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Switching Periodic Membranes via Pattern Transformation and Shape Memory Effect

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We exploited mechanical instability in shape memory polymer (SMP) membranes consisting of a hexagonal array of micron-sized circular holes and demonstrated dramatic color switching as a result of pattern transformation. When hot-pressed, the membrane underwent pattern transformation to an array of elliptical slits (with width of tens of nanometers) to featureless on surface with increasing applied strain, switching the membrane with diffraction color to a transparent film. The deformed pattern and the resulting color change can be fixed at room temperature, both of which could be recovered upon reheating. Using continuum mechanical analyses, we modeled the pattern transformation and recovery processes, including the deformation, the cooling step, and the complete recovery of the microstructure, which corroborated well with experimental observations. We find that the elastic energy is roughly two-orders of magnitude larger than the surface energy in our system, leading to autonomous recovery of the structural color upon reheating. Furthermore, we demonstrated two potential applications of the color switching in the SMP periodic membranes by 1) temporarily erasing a pre-fabricated "Penn" logo in the film via hot-pressing, and 2) temporarily displaying "Penn" logo by hot-pressing the film against a stamp. In both scenarios, the original color displays can be recovered.

Introduction

Shape memory polymers (SMPs) are polymeric smart materials of interest for a variety of applications, including deployable space structures, artificial muscles, biomedical devices, sensors, smart dry adhesives, and fasteners.1, 2 They form a “permanent” shape by chemical or physical crosslinking (e.g. crystallization or chain entanglement). Above a thermal phase transition temperature, either a glass transition temperature (Tg) or a melting temperature (Tm), SMPs can be deformed to different temporary shapes, which can be fixed by cooling the sample. Upon exposure to an external stimulus, such as heat, light, and solvent, the temporary shapes can return to their original (or the permanent) shape. There has been much effort to develop new chemistry for improved shape fixity and shape recovery efficiency, responsiveness to new environmental triggers, achieving multi-shape memory effect, and applications to biomedical devices.1, 3-9 Nevertheless, most of the study focuses on shape memory effect in bulk SMPs. A few groups have created micropatterns in SMPs, such as microprotutions10 and microwrinkles8, 11 by taking advantage of the large modulus change near the phase transition temperature. None of them, however, have reported the recovery to the original shape from the micropatterns. During the shape recovery process, the entropic energy stored in the deformed state is released. It remains to be seen whether the deformed shape can be completely recovered as surface energy becomes increasingly dominant when the size shrinks to micro- and nanoscale.

Recently, we and several other groups have demonstrated pattern transformation in elastic membranes with periodic hole arrays by mechanical compression,12, 13 solvent swelling,14, 15 polymerization,16 and capillary force.17 For example, when swollen by an organic solvent, a poly(dimethylsiloxane) (PDMS) membrane consisting of micron-sized circular holes in a square array buckles to a diamond plate pattern of elliptic slits with the neighboring units perpendicular to each other.14 As a result, the physical properties (e.g. photonic18, 19 and phononic15 band gap18, 19 and mechanical behaviors20, 21) could be significantly altered due to change of lattice symmetry, pore size, shape and volume filling fraction. One question rises whether it is possible to switch a colorful film to transparent one via pattern transformation. The latter state will allow for seeing through or mingling with the surroundings. Therefore, the
dramatic visual contrast between colored and transparent states is of interest for applications such as display, privacy window, and camouflage. In nature, invisibility is an important strategy for many sea creatures to hide from predators in water. For example, bobtail squids are invisible in sand during the day with chromatophores in the skin concentrated into small, barely visible dots; when the muscle fibers stretch out the skin, thereby enlarging the chromatophores, the color becomes visible for signaling or escape from predators. 22

Here we report switching a SMP membrane with diffraction color to a transparent film via harnessing the mechanical instability and shape memory effect. When hot-pressed, the SMP membrane consisting of a hexagonal array of circular holes (1.2 µm in diameter, 2.5 µm in pitch, and 5.0 µm in depth) underwent pattern transformation to an array of elliptical slits to featureless on surface with increasing applied strain, leading to the dramatic change of the hole size and shape, and diffraction color, which could be fixed at room temperature, and later recovered to the original pattern (and color) upon reheating. Using continuum mechanical analyses, we modeled, for the first time, an out-of-plane compression of SMP membrane. We observed the hot-press induced deformation and pattern transformation of the membrane at different strains, the structure fixation at the cooling step, and the complete recovery of the microstructure, in agreement with experiments. We also find that the elastic energy stored in the membrane is roughly 2-orders of magnitude larger than the surface energy, leading to autonomous recovery of the structural color upon reheating. Further, we demonstrated two possible applications of color and transparency change in our SMP periodic membranes, including 1) temporary erasing the pre-fabricated "Penn" logo in the film, and 2) a temporary display of "Penn" logo by hot-pressing the film against a stamp.

Results and Discussion

The ability to simultaneously change the lattice symmetry, pore size and shape, and volume filling fraction through pattern transformation offers an attractive approach to drastically alter the materials properties. Most deformation methods reported so far involves the use of solvent, either through swelling or drying processes. In comparison, application of mechanical force will allow us to independently control the amount, direction (uniaxial or biaxial both in-plane and out-of-plane), and timing of strain applied to the periodic structures. In the case of in-plane compression, however, additional care has to be taken to eliminate the out-of-plane buckling, e.g. by sandwiching the

![Fig.1 Schematic illustration of fabrication and deformation/recovery of a 2D SMP membrane. (a) Fabrication of 2D pillar array by holographic lithography. (b) Fabrication of SMP membrane with periodic holes by replica molding, followed by etching in HF aqueous solution. (c) Hot-pressing of SMP membrane in the vertical direction above \( T_g \). The temporary shape could be fixed by cooling down to room temperature under the load. The original shape could be recovered upon reheating above \( T_g \).](image-url)
membrane is colorful due to the diffraction grating effect.

![Fig. 2 Pattern transformation and recovery in a 2D SMP membrane.](image)

(a-e) Optical images of the (a) original, (b-c) partially deformed, $\epsilon \sim 13\pm2\%$ (b) and $\epsilon \sim 20\pm2\%$ (c), (d) completely deformed, $\epsilon \sim 30\pm2\%$, and (e) recovered SMP membranes. (f-j) Corresponding SEM images of the SMP membranes shown in (a-e). (k-o) Higher magnification SEM images of (f-j).

(Fig. 2a, f, k). Because of the Gaussian distribution of the laser beam in holographic lithography and possible small misalignment of optics, there was gradient laser intensity from center to the edge, resulting in pore size distribution and color variation across the sample size. This can be improved using a beam shaper or patterning the film by conventional photolithography through a photomask. When the applied strain, $\epsilon$, was $\sim 13\pm2\%$, the circular holes of $p6mm$ symmetry were deformed to elliptical slits (width of major axis, 1.25 $\mu$m, minor axis, 500 nm) with $p2gg$ symmetry (Fig 2g, l), in agreement with the observation from the swelling-induced instability in SU-8 membranes with a hexagonal array of pores. When the SMP membrane was compressed in the vertical direction, it expanded in-plane due to positive Poisson’s ratio, hence generating an equivalent in-plane compressive stress to the circular holes. The initial diffraction color diminished significantly after compression although it was not completely lost at this strain level (Fig. 2b). This could be attributed to the smaller pore size and porosity. The width of the minor axes of the ellipse further decreased, from hundreds of nanometers to a few nanometers, as the strain was increased. When $\epsilon$ was increased to $\sim 20\pm2\%$, the holes were almost closed into lines (see Fig. 2e, h and m) and the SMP membrane became quite transparent, much like the bulk film. At $\epsilon \sim 30\pm2\%$, the holes were closed-up and the surface became nearly featureless (Fig. 2d, i and n). No further change of transparency was observed. When any of the above deformed SMP membranes were reheated to 90 °C, the original periodic structure was restored nearly to completion (97.6% of the original hole size and 100% of the original pitch), as evident by the SEM images and the regeneration of strong diffraction color (Fig. 2c, e and i and Movie S1†). Surprisingly, even the one with completely closed pores was restored, suggesting that the adhesive energy between the pore surfaces was much smaller than the elastic recovery energy. The different color displayed in Fig. 2a (the original film) and 2e (the recovered one) could be caused by a small misalignment of incident light during photo shooting could lead to appearance of a different color. When $\epsilon$ was greater than 50%, the 2D grating with air holes and its color could no longer be completely recovered due to the permanent deformation of the polymer network.

The reversible switching between the colorful displays to transparency was repeated successfully for more than 10 cycles with $\epsilon < 50\%$, and the recovery of diffraction color occurred within a few seconds (see Movie S1). According to SEM images, the hole diameter and pitch of the recovered film decreased slightly to 94.4% and 98.4% of the original one after three cycles, respectively, and to 89.7% and 98.0% of the original one after ten cycles, respectively. The diffraction color displayed at any of the temporary state could be reprogrammed on demand by precise control of the applied strain level and temperature/load of deformation. Hence, it is possible to build a color spectrum by carefully tuning the mechanical deformation. Further, we may achieve full-color display by combining the instability and design of the original microstructures with variable structural parameters.

During the pattern transformation and recovery process, the air holes were squeezed out and restored, respectively, which would result in a dramatic transparency change. As a proof-of-concept, we placed two SMP membranes on a paper printed with “Penn” logos: one was hot-pressed at $\epsilon \sim 30\pm2\%$ (the left one), and the other was the original, non-deformed one (the right one, see illustration in Fig. 3a). Due to diffraction from the surface of the original membrane with pores in hexagonal array, the “Penn” letters beneath it could not be clearly viewed, in sharp contrast to that beneath the deformed membrane (see Fig. 3b). The transparency change was further investigated by UV-Vis spectroscopy at different thermal and mechanical treatments (Fig. 3c) using the bulk SMP film as a reference. As expected, the original sample (A) has the lowest transmittance (e.g. 28.1% at $\lambda = 600$ nm). For the hot-pressed samples, sample (B) that was deformed at $\epsilon \sim 13\pm2\%$ shows improved transmittance, 46.9% at 600 nm, and the sample (C), which was deformed at $\epsilon \sim 30\pm2\%$ with closed voids, has the highest transmittance, 88.8% at 600 nm, in comparison with the bulk SMP film The slightly lowered transparency may be attributed to the surface roughness of the SMP membrane introduced by the Teflon sheets and dust.
particles trapped on the sample surface during hot-pressing and press release. Finally, the recovered sample (D) shows low transmittance (32.5% at 600 nm), close to that of the original membrane in the UV-visible region.

**Finite Element Analysis**

Since the deformation results presented here are the first demonstration of instabilities induced by loading in the direction perpendicular to the voids, we built a 3D mechanical model to quantitatively investigate the buckling and post-buckling behaviors. The structure is modeled as an infinite array of infinitely long voids in the x1-x2 plane. 3D analyses are conducted and the constraining effect given by the substrate is accounted for by setting the lateral expansion equal to zero. A periodic representative volume element

\[ \sigma = \sigma_N + V_v \sigma_v \]  

where

\[ V_v = 1 - \frac{1}{1 + \exp(-A_1 + A_2)} \]

material parameters defining the position and width of the zone where mechanism \( V \) becomes significant.

The shape memory behavior is taken into account by having \( \sigma_v \) depend on \((T-T_g)\). When \( T > T_g \) the material is characterized by a rubbery behavior; as \( T \) decreases toward \( T_g \), the material becomes increasingly glassy and locked into the deformation. The constitutive model is implemented into a user-defined subroutine (VUMAT) of the commercial finite element code ABAQUS, and numerical simulations of the whole thermo-mechanical loading history of the structures are performed in four steps (see Fig. 4 and Movie S2) using the model parameters summarized in Table 1.
Step 1) *Hot-pressing.* $T$ increases above $T_g$, so $\sigma_v$ vanishes and the material exhibits rubber-like behavior. The stability of the material; completely closed (Fig. 4f), and the elastic energy is stored in the structure again exhibits a rubbery behavior ($\sigma_v$ vanishes again) and the initial shape and pattern are elastically recovered (see Fig. 4g).

**Table 1.** Material constants for SMP used in the mechanical models.

<table>
<thead>
<tr>
<th>Rubbery Phase (Mechanism N)</th>
<th>Glassy Phase (Mechanism V)</th>
<th>Temperature</th>
<th>Related Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E = 1500\text{MPa}$</td>
<td>$\nu = 0.45$</td>
<td>$T_g = 343\text{K}$</td>
<td>$\gamma_0 = 52 \times 10^9/\text{sec}$</td>
</tr>
<tr>
<td>$\mu = 1.72\text{MPa}$</td>
<td>$N = 4.33$</td>
<td>$A_1 = 20\text{K}$</td>
<td>$\Delta G_0 = 92 \times 10^{-21}\text{J}$</td>
</tr>
<tr>
<td>$K = 16.7\text{MPa}$</td>
<td>$s_0 = 56\text{MPa}$</td>
<td>$A_2 = 5\text{K}$</td>
<td>$S_{\Delta} = 28\text{MPa}$</td>
</tr>
<tr>
<td>$h = 400\text{MPa}$</td>
<td></td>
<td></td>
<td>$\nu C$</td>
</tr>
</tbody>
</table>

$\mu$ is the elastic shear modulus, $N$ is the parameter relating to the limiting chain extensibility, $K$ is the bulk modulus, $E$ is the Young’s modulus, $\nu$ is Poisson’s ratio, $\gamma_0$ is pre-exponential shear strain rate factor, $\Delta G$ is activation energy, $s_0$ is the initial athermal deformation resistance, $s_{\Delta}$ is the athermal deformation resistance value at the steady state, $h$ is the softening slope (the slope of the yield drop with respect to plastic strain).

The press is removed, but the holes remain completely closed (Fig. 4f), and the elastic energy is stored in the material; thus the discrepancy between experiments and simulations observed close to the onset of instability at $\varepsilon = 13\%$ (Figs. 2g and 4h) may be attributed to a small difference in porosity between the model and the tested sample. Additionally, we find that for the considered structures with voids of 1 $\mu$m in diameter the surface energy (22.8 mJ/m$^2$ measured by goniometer) is roughly two orders magnitude smaller than the elastic recovery energy, making the recovery autonomous upon reheating. Since the strain energy is proportional to $L^3$ (with $L$ denoting the characteristic material dimension), while the surface energy is proportional $L^2$, a decrease of the voids diameter will increase the contribution of the surface energy. An approximate analysis suggests that the surface energy will play an important role for voids 10 times smaller than those considered in this study.

**Color displays with SMP periodic membranes**

To demonstrate the flexibility of color and transparency change in our SMP periodic membranes and their potential applications, we exploited two possible renderings of the SMP membranes. First, a “PENN” logo was pre-fabricated within the 2D membrane (Fig. 5a, b). The template for replication was fabricated by exposing the negative-tone photore sist, epoxy POSS, to UV light through a photomask with “PENN” logo, followed by 3-beam holographic molding.

**Fig. 5 Display of “PENN” embedded in a 2D SMP membrane.** (a) Schematic illustration of the fabrication of template. (b-d) SEM images of the photore sist template before replication to the SMP membrane. (b) A low magnification SEM image of the “P” character in the template. (c) SEM image of the structure outside “P” character, yellow square, showing tall pillars. (d) SEM image of the structure inside the “P” character, red circle, showing nearly flat film with shallow voids. e-g. Optical images of the original (e), deformed (f) and recovered (g) SMP films.
lithography to create hexagonal array of pillars in the surrounding area (Fig. 5c). Since the region with “Penn” was mostly crosslinked in the first step, the second exposure did not produce any pillar in this region but shallow voids (Fig. 5d). After replica-molding the template to SMP membrane, there was no or little color disfected from this region in sharp contrast to the bright color from the surrounding area (Fig. 5e, g). When the SMP membrane was hot-pressed above \( T_g \), “Penn” logo disappeared as the film became transparent (Fig. 5f). When reheated, the “Penn” logo reappeared together with its colorful background, confirming the success of shape recovery. Here, the logo was pre-fabricated in the permanent shape, which could be temporarily erased upon deformation.

In a second approach, the “Penn” logo was introduced as a temporary shape by a rubber stamp indented into the SMP membrane during heating (Fig. 6a) at 90 °C. The stamp was released after the film was cooled down to room temperature. As seen in Fig. 6b and 6d, the indented region was transparent, especially at the sharp corners of the letters, presumably receiving higher stress, while the background remained colorful. When reheated, the “Penn” logo was erased (Fig. 6c, e). In this way, different letters or patterns could be “finger-printed” and reprogrammed into the same SMP membrane repeatedly, which could be extremely useful as a user-friendly touch screen display or fingerprinting by tailoring the SMP \( T_g \) near the body temperature. It should be noted that all the displays presented here require no extra energy to maintain the displayed state.

Conclusions

We prepared 2D periodic membrane in SMPs, and studied the mechanical instability and shape memory effect. When hot-pressed, the membrane underwent pattern transformation from a \( \rho6mm \) hexagonal lattice of circular holes (1 μm diameter) to a \( p2gg \) pattern of elliptical slits (width varied from a few hundreds of nm to a few nm), and eventually the holes were completely closed. The original film is colorful because of the diffraction from the periodic micropattern and can be reversibly switched to a transparent state by mechanical deformation above the material’s \( T_g \). Upon reheating, the deformed patterns were able to recover, hence, restoring the diffraction color. The combination of pattern transformation and shape memory effect in a 2D periodic membrane offers several distinctive characteristics. 1) It is the first demonstration of instabilities induced by loading in the direction perpendicular to the voids in microstructured SMPs, which is more desirable in practical applications than approaches such as solvent swelling and in-plane compression. 2) The temporarily deformed structure and the resulting color can be fixed without the need for continuous input of external trigger; they can also be programmed continuously by varying the mechanical strain level. 3) The continuum mechanical analyses have faithfully captured the buckling and post-buckling behaviors of the SMP membrane observed experimentally. Importantly, the model suggests that the surface energy plays a negligible role comparing with elastic energy when the void dimension is comparable to the wavelength of light, leading to autonomous and fast shape recovery of the microstructure.

We emphasize that while the diffraction color change is demonstrated in temperature responsive SMPs here, there are a broad range of stimuli responsive material systems in the literature, allowing for fine-tuning the transition temperature, switching speed, degree of responsiveness, number of temporary states, and the type of stimulus. For example, the \( T_g \) of the epoxy SMP used in our system could be lowered (e.g. to 30 °C) by increasing the concentration of more flexible crosslinker, decylamine.26 SMPs that can store up to three different shapes in temporary states have been reported.7–27 We expect that the study of tuning periodic structures via combined pattern transformation and shape memory effect will shed new light in harnessing the mechanical response of soft materials and advancing a wide range of technologies, including color displays, sensors, camouflage, and energy efficient building components (e.g. smart windows and responsive façade).

Experimental section

Unless specifically noted, all chemicals were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received.
Fabrication of the hexagonal pillar array (Fig. 1a)

The SMP periodic membrane was replica molded from a 2D hexagonal pillar array (1.2 µm in diameter, 2.5 µm in pitch, and 5 µm in height), which was fabricated by 3-beam holographic lithography (HL) from epoxycyclohexyl POSS® cage mixture (EP0408, Hybrid Plastics®) (epoxy POSS) mixed with 0.9 wt % photoinitiator, Irgacure 261 (Ciba Specialty Chemicals). In a typical HL experiment, the epoxy POSS photoresist was spin-coated on a glass substrate, prebaked at 50 °C for 40 min, followed by post-exposure bake (PEB) at 50 °C for 30 s (Fig. 1a). The pillar structures were obtained after development in propylene glycol methyl ether acetate (PGMEA), rinsing in isopropanol (IPA), followed by drying in critical point dryer for 1.5 h and 150 °C by varying the ratio of difunctional D230 and monofunctional DA. Here, the SMP was formulated to have a Tg of 70 °C. After crosslinking EPON 826, the epoxy POSS template and the glass substrate were etched away by aqueous HF solution (48% wt.), resulting in a free-standing SMP membrane of a hexagonal array of holes on a ~500 µm thick bulk film.

Replica molding SMP periodic membrane (Fig. 1b)

The SMP precursor, a mixture with molar ratio 5:1:3 of melted diglycidyl ether of bisphenol A epoxy (EPON 826), poly(propylene glycol)bis(2-aminopropyl)ether (Jaffamine D-230) and decylamine (DA), was infiltrate into the template via capillarity at 50 °C followed by thermal curing at 100 °C for 1.5 h and 150 °C for 1 h, respectively. The Tg can be tuned from 40 °C to 90 °C by varying the ratio of difunctional D230 and monofunctional DA. Here, the SMP was formulated to have a Tg of 70 °C. After crosslinking EPON 826, the epoxy POSS template and the glass substrate were etched away by aqueous HF solution (48% wt.), resulting in a free-standing SMP membrane of a hexagonal array of holes on a ~500 µm thick bulk film.

Hot pressing of SMP membranes

The SMP membrane was compressed in the vertical direction using a manual bench top heated hydraulic press (CARVER 4122, Carver, Inc). The sample (> 0.4 mm thick) was placed inside of a Teflon sample holder (0.4 mm thick), which was then pressed between two Teflon sheets with heated platens. The platens were pre-heated to 100 °C for 10 min to reach equilibrium. Then a pressure of 1000 psi was applied to the sample and kept for 15 min before cooling down to room temperature, followed by release of the pressure to lock the temporary shape. The strain was calculated by comparing the final film thickness with the original one.

Fabrication of SMP membrane with embedded “Penn” letter

The membrane was fabricated by replica molding in the way similar to that from the hexagonal POSS pillar array. One added step was UV exposure (λ=365 nm, 400 ml/cm², 97435 Oriel Flood Exposure Source, Newport) through a “Penn” logo photomask conducted after prebaking and before the three-beam laser exposure. After PEB, the “Penn” region was highly crosslinked and appeared nearly flat or with shallow features depending on the dosage, while the surrounding areas formed pillar structures.

Calculation/modelling

Numerical simulations of stability of the structure were conducted using the nonlinear finite element code ABAQUS/Standard (version 6.8-2) while the thermo-mechanical loading history of the structures was investigated utilizing the nonlinear finite element code ABAQUS/Explicit (version 6.8-2). Each mesh was constructed of 8-node, linear, 3D elements (ABAQUS element type C3D8R). In the hexagonal array the voids have a radius R = 1 µm and a unit cell spanned by the lattice vectors A1 = [2 0 0] µm and A2 = [1 1.732 0] µm and A3=[0 0 0.1] µm is used. RVE consisting of 1x2x1 unit cells is considered in the simulations of the thermo-mechanical loading cycle and an imperfection in the form of the most critical eigenmode is introduced into the mesh to capture the instability upon hot-pressing, the subsequent freezing-in of the transformed pattern and then the shape recovery behavior. The stress-strain behavior of the SMP is captured using the material parameters reported in Table 1.

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Notes and reference

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† Electronic Supplementary Information (ESI) available: Movie showing the shape and color recovery of compressed, transparent SMP membrane after immersing in 90°C water; movie showing FEM simulation of the pattern transformation of 2D SMP membrane through compression and its recovery. See DOI: 10.1039/b000000x/20

reflective structural color, which can be recovered upon reheating.