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Supporting Information

Mechanically Programmed Shape-Change in Laminated Elastomeric Composites

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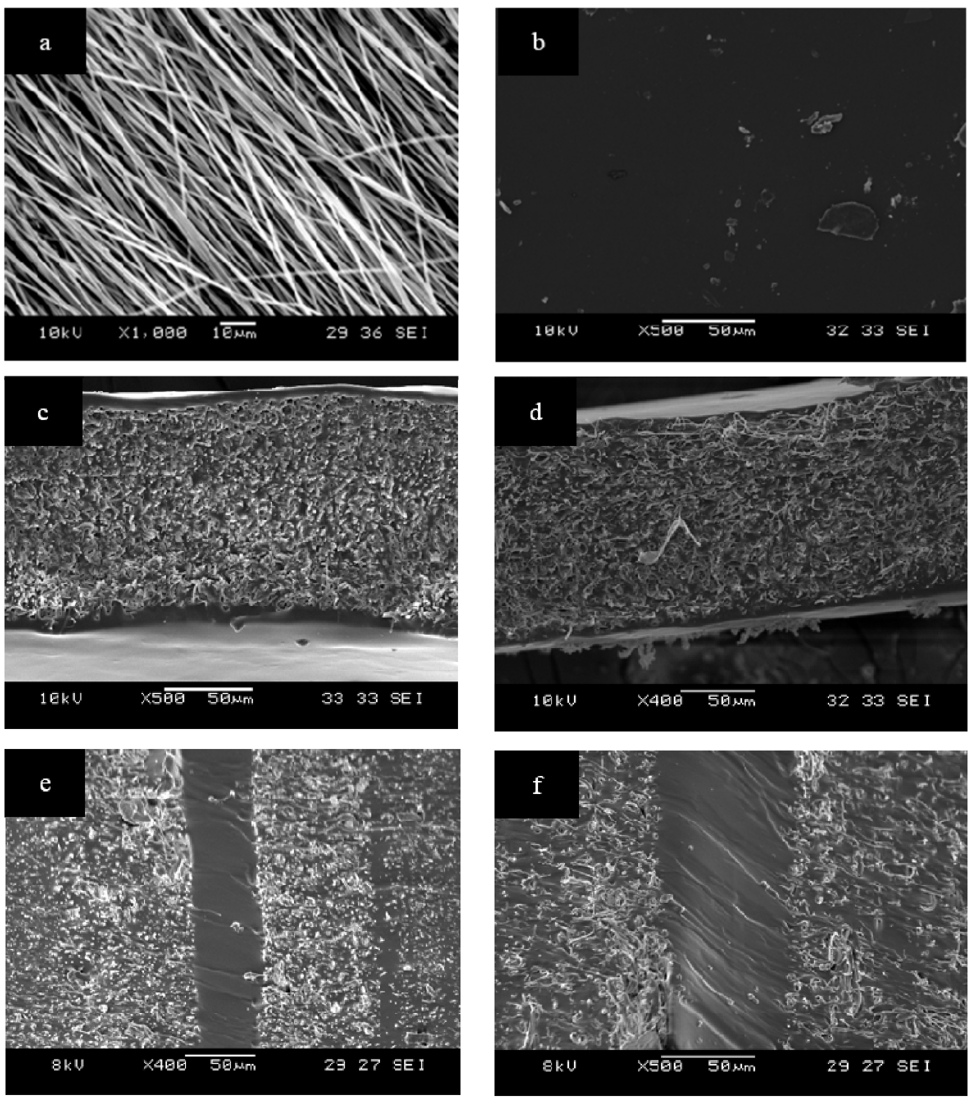


Figure S1. SEM micrographs of (a) aligned PVAc fiber mat, (b) single-layer A-SMEC surface, (c) single layer A-SMEC perpendicular cross section, (d) single layer A-SMEC parallel cross-section, (e) bilayer A-SMEC perpendicular cross-section, and (f) bilayer A-SMEC parallel cross-section. It is noted that the SEM image of the aligned fibers was taken at an angle.

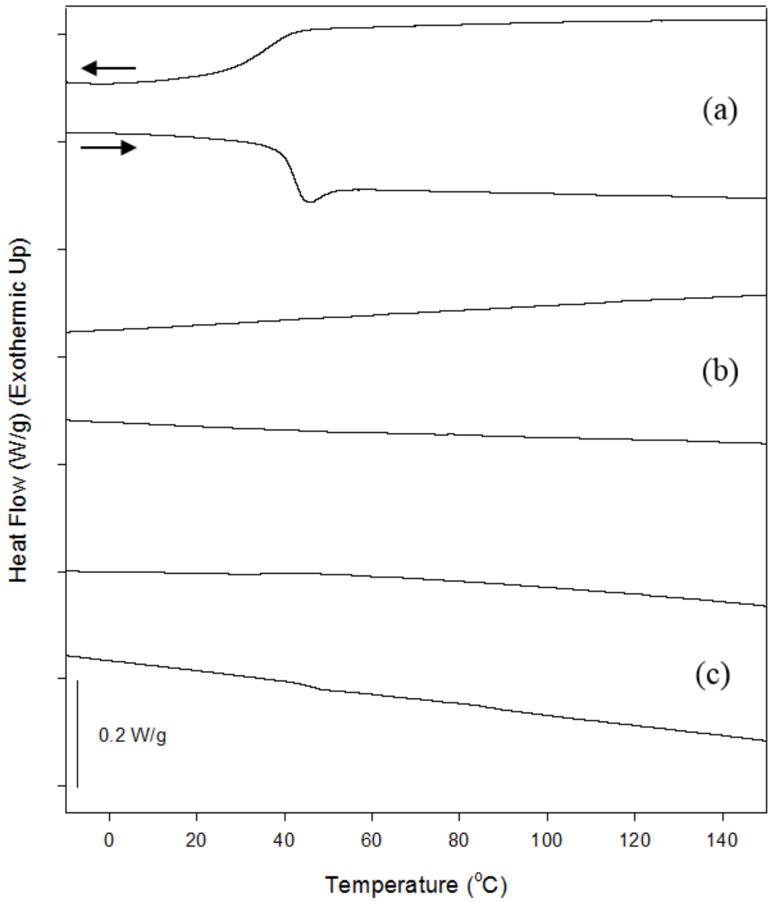


Figure S2. DSC cooling and second heating curves for (a) a PVAc fiber mat, (b) neat Sylgard, and (c) A-SMEC bilayer composite. The measured glass transition temperatures (T_g) are 42 °C and 46 °C for the PVAc fiber mat and the bilayer composite, respectively. The T_g of Sylgard cannot be determined from the DSC results, but it is known to be -115 °C from prior studies.

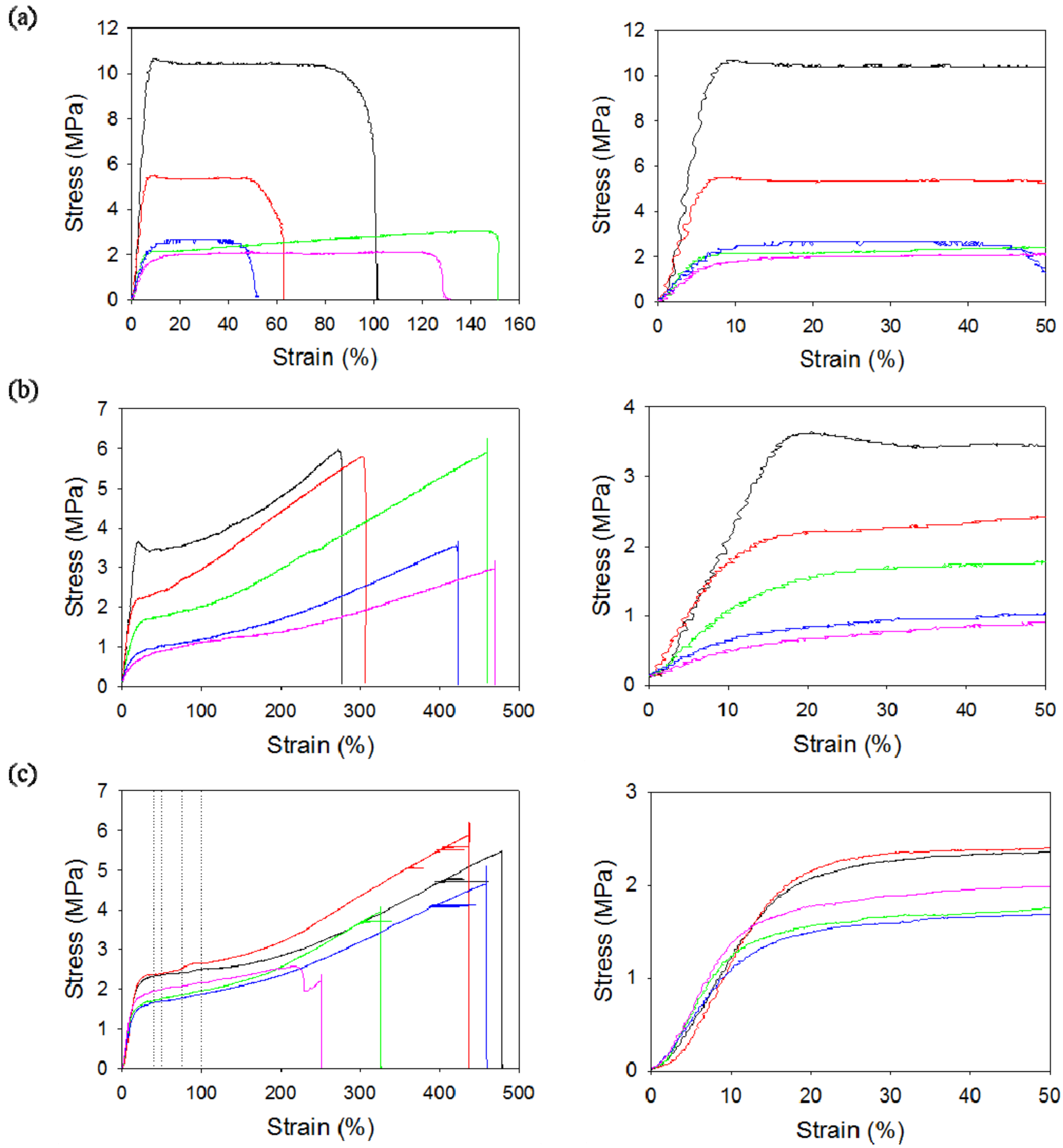


Figure S3. Representative stress-strain curves (first column) and magnified views of the elastic deformation (second column) for (a) anisotropic PVAc fiber mats (b) single-layer composites, and (c) bilayer composites with fiber orientations (θ or Δθ) of 0° (black), 22.5° (red), 45° (green), 67.5° (blue), and 90° (pink). The vertical dotted lines in (c) indicate strains to which the bilayer composites were stretched for mechanically activated shape change.

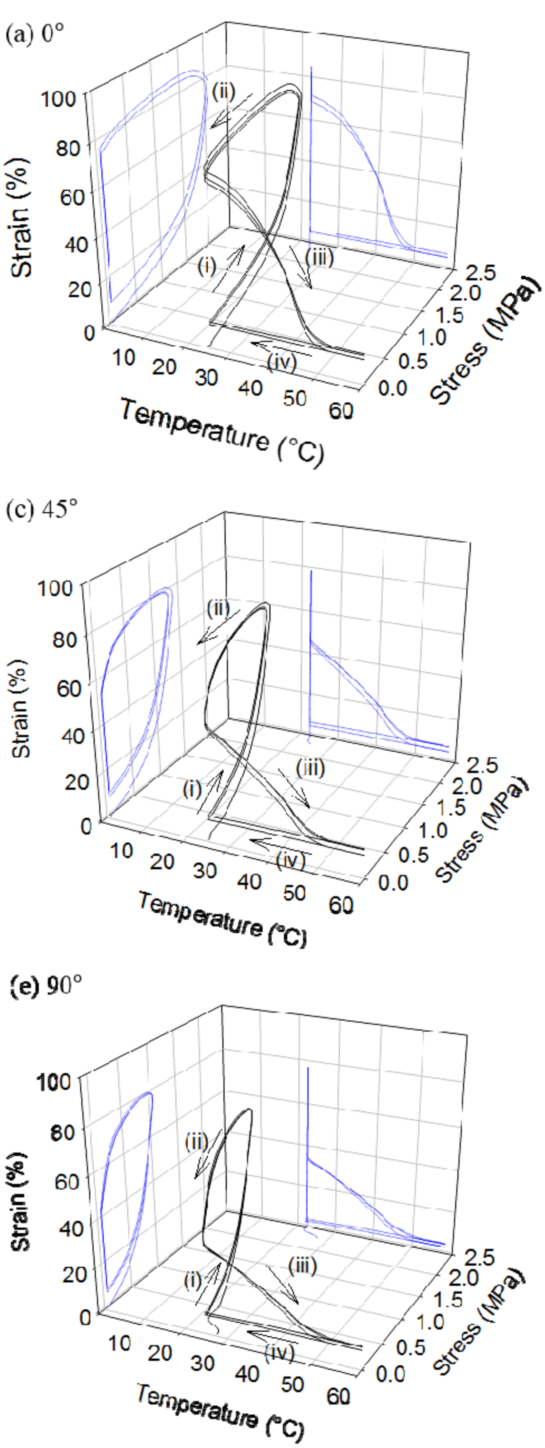


Figure S4. Reversible plasticity shape-memory (RPSM) 3D plots of single-layer A-SMEC for fiber orientation angles of: (a) 0°, (b) 22.5°, (c) 45°, (d) 67.5°, (e) 90°, and (f) neat Sylgard. Each plot shows three cycles and the beginning of the cycles are marked by an asterisk. Projection of cycles onto stress vs. strain and strain vs. temperature planes are shown. Samples were loaded at RT (1), unloaded at RT for fixing (2), heated to 60 °C for recovery (3), and cooled to RT (4).

Table S1. Average fixing (R_f) and recovery (R_r) ratio measurements from the three cycles of the reversible plasticity shape-memory (RPSM) analysis of single-layer A-SMECs with different fiber angles.

Sample	Cycle	R_f %	STDEV	R_r %	STDEV	N
0°	1	87.7	0.9	88.2	1.0	3
	2	86.5	0.9	97.7	0.6	
	3	85.7	1.0	97.6	0.2	
22.5°	1	76.9	6.9	85.4	2.3	3
	2	78.6	3.6	96.8	0.9	
	3	77.2	4.0	96.7	0.0	
45°	1	65.0	6.3	83.1	1.8	3
	2	65.2	5.0	97.1	1.2	
	3	63.9	4.9	96.6	1.1	
67.5°	1	48.0	4.2	78.7	4.4	5
	2	50.2	3.8	96.6	1.1	
	3	49.7	3.3	96.0	0.8	
90°	1	45.6	5.9	75.8	4.0	4
	2	48.6	2.4	96.1	1.3	
	3	48.4	2.5	95.7	0.8	

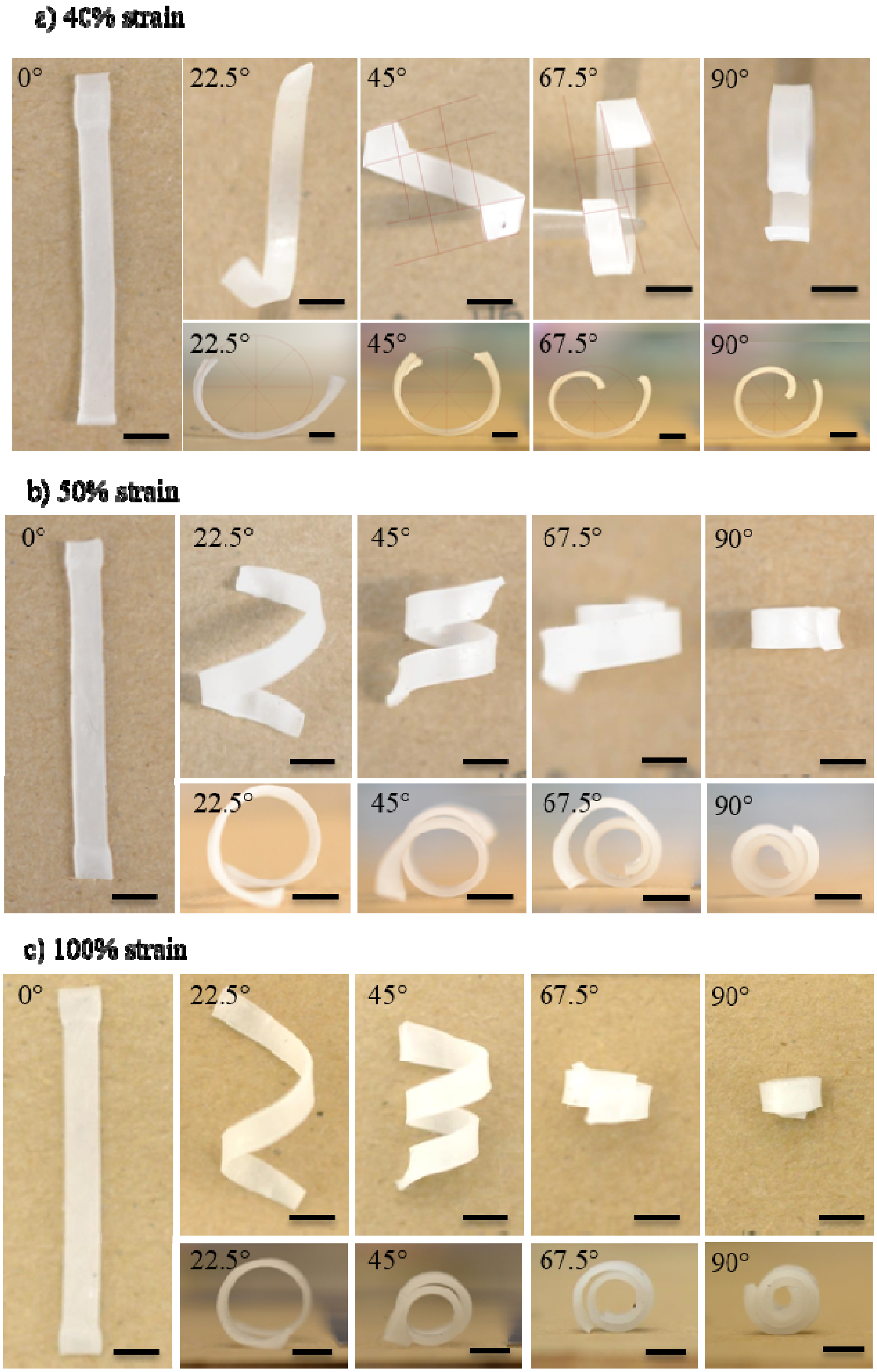
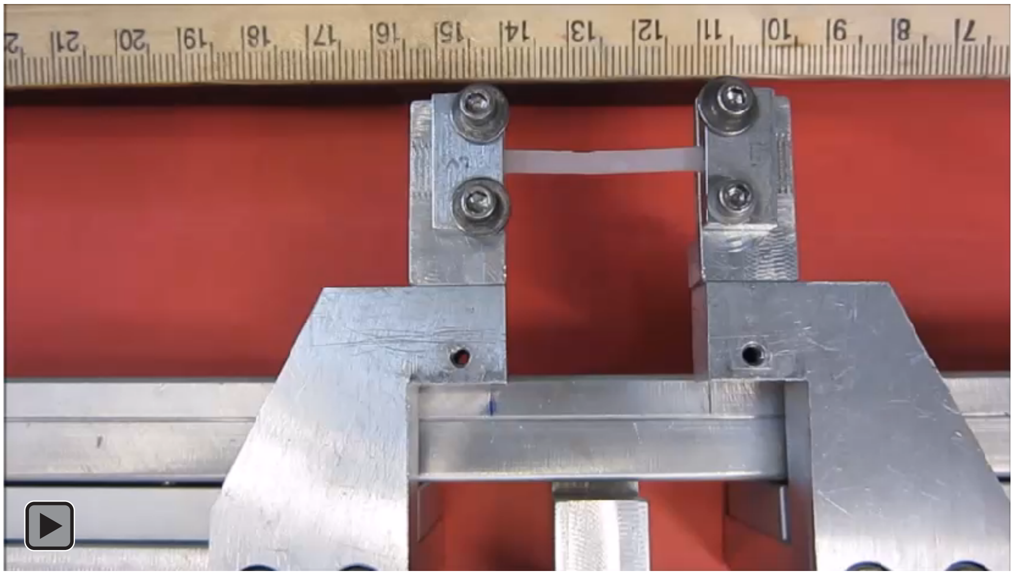


Figure S5. Representative images of curled bilayer A-SMECs stretched to a) 40%, b) 50%, and c) 100% strain indicating the pitch in the corresponding top row and the radius of curvature in the bottom row. $\Delta\theta$ is indicated on top left corner of each image. Scale bars represent 4 mm.

(a)



(b)

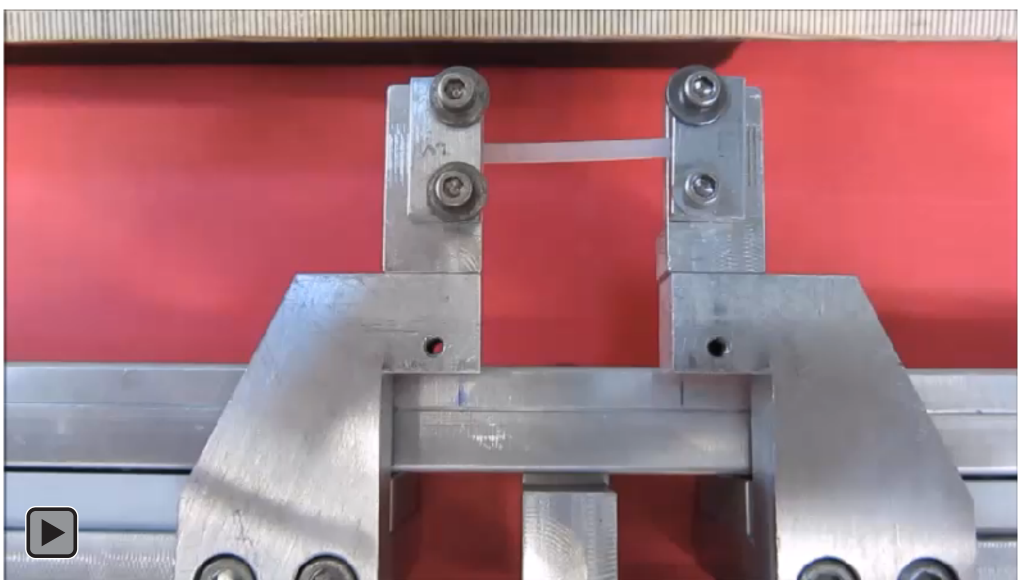


Figure S6. Videos of the mechanical programming and shape recovery of bilayer A-SMECs with (a) $\Delta\theta = 0°$ and (b) $\Delta\theta = 45°$. The bilayer A-SMECs with $\Delta\theta = 0°$ remains flat after stretching since the fixed strain in both layers is equal. The bilayer A-SMECs with $\Delta\theta = 45°$ forms a helix due to the difference in recovery between the layers. Both A-SMECs recover to their original shape upon heating.

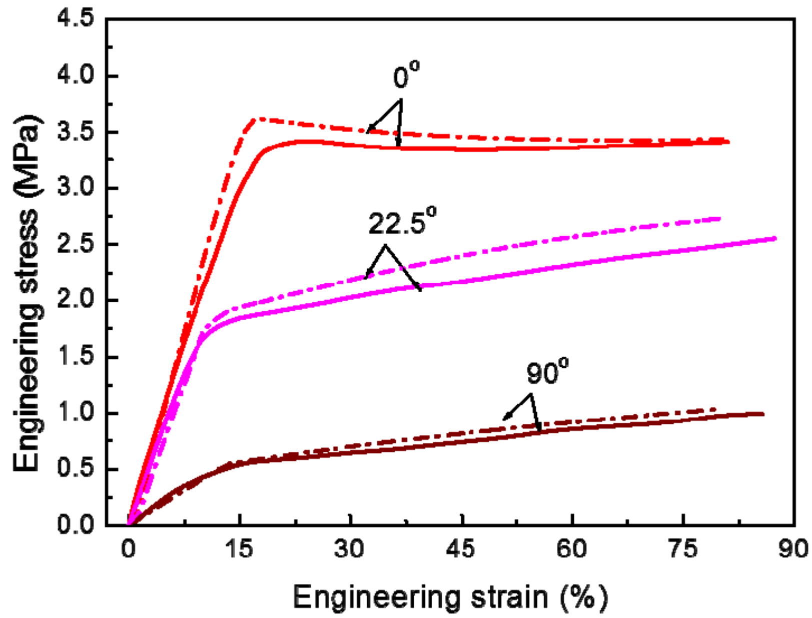


Figure S7. Comparing experimental (solid line) stress-strain behavior for single A-SMECs with fiber orientations of 0°, 22.5°, and 90° to the fitted models (dashed lines). Fitted models to the 0° and 90° cases were used to obtain material parameters for the matrix and fiber mat. Those parameters were used to predict the stress-strain behavior for the A-SMEC with a fiber orientation of 22.5°.

Table S2. Material parameters used in simulations.

	Parameter	**Value**
Matrix		
Crosslinking density	N (m^{-3})	1.96×10^{26}
Fiber mat		
Shear modulus	μ_f (MPa)	6.8
Energy factor	β	100
Relaxation time	τ_0 (s)	9×10^{9}
Yield parameter		
Initial shear strength	s (MPa)	2.5
Saturation shear strength	s_s (MPa)	3.0
Zero stress level activation energy	ΔG (J)	5×10^{-20}
Prefactor parameter	h_o (MPa)	400

Derivation of the Constitutive Relation (Eq.6-Eq.9 in the main text)

Consider the hyperelastic property of the elastomeric matrix and the viscoelastic behavior of the PVAc fiber mat. To analyze the viscoelastic property of the PVAc fibers, the total stress in the fibers is separated into equilibrium and nonequilibrium parts. Then, the total Cauchy stress of the A-SMEC sums contributions by the matrix and fiber mat:[1]

$$\boldsymbol{\sigma} = \underbrace{\boldsymbol{\sigma}_m}_{matrix} + \underbrace{\boldsymbol{\sigma}_F^{eq} + \int_{t=0}^{t} \beta \dot{\boldsymbol{\sigma}}_F^{eq} \exp\left[-\left(\frac{t-r}{\tau}\right)\right] \mathrm{d}r}_{fibrous} \quad \text{(S1)}$$

where τ is relaxation time, $\boldsymbol{\sigma}_F^{eq}$ is the stress of the equilibrium part of the fiber mat, and β is a material parameter.

The Cauchy stress for the matrix is defined as

$$\boldsymbol{\sigma}_m = V_m N k_b T \mathbf{B} \quad \text{(S2)}$$

where V_m is the matrix volume fraction, N is the crosslinking density, k_b is Boltzmann's constant, and $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ is the right Cauchy Green strain tensor.

Several works have successfully captured the anisotropic property of anisotropic fibrous networks.[1-5] Using one such result, the free energy of the equilibrium part of the fiber mat is defined as.[5]

$$\rho_{R\theta} \Psi_F^{\infty} = \frac{1}{2} \mu_F \left(\lambda_F{}^2 - 1\right)^2 \quad \text{(S3)}$$

where $\rho_{R\theta} \Psi_F$ is free energy density per unit volume, μ_F is shear modulus, λ_F is stretch of fiber with definition of $\lambda_F = \sqrt{\frac{I_4}{3}}$, and $I_4 = \mathbf{a}_0 \cdot \mathbf{C} \cdot \mathbf{a}_0$, here $\mathbf{a}_0$ is initial fiber direction vector.

Then, the stress for the equilibrium part of the fibers can be obtained from Eq.(S3) as

$$\boldsymbol{\sigma}_F = 2 V_F \mu_{F(2)} \left(\lambda_F{}^2 - 1\right) \lambda_F \frac{\partial \lambda_F}{\partial I_4} \mathbf{a} \otimes \mathbf{a} \quad \text{(S4)}$$

where V_F is the fiber volume fraction and $\mathbf{a}$ is the fiber direction defined in the current configuration, with $\mathbf{a} = \mathbf{F}\mathbf{a}_0$.

As for uniaxial stretch, the deformation gradient, the right Cauchy Green strain tensor, and the fiber direction tensor can be obtained as

$$\mathbf{F} = \begin{bmatrix} \lambda_1 & \gamma & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}, \quad \mathbf{B} = \mathbf{F}\mathbf{F}^T = \begin{bmatrix} \lambda_1^2 + \gamma^2 & \lambda_2\gamma & 0 \\ \lambda_2\gamma & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{bmatrix}$$

$$\mathbf{a} \otimes \mathbf{a} = \begin{bmatrix} (\lambda_1 \cos\theta + \gamma \sin\theta)^2 & \lambda_2 \sin\theta(\lambda_1 \cos\theta + \gamma \sin\theta) & 0 \\ \lambda_2 \sin\theta(\lambda_1 \cos\theta + \gamma \sin\theta) & (\lambda_2 \sin\theta)^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{S5}$$

Substituting Eq.(S5) into Eq. (S4) yields the specified constitutive relations for the fiber network with consideration of the anisotropic property.

By using Eq.(S4) and Eq.(S2), the axial stress and shear stress components can be written as

$$\begin{aligned} \sigma_1 &= E_M(\lambda_1^2 + \gamma^2) + E_F(\lambda_1 \cos\theta + \gamma \sin\theta)^2 + \\ &\quad E_F 2\cos\theta(\lambda_1 \cos\theta + \gamma \sin\theta)\int_0^T \beta\dot{\lambda}_1 \exp\left[-\left(\frac{T-t}{\tau}\right)\right] \end{aligned} \tag{S6a}$$

$$\sigma_{12} = E_M(\lambda_1^{-1/2}\gamma) + E_F\left(\lambda_1^{1/2} \sin\theta \cos\theta + \lambda_1^{-1/2}\gamma(\sin\theta)^2\right) \tag{S6b}$$

where the incompressibility of the material is assumed and $\lambda_3 = \lambda_2 = \lambda_1^{-\frac{1}{2}}$ is adopted for the uniaxial stretch case. E_M and E_F are deduced material parameters, and

$$E_M = V_M N k_b T \tag{S7a}$$

$$E_F = \frac{1}{3}\mu_F\left(\lambda_F^2 - 1\right) \tag{S7b}$$

Solving the Model

To solve the anisotropic viscoplastic property of A-SMECs, we first rewrite the axial constitutive relation

(Equation 6) and shear stress constitutive relation (Equation 9) following incremental formations as

$$\sigma_1^{n+1} = \sigma_1^n + \tilde{E}_m\left(1+\Delta\varepsilon_1^{n+1}\right) + \tilde{E}_f\left(1+\Delta\varepsilon_1^{n+1}\right) + \beta\tilde{E}_f\left(\left(\sum_{k=1}^{n}\Delta\varepsilon_1^k \exp\left(-\frac{t-k\Delta t}{\tau(k)}\right)\right)+\Delta\varepsilon_{1(e)}^{n+1}\right) \tag{S8a}$$

$$\sigma_{12}^{n+1} = \sigma_{12}^n + E_m'\Delta\gamma + E_f'\Delta\gamma \tag{S8b}$$

where material parameters for the matrix are $\tilde{E}_m = 2E_m\lambda_1$ and $E_m' = E_m\lambda_1^{-1/2}$, and parameters for the fiber are

$$\tilde{E}_f = 2E_f\cos\theta\left(\lambda_1\cos\theta+\gamma\sin\theta\right)$$

and

$$E_f' = 2E_f\lambda_1^{-1/2}\sin\theta\left(\lambda_1^{1/2}\cos\theta\sin\theta+\lambda_1^{-1/2}\gamma\sin\theta\right).$$

For the derivation of Equation S1, the relation $\Delta\lambda_1^{n+1} = 1+\Delta\varepsilon_1^{n+1}$ is applied, where n+1and n indicate time increment steps. By using a compatible relation between the equilibrium branch and the non-equilibrium branch of the standard linear solid model, the elastic strain increment of the non-equilibrium part can be related to the total strain increment as $\Delta\varepsilon_{1(e)}^{n+1} = \left(\Delta\varepsilon_1^{n+1} - \varepsilon_{1(e)}^n\Delta t/\tau\right)\Big/\left(1+\varepsilon_{1(e)}^n\Delta t/\tau\right)$. Here the total elastic strain of the non-equilibrium part is $\varepsilon_{1(e)}^n = \sum_{k=1}^{n}\Delta\varepsilon_{1(e)}^k\prod_{j=k}^{n+1}\exp\left(-\Delta t/\tau(j)\right)$. Therefore, Equation S1 can be rewritten in a compact form as

$$\sigma_1^{n+1} = \underbrace{\left[\tilde{E}_m+\tilde{E}_f+\frac{\beta E_f}{1+\beta E_f\Delta t/\eta(t)}\right]}_{P_A^S}\Delta\varepsilon_1^{n+1} + \left(\underbrace{\sigma_1^n+\tilde{E}_m+\tilde{E}_f+\left(\frac{\beta E_f}{1+\beta E_f\Delta t/\eta(t)}\varepsilon_{1(e)}^n\right)}_{P_B^S}\right) \tag{S9a}$$

$$\sigma_{12}^{n+1} = \underbrace{\left[E_m'+E_f'\right]}_{P_A^T}\Delta\gamma + \underbrace{\sigma_{12}^n}_{P_B^T} \tag{S9b}$$

where $P_A^S = \tilde{E}_m+\tilde{E}_f+\beta\tilde{E}_f\Big/\left(1+\Delta t/\tau(t)\right)$ and $P_A^T = E_m'+E_f'$ are defined as the tangential stiffness at each time increment, $P_B^T = \sigma_{12}^n$ and $P_B^S = \sigma_1^n + \tilde{E}_m + \tilde{E}_f + \left(\beta \tilde{E}_f \varepsilon_{1(e)}^n \big/ \left(1 + \Delta t / \tau(t)\right)\right)$ are defined as the total stress related to loading history, and $\varepsilon_{1(e)}^n = \sum_{k=1}^{n} \Delta\varepsilon_{1(e)}^k \prod_{j=k}^{n+1} \exp\left(-\Delta t / \tau(j)\right)$.

The constitutive relation equations for axial and shear stress were solved incrementally, as is subsequently described. The resultant axial force N^S, resultant shear force N^T and bending moment M in the bilayer can be calculated by summing that of each layer

$$N^S = N_1^S + N_2^S, \quad N^T = N_1^T + N_2^T, \quad M = M_1 + M_2 \tag{S10}$$

where the resultant force and bending moment in layer 1 and layer 2 are

$$\begin{aligned}
N_1^S &= \int_{-h_2}^{0} \sigma_1 \mathrm{d}z = \int_{-h_2}^{0} P_A^S \mathrm{d}z \Delta\varepsilon + \int_{-h_T}^{0} P_A^S \mathrm{z d}z \Delta\kappa + \int_{-h_T}^{0} P_B^S \mathrm{d}z \\
N_1^T &= \int_{-h_2}^{0} \sigma_{12} \mathrm{d}z = \int_{-h_T}^{0} P_A^T \mathrm{d}z \Delta\gamma + \int_{-h_T}^{0} P_B^T \mathrm{d}z \\
M_1 &= \int_{-h_2}^{0} z\sigma_1 \mathrm{d}z = \int_{-h_2}^{0} P_A^S \mathrm{z d}z \Delta\varepsilon + \int_{-h_2}^{0} P_A^S \mathrm{z}^2 \mathrm{d}z \Delta\kappa + \int_{-h_2}^{0} P_B^S \mathrm{z d}z \\
N_2^S &= \int_{0}^{h_1} \sigma_1 \mathrm{d}z = \int_{0}^{h_1} P_A^S \mathrm{d}z \Delta\varepsilon + \int_{0}^{h_1} P_A^S \mathrm{z d}z \Delta\kappa + \int_{0}^{h_1} P_B^S \mathrm{d}z \\
N_2^T &= \int_{0}^{h_1} \sigma_{12} \mathrm{d}z = \int_{0}^{h_1} P_A^T \mathrm{d}z \Delta\gamma + \int_{0}^{h_1} P_B^T \mathrm{d}z \\
M_2 &= \int_{0}^{h_1} z\sigma_1 \mathrm{d}z = \int_{0}^{h_1} P_A^S \mathrm{z d}z \Delta\varepsilon + \int_{0}^{h_1} P_A^S \mathrm{z}^2 \mathrm{d}z \Delta\kappa + \int_{0}^{h_1} P_B^S \mathrm{z d}z
\end{aligned} \tag{S11}$$

Substituting Equation (S9) into Equation (S11), and then into Equation (S10), yields the following compact formation of the resultant force and bending moment at the current time step

$$\begin{Bmatrix} N^S \\ M \\ N^T \end{Bmatrix}_{n+1} = \begin{bmatrix} A & B & 0 \\ B & D & 0 \\ 0 & 0 & G \end{bmatrix}_{n+1} \begin{Bmatrix} \Delta\varepsilon^0 \\ \Delta\kappa \\ \Delta\gamma \end{Bmatrix}_{n+1} + \begin{Bmatrix} N^{S(*)} \\ M^{(*)} \\ N^{T(*)} \end{Bmatrix}_{n} \tag{S12}$$

where

$$A = \int_{-h_2}^{0} P_A^S \mathrm{d}z + \int_0^{h_1} P_A^S \mathrm{d}z \qquad B = \int_{-h_2}^{0} P_A^S z\mathrm{d}z + \int_0^{h_1} P_A^S z\mathrm{d}z$$
$$D = \int_{-h_2}^{0} P_A^S z^2\mathrm{d}z + \int_0^{h_1} P_A^S z^2\mathrm{d}z, \qquad G = \int_{-h_s}^{0} P_A^T \mathrm{d}z + \int_0^{h_1} P_A^T \mathrm{d}z,$$
$$N^{S(*)} = \int_{-h_2}^{0} P_B^S \mathrm{d}z + \int_0^{h_1} P_B^S \mathrm{d}z, \qquad N^{T(*)} = \int_{-h_2}^{0} P_B^T \mathrm{d}z + \int_0^{h_1} P_B^T \mathrm{d}z,$$
$$M^{(*)} = \int_{-h_2}^{0} P_B^S z\mathrm{d}z + \int_0^{h_1} P_B^S z\mathrm{d}z \tag{S13}$$

The midpoint integration method is used to integrate the stiffness matrix, resultant force and bending moment. Thus the strain and curvature increment at the current time step can be calculated by solving the following equation

$$\begin{Bmatrix} \Delta\varepsilon^0 \\ \Delta\kappa \\ \Delta\gamma \end{Bmatrix}_{n+1} = \begin{bmatrix} A & B & 0 \\ B & D & 0 \\ 0 & 0 & G \end{bmatrix}_{n+1}^{-1} \begin{Bmatrix} N^S - N^{S(*)} \\ M - M^{(*)} \\ N^T - N^{T(*)} \end{Bmatrix}_{n+1} \tag{S14}$$

Since during stretching the bilayer is kept flat and no out-of-plane deformation is allowed, the following displacement boundary conditions are applied

$$\Delta\varepsilon^0 = \dot{\varepsilon}\mathrm{d}t \ , \ \Delta\kappa = 0 \ , \ \Delta\gamma = 0 \tag{S15}$$

where $\dot{\varepsilon}$ is the loading strain rate.

Upon unloading the bilayer bends due to difference in fixed strains between the two layers, and the boundary conditions are applied as

$$\Delta N^{S(*)} = \int_{-h_2}^{h_1} \dot{\sigma}_1 \mathrm{d}z, \ \Delta M^{(*)} = \int_{-h_2}^{h_1} \dot{\sigma}_1 z\mathrm{d}z \tag{S16}$$

where $\dot{\sigma}_1$ is the applied loading stress rate.

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