Soft Color Composites with Tunable Optical Transmittance

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A class of soft color composites whose light transmittance can be actively tuned and controlled through mechanical actuation is studied. The design comprises thin sheets of polydimethylsiloxane, an optically clear silicone-based rubber, that is mixed with a colloidal suspension of black micrometer-sized dye particles to provide tunable opacity to the specimens. The thickness of the samples can be reduced by mechanical loading (e.g., pneumatically), which modulates the thickness and, in turn, the transmittance by as much as 40%. The mechanism is independent of the specific method of actuation chosen for loading. Scaling analysis and finite element modeling are combined to predictively describe and rationalize the evolution of the transmittance of our samples as a function of the applied mechanical loading and validate the predictions against biaxial tensile experiments. Compared to existing solutions, the main advantages of this mechanism are that it is remarkably simple and robust, as well as fast and fully reversible. Making use of this framework, pneumatic bulging is then chosen as a representative loading strategy, for which a series of design guidelines is presented, which may be implemented in practical applications, such as smart windows and other visually active materials.

1. Introduction

Color composites, similarly to their mechanical,[1] electrical,[2] and magnetic[3] counterparts, are designed to exhibit enhanced optical properties that are superior to those of their individual components. Recent advances in materials that are able to change color on-demand[4–6] also known as chromogenic materials,[7] are enabling novel applications in electronic displays, camouflage,[8] and strain sensors.[9]

Color composites have also been identified as a promising solution for smart windows, given their ability to modulate their optical properties on demand in order to reduce costs for heating, air-conditioning, and artificial lightning.[10] There has been significant progress in the field, which has resulted in functional materials designed to change transparency under external electrical,[11–13] thermal,[14] chemical,[15] and optical[16] stimuli. However, current commercially available devices are still too expensive and complex for mass production,[17] which highlights there is still a need for new mechanisms for tunable opacity. Recent efforts have turned to devices based on optically clear elastomers, particularly polydimethylsiloxane (PDMS). These studies include surface-texturing with nanopillars,[18,19] mechanically controlled voids,[20] magnetically controlled inclusions,[21,22] nucleation of voids around silica nanoparticles,[23] and paraffin-PDMS composites.[24] Despite the advantages in the handling and manufacturing of a PDMS-based device, fabrication techniques based on a controlled architecture of the microstructure are still cumbersome and challenging to implement. Furthermore, the presence of rigid inclusions in an elastomer accelerates material degradation under cyclic loading[25] and can lead to failure through cavitation and subsequent rupture.[26]

Here, we study a class of soft color composites whose light transmittance (the fraction of incident light that is transmitted through a material) can be actively tuned and controlled through mechanical actuation. Our design comprises thin sheets of PDMS, an optically clear silicone-based rubber, mixed with a colloidal suspension of black micron-sized dye particles that can make the samples opaque. Dyed PDMS has been used to design monolithic band pass filters[27,28] and waveguides[29] in microfluidic devices. By exploiting the exceptional mechanical properties of PDMS, we show how reducing the thickness of our samples is an effective and versatile way to modulate their transmittance. We focus on thin sheets due to their simplicity for actuation, while obtaining homogeneous deformation. Nonetheless, this method could also be applied to bulk specimens since the underlying mechanism is independent of the geometry of the sample, and it is also independent of the specific method of actuation chosen for loading. A significant advantage of our mechanism compared to existing designs is that it is simple, fully reversible, and that the speed at which transmittance can be tuned is only limited by the choice of

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mechanical actuation. Furthermore, by combining scaling analysis and finite element modeling (FEM) we are able to predictively describe the evolution of the transmittance of our samples as a function of the applied mechanical loading. The predictions are validated against biaxial tensile experiments. Pneumatic bulging is then chosen as a representative loading strategy, for which we present a series of design guidelines that can be implemented in practical applications.

2. Results and Discussion

2.1. Sample Fabrication and Characterization

Our experimental samples were made out of PDMS (Sylgard 184, Dow Corning), mixed with a black dye (Silc-Pig, Smooth-on) in suspension prior to curing. In Figure 1a, we present a photograph of a sample with pure PDMS (thickness, \( h_0 = 2.9 \) mm), which illustrates its optically clear characteristics. The dependence of its transmittance on the wavelength of the incident light, \( \lambda \), exhibits an approximate constant level at \( T \approx 90\% \), except for two absorbance gaps in the infrared range (Figure 1c). However, this transmittance can be decreased dramatically by the addition of a relatively small concentration, \( c \), of dye. In Figure 1b, we present an example of a sample of dyed PDMS with the same \( h_0 = 2.9 \) mm as the previous optically clear case (Figure 1a), but with \( c = 0.17\% \) (measured as a mass fraction between dye and base polymer). In the visible range (400 < \( \lambda [\text{nm}] < 700 \)), \( T \) is found to be approximately constant (Figure 1c) and henceforth the mean value over this range, \( \overline{T} \), is taken as the characteristic transmittance of each sample. For example, we find \( T = 92.0\% \pm 0.5\% \) and 7.2\% ± 0.7\% for the clear and dyed samples shown in Figure 1a,b, respectively. Once the specimens are cured, the dye takes the form of an approximately isotropic colloidal composite of micron sized particles embedded in a matrix of PDMS (see Figure 1d,e).

Figure 1. Representative photographs of samples: a) optically clear PDMS with no dye (thickness, \( h_0 = 2.9 \) mm and dye concentration, \( c = 0\% \)); b) dyed PDMS (\( h_0 = 2.9 \) mm and \( c = 0.17\% \)); c) Transmittance, \( T \), as a function of the wavelength of incident light, \( \lambda \), for the clear and dyed PDMS samples shown in (a) and (b), respectively. The two vertical dotted lines represent the limits corresponding to the visible range, 400 < \( \lambda [\text{nm}] < 700 \). Micrographs of specimens with: d) \( c = 0.25\% \) and e) \( c = 1\% \), showing the colloidal suspension of dye particles. f) Mean transmittance, \( \overline{T} \), in the visible range versus surface concentration, \( \Gamma = \epsilon h_0 \), for samples with different values of \( h_0 \) and \( c \) (see legend in the plot). Error bars correspond to the standard deviation of \( T(\lambda) \) in the visible range.
In addition to the concentration of the dye, the transmittance also depends on the thickness of the sample, i.e., length of the optical path. In Figure 1f, we plot \( T \) for a number of samples with values of thickness and dye concentration in the ranges 0.91 \( \leq h_{0}[\text{mm}] \leq 7.4 \) and 0.08 \( \leq c[\%] \leq 0.54 \), respectively. Our data are consistent with Beer–Lambert law \cite{48} for the attenuation of light traveling through a solution, \( T = 10^{-c h_{0}} \), where \( \Gamma = c h_{0} \) is the surface concentration of the dye and the absorptivity of PDMS was determined to be \( \varepsilon = 218.1 \pm 10.9(\text{mm mm})^{-1} \), by fitting the data in Figure 1f.

The mechanical properties of the PDMS samples were varied by changing the ratio between curing agent and base polymer. The stiffness was characterized through uniaxial tension tests on dogbone specimens on an universal testing machine. The experimental stress-stretch curves for the three combinations of curing agent and base polymer are plotted in Figure 2. We find that the curing agent-to-base polymer ratio affects not only the initial linear response, characterized by the initial shear stiffness—\( \mu = [653 \pm 6.255 \pm 4.69 \pm 1] \) kPa for \( 1: 10, 1: 15, \) and \( 1: 25 \) curing ratios, respectively—but also leads to important variations in behavior at large strains. In particular, the strain at which stiffening occurs is lower for the PDMS with higher value of the initial modulus. No effect of the dye was observed for the concentrations used in the study.

The experimental results of the tensile tests were fitted to a three-parameter Gent hyperelastic potential \cite{31} with strain energy density

\[
W = -C_{1} f_{m} \ln \left( 1 - \frac{I_{3}}{f_{m}} \right) + C_{2} \ln \left( \frac{I_{2}}{3} \right) \tag{1}
\]

where \( C_{1}, C_{2}, \) and \( f_{m} \) are the parameters to fit from the experimental data and \( I_{2} \) and \( I_{3} \) are the first and second order invariants of the deformation tensor, \( I_{1} = \lambda_{1}^{2} + \lambda_{2}^{2} + \lambda_{3}^{2} \) and \( I_{2} = \lambda_{1}^{2} \lambda_{2}^{2} + \lambda_{2}^{2} \lambda_{3}^{2} + \lambda_{3}^{2} \lambda_{1}^{2}, \) where \( \lambda_{i} \) with \( i = \{1, 2, 3\} \) are the principal stretches. We assume incompressibility, such that in our test \( \lambda_{3} = \lambda_{1} = 1/\sqrt{\lambda_{1}} \), where \( \lambda_{1} \) corresponds to the stretch along the loading direction. The Gent potential has been chosen since its parameters can be accurately obtained from uniaxial data alone, which is not the case with other hyperelastic potentials \cite{32}. The set of fitted parameters for our three different mixing ratios, as well as the corresponding initial stiffness, are shown in Table 1.

The hyperelastic potential was incorporated in the finite element package Abaqus through an user defined function, UHYPER, and was modified to avoid the singularity at \( I_{1} = f_{m} + 3 \). Even if this corresponds to an unrealistically high stretch, it is sometimes reached by the finite element software during an iteration to find convergence to values within the physical limits of the material. In order to prevent numerical errors, the first term of the strain energy in Equation (1) was substituted at large strains by a quadratic function of \( I_{1} \). The resulting expression is continuous up to the second derivative, which ensures that the resulting stress is also continuous and smooth, up to the first derivative \cite{31}.

\[
W = -C_{1} f_{m} \ln \left( 1 - \frac{I_{1} - 3}{f_{m}} \right) + C_{3} \ln \left( \frac{I_{1}}{3} \right) \\
\text{if } I_{1} \leq 0.9(f_{m} + 3) \tag{2}
\]

\[
W = C_{1} f_{m} \ln 10 + C_{1}(I_{1} - 3 - 0.9 f_{m}) \frac{0.1}{0.01 f_{m}} + 0.5(1 - 3)^{(I_{1} - 3 - 0.9 f_{m})^{2}} + C_{3} \ln \left( \frac{I_{1}}{3} \right) \\
\text{if } I_{1} > 0.9(f_{m} + 3) \tag{3}
\]

2.2. Transmittance under Mechanical Loading

Mechanical loading can now be used to control the transmittance of our samples, by reducing the length of the optical path (i.e., thickness). For simplicity we consider the case where the loading is applied to the sample such that stretching occurs in

<table>
<thead>
<tr>
<th>Mixing ratio</th>
<th>( \mu ) [kPa]</th>
<th>( C_{1} ) [kPa]</th>
<th>( C_{2} ) [kPa]</th>
<th>( f_{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>635 \pm 6</td>
<td>399 \pm 8</td>
<td>-410 \pm 50</td>
<td>1.99 \pm 0.02</td>
</tr>
<tr>
<td>1:15</td>
<td>255 \pm 4</td>
<td>97 \pm 2</td>
<td>128 \pm 15</td>
<td>4.22 \pm 0.03</td>
</tr>
<tr>
<td>1:25</td>
<td>69 \pm 1</td>
<td>31.2 \pm 0.8</td>
<td>15 \pm 3</td>
<td>30 \pm 6</td>
</tr>
</tbody>
</table>

Table 1. Linear stiffness and fitted parameters for a Gent hyperelastic model, obtained from uniaxial tension testing on dog-bone specimens, for different values of the curing agent to base PDMS mixing ratio.
the plane perpendicular to the direction of propagation of light. This results in a reduction of the sample thickness, \( h = h_0 \lambda_z \), where \( h_0 \) is its initial value and \( \lambda_z \) is the stretch in the thickness direction. Due to the incompressibility of elastomers, the volumetric density of dye in any region larger than the colloid particles is not affected by the elastic strain, and neither is the absorptivity \( \epsilon \), which is also a material property. We can then rewrite Beer–Lambert law for our deformed samples of dyed PDMS at a given value of stretch as

\[
T = T_0 e^{-\lambda z} 
\]

where \( T_0 = 10^{-\epsilon h_0} \) is the initial transmittance of the undeformed geometry.

In order to validate Equation (4), we performed biaxial tensile tests of PDMS cruciform specimens (the geometry and detailed dimensions are shown in Figure 3a) with shear modulus \( \mu = 69 \text{ kPa} \) and thicknesses over the range \( 1.1 \leq h_0 [\text{mm}] \leq 2.3 \). The specimens were clamped at their four extremities and then stretched biaxially (imposed displacement, at regular increments of 6.36 mm). During loading, the sample was illuminatd from underneath with a light source of constant intensity, and the transmitted light intensity was measured at its center with a silicon photodiode (LS-BTA, Vernier). Given the nontrivial relationship between the applied in-plane loading and the resulting out-of-plane deformation, the values of \( \lambda_z \) were calculated using FEM of the test (see Figure 3b). In Figure 3c, we compare the data for \( T \) versus \( \lambda_z \) with the prediction of Equation (4), and find excellent agreement between the two. This is further highlighted in Figure 3d, where \( \log T / (\log T_0) \) is plotted as a function of \( \lambda_z \) and, as expected, all the data collapse onto a master curve with unit slope. Note that in this comparison, we have directly measured the initial transmittance \( T_0 \) instead of using the nominal value set by the the initial surface concentration of dye. \( \Gamma_0 = c h_0 \) which typically deviates from the measured value by less than 10%. The accessible transmittance range is limited by the failure strain of the material, which in the case of the cruciform specimens is low due to defects along the free edges, from which fracture is nucleated.

2.3. Application to Bulging

We proceed by considering an alternative specimen geometry comprising the bulging by pneumatic loading of originally planar disks of dyed PDMS, clamped at their circular boundary. Due to the lack of free edges, this configuration enables us to achieve larger variations in transmittance than those attained above by the cruciform specimens. Whereas the bulge test is traditionally used in the linear regime to characterize the mechanical properties of thin films, it has also been used to study large deformations of elastomers. In our case, bulging offers a simple and versatile actuation mechanism that allows us to reach high values of stretch in our soft color composite material.

In Figure 4a,b, we present a photograph and a schematic of our bulging apparatus. The specimens are now disks of initial thickness \( 1.5 \leq h_0 [\text{mm}] \leq 2.5 \), that are clamped with a rigid plate containing a circular hole of radius \( R = 25.4 \text{ mm} \). They were pressurized from underneath, which results in out-of-plane bulging and in-plane stretching of the material. Their transmittance was measured as a function of applied pressure using a light sensor (silicon photodiode) located underneath the center of the specimen, where the deformation is equibiaxial. A sequence of photographs from one of our typical bulging tests \((c = 0.5\%, h_0 = 1.8 \text{ mm}, \text{ and } \mu = 69 \text{ kPa})\) is shown in Figure 4c. As the applied pressure, \( p \), is progressively increased, the disk bulges, its thickness decreases, and, consequently, the transmittance increases. As a result, the image located underneath the sample becomes visible for the higher values of \( p \). This mode of pneumatic actuation allows for repeatable and fast tunability of transmittance of our dyed PDMS samples, as illustrated by the representative time-series of \( p(t) \) and \( T(t) \) shown in Figure 4d,e, where variations of about 40% in transmittance are achieved. Since our approach does not depend on the loading method, it is able to show actuation times much faster than those observed in other PDMS-based pneumatic devices.

For a detailed quantification, we have systematically measured \( T \) as a function of \( p \) for a large set of samples with \( c = \{0.1,0.2\} \%, 0.9 \leq h_0 [\text{mm}] \leq 3.0 \) and shear moduli \( \mu = \{69,255,635\} \text{ kPa} \). In Figure 4f we plot \( \log T / (\log T_0) \) versus

![Figure 3. a) Photograph of a cruciform specimen used in biaxial tension testing. The highlighted region is modeled by finite element method to relate in-plane loading and thickness stretch. b) Representative results from the simulations. The scale bar corresponds to logarithmic strain in the thickness direction. c) Mean transmittance, \( T \), versus thickness stretch, \( \lambda_z \), for samples with different values of dye concentration, \( c \), and initial thickness, \( h_0 \). d) Scaled transmittance, \( \log T / (\log T_0) \), versus \( \lambda_z \). The legend in (d) also applies to (c). The solid lines correspond to predictions according to Equation (4).](image-url)
the dimensionless applied pressure, $pR/(\mu h_0)$. The initial response of all samples collapses into a single line regardless of their stiffness, given the linearity of PDMS at low strains. As the applied pressure is increased further, the difference in behavior at large strains seen in Figure 2 explains the grouping of the samples according to their value of $\mu$. The experimental results are compared with numerical simulations, showing excellent agreement through the complete deformation regime.

Having identified pneumatic bulging as a viable actuation mechanism to change the transmittance of our color composites, we now provide design guidelines for its implementation. First, it is important to consider the mean transmittance over the complete specimen, instead of only the value at its center. We define the average transmittance over a given area, $A$, as $\langle T \rangle = \int A \int 10^{-6} dA$, where $l$ is the light path through the material at a given point. In this case, $l$ depends on the direction of the light (assumed to be perpendicular to the undeformed specimen), as well as the total deformation of the material (i.e., both stretching of the initial thickness and rotations). A region of width $h_0$ around the boundary is neglected from the area used in the calculation of $\langle T \rangle$, in order to avoid edge effects.

In Figure 5a we plot the average transmittance, $\langle T \rangle$, as a function of the normalized pressure, $pR/(\mu h_0)$ ($L$ is the diameter of the specimen), for different values of the initial transmittance, $T_0$. The results are presented for the dimensionless thickness $h_0/L = 0.04$, which corresponds to the average thickness of the experimental samples in Figure 4c. The shaded region represents the results obtained for the range $0.02 \leq h_0/L \leq 0.08$, showing a relatively small spread. Figure 5a also presents the maximum out-of-plane displacement, $u$, normalized by $L$, which can be significant (see Figure 4c) and is therefore an important design constraint for practical applications. The extent of this out-of-plane bulging can be reduced by tessellating smaller units, instead of using a single large disk. The size $L$ of these smaller units is determined by the target change in $\langle T \rangle$ and a maximum desired $u$.

With the above strategy in mind, we also consider bulges with square shape of side $L$, and their transmittance and maximum deflection are found to be similar to those of the circular bulges (see Figure 5b). This independence on the particular geometry highlights the versatility of the proposed method to be adopted to different possible practical scenarios. As an implementation...
example of our design, in Figure 5c,d we show a representative finite element model of an array of circular and square bulges, in an hexagonal and square arrangement, respectively. For both cases, $h_0/L = 0.04$ and the separation between bulges in the lattice is $0.2L$. The interaction between bulges imposes an additional constraint, and in the case of the square bulge $\mu \leq 4.5/\mu h_0 L$ so that the bulges do not touch each other.

3. Conclusions

Our results demonstrate how the transmittance of dyed PDMS can be tuned, on-demand through mechanical loading in a robust, fast, and repeatable manner. Although the mechanism is independent of the geometry and loading conditions, we have focused on biaxial stretching of thin sheets in order to achieve homogeneous variations in opacity. By combining scaling analysis and FEM, we have rationalized the relationship between loading and transmittance. Guided by this optical constitutive relationship, we have chosen pneumatic bulging as a suitable loading strategy, and presented a series of design guidelines. Our system is able to provide variations of over 40% in transmittance, which compares favorably to several commercially available technologies.\[17\] We believe that this mechanism for soft color composites could be applied across length scales, from smart windows for indoor light control, to band pass filters in microfluidic devices. The functionality of such systems could be greatly enhanced by exploiting the novel opportunities offered by coupling large mechanical deformations of a composite material with its optical response.

Although we have focused on the transmittance variation in the visible regime, the spectrophotometry data (see Figure 1c) show that the behavior is similar for infrared radiation. Variation of transmittance across a wider range of wavelengths could be achieved with differently colored dye, or by using submicron solid particles inclusions, whose effect would depend on the relationship between incident light wavelength and inter-particle distance. This could lead to an independent control of illumination and thermal radiation for smart windows.

4. Experimental Section

Sample Fabrication: The experimental samples were made out of PDMS (Sylgard 184, Dow Corning), mixed with a black dye (Silc-Pig, Smooth-on)
in suspension prior to curing. The base elastomer, the curing agent, and the dye were all simultaneously mixed together by first stirring by hand for 5 min, and then in a centrifugal mixer (ARE-310, Thinky) for 2 min, to finish mixing and help degassing. The PDMS was then poured into molds fabricated with rapid prototyping, and placed under vacuum for final degassing. The samples were then cured for 1 h at 100 °C. The mechanical properties of the resulting PDMS were varied by changing the ratio between curing agent and base between 1:10 and 1:25. The micrographs of the samples were taken on different focal planes with an optical Nikon microscope, and then focus stacked using Adobe Photoshop.

**Mechanical Characterization**: Dog-bone samples were fabricated using a set of three curing ratios (1:10, 1:15, and 1:25) and the same procedure of all other samples was used in this study, in order to ensure that the properties were identical and reproducible, throughout. The samples were tested under uniaxial tension until failure in an universal testing machine (Instron 5943 with a 1 kN load cell). The strain was measured over a gauge length of ~30 mm and width 10.5 mm using a a video an in-house image processing code. The large deformation response was fitted to a three-parameter Gent hyperelastic potential[31] assuming full incompressibility. Throughout the main text, for conciseness, the three sets of material properties are referred to by their initial shear stiffness: \( \mu = \{63 \pm 6.25 \pm 4 \text{ and } 69 \pm 3 \} \text{kPa for } (1:10, 1:15, \text{ and } 1:25) \) curing ratios, respectively. The mechanical properties of PDMS were found to be unaffected by mixing it with the dye.

**Transmittance Characterization**: The transmittance of the samples was first characterized in a spectrophotometer (Cary 500i, Agilent Technologies). The measurements on mechanically loaded specimens were taken with a silicon photodiode (LS-BTA, Vernier). The results presented are the average of measurements taken over 5 s under constant applied loading, sampled at 20 Hz. The standard deviation of the measurements yields errors of less than 0.2% in transmittance, and so error bars are omitted from the plots to aid visualization. The illumination was provided by a florescent lamp, which had an intensity of ~1000 lux in the absence of a sample.

**Finite Elements Simulations**: The finite element simulations were performed considering both geometric and material nonlinear behavior using Abaqus/Standard. An user defined function, UHYPERR, was used to model the Gent hyperelastic potential. Due to the incompressibility of PDMS, the analysis used hybrid elements to avoid locking. The number of elements was chosen after a mesh refinement parametric study: \( 5 \times 10^4 \) solid brick element, C3D8H, for the rest of the analysis. General contact was employed to ensure that there was no penetration between the sample and the test rig, which was modeled as a solid surface.

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