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Humidity-responsive actuators from integrating liquid crystal networks in an orienting scaffold†

Alexander Ryabchun, * Federico Lancia, Anne-Déborah Nguindjel and Nathalie Katsonis *

Developing shape-shifting materials requires combining the flexibility needed by shape-shifting properties, with the toughness that is demanded to maintain their mechanical performance. Typically, in liquid crystal networks, the amplitude of the shape transformation can be hindered by large cross-linking densities. Here, we argue that a promising strategy to address this limitation consists in integrating liquid crystal networks into an anisotropic and porous material that acts as an orienting scaffold. This strategy shows similarities with the principles of stimuli-responsive deformation in plants, where inflexible elements with specific orientations are integrated into a stimuli-responsive matrix. By aligning liquid crystals in a porous polypropylene orienting scaffold, we demonstrate liquid crystal networks that respond to humidity with a shape change, yet they display high elastic modulus and toughness. Various chiral shapes can be generated in single and double layers of these films, and the complexity of their actuation modes is enhanced, including twisting, curling or winding. We anticipate that these hybrid composites and the strategy they embody can find application to other stimuli-responsive anisotropic soft materials.

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Introduction

Developing molecular materials that respond with large and complex shape transformation to small changes in temperature, humidity or light remains a contemporary challenge,¹ one of the reasons being that the responsiveness that is required to achieve large amplitude shape changes, also decreases the mechanical strength of a material. Typically, in shape-shifting liquid crystal networks, the amplitude of the shape transformation is hindered by large cross-linking densities.^{2,3} While increasingly sophisticated shape transformations have been reported, with large amplitudes and tunable kinetics,⁴ providing mechanical robustness to liquid crystal actuators while preserving their actuation modes thus remains a challenge.⁵

On the other hand, fibrous-like composite materials have shown versatile shape-shifting properties akin to stimuli-responsive deformation in plants, where inflexible elements with specific orientations are integrated into a stimuli-responsive matrix.^{6–8} In recent work, we have shown that fibrous-like liquid crystal networks display versatile actuation modes, however the mechanical robustness of these systems was moderate.⁹

Here, we propose an approach towards versatile yet mechanically robust actuators, by combining a porous orienting scaffold

with a liquid crystal network. This approach towards robust shape transformation is not limited to a specific stimulus – here we demonstrate its potential by focusing specifically on shape transformations in response to humidity. Humidity is a major stimulus for plant movement, *e.g.* for the opening of pinecones¹⁰ and seedpods,¹¹ self-burrowing of seeds¹² or expansion/contraction of bacterial spores,¹³ and these systems have inspired the design of humidity-driven actuators.^{14–19} In particular, Schenning and coworkers have shown how controlling hydrogen bonding allows designing humidity-responsive bilayers, where active and inactive liquid crystal networks are combined.²⁰ However, this approach requires pre-alignment of the liquid crystals and the design precludes implementing orthogonal deformation modes,³ therefore the performance of these actuators remained limited in terms of control over the shape transformation.

Experimental

Preparation of the samples

We use a photo-polymerizable nematic liquid crystal (Fig. 1a) that is composed by liquid crystal monomers with hydrogen-bonding possibilities A3, A5, and A6 (Synthon Chem.), a nematic cross-linker C6M (Merck), 1.5 wt% of photoinitiator (Irgacure 819, Ciba) and 0.1 wt% of 2-methoxyphenol stabilizer (Sigma-Aldrich). A porous polypropylene film (Celgard® 2500) with thickness 25 µm and porosity 55% was filled by capillary forces with this nematic liquid crystal, at 75 °C. The typical size

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Fig. 1 (a) Composition of the photo-polymerizable nematic liquid crystal used as a humidity-responsive matrix. (b) SEM image of the porous polypropylene film surface. (c) FT-IR spectra of the composite film before and after immersion in and aqueous solution of KOH. (d) Schematic representation of gradients distribution in the composite film upon activation in KOH. The film is a single-layered material, the colors represent a gradient in cross-linking density and swelling ratio.

of the films was about 5×5 cm. The excess liquid crystal was removed from the surface, and photo-polymerization was performed with UV light for 30 min (UV-LED 365 nm, intensity $\sim 6 \text{ mW cm}^{-2}$) in inert atmosphere. Post-curing was allowed at the same temperature for 8 h. In order to fabricate double-layered networks, two polypropylene films with orthogonal aligning direction were folded together, filled and polymerized by following the same procedure as for single layered films.

Ribbons of ~ 1 mm width were cut out at specific angles in respect to alignment direction when the irradiated side of the film was on the top. The cutting angle for double layered composite ribbons has been chosen in respect to the aligning direction of top polypropylene layer when the irradiated side is on the top.

In addition to enhancing the versatility of humidity-responsive helical actuators, this fabrication strategy shows practical advantages too: less liquid crystal is needed than when full films of liquid crystal elastomers are used, and the use of alignment cells is avoided, which also means that the films are less prone to damage upon opening the cells. Moreover, the fabrication involves a one-step procedure only, even in the preparation of double-layered actuators.

Measurements

The hydrogen bonding of the liquid crystal network ribbons was broken by immersion in a 0.1 M aqueous solution of potassium hydroxide (KOH) for 20 min. This procedure was

adapted from Schenning and coworkers.²⁰ The stimuli-responsive deformations were tested at different levels of humidity, at room temperature, in a glass container. A relative humidity of 11%, 33%, 54%, 75% and 98% was obtained by using saturated aqueous solutions of LiCl, MgCl₂, Mg(NO₃)₂, NaCl and K₂SO₄, respectively.

The mechanical properties were measured by using a tensile tester Z1.0 (Zwick Roell). Strain rate: 1 mm min^{-1} ; load sensor: 50N. The phase behavior was studied with a polarized optical microscope BX51 (Olympus) equipped with a heating stage (Instec). UV-Visible transmission spectra were measured with a spectrometer (Ocean Optics). Fourier transform infrared (FT-IR) measurements were performed on a spectrometer Nicolet 6700 (Thermo scientific). The scanning electron microscopy (SEM) measurements were carried out with microscope Neon 40 (Carl Zeiss).

Results and discussion

The orienting scaffold is a porous film of polypropylene (Fig. 1b). Liquid crystals align spontaneously in the elongated pores of such a porous olefin, and the resulting mesoscopic anisotropy can be stabilized by cross-polymerization of the liquid crystal to yield unusual fluorescent, light-scattering or photo-actuating properties.^{21–23} The liquid crystal we use forms a nematic phase up to 102 °C and is composed by carboxylic

Table 1 Mechanical characterization of the single-layered actuators. The elastic modulus (E), the elongation at break (ϵ_b) and the tensile toughness (U_T) are reported for each material

	E (GPa)	ϵ_b (%)	U_T (MJ m ⁻³)
Liquid crystal network ^a	3.83	2	0.92
Porous polypropylene	0.82	38	26.92
Reinforced liquid crystal network	0.92	225	224.18

^a The film was prepared by photo-polymerization of the liquid crystal, in a cell with 25 μ m gap and planar unidirectional alignment.

acids promoting hydrogen-bonding, to which a cross-linker and a small amount of a photo-initiator were added (Fig. 1a). After the porous polypropylene is filled with this nematic liquid crystal, photo-polymerization yields an anisotropic material (Fig. S1a, ESI[†]). This procedure does not require any preliminary alignment.

We compare the mechanical properties of this composite material with those of either the empty scaffold, or the liquid crystal network in the absence of the scaffold. All measurements were performed along the main alignment direction of the liquid crystal; the response to perpendicular strain is described in Fig. S2 and Table S1 (ESI[†]). Table 1 shows the stiffness (E), elongation at break (ϵ_b) and tensile toughness (U_T) of all the materials investigated under parallel strain. The tensile toughness characterizes the energy that can be absorbed by a material before it breaks. As expected, in the absence of the orienting scaffold, the liquid crystal network breaks rapidly when elongated, *i.e.* its elongation at break is only 2%. Also, in spite of a high modulus associated with the carboxylic acid dimers acting as additional crosslinks, the non-reinforced network is characterized by a small value for the tensile toughness, which means that the material can only absorb little energy before fracture. The reinforced network demonstrates a high modulus (~ 1 GPa) and, at the same time, this material breaks down at more than twice the elongation, which results in a remarkable ultimate toughness, which is in ~ 200 times larger in comparison with the reference liquid crystal network (Table 1). The composite material thus demonstrates high performance in terms of absorbing energy and dissipating it, and moreover appears to be a ductile material (with high breaking elongation) while keeping a high degree of toughness. In that regard, this shape shifting network is comparable to spider silks,²⁴ which display a toughness in the range of 10–350 MJ m⁻³, and also comparable to other materials featuring an interplay between soft and hard phases.²⁵ These unique properties emerge from the intimate association between the plasticity the scaffold and the lability of the hydrogen bonds in the liquid crystal network.

The shape-changing properties of the reinforced liquid crystal network were evaluated on different shapes of actuators. The actuators were generated by cutting ribbons out of the film of reinforced liquid crystal network. The angle of cut (φ_s) is defined in respect to the direction of liquid crystal alignment (Fig. 1b). After cutting, the ribbons remained almost flat because the material features a relatively large elastic modulus and only a moderate cross-linking gradient across its thickness

due to low absorbance at photo-polymerization wavelength (Fig. S1b, ESI[†]). Once formed, these objects do not undergo shape transformation before being treated with an aqueous solution of KOH, to make the hydrogen-bonded network hydrophilic.¹⁸ This activation step allows breaking the carboxylic acid dimers transforming them into potassium salts (Fig. 1c). Infrared spectroscopy reveals that after activation, the peak at 1678 cm⁻¹, which is associated with C=O stretching in carboxylic acid dimers, disappears completely. Moreover two new peaks appear at 1544 cm⁻¹ and 1389 cm⁻¹, which are related to asymmetric and symmetric carboxylate stretching, respectively (Fig. 1c). Overall, these signals evidence that KOH has penetrated the network, further deprotonating the carboxylic acid groups and breaking up the hydrogen bonds.

Once water molecules penetrate the liquid crystal network, the film expands preferentially along the director, by swelling. In parallel, the gradient in cross-linking density results in a differential swelling amplitude across the thickness of the film: the face that is more loosely cross-linked undergoes larger shape-transformation by swelling than the other face (Fig. 1d). We note that in the absence of swelling, the gradient in cross-linking density is not pronounced enough to yield bending. Overall, the humidity-triggered actuation reverts the original curvature of the film: upon photo-polymerization, the looser cross-linked face of the film shrinks more,²⁶ which is why it responds to humidity with a larger expansion than its densely cross-linked counterpart.

We have investigated the geometry and response of ribbons cut out of this film systematically, as a response to an increase of humidity. While a ribbon cut at $\varphi_s = 0^\circ$ unfolds in the presence of humidity, in contrast, a ribbon cut at $\varphi_s = 90^\circ$ bends in response to humidity (Fig. 2a). We found that the inversion of curvature takes place for both samples upon increasing humidity, and attribute this behavior to the fact that the water-induced expansion in the direction perpendicular to molecular alignment is up to four times higher than in the parallel direction.¹⁸ In the case of $\varphi_s = 0^\circ$, the direction of the largest expansion at high humidity is along the short axis of the ribbon, which does not lead to any significant changes in the shape and the ribbon remains almost flat. Whereas for $\varphi_s = 90^\circ$ expansion occurs along the long axis of the ribbon causing its bending. On the contrary, at low humidity values, the greatest contraction proceeds along the liquid crystal orientation, which explains the observed opposite curvatures.

At all φ_s angles other than 0° and 90° , treating the ribbons with potassium hydroxide yields chiral shapes. Fig. 2b and c shows two ribbons with the most pronounced spring shapes. These springs are characterized by opposite handedness which is due to the presence of the symmetry breaking element – gradient of cross-linking density across the thickness of the samples. For $0^\circ < \varphi_s < 90^\circ$ springs are right-handed and for $90^\circ < \varphi_s < 180^\circ$, they are left-handed. A diagram summarizing all possible shapes is shown in Fig. S3a (ESI[†]). In all cases, at dry conditions the ribbons are almost flat and when humidity increases, they wind into springs gradually (Video S1 and Fig. S3c, ESI[†]). The movement of these single-layered ribbons takes typically 30–40 s. The humidity-induced shape

Fig. 2 (a) Dynamics of curvature of single-layered actuating ribbons $\varphi_s = 0^\circ$ and $\varphi_s = 90^\circ$, depending on the level of humidity. (b and c) Ribbons cut at $\varphi_s = 75^\circ$ and $\varphi_s = 135^\circ$ wind when the relative humidity increases from 11% to 98%. Scale bars = 2 mm.

changes are reversible and no substantial fatigue or degradation was observed over dozens of cycles.

We utilized a well-known strategy that promotes the generation of helical shapes, in order to expand the library of shapes, actuation modes and their amplitudes.^{6–9} In seed pods for example,²⁷ the valves typically contain two fibrous layers oriented orthogonally (commonly at angles of $+45^\circ$ and -45° relative to the longitudinal axis of the pods), and this structure supports a large number of helical shapes. Accordingly, we have prepared double-layered films with orthogonal liquid crystal alignment in each of layer as it is schematically illustrated in Fig. 3a. The ribbons cut out at different angles (φ_d) form various shapes such as curled, twisted or spring-like (Fig. 3b). Similar forms can be found among diversity of plant seedpods. Curled shapes of the ribbons cut at $\varphi_d = 0^\circ$ or 90° are similar to *Calliandra* seedpods; twisted shape cut at $\varphi_d = 45^\circ$ – to *Parkia speciosa* seedpods; spring shapes cut at $\varphi_d = 15^\circ$ and $\varphi_d = 75^\circ$ are similar to *Wisteria* and *Gleditsia triacanthos* seedpods, respectively. Overall, for $0^\circ < \varphi_s < 90^\circ$, springs are left-handed and for $90^\circ < \varphi_s < 180^\circ$ they are right-handed, which is opposite to what is observed with single layered ribbons (Fig. S3b, ESI†).

Let us consider the dynamics of the shape transformation of these double layered ribbons, upon increasing the ambient

humidity (Video S2, ESI†). The ribbon cut at $\varphi_d = 0^\circ$ undergoes large amplitude curling in response to water, accompanied by an inversion in the sign of curvature (Fig. 4a). The actuation mechanism involves in-plane anisotropic swelling, but each layer expands orthogonally to each other, which is accommodated by an increase in curvature. By humidity increase the twisted ribbon cut at $\varphi_d = 45^\circ$ gradually unwinds the right-handed structure to a completely flat/non-chiral state, and further inversion of handedness and winding of the left-handed shape occurs as illustrated in Fig. 4b. Fig. 4c demonstrates the changes in the radius of curvature and the half-pitch of the enantiomerically paired ribbons cut at $\varphi_d = 0^\circ/90^\circ$ and $\varphi_d = 45^\circ/135^\circ$. The pitch of the macroscopic helix is defined as positive for a left-handed shape. The shape transformation typically persists for about 40–60 s, depending on actuation mode. The kinetics of humidity-driven curling and humidity-driven twisting are described in Fig. S4 (ESI†). In all cases, the inversion of the sign of curvature or twist occurs at $\sim 40\%$ humidity, and geometrical parameters evolve similarly with humidity, for both curled and twisted shapes. For enantiomeric springs, the evolution shows mirror symmetry. A diagram summarizing all shapes generated by the double layered ribbons is provided in Fig. S3b and d (ESI†). We observed large water-induced deformations in a range of relative humidity percentages that are commonly encountered in

Fig. 3 (a) Representation of the double-layered actuators. (b) Shapes of the double layered ribbons cut at angle φ_d .

Fig. 4 (a) Curling and (b) twisting of the double-layered actuators cut at $\phi_d = 0^\circ$ and $\phi_d = 45^\circ$, respectively, upon humidity increase. (c) Humidity-induced changes in the geometric parameters of the double-layered actuators (radius of curvature, r , and half-pitch of helix, $p_{1/2}$).

ambient conditions (40–100%). Combined with the straightforward processing method and the advanced mechanical properties that characterize the double-layered reinforced networks, we envision that these materials may be integrated with soft piezo-electric materials for energy harvesting, for example to generate electricity based on the alteration of humidity that occurs during the day-night cycle.

Conclusion

We demonstrate that combining the responsiveness of liquid crystal networks with the mechanical stability and anisotropy of porous polypropylene, yields humidity-responsive materials that convert anisotropic expansion into versatile macroscopic motion. The shapes and actuation modes of single layer actuators were pre-programmed by (i) the anisotropy induced by the scaffold; (ii) a gradient of crosslinking density across the thickness of the liquid crystal network, and (iii) the orientation of the liquid crystal with respect to the long axis of the ribbon. In the double layered actuators, these factors are complemented by (iv) the relative orientation of the scaffold on the top layer and the bottom layer. Based on this complex interplay, we demonstrate a large range of robust shapes and actuation modes, and even humidity-driven helical inversion. Essentially, this strategy can be extended to other stimuli-responsive liquid crystal networks. The enhanced control over the shape transformation of these actuators and their versatility, added to their resistance to fracture when stressed and to their ease of preparation, opens perspectives in the field of soft actuation.

Note added after first publication

This article replaces the version published on 20th October, which contained an incomplete version of Fig. 3.

Conflicts of interest

There are no conflicts of interest to declare.

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