In-plane deformation of shape memory polymer sheets programmed using only scissors

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1. Introduction

This paper describes a simple strategy to program polymer sheets to shape-shift in-plane into a variety of structures in response to heat. The process begins by cutting (e.g., using scissors) a pre-strained, inexpensive, chemically-homogeneous, and commercially available thin polymer sheet into an initial geometry. Subsequent heating of the polymer above its glass transition allows the strain to relax, which produces a final shape. The appeal of the method described here is that an easy, low-cost cutting method can achieve a similar shape memory effect attained by more complex processing techniques. Unlike conventional methods, where the final shape of a shape memory polymer must be defined a priori, the direction of cutting of the polymer defines its final shape without any complex pre-programmed strain profiles. A geometric model relating the resolved 2D polymer shape to the initial shape and strain orientation reveals linear correlation between the model-predicted and experimentally-observed shapes. In addition to demonstrating the principle with simple rectangular shapes, we suggest geometries related to encryption and high aspect ratio fibers.

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The approach here has a similar appeal; it creates a variety of in-plane (i.e., 2D shapes) from a single pre-strained polymer sheet that may be fabricated in mass production at low cost. In-plane shrinkage is useful for a number of applications including heat-shrink packaging, unconventional fabrication of microfluidic channels [16], and densification of lithographic features [17,18].

We demonstrate this alternative approach for shape programming, characterize the geometric response, develop a predictive model, and show a few illustrative examples of the method.

2. Discussion

We chose to use 0.05 mm thick Embrace films manufactured by Eastman as model substrates because these uniaxially-strained films are available commercially. These films—used industrially as labels for plastic bottles—shrink ≈ 50–60% in plane (along the direction of strain) when heated above the glass transition temperature (T_g). Polyester films similar to Embrace films quickly reach ultimate shrinkage without significant heating above T_g [19]. In some of our experiments, we print patterns of ink on these films to help visualize shape change and monitor the degree of shrinkage. This principle is similar to patterns printed on industrially-produced heat shrink polymer films. However, industrial applications scale the printed patterns before shrinking so that the final image does not appear distorted after shrinking.

We used a hot water bath at 70 °C to induce shrinkage in most of the samples. We chose this temperature because it is above T_g, produced significant shrinkage of the polymer sheet in less than a minute, and provided a relatively safe working temperature (i.e., no risk of boiling) with minimal evaporation of water. For convenience, we placed the film samples in the gap of a ‘cartridge’ composed of two glass slides in a Plexiglass holder (the completed sample housing is shown in Figures S1 & S2 in the Supporting Information) and submerged it in the water bath. Although the cartridge is not a necessity, it kept the samples dry during shrinkage. We removed the samples from the water bath after being submerged for 45 s, at which point the shrinkage appeared to halt.

As a concept demonstrator, we cut identical rectangles (2.5 cm x 5 cm) from these films and oriented the cut-outs at angles defined relative to the direction of strain. By arbitrary definition, an angle of zero degrees aligns the long axis of the rectangle with the direction of strain. Fig. 2a illustrates the shape and orientation of the samples, while Fig. 2b provides photographs of the films before and after heating at 70 °C. Black ink from a marker added to the perimeter of the films after processing enhances photographic contrast. The Supporting Information (Video S1 and Figure S3) contains a video capturing the strain relaxation of a rectangle cut from the film at 45°.

It is possible to achieve a variety of final shapes from identical starting patterns by varying only the orientation relative to the
strain axis. At the two extreme angles, the initial rectangle converts into a square (at 0°, relative to the initial strain direction) and to a high-aspect ratio rectangle (at 90°, relative to the initial strain direction). Intermediate angles convert the same initial rectangle into parallelograms with different vertex angles. This family of shapes is unique to the rectangular starting shape; other shapes are possible with different initial shapes.

Given the stored uniaxial strain in the polymer film, the shrinkage of a shape of known dimensions and strain angle can be predicted geometrically. Fig. 3 shows a rectangle with long dimension before (L₁) and after (L₂) shrinking. To facilitate modeling, we define additional terms H and W that correspond to the resolved vectors of L parallel and perpendicular to the direction of strain in the film, respectively (Supporting Information, Figure S4). Before shrinking, the long dimension is oriented at an angle θᵢ relative to the direction of the initial strain (in this example, θᵢ = 30°). After shrinking, the angle becomes θₑ.

Equation (1) relates Lᵢ and Lₑ to θₑ, while Equation (2) enables calculation of θᵢ. The Supporting Information provides the rigorous mathematical derivation of Equations (1) and (2):

\[
\left( \frac{L_1}{L_2} \right)^2 = S^2_H + (S^2_W - S^2_H) \sin^2 \theta_i
\]

(1)

\[
\theta_F = \sin^{-1}(S_W \frac{L_1}{L_2} \sin \theta_i)
\]

(2)

In Equations (1) and (2), Sᵢ denotes the shrinkage in the i dimension (i.e., H or W), Sᵢ is defined as:

\[
S_i = \frac{L_2 - L_1}{L_1} = 1 - \frac{L_1}{L_0},
\]

(3)

where L₀ and L are the initial and final lengths, respectively, for both the H and W vectors (note: these lengths are directly related to L₁ and Lₑ via geometry). Values of Sᵢ < 1 correspond to shrinkage and Sᵢ > 1 denotes expansion.

To test the model, we measured experimental geometric values (cf. Fig. 1) and plotted them in Fig. 4. Raw data are included in the Supporting Information. The best fit of the data in Fig. 4 verifies the prediction using Equation (1) and enables determination of S_H and S_W from the intercept and the slope of the line, respectively. From the data, we determine S_H = 0.512 and S_W = 1.046. Thus, upon heating, the sheet shrinks in the H direction by 48.8% while it expands in the W direction by 4.6% (cf. Equation (3)).

After completing these experiments, we heated the sheets directly in a water bath at 70 °C (as well as other temperatures, as reported in Supporting Information Figures S5 & S6) for several minutes to verify the ultimate shrinkage. The ultimate shrinkage was 60–65% at this temperature and 55.6 ± 1.8% at 63 °C, which is closer to the Tg of the film (59.5 °C as verified by DSC). Thus, samples placed directly in water at temperatures ranging from 63 to 70 °C all reached ultimate shrinkages greater than 51.2%, and notably, required more than 45 s to reach these ultimate shrinkages. Data collected from control experiments directly in water at 65 and 70 °C reveals that it takes 22–33 and 80–100 s to reach S = 51.2%, respectively, at these temperatures. Taken in sum, these results suggest the experiments performed in the plastic sleeve at 70 °C had insufficient heating time (45 s) to reach the ultimate shrinkage. The use of a consistent temperature for a consistent time resulted in consistent geometric changes even though the samples did not quite reach the ultimate shrinkage, which is satisfactory for demonstrating the concept of in-plane shape memory.

The unique shapes that result from the in-plane shape-shifting provide an opportunity to demonstrate new shape memory concepts. For example, we demonstrate lock-and-key structures in which the lock and key can both be encoded to be re-keyed synchronously. We created three “lock-and-key” structures with identical geometries but cut with different initial orientations relative to the axis of strain (i.e., θᵢ). We patterned each structure with a checkerboard design using an inkjet printer to facilitate observation of the strain relaxation. As shown in Fig. 5, the contracted samples form “locks” that only mate with their initial “keys”. In addition to physical structure, the post relaxation checkerboards are unique to each lock-and-key set, although the lock and key concept would work equally well without the ink.

Fig. 4. Measured geometric values versus values determined from the geometric model. The line is a best fit line (L₁L₂)² = 0.262 + 0.831sin²(θᵢ).

Fig. 3. Graphical depiction of the geometric basis used to develop a model that relates the geometry of the sample to the orientation angle. The images show the geometry of a sample before (left) and after (right) shrinking induced by heating. Ink is added to the perimeter of the shapes for visualization and the long axis is colored blue to distinguish it. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3. Summary

We demonstrate and model a new technique to program shape memory polymers using only cutting to ‘program’ the final shape. The appeal of this technique is that a single polymer shape cut from a chemically homogeneous, commercial, pre-strained shape memory polymer sheet can be converted into a variety of final 2D shapes using only the orientation of cutting and relaxation of the initial strain. We demonstrate an ‘encoded’ lock-and-key structure in which both the lock and key change in sync depending on the orientation. Upon heating, the three seemingly identical patterns resolve into separate shapes, with each having a unique key. As another demonstration, we fabricated high aspect ratio fibers by cutting thin fibers at angles greater than 45° and heating above $T_g$.

Most shape memory polymers start from the desired final shape, which is physically distorted into a temporary shape that resorts back to the final shape upon heating. This physical distortion requires careful control of complex strain profiles at elevated temperatures. Here, we show the ability to define the final shape by starting with a uniformly distorted sheet that is cut into a ‘programmed’ shape. This characteristic may be particularly useful for applications involving shape memory polymers with shapes that are difficult to pre-program or distort. Although shrink films have been used in microfabrication and packaging, the work here is the first to program the final shape by orienting and cutting the initial geometry relative to the direction of uniaxial strain relaxation.

The approach here could, in principle, apply to any polymer that can be pre-strained and cut. Although the polymer used here cannot convert back to the original shape after shrinking, the approach should apply to other versatile polymers such as cross-linked, semicrystalline polymers or liquid crystal elastomers with two-way shape memory effects that provide reversible actuation [20,21]. Although the approach can produce a variety of shapes, it is limited by the initial shapes that can be cut. Here, we used scissors, but it should be possible to achieve more precise shapes by employing a laser cutter, which has resolution closer to tens of microns. We also limited ourselves to 2D shapes, but in principle, the concept could be extended to 3D shapes with appropriate cutting tools. An appeal of the 2D approach is that it should be compatible with in-plane processes such as lithography, roll-to-roll, and inkjet printing although the necessity to cut the polymer is inherently more wasteful than conventional approaches to shape memory polymers. Ultimately, the shapes created by the technique described here are limited by the complexity of the starting strain profiles in the polymer (prior to cutting), but nevertheless, the simplicity of the approach has appeal as an alternative method for programming shape memory polymers.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.07.042.

References


Supporting Information:
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Sample Preparation

Desktop inkjet printers are not capable of printing on Embrace films directly. To print the checkerboard graphic onto these shrink films, we coated a section of the film substrate with a thin layer of craft glue (Elmers) and ‘dried’ the coating with a fan at room temperature. To help feed the sheets through an inkjet printer, we taped the film sections to a thicker 21.6 cm x 28.0 cm plastic sheet. Scissors cut the desired designs out of the checkerboard printed film.

Water Bath Heating

We used a hot water bath to induce shrinkage in most of the samples, although other heating sources (e.g., an oven) were used for shrinking the fiber samples due to size restrictions. We placed the film samples between two poly(dimethylsiloxane)-treated glass slides that allow the sample to shrink in plane without deforming out of plane. Although we did not anticipate out of plane shrinkage, the films are thin enough that they can deform unevenly when heated; thus, we confined them between two glass slides and inserted them inside a Plexiglas ‘cartridge’ (two Plexiglas sheets separated by a small gap) designed to allow heat transfer but prevent water contact with the film. The dimensions of the cartridge were such that two glass slides, each 75 mm x 50 mm x 1mm, would loosely fit within the housing. The completed sample housing is shown in Figure S1, with the glass slides inserted into the water-proof cartridge.

![Figure S1](image)

**Figure S1.** A polymer sheet patterned with a checkerboard (for visualization) and placed between two glass slides housed in a Plexiglass cartridge.

As shown in Figure S2, the Plexiglass (polymethylmethacrylate, PMMA) cartridge is immersed in a water bath at 70°C to relax the strain in the film.
Figure S2. Submersion of the sample in 70°C water bath relaxes the strain of the film.

A video capturing the strain relaxation accompanies this supporting information. Screen captures of the shrinking demonstration video showing pre- and post-relaxation samples are given in Figure S3.
Figure S3. A 5.0 cm x 2.5 cm rectangle cut at 45 degrees (top) before shrinking and (bottom) after shrinking.
Geometric Model

The following is a derivation of the geometric model used to determine the sizes of post-relaxation shapes based on initial lengths and relative strain angles. In each equation, L refers to the length of an arbitrary line in the same plane as the shrink film. H and W correspond to the resolved vectors of L parallel and perpendicular to the direction of strain in the film. θ is the angle between L and the strain direction, while subscripts I and F denote pre- and post-relaxation. Figure S4 denotes graphical depiction of each quantity.

**Figure S4.** Graphical depiction of the geometric basis used to develop the model that relates $L_F$ (i.e., dimension before film shrinking, Figure S1a) and $L_I$ (i.e., dimension after film shrinking, Figure S1b) and enables the determination of θ. (a) Before and (b) after shrinking.

L is initially resolved into the two vectors H (parallel to strain) and W (perpendicular to strain) as:

$$L_F^2 = H_F^2 + W_F^2$$  \hspace{1cm} (S1)

$H_F$ and $W_F$ are related to $H_I$ and $W_I$ via:

$$H_F = H_I \cdot S_H$$  \hspace{1cm} (S2)

$$W_F = W_I \cdot S_W$$  \hspace{1cm} (S3)

In Equations (S2) and (S3), $S_i$ denotes the shrinkage in the i direction (i.e., H or W). $S_i$ is defined as:

$$S_i = \frac{L_0 - L}{L_0} = 1 - \frac{L}{L_0}$$  \hspace{1cm} (S4)

where $L_0$ and L are the initial and final lengths, respectively. Combination of Equations (S1)-(S3) yields:
\[ L^2_F = H^2_I \cdot S^2_H + W^2_I \cdot S^2_W, \]  
which after substitution for \( H_I \) and \( W_I \) results in:

\[ L^2_F = L^2_I \cdot \sin^2(\omega_I) \cdot S^2_H + L^2_I \cdot \cos^2(\omega_I) \cdot S^2_W. \]

By invoking the law of sines and cosines, Equation (S6) can be rewritten as:

\[ \frac{L^2_F}{L^2_I} = (1-\cos^2(\omega_I)) \cdot S^2_H + \cos^2(\omega_I) \cdot S^2_W = S^2_H + (S^2_W - S^2_H) \cdot \cos^2(\omega_I). \]  

Recognizing that \( \theta = 90^\circ - \omega_I \) one can rewrite Equation (S7) as:

\[ \left( \frac{L^2_F}{L^2_I} \right)^2 = S^2_H + (S^2_W - S^2_H) \cdot \sin^2 \theta_I. \]  

The angle \( \theta_F \) can be obtained as follows. We first express \( W_I \) and \( W_F \) as:

\[ W_I = L_I \cdot \cos(\omega_I), \]
\[ W_F = L_F \cdot \cos(\omega_F). \]

By combining Equations (S9)-(S10) with Equation (S3) one arrives at:

\[ L_I \cdot \cos(\omega_I) = \frac{L_F}{S_W} \cdot \cos(\omega_F). \]

Using \( \theta_I = 90^\circ - \omega_I \) and \( \theta_F = 90^\circ - \omega_F \) one can rewrite Equation (S11) as:

\[ L_I \cdot \sin(\theta_I) = \frac{L_F}{S_W} \cdot \sin(\theta_F), \]

which after some algebra yields the expression for \( \theta_F \):

\[ \theta_F = \sin^{-1} \left( S_W \cdot \frac{L_I}{L_F} \cdot \sin \theta_I \right). \]

These derivations provide a predictive tool for use in designing shapes, as the two relevant post-relaxation quantities \( (L_F \) and \( \theta_F) \) are defined in terms of initial parameters \( (L_I \) and \( \theta_I) \). Desired final shapes can then be programmed by cutting the related initial designs out of the film. Table S1 lists experimental data used to plot Figure 4 in the main text and provides estimates of \( \theta_F \).
Table S1: Experimental data used for model validation

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**Shrinkage:** We performed additional shrinkage experiments by placing a 5 cm x 2.5 cm piece of the film directly in a water bath with controlled temperature. In contrast to the previous experiments, these samples were in direct contact with the water and not placed in a sleeve. We used a video camera to record the changes in geometry versus time and converted those changes into shrinkage. Differential scanning calorimetry (DSC) estimates a $T_g$ of $\approx 59.5^\circ$C; we observe shrinkage of the film as low as 63°C but none at 60°C. Figure S.5 plots the time dependent shrinkage at various temperatures in the direction of the initial strain (red) and the direction perpendicular to the initial strain (black). As expected, the shrinkage occurs faster with increasing temperature. In addition, the ultimate shrinkage (i.e., shrinkage plateau at long times) increases with increasing temperature; the films shrink $\approx 55\%$ at temperatures close to the $T_g$ and tend achieve plateau in shrinkage of $\approx 70\%$ at 80–90°C. Figure S.6 summarizes the ultimate shrinkage along the direction of the initial stain as a function of the sample annealing temperature.

![Figure S5](image)

**Figure S5.** The shrinkage of an Embrace rectangle (dimension: 5.0 cm x 2.5 cm) versus time for various temperatures. The red and black symbols represent three independent trials depicting shrinkage in the direction along (red) and perpendicular (black) to the initial strain.
Figure S6. Ultimate (i.e., long time) shrinkage of an Embrace rectangle (dimension: 5.0 cm x 2.5 cm) as a function of heating temperature. The open and solid symbols represent shrinkage obtained by averaging over two and three experiment trials, respectively.