Preparation of a Mechanochromic Elastomer using Liquid Crystal Dispersed in Polymer

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***Abstract*— We have designed an inexpensive and sensitive mechanochromic system. Our system is prepared by a simple emulsion procedure of nematic liquid crystal in polydimethylsiloxane (PDMS). The resulting polymer dispersed liquid crystal (PDLC) exhibits a transmission change of 50% as a response to strain. Here we characterize the morphological, optical, and mechanical factors behind this transmission change. Understanding this mechanochromic behavior is essential for developing precise and reliable methods to tune a material's optical properties. We propose a new model that illustrates how mechanical strain modifies the polymer-liquid crystal interface and the nematic director fluctuation within the liquid crystal droplets. We propose that both of these factors play critical roles for the transmission change in PDLC samples. This work lays a new foundation for developing innovative mechanochromic devices, including smart windows and biomedical pressure sensors.**

***Index Terms*—elastomer, liquid crystal, mechanochromism, optics, PDLC, sensor**

I. Introduction

Many types of living systems use optical tools to communicate with each other, control their surroundings, and sense changes in their environments. The cuttlefish, for example, use elastic pigment sacs called chromatophores to quickly camouflage themselves and evade potential predators. Muscles surrounding these sacs contract and induce a change of color [4]. This mechanism is considered a mechanochromic system because it uses a mechanical stimulus to evoke an optical response. Mechanochromic systems are promising solutions to modern problems, such as energy conservation and biomedical sensing. For example, a smart window would conserve heating and cooling energy if it could control sunlight transmission by contracting and expanding its glass panes [1]. In addition, effective compressive bandages are being developed to visually indicate when an effective amount of pressure is applied to a patient [2]. Despite a wealth of mechanochromic research, we do not see many of these systems implemented commercially [6]. Barriers, such as cost and complex preparation methods, have limited mechanochromic applications. We aim to develop an inexpensive and simple method to prepare a mechanochromic system that requires low mechanical energy and enables a high level of optical control.

To this end, we have designed a polymer dispersed liquid crystal (PDLC) system. Liquid crystal adopts properties from liquid matter and crystal solid matter [3]. We use a nematic liquid crystal, which consist of nanosized rods that flow like a liquid but are uniformly oriented with a director [9]. Dispersing liquid crystal droplets in a polymer allows researchers to utilize the unique optical properties of liquid crystal while harnessing the mechanical properties of a polymer [3]. To create an inexpensive and sensitive system, we use a low concentration of liquid crystal immersed in soft polydimethylsiloxane (PDMS). Our system changes from opaque to transparent upon compression. In the following sections, we describe the mechanical, optical, and morphological mechanisms underlying this mechanochromic response.

II. Background

PDLC has been extensively studied in the past thirty years due to its unique optical properties. In its traditional, "swiss cheese" morphology, very small spherical liquid crystal droplets are suspended in a polymer matrix [7]. In this state, the refractive index of the liquid crystal does not match that of the polymer, causing light to scatter and the material to appear opaque. When the material undergoes stress, the droplets become increasingly oblate and the liquid crystal refractive index changes to match that of the polymer [3]. Deformation can be caused mechanically by shear, stretch, or compression; or electrically, such as putting a voltage across the material [7]. On the macro scale, these subtle deformations cause the material to change from opaque to transparent, making PDLC an intriguing material for window, display, and sensor applications.

Current mechanochromic techniques include: rearrangement of bonds, dye-dispersed systems, and photonic gels [8]. A PDLC-based mechanochromic device would most generally resemble the dye-dispersed system. In such a system, organic or organometallic small molecule dyes change their optical properties upon grinding, smearing, or pressing. The dyes form aggregates (in this case, liquid crystal clusters into droplets) when dispersed in an elastomeric matrix and these aggregates are deformed upon straining the matrix [8]. Key hurdles in current mechanochromic research include increasing the predictability and precision of optical changes and optimizing the amount of color or transmission change of a material with minimal mechanical strain [6]. In this paper, we discuss a simply designed PDLC material and demonstrate key properties that address how PDLC can be tuned to increase predictable optical changes and enhance mechanochromic sensitivity.

III. Experimental Details

A. Materials

The PDLC samples in the subsequent experiments consisted of nematic 4-Cyano-4'-pentylbiphenyl (5CB) liquid crystal dispersions (Kingston Chemicals Ltd.). Dow Corning Sylgard 184 elastomer kit was used for preparing PDMS.

B. Fabrication of Mechanochromic PDLC Samples

Dow Corning Sylgard 184 silicone elastomer and curing agent were mixed at a weight ratio 30:1. 5CB was added to the solution at 5 wt% and the mixture was mechanically stirred for one minute. After degassing, the mixture was cast in a 25×15×1 mm glass curing cell and the thickness of the sample was controlled at ~ 1 mm. The sample was then cured at 120 °C for 20 minutes.

C. Characterization

Scattering spectra and transmission at various strains and angles were collected from a USB400 fiber optical spectrometer (Ocean Optics) with a custom-built compressor and an angle-resolved stage.

Optical images were obtained by optical microscopy (BX 1, Olympus) using polarizing condensers. Large droplet optical samples were created by preparing 30:1 Dow Corning Sylgard 184 silicone elastomer and curing agent. After degassing, the sample was cast in a petri dish. 1 µL 5CB droplets were pipetted into the elastomer and stirred slowly for 10 seconds. The sample was cured at 65°C overnight. SEM images were taken by the Scanning Electron Microscope (JEOL 7500) at 5kV.

Mechanical PDMS samples were prepared by mixing elastomer and curing agent at 10:1, 20:1, 30:1, 40:1 and 50:1 weight ratios. Each sample was cured at 65°C overnight and cut into 30×7×1 mm films. Mechanical testing of PDMS samples at different curing agent ratios was completed using Instron tensile testing with a crosshead speed of 1 mm/min.

IV. Experimental Results and discussion

The following three subsections describe the mechanical, morphological, and optical characterization of our system.

A. Curing Agent Effect on Mechanical Sensitivity

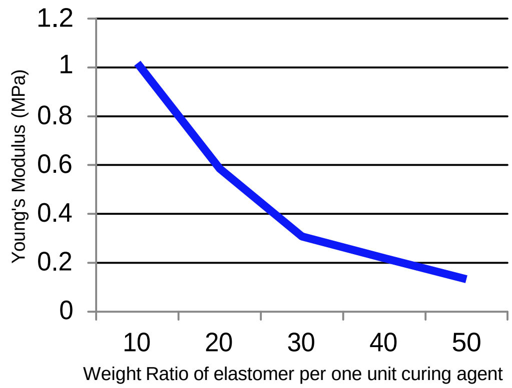
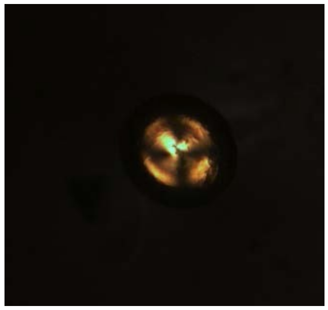


Fig 1. Young's Modulus versus Elastomer-Curing Agent Ratio

In a mechanochromic PDLC system, liquid crystal droplets are deformed by changing the shape of the elastomeric matrix that contains them. The Young's modulus is a measure for how sensitive a material will be to deform. The modulus for each PDMS sample was found by calculating the linear slope of the stress versus strain relationship from Instron testing. Fig 1 demonstrates the relationship between the Young's modulus of PDMS and the amount of curing agent used. A sample with a high elastomer ratio, such as a 50:1 mix, will have a lower Young's modulus. Using less curing agent consequently limits the amount of cross-linking that will occur during the curing process and result in more flexible elastomeric matrices. The rate of change for the Young's modulus of a sample becomes more stable as the elastomer ratio increases. Therefore, a higher elastomer ratio, such as a 30:1 or 40:1 mix, could be used in sample preparation to make systems with reliable mechanical flexibility. For our mechanochromic system, a high elastomer ratio is desirable for producing a flexible matrix with predictable deformation behavior.

B. Morphological Droplet Response to Stress

ImageJ software was used to analyze the size distribution of liquid crystal droplets in the mechanochromic films. Optical imaging of a 20:1 elastomer with 5% liquid crystal showed a mildly uniform distribution of droplets with a mean diameter of 5.1 µm with a standard deviation of 1.84.



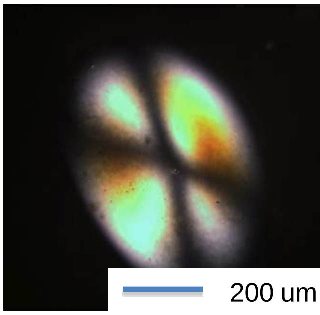


Fig 2a. Polarized view of relaxed and compressed droplet

Optical imaging in Fig 2a show the radial configuration of 5CB liquid crystal droplets in the PDMS. Radial droplets result from homeotropic, or perpendicular, anchoring of nematic rods to the PDMS interface. A central defect results from the nematic director fluctuations that point toward the center of the spherical droplet. As the large droplet sample was compressed, the cross-sectional area of the droplet expands biaxially.

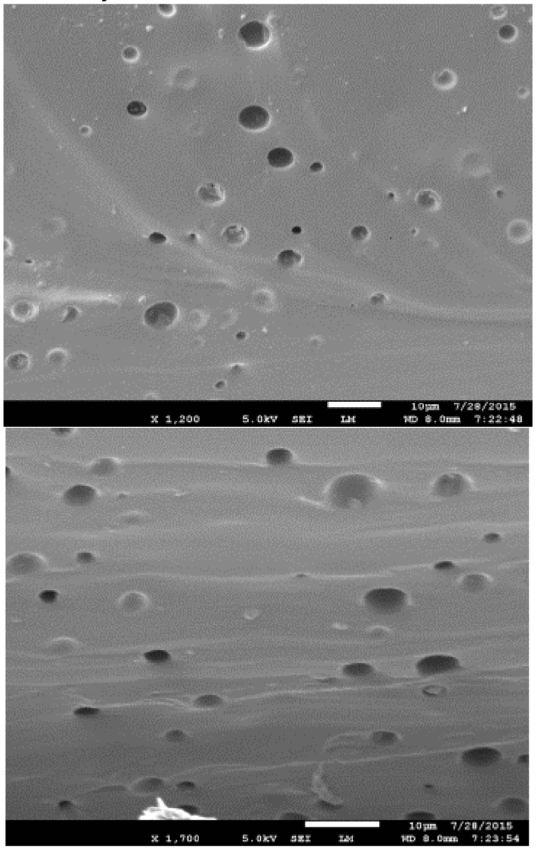


Fig 2b. SEM images of relaxed and compressed matrix

SEM images in Fig 2b depict a cross section view of the elastomeric matrix after liquid crystal was washed out of the sample with acetone. The relaxed sample shows circular cross sections of the droplets, indicating spherical three-dimensional shapes. As compression is applied, the droplets become oblate. As compression increases, the top of the droplet becomes flatter and its sides become more sharply curved. These new boundary conditions may inhibit homeotropic anchoring and change the liquid crystal morphology within the droplet.

C. Mechanochromic Modulation of Light

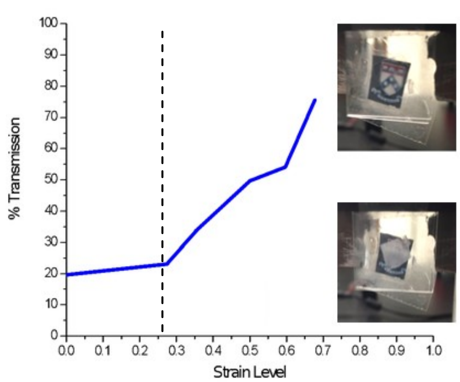


Fig 3a. Transmission versus Strain for 5% 5CB sample

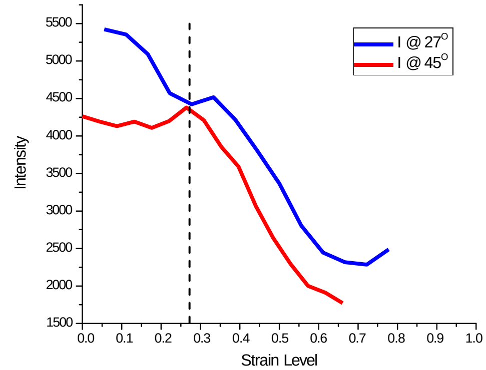


Fig 3b. Backscattering versus Strain for 5% 5CB sample

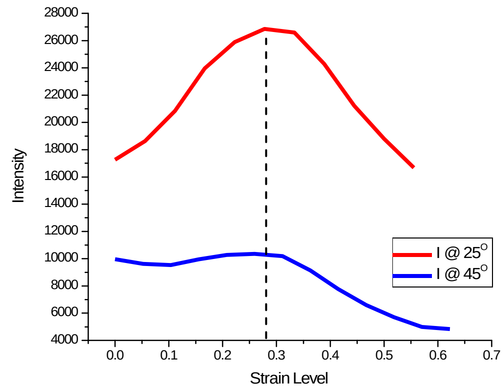


Fig 3c. Front Scattering versus Strain for 5% 5CB sample

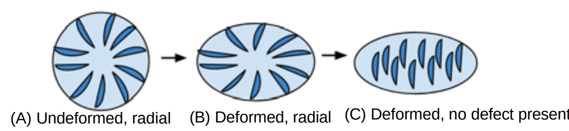


Fig 3d. Cycle of morphology change for droplets

Our mechanochromic PDLC sample exhibit an absolute change of 50% transmission between its relaxed state and stressed state, as seen in Fig 3a. The change in transmission is not uniform; it has two discrete slopes. This suggests that two distinct processes are contributing to transmission change.

These two processes are also observed in Fig 3b and 3c. When the sample experiences strain levels less than 30%, back scattering is constant and frontscattering increases. After 30% strain, both backscattering and frontscattering decrease.

As seen in Fig 3d, compressive force can have two effects on a liquid crystal droplet. By changing the shape of the elastomeric voids, the elastomer-liquid crystal interface is altered. This changes the refractive index of the droplet, from its ordinary to extraordinary values. However, at a certain degree of compression, it is possible to reorient the director of nematic liquid crystal fluctuations. As the aspect ratio of the compressed droplet increased along the major axis, it becomes more difficult for rods to perpendicularly anchor to the droplet boundary. This suggests that a change in nematic director fluctuations at a particular strain level could contribute to an increase transmission and a decrease in light scattering. The data suggests that the change in droplet shape and the change in nematic order contribute to two distinct changes in transmission and light scattering.

V. CONCLUSION

In this paper, we discussed a procedure for preparing a new mechanochromic PDLC film. Using a low concentration of liquid crystal decreases the cost of production for such samples and makes this technology more viable for commercialization. Also, our results show that large changes in transmission can be obtained by compressing the PDLC film by less than a millimeter. This level of mechanical sensitivity also makes this system viable for many commercial applications.

In addition, our characterization of the mechanical, optical, and morphological behavior of liquid crystal droplets in the elastomer matrix demonstrated a more in-depth picture of how transmittance and scattering can be tuned. Changes in the shape of the liquid crystal droplet will modestly increase transmission and increase frontscattering. However, changes in nematic director fluctuations will sharply increase transmission while decreasing scattering. These mechanisms can be harnessed to create precise mechanochromic controls and sensors.

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REFERENCES

[1] Baetens, Ruben, Bjørn Petter Jelle, and Arild Gustavsen. "Properties, Requirements and Possibilities of Smart Windows for Dynamic Daylight and Solar Energy Control in Buildings: A State-of-the-art Review." *Solar Energy Materials and Solar Cells* 94.2 (2010): 87-105.

[2] Compression Bandage Having an Integrated Strain Gauge. Patent.

[3] Cairns, Darran R., Guy M. Genin, Amy J. Wagoner, Clyde L. Briant, and Gregory P. Crawford. "Amplified Stain-rate Dependence of Deformation in Polymer-dispersed Liquid-crystal Materials." *Applied Physics Letters Appl. Phys. Lett.* 75.13 (1999): 1872.

[4] Chan, Edwin P., and Edwin L. Thomas. "Mechanochromic Photonic Gels." *Advanced Materials* 25 (2013):.3934-3947

[5] Deravi, L. F., A. P. Magyar, S. P. Sheehy, G. R. R. Bell, L. M. Mathger, S. L. Senft, T. J. Wardill, W. S. Lane, A. M. Kuzirian, R. T. Hanlon, E. L. Hu, and K. K. Parker. "The Structure-function Relationships of a Natural Nanoscale Photonic Device in Cuttlefish Chromatophores." *Journal of The Royal Society Interface* 11.93 (2014): 20130942.

[6] Jiang, Ying. "An Outlook Review: Mechanochromic Materials and Their Potential for Biological and Healthcare Applications." *Materials Science and Engineering* 45 (2014): 682-89.

[7] Korner, W., H. Scheller, A. Beck, and J. Fricke. "PDLC Films for Control of Light Transmission." *Journal of Physics D: Applied Physics J. Phys. D: Appl. Phys.* 27.10 (1994): 2145-151.

[8] Pucci, Andrea, and Giacomo Ruggeri. "Mechanochromic Polymer Blends." *Journal of Material Chemistry* 21 (2011): 8282-291.

[9] Whitmer, Jonathan K., Xiaoguang Wang, Frederic Mondiot, Daniel S. Miller, Nicholas L. Abbott, and Juan J. De Pablo. "Nematic-Field-Driven Positioning of Particles in Liquid Crystal Droplets." *Phys. Rev. Lett. Physical Review Letters* 111.22 (2013).