) (see Figure 4). These spectra are from the white light source and include Fresnel reflections from light sources. However, in contrast to our earlier studies of highly viscous cholesteric systems sandwiched between two silicone strips [1, 2], shear deformation results in a quite different type of behaviour. The reflection

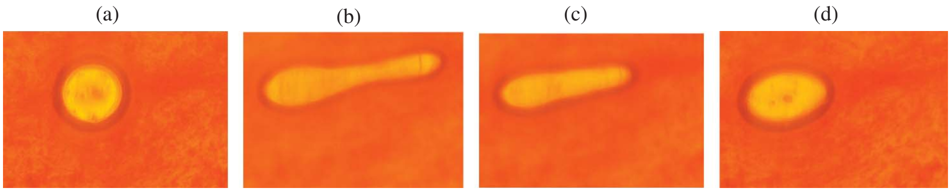

Figure 3. Relaxation of air bubbles trapped in cholesteric sample consisting of ca. 15% MBBA and 85% Wacker oligomer: (a) initial round shape; (b) at a maximum deformation; (c) 10 min after cessation of shear; and (d) 25 min after cessation of shear.

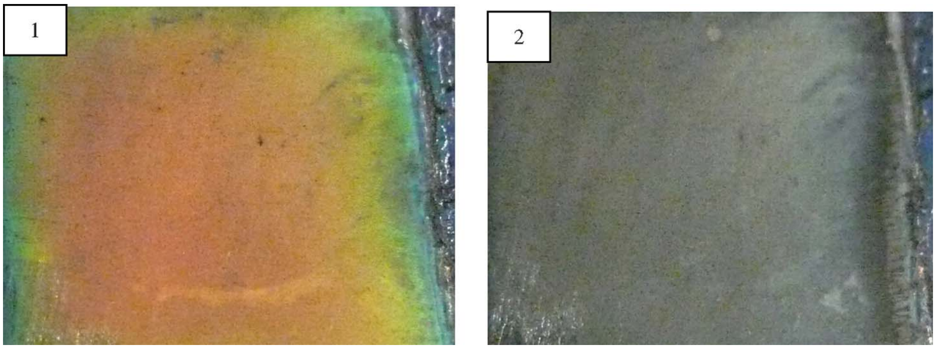

Figure 4. Colour changes before (1) and after (2) shear deformation.

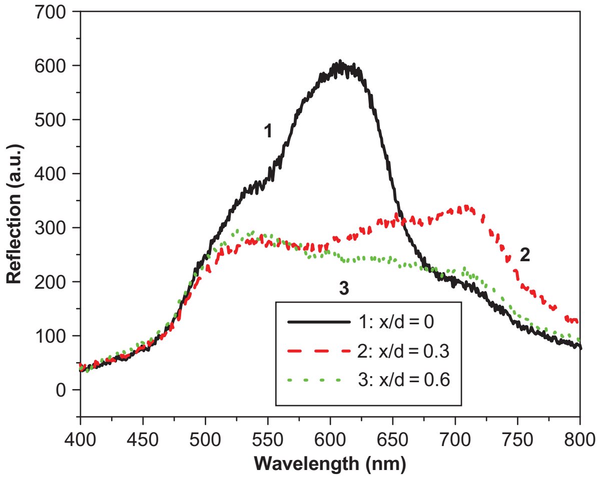

Figure 5. Changes in the reflection spectra under deformation: stage I occurs between spectrum 1 and 2, stage II corresponds to spectrum 2, and stage III corresponds to spectrum 3.

spectra of the sample are given in Figure 5. The shift of the upper plate occurred during ca. 5 s and its magnitude did not exceed 1.5 mm. At the very initial stage of deformation (stage I, when deformation is less than ca. 0.3), the reflection spectrum from white light source actually shifts towards longer wavelengths, then moves towards shorter wavelengths (stage II) and then does not change even if deformation persists (stage III). Stages II and III are characterised by increased light scattering that reaches a maximum at stage III.

The increasing reflection at longer wavelengths at the initial stage of shear (stage I) means that the helical pitch inclines and extends towards the direction of upper plate motion. If we assume that the process is purely elastic at early stage I, then from simple geometrical considerations, the extension of the helical pitch in ideal sample is

$$P = \frac{\sqrt{d^2 + x^2}}{m},$$

where d is the thickness of the sample, x is the displacement of the upper glass of the sample and m is the number of helical periods in the non-deformed sample. If the number of helical twists does not change, then $P = P_0 \frac{\sqrt{d^2+x^2}}{d}$ and the spectral position of the selective reflection band is characterised by the condition

$$nP\cos(\alpha + r) = \lambda, \tag{1}$$

where α is the angle of incidence on the CLC surface, $r = \arcsin(\frac{x}{\sqrt{x^2+d^2}})$ is the inclination of cholesteric helix, $\alpha + r$ is the angle of incidence on cholesteric planes, and n is the average refractive index.

The shift of the selective reflection band calculated from Equation (1) for the experimental condition $\gamma = 20^{\circ}$, a sample thickness of 100 μm and a deformation of about $x/d = 0.2$ gives ca. 60 nm, which corresponds approximately to the transition between spectra 1 and 2 in Figure 5. Thus, we conclude that this equation works well at a very initial stage of deformation and then breaks down as the cholesteric helix shortens back to its initial value and the cholesteric planes deform (stages II, III). At these later stages the helix deforms, cholesteric planes bend and fold, and the number of domains rises, which lead to the increasing light scattering. If deformation continues at stage III, the colour of the sample diminishes and the CLC becomes almost colourless.

If shear deformation is relatively small (the ratio x/d is less than ca. 0.2), the colour of the sample consisting of 20% MBBA and 80% Wacker 540 is restored in about 5 min. For the sample consisting of 30% MBBA and Wacker 540, full restoration of the colour takes a much shorter time.

It is important to note that the mechanism of colour restoration in sheared samples is different from that of samples placed between silicone strips [1, 2], which compress the cholesteric helix when stretched. The time needed to restore the colour of the sheared sample also depends on the magnitude of deformation, in other words, on how far stage II (folding of cholesteric planes and formation of the domains) has progressed. After significant shift of the upper glass, the colour of the sample restores more slowly by a factor of approximately 2–3 than in the case of small deformation. The relaxation time calculated from the simple equation $\frac{K}{\gamma P^2} = 360\,\mathrm{s}$ which assumes $\gamma = 10^4$ Pa s, $P = 600$ nm and $K = 10^{-11}$ N correlates well with the measured relaxation of the sample of ca. 5 min.

The effect of the selective reflection band shift and its slow relaxation back to the original position was used to build a deformation sensor consisting of two plates with the CLC sample placed in between. Such a sensor consists of two glass plates, one of which is free to move. The plates are irradiated by a light-emitting diode (LED) and the intensity of reflected (or transmitted) light is measured by another diode. The system was graduated in terms of photodiode voltage as a function of displacement. The viscoelasticity of the sandwiched CLC leads to a good reproducibility and high sensitivity of the measurements in case of small deformations (Figure 6). The hysteresis effect is almost negligible at stage I. Such sensors can also have different geometrical shapes; for example, they can be made of two concentrically mounted cylinders with CLC placed in between them. The small angles of rotation could then be measured. Other configurations suited for particular application are also possible.

3. Conclusions

The reflection from highly viscous cholesteric materials based on cyclic Wacker oligomers that reversibly change colour under shear deformation has been studied and three stages of deformation related to changes in optical spectra have been identified. The relaxation processes in these materials are slow and depend on the viscosity of the samples, which in turn depend on the concentration of low molar mass liquid crystal in a polymer matrix. The viscoelastic behaviour allows us to build simple and sensitive prototypes of mechanical sensors.

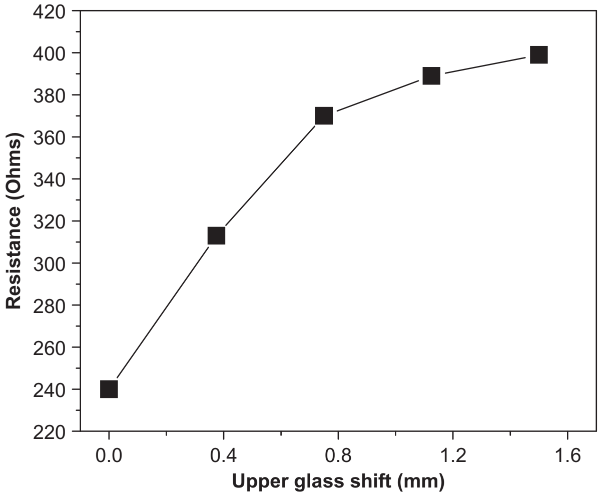

Figure 6. Resistance of the photodiode as a function of deformation.

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