“2D or Not 2D”: Shape-Programming Polymer Sheets

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Abstract

This review summarizes progress toward programming two-dimensional (2D) polymer sheets which respond to a variety of external stimuli to form three-dimensional (3D) shapes or macroscopically planar sheets comprising topographical features. Shape programming strategically adds value or function to 2D sheets, films, or coatings that can be created inexpensively. 2D substrates are common form factors that are compatible with ordinary 2D patterning techniques (*i.e.*, inkjet, photolithography, roll-to-roll printing) and may be stored, packed, and shipped efficiently. Polymer materials are attractive due to their flexibility, light weight, low price, and compatibility with high throughput processing. This review highlights strategies for triggering shape change in planar polymeric materials. The strategies are divided into four broad categories: 1) 2D substrates with latent topography “programmed” using conventional microfabrication, 2) 2D substrates that form topography due to imposed or self-generated stress, 3) 2D substrates form 3D shapes by out-of-plane bending, and 4) 2D substrates that use “hinges” to achieve out-of-plane folding. The review highlights all strategies while focusing primarily on last two approaches.

Keywords

Shape programming, Active materials, Folding, Polymer sheets.

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1. Introduction

1.1 Overview

This review focuses on strategies for shape-programming polymeric materials that can convert planar two-dimensional (2D) polymer sheets to three-dimensional (3D) shapes. Shape-programming changes the physical geometry of materials in response to an external stimulus. The desire to create 3D shapes is stimulated by the premise that shape defines function of most materials. Employing 2D planar sheets to fabricate 3D shapes brings several technological advantages and appeals: 1) 2D polymer sheets and coatings can be mass-produced inexpensively using high-throughput processing methods and find use in our daily lives including the substrates for printed electronics, laminate coatings, and plastic films; 2) 2D polymer sheets are compatible with most planar processes developed for the semiconductor industry as well as other patterning techniques, such as, screen printing, roll-to-roll processing, gravure printing, and inkjet printing; 3) planar sheets can be stacked efficiently for storage, transport, or remote deployment.

We divide shape-programming of 2D materials into four broad categories as illustrated in **Figure 1**: 1) 2D substrates that use additive or subtractive processes, such as lithography, to create topography; 2) 2D substrates that form topography, *e.g.*, wrinkles or creases, on their surface in response to an external stimulus; 3) 2D substrates that can form out-of-plane 3D shapes by bending, and 4) 2D substrates that use “hinges” to achieve out-of-plane folding. Unlike shape transformation, which describes the immediate alteration of the shape due to mechanical processing, shape programming involves a processing step (or a design strategy) to change shape rationally and controllably at a desired time and defined location in response to an external stimulus. It could be argued that Strategy 1 does not involve true shape programming steps since the shape change happens during processing and not in response to a subsequent external stimulus. However, we include it here for completeness and because it can be used to create latent shape change.

Figure 1

The importance of shape programming in planar materials unifies the four strategies depicted in **Figure 1** and points to some similarities among them. For example, while samples prepared by strategies 1 and 2 result in macroscopically planar substrates that support microscopic (typically sub-millimeter) surface topography, strategies 3 and 4 describe the formation of 3D out-of-plane shapes by bending, folding, or rolling to produce dramatic macroscopic shape changes as well as microscopic ones, often in a facile manner. Shape programming characterized by strategies 3 and 4 can occur due to asymmetrical distortion of the material, expansion (*e.g.*, thermal expansion, swelling), contraction (*e.g.*, strain relaxation, de-swelling), or flow or deformation (*e.g.*, displacement of material due to a stress).

Figure 2 differentiates the subtle differences between ‘bending’ (strategy 3) and ‘folding’ (strategy 4). These terms are sometimes used interchangeably since there is not a universally agreed upon definition that differentiates them. Several recent publications discuss the difference between bending and folding in shape programming materials.[1–5] Simply stated, folding involves localized deformation whereas bending is global. Lauff *et. al* provide a thorough summary of the literature on this topic and define bending as the “distributed deformation of a material along the deflected area that creates curvature” (*i.e.*, distributed curvature) and folding as the “localized deformation of a material along crease patterns to create new shapes” (*i.e.*, localized curvature along a crease). [1,2] **Figure 2a** shows a clear case of folding (where the ratio of red to blue approaches zero) and **Figure 2d** shows a clear case of bending (where the ratio of blue to red approaches zero). **Figures 2b and 2c** illustrate why it is difficult to definitively distinguish bending from folding. **Figure 2e** demonstrates that a series of local folds can lead to global bending.

Figure 2

Other excellent reviews cover aspects of shape programming by focusing on common materials (*e.g.*, hydrogels, elastomers) or highlighting adaptive composites. [2,4,6–16] In this review we provide a general roadmap for different strategies and materials used in shape programming. Specifically, we concentrate only on polymeric materials with an occasional mention of other materials that might be utilized in

conjunction with polymers for shape programming. Polymeric materials are attractive for shape programming due to their flexibility, light weight, low price, and compatibility with high throughput processing. We also focus primarily on Strategy 3 and 4; that is, conversion of 2D planar polymer sheets to out-of-plane structures by bending and folding. We limit our discussion of strategies 1 and 2 to a brief review with highlights of previously published reviews and references on these topics.

1.2 Why is shape programming from 2D to 3D interesting?

2D polymeric substrates may be manufactured industrially using low-cost, high-throughput processes, including, melt extrusion, injection molding, vacuum forming, pultrusion, or transfer molding [17,18]. In general, 2D substrates are compatible with many inexpensive 2D patterning techniques (*e.g.*, lithography, screen printing, inkjet printing, gravure printing, roll-to-roll processing, and laser cutting) and more sophisticated microfabrication and nanofabrication techniques (*e.g.*, spin casting, photolithography, thin film deposition, etching, and other additive/subtractive processes including unconventional patterning techniques such as dip pen lithography, colloidal lithography, imprint lithography, and directed self-assembly) [19].

Converting 2D sheets to 3D structures may be beneficial for a variety of purposes. Examples include, but are not limited to: 1) changing the shape of a polymer sheet to achieve a final product (*e.g.*, packaging); 2) assembling structures (*e.g.*, electronics or optics) that are fabricated in 2D to achieve final desired 3D shape; 3) reconfiguring the shape, and thus, function of a substrate for applications that are both low-tech (*e.g.*, responsive toys for children) and high-tech (*e.g.*, shape reconfigurable devices or non-fouling surfaces); [20–24] 4) deploying materials conveniently and compactly in a flat 2D form and have a 3D shape assemble at the destination site; 5) tuning the properties of a surface (*e.g.*, wetting or optical properties) that depend strongly on surface topography; and 6) implanting a structure in a compact form factor and have it assemble in situ (*e.g.*, a boat in a bottle, or an implantable device). [25–27]

There are many compelling applications of 2D to 3D transformations that have been proposed and demonstrated. For example, sensors constructed in 3D space allow for the measurement of signals from three independent axes to obtain accurate angular

and orientation parameters.[22] Morphing structures such as “Morphees” (*i.e.*, shape-shifting mobile devices) and “MorePhone” (*i.e.*, a cellphone curls upon a call) have been proposed for next-generation mobile devices. [28] In addition, shape programming from has also been applied in smart adhesives, [29] anti-fouling coatings, [30,31] sensors. [32,33]

2. Strategies for transforming 2D planes to 3D shapes

Many materials strategies and stimuli can be utilized for shape programming polymers. Following the scheme in **Figure 1**, we first overview those four strategies to convert 2D planes to 3D shapes and then narrow our focus to strategies 3 and 4.

2.1 Conventional fabrication (Strategy 1)

Additive or subtractive microfabrication can generate topography on 2D substrates.[19] Of the four strategies introduced in **Figure 1**, this approach is the most commonly used because of its importance for the mass production of electronics and computer chips. It could be argued that these techniques are not truly shape programming because the shape change usually takes place during processing, and not at some later time programmed into the material. However, conventional photolithography may be considered a shape programming method since the latent topography can be revealed only upon exposure to a liquid developer which may be thought of as “an external stimulus”.

Figure 3 illustrates the two general types of conventional lithographic methods, which expose polymeric films (*e.g.*, photoresists) to photons (*e.g.*, UV light, X-ray) or particles (*e.g.*, electrons and ions) to form relief structures in the film. Chemical changes in the films alter the solubility of the polymer in a liquid developer relative to the unexposed regions.[34,35] Positive photoresists become more soluble in a developer solution after exposure to the incident beam, while negative photoresists become less soluble after exposure. The most common lithographic method utilizes a mask to transmit patterns of photons onto selected regions on the substrate. Alternatively, a focused beam of photons or electrons may be rastered across a substrate, but these serial processes generally cannot achieve the high throughput patterning realized using a mask. Lithographic methods are dominant technologies in the fabrication of

microelectromechanical systems (MEMS), optics, and computer chips. These processes are inherently 2D and thus are poorly suited for patterning curved and out of plane surfaces. However, features created by lithography may be patterned on a 2D surface and then assembled into 3D shapes by, for example, bending or folding (discussed later in this review).[36–38]

Figure 3

In addition to conventional lithographic methods, there are many additive techniques (*e.g.*, sputtering and evaporation [39,40]) or subtractive methods (*e.g.*, etching, machining process [41,42]) for defining topography on a surface.

There are also numerous “unconventional” lithographic approaches for introducing surface topography on 2D substrates. [34,43,44] Examples include imprint lithography,[45–49] directed self-assembly,[50] dip pen lithography,[51] direct-write lithography, [52] colloidal lithography,[53,54], or soft lithography. [55,56] Self-assembly processes (*e.g.*, crystallization, phase separation, order-to-order transition, colloidal assembly) can also be employed to alter surface topography spontaneously by interaction-driven association of individual (often disordered) building blocks into organized arrays.[34,57–59] There are also numerous low-cost, low-resolution patterning techniques, including, inkjet printing, screen printing, and roll-to-roll patterning. In addition, 3D shapes can be realized by, for example, stereolithography [60–64] or ink-based direct-write methods [65–68]. The examples given here are by no means comprehensive and are only given to suggest the wide range of patterning techniques available. The reader is referred to several monographs and references on unconventional fabrication and printed electronics[69–73].

In summary, most of these techniques are “shape transforming” rather than “shape programming” because the topography change occurs directly during the patterning processes themselves rather than in response to an external stimulus. For this reason, these conventional microfabrication methods will not be discussed in more detail in this review despite their prevalence industrially and in laboratory environments.

2.2 Induced surface topographies (Strategy 2)

There are many strategies to induce surface topography onto smooth 2D substrates. Unlike materials addition or subtraction (Strategy 1), the surface topographies discussed here form due to the inherent properties designed into the substrates.

Wrinkling (or “buckling”) is a prominent mechanism to form tunable periodic sinusoidal surface topography, which has been reviewed in detail previously. [6,74–80] Buckles typically form due to compressive forces acting on a thin rigid film attached to a soft substrate (**Figure 4a**). Elastomers are usually used as the substrate. PDMS is employed often for these applications due to its outstanding flexibility and ability to be stretched [74,81]. Other materials, such as viscoelastic polymers (*e.g.*, polystyrene), hydrogels and polymer brushes can also be used to form buckles.[82–86] The stress may be imposed externally (*e.g.*, thermal expansion or mechanical strain) or by chemical modification of the surface of the polymeric substrate. For example, the bottom substrate may be heated and expanded uniformly either by an external heat source before the deposition of the top film or by thermal energy generated during the deposition. Upon cooling, compressive stress develops in the top metal film, which competes with the tensile stress in the bottom substrate and results in the formation of randomly oriented wrinkles (isotropic wrinkles).[82,87–89] Wrinkles can also form on a mechanically pre-stretched polymer sheets with a rigid top film (*e.g.*, metal, oxide or oxidized original surface with high degree of crosslinks) when introducing or releasing mechanical strain.[80,90,91] Imposing larger pre-strains (>10%) results in topography comprising hierarchically-structured wrinkles, in which smaller wrinkles reside on top of larger ones. (**Figure 4b**). Wrinkles can also be induced by swelling bilayer structures or by employing gradients in crosslink density. These techniques are applied commonly in hydrogel systems.[76,78,86,92–95] In addition, wrinkles can occur due to the surface modification (*e.g.*, oxidation) of an elastomer during sputter deposition. The oxidation creates a stiff layer on the surface of the elastomer and the mismatch between the mechanical properties of such skin and the base material generates a compressive stress during strain release that induces buckling.[96] The resulting buckles possess characteristic wavelength that depends on the mechanical properties and geometry of the system. The in-plane organization of the wrinkles depends on the direction of the

imposed strain, as illustrated in **Figure 4c**.^[76] During the past several decades various models have been developed to study the mechanism for wrinkle formation.^[80,82,97–102] The geometry and size of wrinkles (including the wavelength, amplitude) has been found to depend on the thickness of the top film and the foundation as well as the materials properties (*e.g.*, Young's modulus, Poisson's ratio) of the two layers and applied strain.

Figure 4

The ability to form wrinkled/buckled surfaces has been used in various applications, including, anti-fouling coatings,^[31,103] microfluidic devices to direct the cell growth,^[104] “smart” adhesive surfaces,^[105] optical devices such as microlenses^[106] and diffraction gratings.^[87,107] By making use of the buckling mechanism, buckled structures can be applied as a characterization tool to assess the modulus of materials employed as rigid thin layers.^[75,77,107,108] The application of buckled structures in light trapping materials has also been explored.^[109–112] Hierarchical buckles are well-suited topographical structures that enhance trapping of light with various wavelengths since the buckle wavelengths range from micro- to nano-scale.^[81]

Besides wrinkling (continuous undulations on the surface), other thin-film instabilities can form in response to stress, including, craters, creases, folds, localized ridges, or delamination (non-continuous deep folds on the surface). The type of topography depends on the degree of adhesion and difference in modulus between the film and the substrate. These instabilities form self-organized topographies such as wrinkles, creases, and buckles in response to a stimulus (**Figure 5**).^[90,113–121] The use of electric fields to induce film instabilities is another means of generating functional surfaces and on-demand creases or folds.^[113,114]

Figure 5

Dewetting instabilities of polymer thin films (thickness ~100 nm) offer a low-cost and lithographic free approach for patterning surfaces with tailored topographies. Molecular interactions (*e.g.*, van der Waals interactions, residual stresses due to long chain entanglement) or surface heterogeneities drive the spontaneous rupture of these thin

films (*e.g.*, spinodal dewetting). (**Figure 6a,b**) [122–130] Desired patterns can be generated by tuning physical or chemical heterogeneity on the substrate.[122,123] Surface patterns created by rational dewetting have been applied for optoelectronics and semiconductor devices. [122–124]

Figure 6

Dewetting of thicker films (thickness >100 nm) can be induced by applying external field, *i.e.*, temperature, electric or magnetic field.[124] For example, electrohydrodynamic instabilities utilize electric fields to overcome the stabilizing forces of surface tension and thereby form surface topography (*e.g.*, pillars) out of molten polymer films or planar liquids with an air gap (or the other polymer film) sandwiched between two rigid electrodes (**Figure 6c-f**).[131–137] In general, patterns formed by instabilities are difficult to control precisely over large areas and usually result in features with characteristic length scales that lack long range order.

Light-induced chemical transformation can also create stress that results in surface topography. For example, films containing azobenzene moieties undergo a *cis-trans* transition in response to light and generate surface topography when exposed to patterned light by employing surface-plasmon field (**Figure 7**).[138] It could be argued that this approach is a shape transformation rather than shape programming since the topography forms during light irradiation, but we include it since the topography is ‘dormant’ until stimulated by light, the response is ‘programmed’ within the composition of the molecules, and topography forms in the material without human (mechanical) intervention. The mechanism for this response will be discussed in more detail in section 2.3. Moreover, the surface topography can be triggered by light-induced Marangoni effect (*i.e.*, mass transfer through the interface due to surface energy gradients). For example, the surface energy of polystyrene increases due to dehydrogenation under patterned UV irradiation so that the polymer in liquid state flows from unexposed area to exposed area to form surface feature.[139]

Figure 7

Formation of surface topographies on planar substrates can be also triggered by the shape memory effect.[32,140,141] Shape memory polymers, *i.e.*, materials that can be programmed into a temporary shape that recover to a permanent shape upon heating, will be discussed in detail later in this review. As shown in **Figure 8**, surface topography can form in these structures by releasing the local stress formed by indenting or embossing, or by releasing a uniform stress generated by pre-stretching the film.[142] For example, grating patterns can be flattened into a stable temporary, flat substrate. The surface topography recovers by heating the samples above the glass transition temperature (T_g) of the polymer (**Figure 9**).[140] Light diffraction due to the grating pattern reappears, as evident from the apparent color change of the surface. Moreover, the surface topography recovered from a shape memory polymer can form a multi-use dry adhesive to a glass substrate that is strong and reversible.[29]

Shape memory materials are also applied widely for forming 3D structures in a responsive fashion, which will be elaborated in more detail in the section 2.4.

Figure 8

Figure 9

2.3 Bending (Strategy 3)

This section focuses on bending as a mechanism to form out-of-plane 3D structures. Expansion (*e.g.*, swelling, thermal expansion and pneumatics) and contraction (*e.g.*, deswelling, thermal shrinkage, and deflation) generate usually stresses necessary to convert 2D polymer sheets into 3D shapes by bending.

Polymer gels (or polymer networks) are often used for bending because they can swell dramatically in the presence of ‘good’ solvents and contract when exposed to poor solvents while retaining their overall network structure. Polymer gels can be classified as either hydrogels or organogels. Hydrogels are hydrophilic polymeric networks that can absorb water and swell.[143,144] Hydrogels are noted for their ability to swell or deswell in response to environmental changes in aqueous environments including pH, temperature, ionic strength, solvent type, or electrical potential.[143–150] These environmental cues can be employed as stimuli to induce shape change.

Temperature is an appealing stimulus for altering the swelling behavior of hydrogels because it is easy to control and reverse externally. While technically all polymers undergo conformational changes in response to temperature, in some cases changes of polymer solubility in water are very dramatic and lead to large changes in swelling. Poly(N-isopropylacrylamide) (PNIPAAm) and its derivatives are popular temperature-responsive hydrogels due to a reversible coil-to-globule transition that occurs upon exceeding the lower critical solution temperature (LCST $\approx 32^{\circ}\text{C}$).^[143,144,151–154] Other hydrogels also exhibit LCST.^[155,156], for example, poly(N-vinylcaprolactam) or poly(N-vinylpyrrolidone).

Hydrogels often contain charged (*i.e.*, strong polyelectrolytes) or chargeable (*i.e.*, weak polyelectrolytes) groups. The presence of charges causes gels to swell in water. The concentration of chargeable groups in weak polyelectrolytes depends on the nature of the polymer (*i.e.*, polycation *vs.* polyanion), pH, and ionic strength of the solution. Changing the pH of the solution (for weak polyelectrolytes) and/or ionic strength (for all polyelectrolytes) alters the swelling behavior of the gel and are therefore useful stimuli for gel shape change.^[148,157,158]

The ability to control the degree of swelling or de-swelling in hydrogels using external stimuli offers opportunities to program shape change. Isotropic swelling or de-swelling results in uniform changes in volume; *i.e.*, each dimension of the gel shrinks or expands proportionally. To induce out of plane motion, the generated stress must be asymmetric, which can be induced by employing a number of approaches.

One approach to achieve asymmetry may be realized by laminating bimorph structures with different responses to the same stimuli (*i.e.*, temperature, solvent, ionic strength) or by patterning stimuli-responsive hydrogels.^[23,154,159–162] The mismatch in mechanical response of the two layers in the bilayer governs the folding behavior in response to an external stimulus. A theoretical analysis pertaining to the bending behavior of bilayered laminates offers useful insight into folding, which is induced by mismatch in stress (or strain) between the two layers. The bending curvature of bilayered systems offers a measure of the effect of stress (or strain).

The general theory of bilayer bending is derived from the model of a bi-metallic strips proposed originally by Timoshenko in 1925.^[163] A classic example of a bilayer

structure is a thermal bimorph, featuring two layers of materials with different thermal expansion coefficients. The bilayer curls in response to heat since one layer expands more than the other. This concept may also be employed in polymeric systems; a laminate structure composed of a layer of hydrophobic polymer (*i.e.*, polycaprolactone) and a layer of thermo-responsive hydrogel (*e.g.*, PNIPAAm) can bend to generate a 3D structure by tuning the solution temperature (**Figure 10a**).[160] Similarly, a closed micro-cage made of an SU8 epoxy (high thermal expansion coefficient) laminated with diamond-like carbon (DLC) layer (low thermal expansion coefficient) can open upon heating.[164] In addition, the curvature of bilayer structures can be controlled by employing patterned polymers with various Young's moduli on the active layer which is stimuli responsive. (**Figure 10b**). [165] Humidity can also trigger the bending of bilayer structures. For example, a bilayer laminate comprising cross-linked poly(acrylic acid) and a layer of polymer that absorbs water from humid air (*e.g.*, poly(allylamine hydrochloride)) will bend in response to humidity.[166–168] Hydrogel bilayers with a copolymerized layer of N-isopropylacrylamide (NIPAm) and acrylic acid (AAc) or poly-hydroxyl ethyl methacrylate (HEMA) show asymmetric swelling and trigger 3D structures in solutions with different pH and ionic strengths.[23]

Figure 10

Another approach to bending creates out-of-plane motion by generating crosslink patterns in a hydrogel.[169] The process utilizes “halftone” photolithography of photo-crosslinkable PNIPAAm copolymers containing pendent benzophenone units for crosslinking to induce the crosslink patterns. The crosslinked regions of the gel swell less than the rest of the gel, which generates the stress necessary for out of plane deformation with nearly constant Gaussian curvature (**Figure 10c**).[170] Various 3D shapes form by bending if the stress distribution on the film can be controlled. [171–175] For example, hydrogels can form complex 3D helical structures using sheets with alternating stripes of different chemical composition and thus different swelling response (**Figure 10d**).[176] In addition, chemical oscillations of ruthenium ions between reduced and oxidized states within gels can cause cyclic swelling.[177]

Materials containing gradients of fillers or crosslinks through the depth of the sheet also bend. The asymmetry of these embedded active materials results in out-of-plane motion in response to a uniform stimulus (**Figure 11**).^[178–183] For example, rolling of a photo-crosslinkable copolymer based on PNIPAAm can be triggered thermally in aqueous medium by patterning both high and low swelling regions using UV light (**Figure 3b**).^[170,179]

Figure 11

Electric fields represent another attractive stimulus that can moderate swelling of polymeric gels. Electric fields can disrupt the distribution of ions in gels and therefore change the local osmotic pressure. Significant effort in this field has been achieved during the past few decades following the pioneering work by Tanaka and colleagues.^[92,184] For example, electrical potential can drive cations from the electrolyte (*e.g.*, sodium dodecylbenzenesulfonate, Na^+DBS^-) into a polymer and cause asymmetrical swelling.^[185,186] More recently ‘ionoprinting’ was introduced to introduce local folding and global bending of flat hydrogel sheets. Ionoprinting uses metal electrodes under anodic conditions to inject ions into a polyelectrolyte hydrogel (*e.g.*, sodium polyacrylate).^[147,187,188] Divalent metal cations (*e.g.*, Cu^{2+}) bind within the anionic network to form crosslinks that generate sufficient mechanical stress to create a hinging response in air (**Figure 12a**). Whereas actuation of most gels relies on swelling/de-swelling, which is a slow process, ionoprinting results in rapid actuation (a few seconds) without the need for submersion in electrolyte. In addition, the ionoprinted lines are stiffer than the rest of the gel. These stiff lines can generate an anisotropic response to de-swelling of the gel in ethanol (*i.e.*, the water diffuses out of the gel), as shown in **Figure 12b**.

Figure 12

Organogels, *i.e.*, crosslinked polymer networks that swell in the presence of organic solvents, can also be utilized for shape programming.^[189–191] For example, many elastomers such as those based on poly(dimethylsiloxane) (PDMS)^[192] swell to different extents based on the solubility of solvents in the networks.

The major appeal of swelling/de-swelling for controlling the shape of a polymer sheet is its simplicity and ability to operate in wet environments. Furthermore, many hydrogels are biocompatible because they are largely composed of water. Swelling/de-swelling, however, suffers from least two notable drawbacks: 1) it requires solvent media, and 2) it is generally slow due to the reliance on diffusion of solvent into the polymer (although approaches like ionoprinting can operate in air). Here, we limit the discussion of gels because there is a rich literature describing strategies (temperature, solvent, electrical potential, pH, *etc.*) for shape programmable gels; the examples given here are just illustrative and not comprehensive.[12,143,144,146,152,153,193–196]

In addition to swelling, pneumatics can also induce out of plane motion from a 2D substrate via the volumetric expansion and contraction achieved by applying pressurized gas inside a cavity (*e.g.*, a balloon) made of elastomeric materials such as PDMS and Ecoflex (a commercial elastomer) to be utilized as grippers (**Figure 13**).[24,197–200] To realize bending, asymmetrical inflation has to be achieved using material and design strategies. A downside of this method is the inconvenience of tethering of the inlets/outlets for the gas, although it is possible to induce chemical reactions to rapidly create gas in situ.[201]

Figure 13

Liquid crystal elastomers (LCEs) are popular shape programmable polymers. Whereas there are few strategies for creating shape reversible SMPs, LCEs can actuate reversibly, which is a salient feature. LCEs are hybrid materials, which combine oriented liquid crystals and polymeric elastomers. Usually, chemical synthesis couples the liquid crystal units with polymer chains to form the LCE networks. Polymer chains in the network experience anisotropic conformation due to the crystalline phase of liquid crystals, while the polymer chains return to their coil conformation upon heating. Therefore, the shape change in LCEs can be triggered by a temperature jump (**Figure 14a**).[202–210] LCEs incorporating photoresponsive functional groups constitute another large group of light-induced shape programmable materials (**Figure 14b**).[202–208,211] Many excellent reviews and books have summarized the development in this field.[204,212–217]

Figure 14

Light can also induce shape changes to polymers by incorporating photosensitive groups, such as such as azobenzene. Photoresponsive SMPs (or so-called light-activated SMPs) involve materials with photosensitive functional groups or fillers in the polymer networks, such as photoisomerizable molecules, *i.e.*, azobenzenes, triphenylmethane leuco derivatives, and photoreactive molecules (**Figure 15a-c**).[218–225] Triggered by appropriate UV wavelengths, the photoinduced effects on the molecular level (*e.g.*, photoisomerization, ionic dissociation, or photodimerization) lead to macroscopic volume changes (shrinking or swelling) of polymers. For example, the *cis-trans* isomerization reactions of azobenzene generate reversible conformation changes at the molecular level in response to specific wavelengths and, in turn, induce shape change macroscopically. Azobenzene molecules may be introduced into liquid crystal elastomers [205,206,226–228] or photosensitive polymer films.[5,138,229,230] **Figure 15d** demonstrates bending of the polymer sheet with azobenzene molecules in response to light polarized at different angles.

Figure 15

It is also possible to use electric fields to actuate elastomers and dielectric polymers by a number of mechanisms including the Maxwell stress. These topics have been reviewed elsewhere [231–236]. Likewise, piezoelectrics can convert voltage signals into displacement, but involve generally ceramic materials (with the noted exception of poly(vinylidene fluoride), PVDF [237–243]) (**Figure 16**). We thus do not review them in detail here but mention them for thoroughness.

Figure 16

The examples we have provided within Strategy 3 rely primarily on bulk changes in volume to induce bending. However, it is possible to localize those changes to just the surface. Changes in surface topography can be induced by employing polymer brushes that behave similarly to gels by responding to external stimuli, such as, pH, temperature, salt concentration, or type of solvent; those structures have been reviewed

before.[153,245,246] The conformational change of brushes due to an external trigger can be employed in controlling surface wettability,[247,248] or adhesion properties.[249,250] The changes in surface topography due to brush expansion or contraction are relatively small compared to the other techniques discussed here and we therefore limit our discussion of this topic.

2.4 Folding (Strategy 4)

While there is some phenomenological overlap with the examples of bending in Strategy 3, Strategy 4 is distinguished by its focus on folding as defined in **Figure 2**.

Folding occurs commonly in nature (*e.g.*, certain sensitive plants close their leaves in response to gentle touch; folding and unfolding of leaves and wings) and in the ancient art of paper folding.[251–253] Here, we discuss folding of polymeric materials using external stimuli in a hands-free manner; these approaches are often called ‘self-folding’. It is a deterministic self-assembly approach that converts a 2D template with pre-defined hinges into a 3D shape in response to an external stimulus, as shown in **Figure 17**.^[57] Hinges are regions on the substrate that get activated (*i.e.*, fold) in response to an external stimulus.^[57] for the need for reconfigurable devices, actuators, and sensors motivates research on folding utilizing different driving forces and a variety of active (*i.e.*, stimuli responsive) materials.[4,14,20,57,175,186,252,254–256] While strategies can originate from or be inspired by biological systems, the approach discussed here will not include cases of responsive biomolecules or living organisms, although they can be applied for folding processes as well.[257–264]

Figure 17

Folding can be achieved by at least three means: 1) defining locally responsive hinges fabricated using materials with a different composition from the rest of the sheet; 2) combining, laminating, and patterning non-responsive sheets with responsive sheets; 3) modifying physically an otherwise homogeneous sheet (*e.g.*, shape memory polymers) in local regions to define hinges that fold upon exposure to the external stimuli; 4) stimuli can be applied to only the hinge region of a sheet or composite (*e.g.*, Joule heating, focused laser).[20,254,265,266] The following paragraphs describe these different means.

One approach to fold 2D substrates is to define hinges that differ in chemical composition from the rest of the sheet. These hinged regions may be composed of a variety of materials that actuate in response to an external stimulus. For example, polyimide shrinks at high temperatures (*e.g.*, >200°C [165, 166]) due to out-gassing of strongly-bound solvents (**Figure 18a**). Likewise, pre-strained polymer films shrink upon heating and can be utilized as local hinges different from the bulk materials to induce folding (**Figure 18b**).[269] Stimuli-responsive polymers patterned as hinges can also control folding and unfolding of non-responsive laminates (**Figure 18c**).[38] For instance, a polymer (*e.g.*, poly(caprolactone) [270]) or molten metal (*e.g.*, solder [36,271]) can be patterned as a hinge and cause folding of polymer sheets when heated due to surface tension. Some gels swell in response to selected solvents and may therefore be used as hinges as well. For example, hydrophilic hinges based on polyurethane (PU)/2-hydroxyethyl methacrylate (HEMA) swell significantly in acetic acid for folding planar sheets of PDMS into 3D structures.[175]

Figure 18

Another approach employed to fold planar sheets applies multilayer laminates comprised of responsive films combined with non-responsive, rigid films that locally limit deformation. **Figure 19a** shows a schematic of rigid plates held together by a shrink film which can actuate in response to an external stimulus. The folding angle can be controlled by the gap distance, thickness and shrinkage (or swelling) of the active sheet.[2,272–277] One implementation of this strategy consists of sandwiching a temperature responsive hydrogel (*e.g.*, PNIPAAm) sandwiched between two glassy polymer layers. Patterned openings in the top glassy layer allow the gel to swell only locally and therefore create a hinging response, which enables micro-scale origami including the creation of the classic origami crane (**Figure 19b**). A similar strategy sandwiches a pre-strained thermoplastic between two layers of structural panels. When placed in an oven, the thermoplastic shrinks only in the gap between the panels (**Figure 19c**). Folding occurs due to asymmetric openings in the panels. Another example is bonding the elastomeric polymers with a layer of magnetic material and fold can be

induced in response to external magnetic fields. [279] This approach requires multiple (yet simple) fabrication steps and results in folds that are very reproducible.

Figure 19

A third approach to fold planar sheets utilizes physical pre-programming of chemically homogeneous substrates. For example, thermally-responsive SMPs can be locally pre-programmed to a temporary shape and return back to a permanent shape at $T > T_{\text{trans}}$ to achieve shape changing from 2D to 3D. The heat may be delivered by using either uniform or local stimuli, including focused light, Joule heating, or thermal radiation. [280,254,281–286] An illustrative example is shown in **Figure 20**.

Figure 20

In general, shape memory materials have been used extensively for 3D shape programming. These structures demonstrate the so-called shape memory effect in response to various external stimuli. The shape memory effect describes a phenomenon wherein a material can return to its original shape from a temporary shape, defined by deforming the material and fixing it in a metastable state.[287] The temporary shape does not have to be flat, although it can be, as shown in **Figure 20**. Although the final shape could be either a bend or a fold, we discuss it within Strategy 4 because it provides a popular approach for folding.

Swedish physicist Arne Olander discovered the shape-memory effect in the early 1930s in gold-cadmium (Au-Cd) alloys, which can be plastically deformed upon cooling and can return to the original shape by heating.[288] Shape memory materials include not only metal alloys but also other materials such as ceramics, liquid crystalline elastomers, polymers, and gels.[202,203,289–292] Shape memory alloys (SMA) and shape memory polymers (SMPs) are two of the most popular shape memory materials, which will only be briefly introduced here since they have been reviewed thoroughly in the literature.[287–289,293–299]

Although SMAs are not necessarily polymeric, they may be combined strategically with polymer sheets to program shape changes. The most common SMA is nickel-titanium alloy (Nitinol) [288,289,280,300] Those metal alloys demonstrate the

shape-memory effect due to the thermally-driven reversible phase transition from a symmetrical austenitic phase at high temperatures to an asymmetrical martensitic phase.[287,289,280] SMAs can be patterned as thin films to deflect substrates into 3D structures,[301–305] or as actuating hinges that induce the folding of 2D planes when heated (**Figure 21**).[20,254]

Figure 21

SMPs were first developed commercially in 1980s and received much attention due to their light weight, flexibility, high transformation strain, and low actuation forces compared to similar properties observed in metal alloys.[280] SMPs possess a great potential in a variety of applications such as automatic switches or sensors, intelligent packaging and tissue engineering, and have been reviewed thoroughly.[281,282,289,294–296,298,306–315] Both the molecular architecture of polymers and the “programming process” govern the shape memory behavior of SMPs. A typical programming process uses a thermo-mechanical cycle (**Figure 22a**) that starts with the polymer in the permanent shape, deforms the polymer to a temporary shape by applying an external force over the thermal transition temperature (T_{trans}) (*e.g.*, T_g or melting temperature, T_m), and cools the polymer to preserve that temporary structure. Upon heating above T_{trans} , the polymer recovers to the permanent shape (*i.e.*, the recovered shape) because the polymer chains relax back to the entropically favorable state. The shape memory effect is commonly characterized by a cyclic thermo-mechanical strain-temperature-stress diagram (**Figure 22b**). [316] The strain recovery rate, which describes how much the polymer memorizes the permanent shape, and the strain fixity rate, which shows how well the polymer can be fixed at the temporary shape, quantifies the shape memory performance.[287] Most SMPs have one temporary shape. Several researchers have developed clever ways to introduce more than one temporary shape into a SMP.[317–321]

Figure 22

As shown in **Figure 23**, the ability for polymer to “remember” its permanent shape relies on cross-links in the form of either covalent bonds (*i.e.*, chemical cross-

linking) or strong intermolecular interactions (*e.g.*, chain entanglement or crystalline domains). So-called “switching segments” fix the temporary shape of the polymer network and prevent the flow of polymer chains below the transition temperature. Although **Figure 23** summarizes switching approaches, the most common switching segments are “frozen” polymer chains at $T < T_g$ for amorphous polymers or polymers in crystalline domains at $T < T_m$ for semi-crystalline polymers. [280,287,309,310]

Some macroscopically-homogeneous planar materials adopt 3D shapes under uniform stimuli due to the gradients of crosslink densities that form across the sheet in response to a uniform stimulus (*e.g.*, light, heat, *etc.*) (**Figure 24**).

Figure 23

Figure 24

In addition, stimuli can be applied locally to the hinge region, by, for example, Joule heating, [20,254,322] focused laser light, [265,266] or pneumatics. [323]

Recently, our group reported on a simple approach to achieve folding using homogeneous 2D pre-strained polymer sheets with inkjet-printed hinges on a planar surface.[324] Pre-strained polymer sheets are a type of shape memory polymer that shrinks in-plane if heated uniformly. Black toner patterned on the surface provides localized absorption of light, which heats the underlying polymer to temperatures above the T_g to induce the local shrinkage of the polymer so that the planar sheet folds into a 3D shape. Various 3D structures have been demonstrated using this approach from simple folding to complex structures (**Figure 25**) and a simple geometric model predicts its folding angle based on strain relaxation.[325] It is also possible to induce the folding by irradiating the samples with light patterned in the shape of a hinge.[266]

Figure 25

2.5 Discussion for out-of-plane shape programming (Strategies 3 and 4)

The approaches described in Strategies 3 and 4 often present trade-offs. For example, patterned hinges frequently require multiple fabrication steps but can result in a range of complex 3D structures (**Figures 18 & 21**). In contrast, bilayer laminates are simple, but deform into a limited set of geometries and only produce sharp folds when combined

with patterned, rigid sheets (**Figure 19**). SMPs require pre-programming and are usually actuated by heating (**Figure 20**). Hydrogels are biocompatible but their use is usually limited to liquid environments and materials that are often very soft. Thermal actuation is one of the most popular means to induce folding or bending due to its simplicity and the availability of thermal triggers (*i.e.*, light, resistive heating and thermal radiation), but the high temperatures required often limit the applicability of such structures. More generally, selecting materials for shape programming often presents a trade-off between elastic strain and modulus. **Figure 26** summarizes the mechanical characteristics of a wide range of existing materials applied for reconfigurable and morphing structures.[326–328] The red dashed curve in the upper right corner of **Figure 26** depicts the trade-off between strain and stiffness for those structures. Materials that can be deformed significantly (*i.e.*, large strain) tend to have a lower modulus, which limits their utility. Polymers included in the diagram in **Figure 26** are no exception; elastomers or gels possess a low modulus and can be extended to large strains. For many applications, it is desirable to have large deformations and large moduli to store mechanical energy. Development of materials that meet these criteria represents a great research challenge as well as opportunity.

Figure 26

Table 1

Table I summarizes representative stimuli for folding and bending of polymeric materials typical materials, length scales, and reversibility. [4,57,288,255] Among all parameters listed in **Table I**, reversibility is one of top considerations for realizing practical applications of out-of-plane actuation. Hydrogels, electroactive polymers, and LCEs have exhibited various degrees of reversibility. Swelling/de-swelling of gels is a reversible process but it takes place typically only in liquid environments, diffusion of liquid in and out of the gel limits the rate of actuation, and gels are typically soft and brittle. The actuation of photoresponsive shape memory polymers and liquid crystal elastomers with photosensitive groups is reversible by switching the exposure wavelengths (usually in the UV range). Bilayers with differential thermal expansion

bend reversibly over small displacements. In contrast, the folding of most SMPs is usually irreversible (*i.e.*, the so-called one-way shape memory effect) due to the strain relaxation that occurs. Likewise, actuation of pre-strained polymers is typically irreversible because the first actuation relaxes (often completely) the stored strain. Several recent reports discuss polymers with two-way shape memory effects.[310,329–338] The term ‘two-way’ implies that the polymers can change shape reversibly multiple times simply by changing the stimulus. The two-way shape memory effect has been explored in semicrystalline polymers. [310,329,330,332,336,337,339–345] In general, these systems shrink due to chain relaxation at elevated temperature, but revert to a different shape due to stresses generated by the reformation of crystals at lower temperatures.

Response time for folding is an important parameter not listed in **Table I**. Swelling/de-swelling in solvents is usually slow due to inherently slow diffusion process which takes minutes to hours. Chemical changes induced by light cause folding relatively slow (few minutes). Pneumatic actuation occurs typically within seconds or less and can be done reversibly. Actuation in magnetic field is also relatively fast (seconds), and can be done reversibly. Thermal actuation (including light irradiation for heating) can also be fast (a few seconds).

Another challenge facing the field of out-of-plane actuation is the relatively simple 3D structures that have been demonstrated to date, such as single folds and cubes. There are some more complex structures beginning to appear in the literature. [277,279] The ability to provide sequential folding of hinges (rather than all hinges folding at once) may help increase the level of complexity.

Although most current research on converting 2D planar sheets to 3D out-of-plane structures by folding does not use paper, it is often called ‘origami engineering’ which covers a wide range of topics including development of responsive materials, the study of algorithms and mechanics for designing folded structures, [346–353] the establishment of physical models (*e.g.*, to predict and understand compliant mechanisms and its link to origami folding[354–358]), the development of new design tools for fabrication, [359] and the implementation of novel concepts for structure or topography optimization (*e.g.*, hinge design and layout, folding sequence, reconfiguration).[360–362]

In summary, currently there is no universal, ideal approach that provides reversibility, fast response, large forces or torques, geometric and sequential control, and ease of fabrication. Realizing systems that have most or all of these properties is a primary goal of materials researchers working on shape programming.

2.6

2.7 Applications for out-of-plane shape programming (Strategies 3 and 4)

Out-of-plane shape transformation from 2D to 3D is an appealing strategy to generate 3D structures from 2D patterns for many applications spanning microscale to macroscale. Examples include containers for drug delivery and biomedical devices,[25,38,255,281,381–385]; actuators, grippers and robotics (**Figure 27a**); [24,164,185,186,363,364,386] robotic microhand or minimally invasive surgery; [26,257,281,387–390] optical sensors and devices; [22,32,265,391] 3D microfluidic devices (**Figure 27b**); [178,392,393] reconfigurable devices or robots; [20,33,68,254,322,394–396] adhesives and interlocks [29,397] nanoinjector; [398] programmable lithography for nanostructures [399] smart packaging; deployable structures (**Figure 27c**); [251,400–404] and shape-shifting mobile devices.[28]

Figure 27

3. Conclusion, opportunities, and challenges for shape programming

Shape-programming of materials from 2D sheets to 3D shapes is appealing in many applications including reconfigurable devices, responsive actuators, and assembly processes. This review motivates the advantages of creating 3D shapes from 2D sheets and introduces several representative strategies and mechanisms for shape programming polymeric materials involving out-of-plane deformation, *i.e.*, folding, bending, rolling, contraction, expansion, induced surface topography, and conventional lithographic processes. This review focuses primarily on strategies for out-of-plane actuation, of polymeric materials from 2D sheets to 3D shapes, as well as relevant programmable materials within the context of folding.

Although great progress has been made toward shape programmable materials and relevant methods from 2D to 3D, there many opportunities still exist for new shape

programming approaches, especially folding/bending, to evolve regarding design optimization and materials development.

In this context, novel strategies need to be developed that lower the complexity of fabrication of folding substrates, without the loss of high fidelity (*i.e.*, with few defects such as over-folding or under-folding). Many current strategies rely on multi-step microfabrication processes. Second, the most popular stimulus is thermal actuation due to its ease of implementation. However, other stimuli such as chemical and mechanical responses are also desired. Third, although efforts have been made to control and program the folding pathways, [20,254,265,405–407] there more opportunities exist to better control the folding/unfolding pathways that may lead to sequential or programmed folding to create more complex geometries and more sophisticated applications, which is interesting for “4D assembly” (*i.e.*, 3D structures that change shape with time) or printing where the motion or shape is highly correlated with time as well [80,408,409]. Fourth, the rate of folding could be improved along with precise control over folding dynamics. Employing strategies such as snap-buckling instabilities (*e.g.*, those employed by the Venus fly trap [161,410,411]) may allow for more rapid folding relative to mechanisms that rely on polymer shrinkage or gel swelling, which are generally slow. In addition, most folding occurs slowly and often requires large inputs of energy, which represents new opportunities for optimization and improvement. Fifth, the actuation associated with many folding strategies does not generate significant force (or torque), which limits the utility. Lastly, effort in modeling and folding algorithms is needed to guide the optimal design of folding/bending processes.

Current materials and processes often do not meet the needs of applications. For example, shape reversible materials are desired for practical applications that call for reconfigurability. Many current polymers undergo irreversible shape change in response to a stimulus (*e.g.*, shape change usually represents a minimization of energy), while the approaches and materials that are reversible are limited to a narrow range of external stimuli that are often inconvenient such as large changes in temperature or the need to operate in a liquid environment (for controlling pH, ionic concentration). Thus, there are opportunities to develop new polymers or mechanisms for reversible shape change.

There are also opportunities for modelers and theoreticians to provide guidance for optimized design. Most applications are case-dependent regarding materials selection and stimuli utilization. The performance metrics (*e.g.*, energy efficiency, performance versus fabrication complexity and economic costs, pathway, accuracy, fidelity, durability, packing ratio) should guide the design strategy and materials selection.

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Figure Captions

- Figure 1.** Cross-sectional illustrations of strategies to generate 3D shapes by using shape-programming of polymeric materials in four categories: 1) conventional fabrication; 2) induced surface topography on a macroscopically flat substrate; 3) 3D structures by bending ; and 4) 3D structures by folding. The dashed black line marks the original 2D substrate prior to shape change.
- Figure 2.** Illustration of the difference between folding and bending of sheets (in a cross-sectional view): a) ideal case of folding with localized deformation; b) in practice, folding is defined when the deformed region (red) is small relative to the sample size (blue); c) in practice, bending is defined when the deformation region is commiserate with the sample size; d) ideal case of bending with global deformation; e) a series of local folds can lead to a global bend. Red colors denote the regions of deformation.
- Figure 3.** Schematic of conventional lithographic methods that expose polymeric films to patterns of photons, electrons, or ions. Only negative photoresists are shown here for the sake of illustration.
- Figure 4.** a) Schematic of the formation of wrinkles on an elastic substrate by pre-stretching ; b) Wavelengths of multiple generations of wrinkles can form on PDMS sheets by using large pre-strains. [81], Copyright 2050. Adapted with permission from Nature.; c) optical microscopy images (top view) of wrinkles with different orientation preference due to the applied strain in different directions. [76], Copyright 2010. Reproduced with permission from John Wiley & Sons Inc.
- Figure 5.** a) Schematics and optical microscopy images from b) top view and c) side view for typical wrinkles (left column), creasing (middle column) and delamination (right column). [118], Copyright 2013. Reproduced with permission from the ASME.
- Figure 6.** a) Schematic of the time evolution for spinodal dewetting (left) and corresponding experimental result (right). [122], Copyright 2012. Adapted with permission from the Royal Society of Chemistry.; b) Optical microscope image of dewetting of poly(methyl methacrylate) (PMMA) on a patterned PDMS substrate. [130], Copyright 2007. Reproduced with permission from Elsevier Ltd.; c) Schematic of 3D structures induced by an electric field at polymer/air bilayer. [132], Copyright 2000. Reproduced with permission from Nature; d) Schematic of 3D structures induced by electric field at polymer/polymer/air trilayer. [136], Copyright 2006. Reproduced with permission from the American Chemical Society.; e) SEM images of cage-type [136], Copyright 2006. Reproduced with permission from the American Chemical Society. ; f) column structure made of PMMA while removing polystyrene with electric field on PMMA/PS/air trilayers with different electrode set-up. [137], Copyright 2002. Reproduced with permission from Nature.
- Figure 7.** AFM image of surface topography on a polymer film containing photosensitive azo groups after exposing to patterned UV light to generate a surface-plasmon field. [138], Copyright 2011. Reproduced with permission from the Royal Society of Chemistry.

- Figure 8.** Illustration of sample preparation procedures on shape memory polymer to form surface topography (*e.g.*, wrinkling). [142], Copyright 2011. Reproduced with permission from IOP Publishing.
- Figure 9.** Surface topography due to shape memory effect in an acrylate-based SMP (cured from methyl methacrylate (MMA), poly(ethylene glycol dimethacrylate) (PEGDMA) as crosslinker and 2,2-dimethoxy-2-phenylacetodphenone (initiator)). Schematics (top) and images (bottom) for different stages: a) permanent pattern molded by thermally embossing nanoimprint lithography at $\sim 180^{\circ}\text{C}$; b) 2D planar surface after programing with a flat mold; and c) recovered surface topography after heating at $\sim 120^{\circ}\text{C}$. The pattern has a pitch of ~ 800 nm and a height of ~ 180 nm. [140], Copyright 2011. Adapted with permission from John Wiley & Sons Inc.
- Figure 10.** Examples of 3D structures induced by controlling the stress within sheets of polymer gels: a) bending is triggered by a temperature change to a thermal responsive PNIPAAm bilayer laminate. [160], Copyright 2011. Adapted with permission from the Royal Society of Chemistry.; b) bilayer structure with one passive layer (colors other than green, top layer) and one temperature-sensitive hydrogel (green layer) to induce the bending. [165], Copyright 2013. Adapted with permission from IOP Publishing.; c) 3D curved shapes are generated when asymmetrical swelling occurs due to highly crosslinked dots within a low crosslinked matrix. [170], Copyright 2012. Reproduced with permission from the American Association for the Advancement of Science.; d) complex helical structure can be formed when a planar sheet patterned with chemically distinct regions of hydrogel swells. [176], Copyright 2013. Adapted with permission from Nature.
- Figure 11.** a) Schematic to illustrate the light-induced crosslinking gradient across the film thickness of SU-8 film, and resulting bending of the film in different solvents; b) Fluorescence images of actuation of flower-shaped structures. Scale bars are $100\text{ }\mu\text{m}$. [178], Copyright 2011. Reproduced with permission from Nature.
- Figure 12.** a) 3A hydrogel bends into a 3D coil by using multiple folds patterned via ionoprinting lines of copper ions in a hydrogel via the use of a copper electrode; b) ionprint lines are stiffer than the rest of the gel, which causes gels to swell asymmetrically. A consequent gel gripper is demonstrated to catch and release a small blue cube of PDMS (~ 1 g) in ethanol and water, respectively. The scale bar is 10 mm. [187], Copyright 2013. Adapted with permission from Nature.
- Figure 13.** a) Schematics of asymmetrical inflation of a 2D sheet by applying different thickness of elastomers (top row) or using composite materials with different Young's Modulus (E_a , E_b). [24], Copyright 2011. Adapted with permission from John Wiley & Sons Inc.; b) Example of a paper-Ecoflex composite showing asymmetrical actuation. [197], Copyright 2012. Adapted with permission from John Wiley & Sons Inc.; c) Micro hand robotic system driven by pneumatic balloon actuator. [199], Copyright 2007. Reproduced with

permission from the IEEE.; d) Demonstration of gripping an uncooked egg. [24], Copyright 2011. Reproduced with permission from John Wiley & Sons Inc.

- Figure 14.** a) 3D shape change of a liquid crystal elastomer film upon heating. [209], Copyright 2015. Reproduced with permission from American Association for the Advancement of Science.; b) Bending of a cantilever made of azo-liquid crystal network under the exposure of 442 nm light with different polarization angles. [218], Copyright 2011. Reproduced with permission from the Royal Society of Chemistry.
- Figure 15.** Illustration of representative photoisomerizable molecules: a) trans-cis photoisomerization of azobenzenes; b) ionic dissociation of triphenylmethane leuco derivatives; c) cinnamic acid group; and d) photos demonstrating bending of polymer sheet by applying polarized light with different angles. [220], Copyright 2006. Reproduced with permission from John Wiley & Sons Inc.
- Figure 16.** a) A typical piezoelectric sheets sandwiched by electrodes. The dashed lines indicated the deformed shape in response to an electric field. [244], Copyright 1991. Reproduced with permission from Elsevier Ltd.; b) Schematic of piezoelectric PVDF films used as a pressure sensor due to the charge arises from deflection of the film. [238], Copyright 2008. Reproduced with permission from Elsevier Ltd.
- Figure 17.** Schematics of the comparison between (a) conventional self-assembly and (b) folding. [57], Copyright 2010. Adapted with permission from John Wiley & Sons Inc.
- Figure 18.** a) Schematic of shrinking polyimide fabricated as a hinge. [268], Copyright 2006. Reproduced with permission from Springer .; b) 3D structure (right) generated from the template (left) of patterned copper/Kapton sheet with pre-strained polymer strips as hinges that respond to temperature. [269], Copyright 2011. Reproduced with permission from the International Society for Optics and Photonics.; c) Microgripper triggered by temperature or chemicals in the biological environment with a patterned responsive polymer (red, top layer). [38], Copyright 2009. Reproduced with permission from the National Academy of Sciences of the USA.
- Figure 19.** a) Folding of a sandwiched sheet with shrink film in the middle while heat resistant materials on the top and bottom layers. The arrows show the shrinking directions. [274], Copyright 2014. Reproduced with permission from the IEEE.; b) a fluorescence image of a folded flapping bird (bottom) made from the trilayer film (top) with photo-crosslinkable temperature-responsive polymer (PNIPAM) in between. [279], Copyright 2015. Reproduced with permission from John Wiley & Sons Inc.; c) An icosahedron (bottom) made from the template (top) incorporated with pre-strained polymers inside a trilayer laminate. The folding is actuated with uniform heating in an oven. [273], Copyright 2014. Adapted with permission from IOP Publishing.

- Figure 20.** Photographs of folded cubes from a pre-programmed 2D shape-memory polymer sheet that folds in response to heat. [282], Copyright 2010. Reproduced with permission from John Wiley & Sons Inc.
- Figure 21.** a) SMA actuators can be folded by applying Joule-heating (red arrows show the heating location). b) Demonstration of folding a “boat” from a 2D planar composite sheets patterned with SMA hinges which can cause the folding through Joule-heating. [20], Copyright 2010. Reproduced with permission from the National Academy of Sciences of the USA.
- Figure 22.** a) Schematic of a typical thermo-mechanical process for programming shape-memory polymers. $T < T_{\text{trans}}$ is represented in blue color while $T > T_{\text{trans}}$ is in red color; and b) A representative cyclic strain-temperature-stress diagram. In this specific case, a heated sample starts from the “asterisk” (*i.e.*, low stress, high temperature) and is (i) deformed (elongated by stretching), (ii) cooled and then (iii) the stress applied for deformation is released. (iv) The original shape of the sample is recovered by heating again. [130], Copyright 2007. Reproduced with permission from the Royal Society of Chemistry.
- Figure 23.** Summary of molecular structures and switching mechanisms of SMPs. [310], Copyright 2013. Adapted with permission from the Royal Society of Chemistry.
- Figure 24.** a) Schematic of patterned hinge through a photomask due to photo-induced stress relaxation in a polymer (left) and a closed box with multiple hinges created (right). [5], Copyright 2012. Reproduced with permission from the American Institute of Physics.; b) Schematic of local crosslink gradient through poly (N-isopropylacrylamide-co-acrylic acid) (pNIPAM-AAc) and induced folding, and the demonstrated folding and unfolding of the gripper. [272], Copyright 2014. Reproduced with permission from IOP Publishing.
- Figure 25.** Photographs of 3D structures formed by folding of pre-strained polymer sheets patterned with black “hinges” using a desktop printer. The black ink absorbs light from a lamp to induce folding via localized heating. a) Single line with hinge width (w) of 1 mm; b) three lines patterned on alternating sides with hinge with of 1 mm and 12 mm spacing; c) rectangular box (20 mm x 10 mm x 10 mm, $w = 1.5$ mm); d) tetrahedral box with a square bottom facet (10 mm x 10 mm) and hinge widths of 2.0 mm). [324], Copyright 2012. Reproduced with permission from the Royal Society of Chemistry.
- Figure 26.** Summary of existing active materials applied for reconfigurable or morphing structures show a trade-off between maximum strain and modulus. Red dash curve on the top right part shows the limit of existing materials for these two materials properties. Abbreviations of the various compounds (added by the authors of this review, not the authors of the original article): CFRP: carbon-fiber-reinforced polymer; FSMA: ferromagnetic shape memory alloys; G-10: fiberglass epoxy laminates ; IPMC: ionic polymer metal composite; LCE: liquid crystal elastomers; PAN:polyacrylonitrile; PMMA: poly(methyl methacrylate); PVDF: poly(vinylidene

fluoride); PZN-PT: $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_x\text{PbTiO}_3$; PZT: lead zirconate titanate ($\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$); SMA: shape memory alloys. [327], Copyright 2010. Reproduced with permission from SAGE Publications.

Figure 27. Additional examples of applications for out-of-plane shape programming. a) A self-assembled robot by folding. [277], Copyright 2014. Reproduced with permission from the American Association for the Advancement of Science .; b) 3D dual-channel microfluidics. Scale bar is 500 μm . [178], Copyright 2011. Reproduced with permission from Nature.; c) Partially opened deployable array for solar panel. [403], Copyright 2015. Reproduced with permission from SPIE Proceedings.

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Table I. Representative approaches for folding and bending of polymer sheets. The table is organized by the phenomena and stimuli. The term “scale” here refers to the length scale of the hinges or curvature of bending.

Phenomenon	Stimulus	Materials	Length scale	Advantages	Disadvantages	Reversibility	Reference
Differential thermal expansion (<i>e.g.</i> , bimorph)	Heat	Bilayers with different thermal expansion coefficients (<i>e.g.</i> , polymer/metal)	μm-mm	Simple and available thermal actuation	Elevated temperature required, curvature depends on degree of mismatch; limited curvature induced	Yes	[160,164,363–365]
Volumetric expansion/contraction	Solvents	Gels	μm-mm	Simple triggering in liquid	Restricted to liquid environment	Yes	[161,166,366]
	Temperature	Thermal-responsive polymers (<i>e.g.</i> , temperature-responsive hydrogels)	μm-mm	Simple thermal actuation	Asymmetry needed.	Yes	[160,170,176,367,368]
	Pressure (pneumatics)	Elastomers (<i>e.g.</i> , Ecoflex, PDMS); Parylene	mm-cm	Inexpensive, light weight, high loads; fast response time (ms~s depending on air flow rate)	Source/control of fluid pressure needed; requires mismatch in flexibility/modulus between layers for asymmetrical bending	Yes	[197–199,369]
	pH, ionic concentration	Gels	μm-mm	Simple operation	Restricted to liquid environment	Yes	[144,148,152,370]
	Electric field/chemical potential	Piezoelectric polymers (<i>e.g.</i> , PVDF); electroactive hydrogels; ionic polymers	μm-mm	Simple application of electric field or chemical potential	Requires liquid environment, usually slow response except piezoelectric polymers	Yes	[11,185–187,237,238,371,372]
Surface tension	Heat	Solder, tin, polymers, etc.	nm-mm	Hinges can be sealed (locked) after folding	Elevated temperature to melt metals	No	[36,271]
Magnetism	Magnetic fields	Ferromagnetic materials	nm-mm	Remote control by magnetic field	Locking mechanism required to keep it in position	Yes	[181,373–377]
Shape memory	Heat	Shape memory polymers	μm-mm	Simple thermal actuation	Programming required for SMPs or heat must be delivered locally	No	[287,254,281,282]
	Light to induce molecular changes	Liquid-crystal elastomers and gels or photosensitive polymers	μm-mm	Remote; room temperature	Usually requires UV light	Yes	[168,291,205,219,220,378–380]
	Light to deliver heat	Pre-strained shrink films	μm-cm	Simple printing approach	Unproven at small length scales	No ^{a)}	[254,324,269]
Shrinkage	Heat	Polyimide (PI)	μm	Different angle displacement can be achieved depending on curing temperature	High temperature needed (250~500 °C); pattern PI hinge	No ^{b)}	[267,268]

^{a)} also includes approach as described in Figure 25.

^{b)} but can dynamically control angle by heating due to thermal expansion of polyimide [267]