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Mechanism of colour changes in stretchable cholesteric films

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Large shifts of the selective reflection band and colour changes are achieved in highly viscous mixtures of cholesteric polymers and low molar mass liquid crystals subject to mechanical deformation. The liquid crystal mixture was sandwiched between two silicone strips and stretched. The colour of the material changed instantaneously during stretching, and the time for the colour to be completely restored increased with the viscosity of the polymer mixture. A quantitative model considering the material as an incompressible viscoelastic fluid is proposed. The model accurately describes colour changes (shift of the selective reflection band) and its relaxation back to the original spectral location.

Keywords: cholesteric; colour; deformation; stretching

1. Introduction

Cholesteric liquid crystals (CLCs) with a helical structure that may be very sensitive to mechanical stress present a class of materials almost ideally suited to build a variety of mechanical sensors and to visualise a distribution of stress. It is well known that the colour of a cholesteric sample and the position of a centre of the selective reflection band (SRB) is determined by $\lambda = nP$ (where P is the helical pitch of the chiral liquid crystal, and $n = (n_e + n_o)/2$, that is the average refractive index of the cholesteric planes [1]). However, in common thermotropic low molar mass liquid crystals the alteration of helical pitch quickly vanishes due to low viscosity and a fast relaxation rate that is proportional to $\frac{\kappa}{\gamma P} = 10^{-3} \text{ m s}^{-1}$ (see [2]). Quick relaxation does not permit to visualise a deformation and store its current state.

Recently, considerable efforts were directed towards the design of cholesteric materials, namely cholesteric elastomers that could respond reversibly to different types of deformation by changing the helical pitch and keeping these changes in the deformed state [3–6]. Finkelmann *et al.* synthesised and studied cholesteric elastomers under uniaxial and biaxial stress [3]. Terentjev *et al.* studied deformation of elastomers and changes in their photonic band gap [4–7]. Cholesteric elastomers represent a group of chiral polymers, whose behaviour, in theoretical terms, can be described by purely elastic deformation; a number of such models were recently suggested [8, 9].

In this paper we present novel highly viscous CLC materials and discuss the mechanical properties that we believe make them very attractive for a new generation of mechanical sensors or materials able to

visualise mechanical stress. The dissipation of energy in these mechanically stressed materials cannot be neglected; therefore, the exact models developed for CLCs and elastic cholesteric polymers cannot be applied [10–12].

Some attempts were made to use regular CLCs with moderate viscosity to visualise a distribution of shear stress. For example, in Reda and Wilder's research [13], the common mixture of cholesteric derivatives was used for aerodynamic applications on airplane models. However, low viscosity of common cholesteric mixtures makes it difficult to keep a layer of liquid crystal on the surface of the model. One could imagine an ideal CLC material that is able to visualise a deformation by quickly changing and storing the colour following the applied strain. The classes of materials that may possess such an attractive property are viscous chiral polymer solutions, for example lyotropic cholesteric liquid crystals [14].

High viscosity of CLCs may also be achieved by dissolving cholesteric polymers in low molar mass liquid crystals. Care must be taken to account for miscibility of the polymer and low molar mass compounds. Once the appropriate combination is found, the mechanical properties of the mixture are expected to be quite different from the original compounds; the viscoelastic properties will make the behaviour of the mixture more complex, and it is not possible to consider it in terms of only pure elastic deformation.

The CLCs discussed here were obtained by mixing polymers and low molar mass compounds and, as we show below, belong to a class of highly viscous materials. As such, they display a much larger shift of the photonic band gap than cholesteric elastomers. Being

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doped with laser dyes, they may also display mechanically tunable optically pumped lasing; we have previously discussed this effect elsewhere [15].

2. Results and discussion

Highly viscous materials were prepared by mixing 70–80 wt% of silicone-based cholesteric liquid crystals C4745, C4754 or C4768 (Wacker Co.) and 30–20 wt% of a nematic liquid crystal, MBBA (Sigma-Aldrich Co.); see Figure 1 for the chemical structures of liquid crystalline compounds.

In a search for a miscible mixture we tried many low molar mass liquid crystals, and the combination discussed here seems to give the best results. The concentration of chiral groups in the Wacker polymers decreases from C4745 to C4768, leading to a longer selective reflection wavelength (450 nm, 540 nm and 660 nm, respectively). The viscosity of the mixtures was measured either by the vibrating fork or by the two plates method, and was found to significantly increase with polymer concentration (Figure 2).

The vibrating fork method works well only at relatively low viscosities and concentrations of polymers in a mixture (less than 18%). At higher concentrations the vibration of the fork is completely damped; the two plates technique was used to measure viscosity at

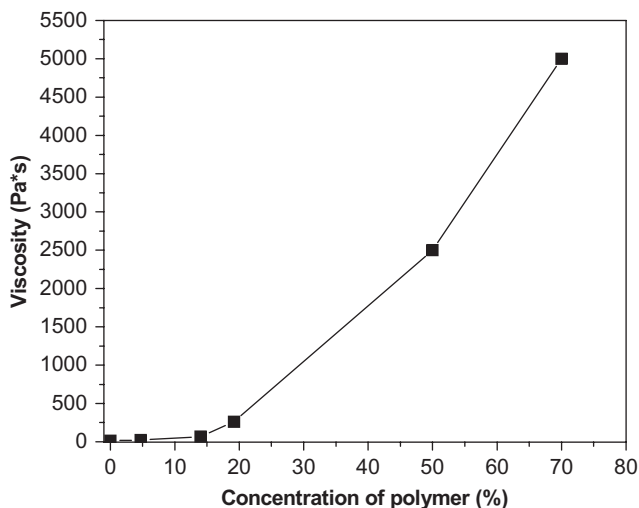


Figure 2. Viscosity of the sample as a function of polymer concentration.

higher polymer concentrations. The CLC mixture was placed between two glass plates, the varying pushing force induced the motion of the upper plate with respect to the lower one with constant velocity. The effective viscosity can be estimated from the equation

$$\gamma = \frac{Fd}{Av}, \quad (1)$$

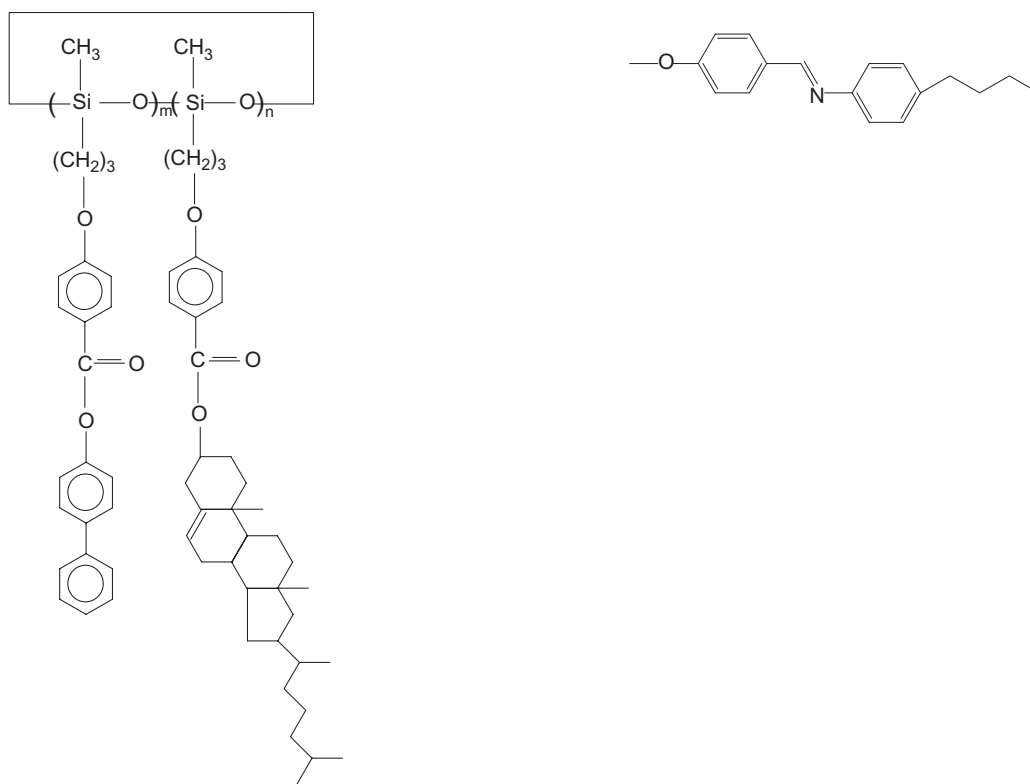


Figure 1. Chemical structure of the components of the mixture.

where d is the distance between plates, F is the pushing force, A is the area of the sample, and v is the velocity of upper plate motion.

It is important to note that in the two plates method the measured viscosity is not related to permeation flow (the flow of liquid crystal occurs parallel to cholesteric planes); therefore, the viscosity must be significantly lower (by three to four orders of magnitude) than in the case of flow in the direction perpendicular to the planes [1]. By combining different polymers and changing the concentration of the nematic liquid crystal in the mixture, it was possible not only to change the helical pitch of the mixture and adjust the position of the SRB to any point in the visible light spectrum of the undeformed material, but also to choose the desired viscosity of the sample. We found that the most stable and pronounced colour changes occur at polymer concentrations ranging from 65% to 80%. All measurements were made at room temperature ($22^{\circ}\text{C} \pm 1^{\circ}\text{C}$).

The CLC mixture was placed between two transparent silicon strips, one side of which was treated using a 20% NaOH water solution, and was subsequently rubbed. Alternatively, a thin layer of cholesteric paste can be deposited on just one strip.

The schematic representation of the CLC placed between two transparent strips under stretching deformation is given in Figure 3. Stretching of such a sandwiched structure induces a shift of the SRB from a longer wavelength towards a shorter wavelength. The shift is accompanied by a colour change, which depends on the degree of stretching and the composition of the cholesteric liquid crystal. A film exemplifying a red to green colour shift under 20% deformation is shown in Figure 4.

Colour is immediately and completely restored after deformation, when the sample returns to its

original length. If the film is kept stretched, the centre of the SRB slowly shifts back to its original position. The rate of the colour restoration in a stretched state depends on the viscosity of the sample. Higher viscosity leads to a slower rate. Complete restoration of colour takes several hours under a 30% deformation for a sample consisting of 80 wt% of C4745 and 20 wt% of MBBA.

We suggest the following major mechanism as a potential cause for the observed colour changes and the shift of the SRB. Contraction of the sample occurs along the axis perpendicular to the surface of the film. As the liquid crystal is attached to the silicone strips, a decrease in the distance between them results in readjustment of the helical pitch. Thus, the mechanism of the pitch decrease is somewhat similar to the mechanism resulting from confinement in a Grandjean-Cano wedge [1]. Similarly, the contraction was partially responsible for changes of the selective reflection band in cholesteric elastomers [7]. However, the major difference between this system and cholesteric elastomers is that viscous CLC, as we show below, can be represented by a simple rheological Maxwell model [16]. Under stretching, the liquid crystal moves with the strips without any flow of CLC with respect to the strips. The volume of the liquid crystal, V , does not change during deformation:

$$V = l * w * t, \quad (2)$$

where l is the length, w is the width of a silicone strip and t is the thickness of the sample. After uniaxial deformation, the length of the sample increases to $l + dl$, the width of the sample decreases to $w - dw$ and the thickness becomes $t - dt$. Subsequently, the volume of the sample becomes

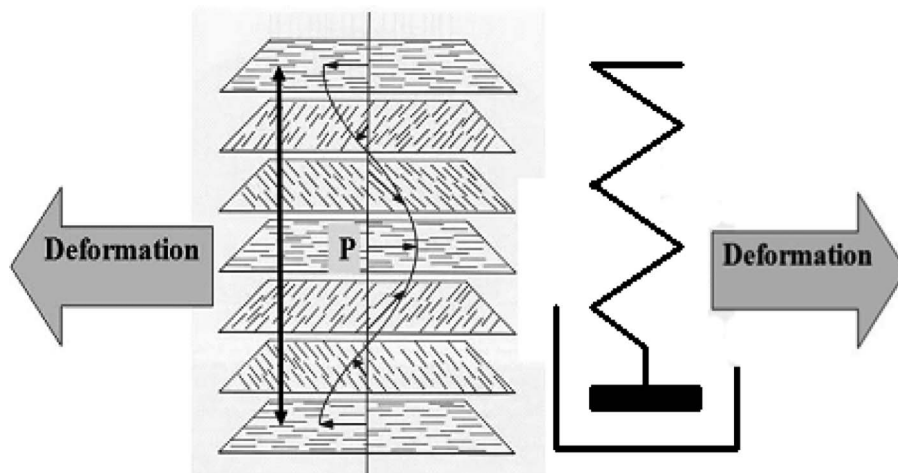


Figure 3. Schematic representation of cholesteric helix and its deformation.

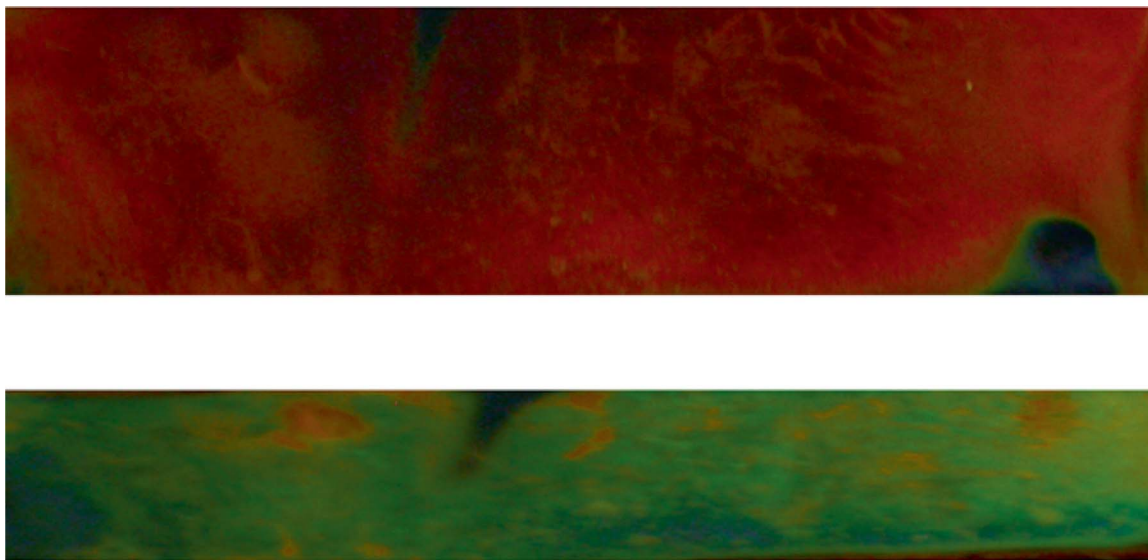


Figure 4. Colour changes in a stretched film (degree of stretching changes from 0 on the top to around 20% on the bottom).

$$V = (l + dl)(w - dw)(t - dt). \quad (3)$$

CLC deforms in the same manner as the underlying strip; therefore, the change of the width and the length of the CLC sample are exactly the same as for the strip. Comparing (2) and (3) and taking into account that the CLC's motion just follows the deformation of the strips and $\nu = (dw/w)(l/dl)$ is Poisson's ratio, we will immediately obtain

$$dt/t = 1 - \frac{1}{(1 + dl/l)(1 - \nu dl/l)}. \quad (4)$$

Note, that deformations dl and dw are entirely determined by mechanical properties of the silicone strip, and not the cholesteric liquid crystal. The change of thickness calculated from Equation (4) is plotted as a function of deformation in Figure 5(a). However, changing geometry of the strips results in the decreasing gap between them and readjustment of the cholesteric pitch of the sample shown in Figure 5(b). It can be seen that the trend of pitch changes is perfectly described by Equation (4). In derivation of Equation (4), the squeezing of the liquid crystal out of the gap between the strips was not considered; therefore, the same equation can be used in the case of just a layer of CLC deposited on a single strip.

The visual restoration of the initial colour of the sample that is kept under the deformation depends on the sample's viscosity, and requires several hours. The complete return of the SRB to the same wavelength requires an even longer time. A high measured viscosity of the CLC ($5 \cdot 10^2 - 5 \cdot 10^3$ Pas) leads to a low relaxation rate of cholesteric pitch, proportional to

$\frac{K}{\gamma P} = 10^{-7} - 10^{-6} \text{ m s}^{-1}$ (we used $K = 10^{-11} \text{ N}$ and helical pitch $P = 600 \text{ nm}$) or even to a much lower value if the flow in the direction perpendicular to cholesteric planes is allowed (in this case the effective viscosity becomes three to four orders of magnitude larger than the measured value of γ). In contrast to the low relaxation rate, the sample is deformed very quickly with the rate from 10^{-3} m s^{-1} to 10^{-2} m s^{-1} . Since deformation is fast, the contraction of the sample leads to an elastic decrease of the cholesteric pitch.

In accordance with the simple Maxwell model for isotropic material, the deformation of the viscoelastic

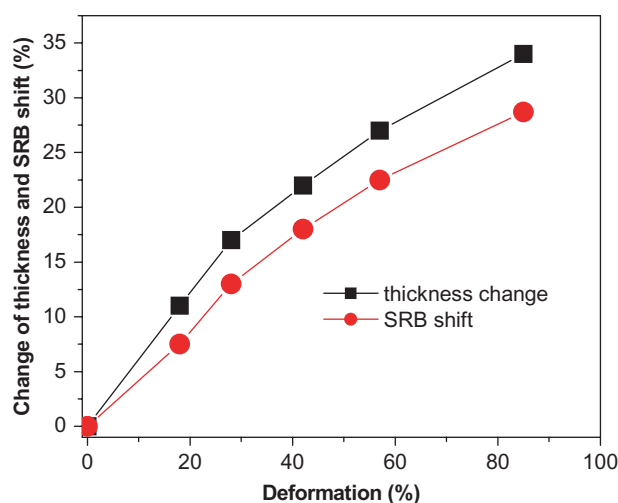


Figure 5. (a) Calculated change of thickness (dt/t) as a function of uniaxial deformation ($(dl/l) \cdot 100\%$) (b) Shift of the selective reflection band ($d\lambda/\lambda$) as a function of uniaxial deformation ($(dl/l) \cdot 100\%$).

sample consists of an elastic part ε_{el} and an inelastic part ε_{in} , which is schematically represented in Figure 3. The stress σ is distributed uniformly between elastic and inelastic subsystems. In the elastic subsystem $\sigma = E\varepsilon$, and in the viscous subsystem $\sigma = \eta \frac{d\varepsilon}{dt}$, where η is a viscosity of the subsystem.

The total deformation of the CLC is governed by the equation:

$$\varepsilon(t) = \frac{\sigma(t)}{E} + \frac{1}{\eta} \int_0^t \sigma(\tau) d\tau. \quad (5)$$

This equation gives a relaxation time of the order $\tau_{relax} = \frac{\eta}{E}$. If the sample is suddenly deformed to a certain degree of strain ε_0 , the stress will decay exponentially:

$$\sigma = \sigma_0 \exp(-t/\tau_{relax}). \quad (6)$$

The deformation of the helical pitch is associated with the first term in Equation (5). In accordance with a 'naïve' approximation, the elastic deformation can be directly related to changes in the free energy of a helical cholesteric structure. Then, the following equation for the free energy of the system [17] can be written as:

$$F = F_0 + \frac{1}{2} B \left[\frac{P - P_0}{P} \right]^2 + \frac{1}{2} \text{div} [\vec{d}(r)]^2 + \sigma \varepsilon, \quad (7)$$

where B is the twist constant, P is the current helical pitch of CLC phase, P_0 is the helical pitch of non deformed CLC phase, σ is the imposed stress, ε is the strain, \vec{d} is the vector perpendicular to cholesteric planes. Note that Equation (7) is valid only for a stretching deformation and a system with cholesteric planes parallel to the surface of the strips. In the case of very small deformations of helical pitch, the following relationship holds: $\varepsilon \approx \frac{P_0 - P}{P_0} m$, where m is the number of helical twists along the thickness of the sample. By inserting this into (7) and minimising over P we will obtain

$$P = P_0 - \frac{\sigma m}{B}. \quad (8)$$

In this equation B plays the role of Young modulus E . From Equation (8), one can observe that the helical pitch decreases with increasing tension. Since the stress decays exponentially (see Equation 6), for the relaxation of the helical pitch P back to initial value P_0 , we will obtain

$$P = P_0 \left(1 - \frac{\sigma_0 \exp(-t/\tau_{relax})}{B_0} m \right). \quad (9)$$

Relaxation time $\tau_{relax} = \frac{\eta}{E}$, and viscosity associated with the relaxation are most likely related to permeation

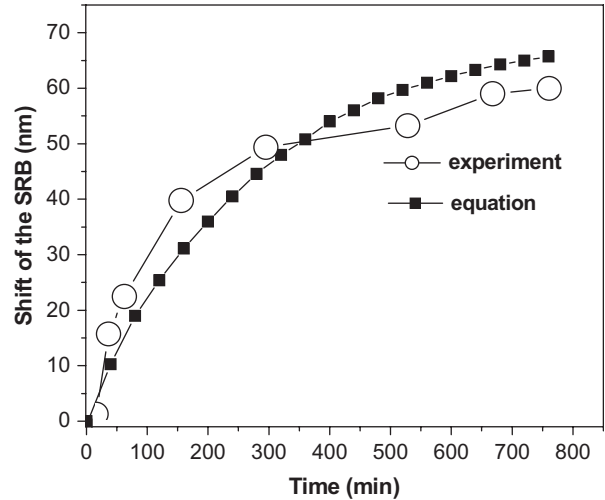


Figure 6. (a) Experimental shift of the SRB due to relaxation in Wacker polymer/MBBA mixture as a function of time and (b) calculated shift of the SRB from Equation (9).

flow and therefore must lie in the range $\eta = 10^6 - 10^7$ Pas. The Young modulus $E = B$, where $B_0 = K_{22} q_0^2 = 6 * 10^3 N/m^2$. This will give the relaxation time of about $\tau_{relax} = 10^4 - 10^5 s$ and that is indeed observed in the experiments. The experimental data for the back shift of the SRB as a function of time are shown in Figure 6(a). Equation (9) was used to find the best fit curve reproducing the relaxation of the SRB in a stretched system (Figure 6(b)). It is easy to see that Equation (9) correctly reproduces experimental data for relaxation. Overall, the simple theoretical approach outlined in this article explains the peculiarities of stretching deformation of the CLC deposited on an elastic strip.

3. Conclusions

Cholesteric materials that change colour under deformation may serve as reversible colour-changing deformation sensors as well as photonic materials with a tunable position of the band gap. The shift of the SRB towards shorter wavelengths depends on the viscosity of the matrix. At higher viscosity, the relaxation processes are very slow, allowing then to reach the largest band gap shift under stretching. A simple theoretical approach taking into account the rheological Maxwell model is able to describe the shift of the SRB under stretching as well as relaxation of helical pitch.

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