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A Patterned Mechanochromic Photonic Polymer for Reversible Image Reveal

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Mechanochromic photonic polymers, which can change structural color upon mechanical deformation, are promising for many applications including strain/stress sensors and security features. Here, a patterned poly(dimethylsiloxane) (PDMS)/cholesteric liquid crystal elastomer (CLCE) photonic mechanochromic bilayer film for reversible image reveal is reported, in which the PDMS component determines the mechanical properties and the CLCE determines the mechanochromic properties. The structural color pattern is achieved by locally crosslinking the CLCE layer at different temperatures using a photomask and utilizing the temperature response of the cholesteric liquid crystal main-chain oligomers. The resulting PDMS/CLCE bilayer is able to reversibly reveal the predesigned invisible pattern upon stretching, showing that this method can be used to convey more advanced information to a potential user than would be possible with a simple homogeneous color change. It is also demonstrated that the bilayer film can be used as a stimuli-responsive sticker able to detect bending deformations.

1. Introduction

Structural colors that arise due to the presence of periodic alteration of refractive indices in photonic nanomaterials are prevalent in nature and are important for various biological functions, including camouflage, warning and information delivery.[1–6] For instance, cephalopods (squid, cuttlefish, octopus, and so on) are able to produce a wide range of structural colors and photonic patterns to signal and communicate with their own species and others.[4,7] Inspired by nature, scientific efforts have been devoted to develop smart photonic materials which inform the user by changing their structural color.[8–10]

Mechanochromic photonic materials, which change structural color in response to mechanical stimuli, are attractive for a wide range of applications such as strain mapping,[11,12] stress sensing,[13–16] anti-counterfeiting,[17–19] tunable optical devices,[20,21] and so on. Different materials, such as inorganic, polymeric, and hybrid components have been used to fabricate these mechanochromic photonic devices.[11–25] Among these smart materials, cholesteric liquid crystals (CLCs) have garnered significant attention in the last few decades, as they have a helical structure that acts as a photonic nanomaterial with a reflection peak that depends on both the helical pitch, which is the distance over which the molecular director makes one full rotation, and the average refractive index.[10,26–29] Such a helical CLC phase arises when a chiral dopant is added to a nematic LC mixture. When the CLCs are crosslinked, the cholesteric pitch affinely deforms with the macroscopic dimension of the network, resulting in a structural color change. Considerable effort has been devoted to design systems based on cholesteric liquid crystals that have mechanically induced color changes.[14,21,30–33] However, fabricating patterned mechanochromic photonic systems that can reveal hidden information as well as detect different deformations remains a challenge.

Previously we reported that a cholesteric liquid crystal elastomer (CLCE) thin film can be patterned in full color by multiple crosslinking steps using main-chain CLC oligomers.[14] Here, we report on the development of a versatile photonic bilayer system that can reversibly reveal and conceal a pattern upon stretching and releasing. Robustness is achieved by laminating a soft transparent stretchable polydimethylsiloxane (PDMS) layer on top of a patterned CLCE photonic layer. An invisible IR-reflective pattern which can reversibly be revealed and concealed upon stretching and releasing is fabricated by using a photomask and multiple crosslinking steps. We also show that the responsive photonic material can be applied as a sticker to an elastic object, giving visual information about the stretching and/or bending. This mechanochromic device overcomes the shortcomings of previously reported photonic...
strain sensors, such as incapability of information delivery, humidity dependence, and lack of scalability, and has various potential applications including stress, strain and bending sensors, data encryption and security labels.

2. Result and Discussion

The CLCE layer was prepared using the method reported in our previous work. Diacrylate LC monomer 1 (83.07 wt%) and chiral diacrylate dopant 2 (8 wt%) were mixed with butylamine 3 (8.93 wt%) (Figure 1A). The mixture was stirred at elevated temperature to form the main-chain LC oligomer, having an average degree of polymerization of 3.1 (Figure S1, Supporting Information) and a cholesteric-to-isotropic phase transition temperature of 82 °C (Figure S2, Supporting Information). The oligomer was then applied to a rubbed polyvinyl alcohol (PVA) functionalized glass substrate via blade coating. The purpose of the PVA functionalized glass was to help the oligomer form a planar cholesteric liquid crystal alignment and make it easy to peel the coating from the substrate by immersing it in water. Upon changing the temperature, the reflection band of the non-crosslinked coating showed a few hundred nanometers of shift. For example, upon cooling from 61 to 24 °C, the reflection band shifted from 715 to 1100 nm, out of the visible spectrum (Figure S3, Supporting Information). Prior to being applied to the substrate, 1 wt% photoinitiator 4 was added to this mixture to allow photopolymerization and fix the color by crosslinking. A photonic polymer bilayer was then prepared in two steps. In the first step, the fabricated photonic coating was exposed to UV light at the desired temperature to polymerize the film. The resulting CLCE layer typically had a thickness of about 10 µm. It is noted that when the CLCE layer was made too thick, it was difficult to obtain a well aligned CLCE layer, and strong light scattering would be observed. The thickness of the CLCE layer was controlled around 10 µm, which was enough to have a good reflection band, while still having good transparency of the film. At this thickness, the layer could not

Figure 1. A) The molecular structures of the materials used to synthesize the main-chain CLC oligomer. B) Schematic representation of the fabrication of the PDMS/CLCE bilayer film. C) Stress–strain curves for only the PDMS film (1), the PDMS/CLCE bilayer film where both layers were clamped (2), and the bilayer film with only the PDMS layer clamped (3). The schematics on the right show how the films were clamped during the different measurements.
be handled as a free-standing film. Therefore, in the second step a soft PDMS layer was laminated on top of the crosslinked liquid crystal elastomer layer by spin-coating and thermally cured. The PDMS had a thickness of about 120 µm. By peeling off the PDMS/CLCE from the glass substrate, the bilayer free-standing film was obtained (Figure 1B). More information on the preparation procedure can be found in the Supporting Information.

The stress–strain curve of the PDMS/CLCE bilayer film was measured, and the result was compared to that of a PDMS single layer (Figure 1C). Surprisingly, the Young’s modulus of the PDMS/CLCE bilayer film was lower than that of the PDMS single layer (curves 1 and 2 in Figure 1C). To verify if the modulus of the PDMS itself was changed by the presence of the LC layer, or if the modulus of the combined system was lower, a control experiment was carried out on a bilayer in which only the PDMS layer was clamped (curve 3 in Figure 1C). The result was similar to the experiment where both CLCE and PDMS were clamped, which means that the mechanical properties of the PDMS were affected by the LC layer, for example by the LC layer absorbing some of the curing agent. However, the results of these experiments also show that the PDMS layer largely determines the mechanical properties of the bilayer. This adds to the versatility of the system, as the mechanical properties of the PDMS can easily be adjusted by changing the crosslink density, changing the mechanochromic sensitivity to the application of a certain stress. An experiment was carried out to determine the effect of CLCE and PDMS layer thickness on the mechanical properties of the bilayer film. Initially, the CLCE layer was kept at the same thickness of 10 µm, while the thickness of the PDMS was changed from 121 to 131 µm. The strain–stress curves of the two films were almost identical (Figure S4, Supporting Information). Upon further tuning the thickness of the PDMS to 169 µm and changing the CLCE layer thickness to 6 µm, the stress–strain curve shifted slightly but was still very similar to the previous two, indicating that the thickness of both the PDMS and the CLCE did not significantly affect the mechanical properties of the bilayer.

The mechanochromic properties of a nonpatterned PDMS/CLCE bilayer were studied first by photo-polymerizing a film with a reflection band notch of 600 nm (Figure S5, Supporting Information) at 53 °C. The structural color of the resulting bilayer changed from yellow to green upon stretching and was restored to yellow when released (Figure 2A). The mechanism of the reflection band shift is that during the uniaxial extension of the bilayer film, the contraction of the CLC layer in the thickness direction leads to a reduction in pitch length,[14,21,31] causing the reflection band to shift to 496 nm, resulting in an overall shift of 104 nm of the reflection band. An average sensitivity, which was defined as the total reflection band shift divided by the total strain, of ~3.4 nm/% was observed. The relatively large wavelength shift resulted in a color change of the film from yellow to green. The reversible behavior was investigated by measuring the reflection band during multiple loading–unloading cycles. The film was loaded to a specific strain and the reflection band was measured, after which the strain was released to the unloaded state. This was repeated five times before the film was further stretched to a higher strain. As is shown in Figure 2D, the sample with a starting band of 600 nm was tested with strains of 6.33%, 15.83%, and 30.67%. For all the cycles, the reflection band shifted to the same position at the stretched state and was restored to the original reflection band at the released state. As we applied each strain five times, and we measured at least seven different strains for each sample, the number of applications of load and unload were at least 35 for each sample, and we observed no change. This result indicates the stretch-induced reflection band shift has good reversibility and there is no creep within the measured strain range.

Other bilayer films with start reflection band notches of 731, 710, and 642 nm were studied with an aspect ratio of around 5, and the reflection bands for all the films showed again a blue shift upon stretching and showed good reversibility (Figure 2E; Figure S7, Supporting Information). As expected, the relative reflection band shift (ΔA%) upon applying a certain strain is the same for all the films with different starting bands, and only the absolute reflection band shift is depending on the starting band of the film. This means the mechanochromic properties, i.e., the relative color change of the PDMS/CLCE bilayer, are consistent for the bilayers that have different original structural color, which is desired for a sensor to give accurate information. To investigate the effect of aspect ratio on the reflection band shift, the reflection band shift upon stretching of a PDMS/CLCE bilayer film with a starting band of 731 nm was measured using different aspect ratios. As shown in Figure 2F, the relationship between the reflection band shift and applied strain for aspect ratios of 5.09, 6.56, and 9.80 was similar, indicating the aspect ratio of the film makes no difference to the stretch-induced reflection band shift. As the lateral contraction at such high aspect ratios should be heavily influenced by the aspect ratio, this means that there is negligible lateral contraction in the measured area, and the stretch is directly converted into pitch contraction. Upon changing the starting band to 817 nm as well as the aspect ratio to 1.185 (green star in Figure 2E), the percentage of reflection band shift versus strain still showed good agreement with the films with different starting band that all have an aspect ratio around 5. This further indicates that the stretch induced reflection band shift is independent of the starting band and the aspect ratio of the film during stretching.

The expected contraction of the thickness of the CLCE layer upon application of strain can be estimated and compared to the measured reflection band shift. There seems to be negligible lateral contraction in the area where the reflection band is measured. If we assume no volume change takes place (a Poisson’s ratio of 0.5) so all of the applied strain is converted into pitch contraction, the correlation between the length...
(l) and thickness (d) of the film can be described as \( l_0 \times d_0 = l_s \times d_s \), where \( l_0 \) and \( l_s \) represent the length of the film in the unstretched and stretched states, and \( d_0 \) and \( d_s \) represent the thickness of the film in those two states. When the film is stretched by 30.67% in length, the maximum possible contraction of the thickness of the film is calculated to be 23.5%. We can calculate the pitch change from the reflection wavelength change using \( \lambda = \pi \times P \times \cos \theta \), where \( \lambda \) is wavelength of reflection, \( \pi \) is the average refractive index, \( P \) is pitch, and \( \theta \) is incident angle of light. We assume the average refractive index \( \pi \) does not change during stretching and the incident angle of light is 0°, so the pitch \( P \) will directly correlate with the reflection wavelength \( \lambda = \frac{\pi}{P} \). When further assuming that the crosslinked nature of the CLCE fixes the number of pitches across the thickness, the pitch change should correlate with the dimensional changes in the thickness. When stretched to 30.67%, the pitch \( P_s \) is calculated as 0.83 \( P_0 \), a contraction of 17% in pitch, i.e., 17% contraction in thickness. Comparing the maximum expected thickness change of 23.5% with the experimental result of 17% and taking into consideration that there might be a volume increase, it can be concluded that the reflection band shift is in good agreement with the thickness change.

As reported earlier, photonic coatings with patterns can be prepared using a mask and multiple crosslinking steps at different temperatures (illustrated in Figure 3A). When the reflection bands of the pattern and the background are different and fixed in the infrared (IR) range, the patterns are invisible and the film will be colorless and transparent. Upon stretching, the reflection band of the pattern will blue shift to the visible range, making the pattern appear. When the strain is released, the reflection band of the film will go through a red shift, during which the pattern will become invisible again.
An IR patterned film was prepared by using the CLC mixture 1 and locally fixing the reflection band of the CLCE at two different temperatures. After blade-coating, the sample was locally cured in nitrogen atmosphere at 43 °C for 60 s with a UV light intensity of 3.73 mW cm⁻² through a mask in the image of a warning sign. The mask was removed and the coating was heated up to 51 °C and cured with UV light of an intensity of 16.37 mW cm⁻² for 10 min. By being exposed to UV light at different temperatures, a coating with an IR reflecting patterned warning sign was prepared. A PDMS/CLCE bilayer was then fabricated using the method described in Figure 1B. The patterned bilayer film showed good transparency, with the reflection band notch of the pattern and the background located at 807 and 888 nm, respectively (Figure 3C). Upon stretching to 38%, the warning sign image appeared, and it disappeared when the device was released. If the reflected light becomes visible at a wavelength of 740 nm or smaller, the reflection of the background decreased by at most 17%, which agrees well with the earlier measured shifts and places the reflected wavelength of the image at around 672 nm, which is in the middle of the wavelength range of red light (625–750 nm). This leads to a good contrast between image and background. The stretching could be repeated several times and the effect was fully reversible (Figure 3D; Video S1, Supporting Information). The constructed device show that our method can be used to convey more information to a potential user than would be possible with a simple homogeneous color change.

Finally, we show that the photonic bilayer film can also be used as a stimuli-responsive mechanochromic sticker. For this, a blue-colored PDMS/CLCE bilayer film with a reflection wavelength of 441 nm (Figure S9, Supporting Information) was cut out, and glue was applied to it to turn it into a sticker. The film was then stuck onto a thick PDMS block prepared in the lab (Figure 4A). The PDMS block was only used for demonstration purposes, and another elastic object could be used as well. The original color of the film was blue (Figure 4B). When bent downwards, the CLCE film was stretched and a blue shift happened, resulting in the blue color shifting to the UV region, i.e., becoming colorless at any viewing angle (Figure 4C; Video S2, Supporting Information). When bent upwards, the CLCE film was compressed and a red shift happened, resulting in the blue color shifting to green (Figure 4D). This bending-induced color change proves the PDMS/CLCE bilayer film can work as a photonic sensor sticker to visualize the bending deformations.

3. Conclusions

We have demonstrated a patterned mechanochromic bilayer film that reversibly changed its color upon stretching, prepared by laminating a soft PDMS layer on top of a cholesteric main-chain liquid crystal elastomer coating. The thickness and the mechanical properties of the bilayer are mostly determined by the PDMS layer, while the CLCE film is responsible for the mechanochromic photonic properties. The film was patterned in the near infrared region utilizing the temperature response of the main-chain cholesteric liquid crystal oligomers, and this invisible pattern can reversibly be revealed and concealed by applying strain. In the device demonstrated in our work, it is an image of a warning sign which appears upon stretching, which could notify a user of a potential danger to a degree that a simple homogeneous color change could not, and the
amount of information that can be transferred is significantly larger. Of course, this is only one example of a pattern that can be made for a specific situation, and due to the versatility of the technique the possibilities are virtually endless. The possibility of this bilayer to be employed as a strain-responsive information sticker for everyday use was also demonstrated by gluing the bilayer on bulk PDMS and showing the mechanochromic response to bending. The photonic bilayers have excellent potential for developing versatile sensors capable of visualizing strain and bending deformation, data encryption where various information can be recorded, or as anti-counterfeit measures.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
cholesteric liquid crystals, image reveal, liquid crystal elastomers, mechanochromic

Figure 4. The PDMS/CLCE bilayer film as a bending sensor. A) The PDMS/CLCE bilayer film is glued on a PDMS bulk substrate. B–D) Schematic representation of the PDMS/CLCE bilayer film in the original state, bending downwards and upwards and the color of the film in the different states.

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