Electronic Supplementary Material (ESI) for RSC Advances

Water-triggered shape memory of PCL-PEG multiblock TPUs

Xinzhu Gu, and Patrick T. Mather*

Supporting Information

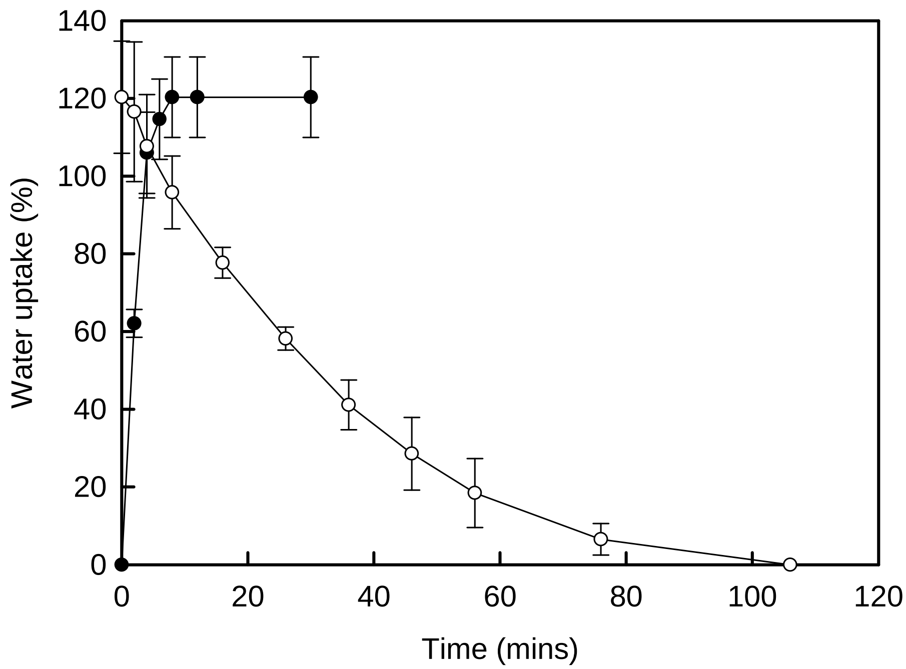


Figure S1. Swelling (closed circle) and deswelling kinetics (open circle) of $[PCL]_{50}$-$[PEG]_{50}$ in water at room temperature. The dimension of the film is 10 mm x 10 mm x 0.35 mm (thickness).

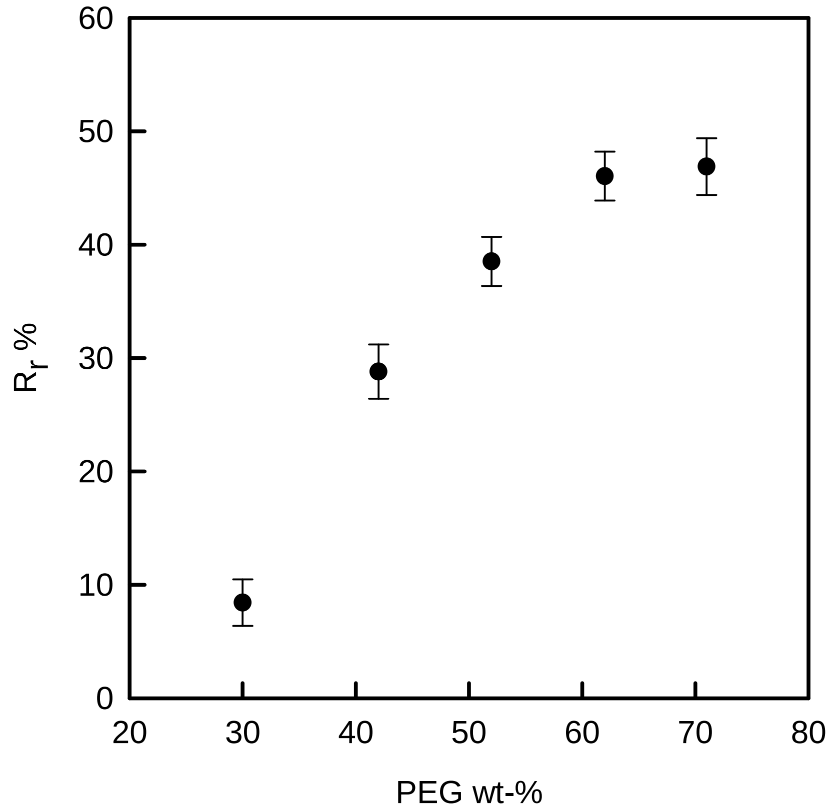


Figure S2. Dependence of shape recovery during water-triggered recovery, R_r (%), on PEG wt-%.

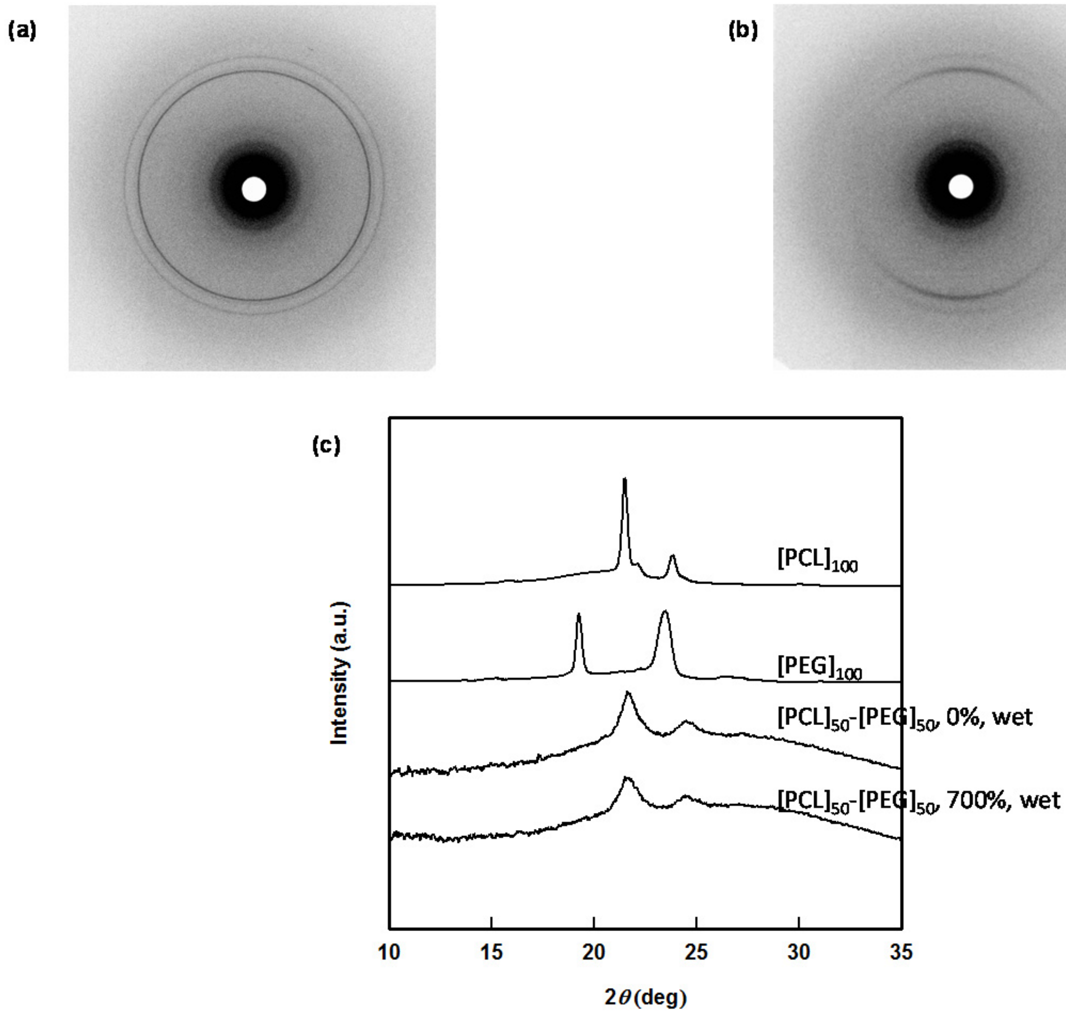


Figure S3. (a) 2D WAXS patterns of $[PCL]_{50}$-$[PEG]_{50}$ after immersed in water at RT for 1 h. (b) 2D WAXS patterns of $[PCL]_{50}$-$[PEG]_{50}$ after deformation to 700% and immerse in water at RT for 1 h; and (c) 1D WAXS profile of samples shown in (a) and (b). Data of $[PCL]_{100}$ and $[PEG]_{100}$ in dry state are shown here for comparison. For samples at swelling state, films were sandwiched between two layers of Kapton tapes and x-ray experiments were operated under no vacuum to prevent from water evaporating. The two-layer tapes were also tested and used as baseline and all reported WAXS curves for samples at "swelling state" have been subtracted by the pure two-layer tape. Samples at dry state were exposed under vacuum to eliminate air exposures.

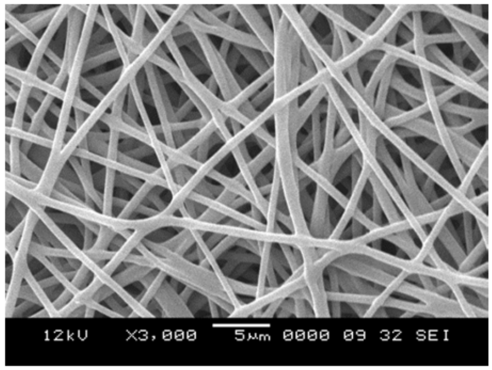
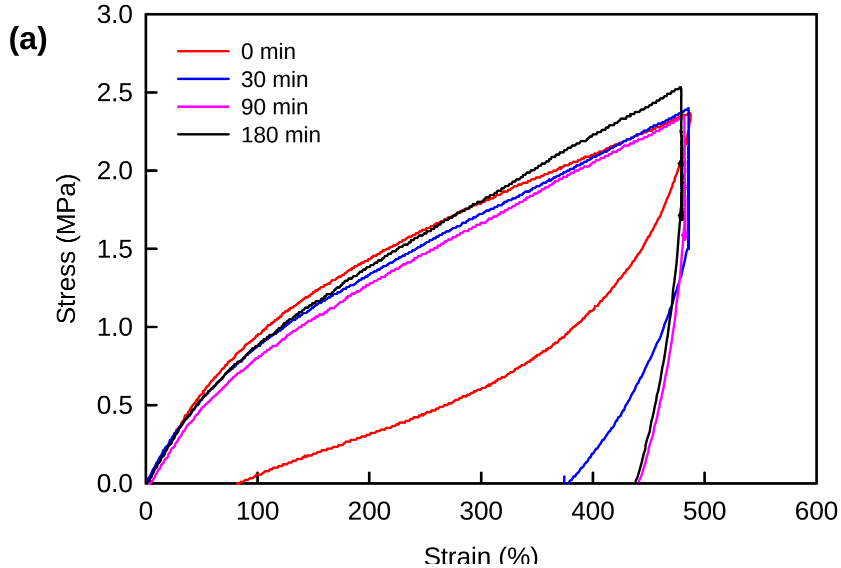


Figure S4. Scanning electron microscopy (SEM) image of fibrous mats made by electropsinning.

The number-average fiber diameter was 810 ± 28 nm.



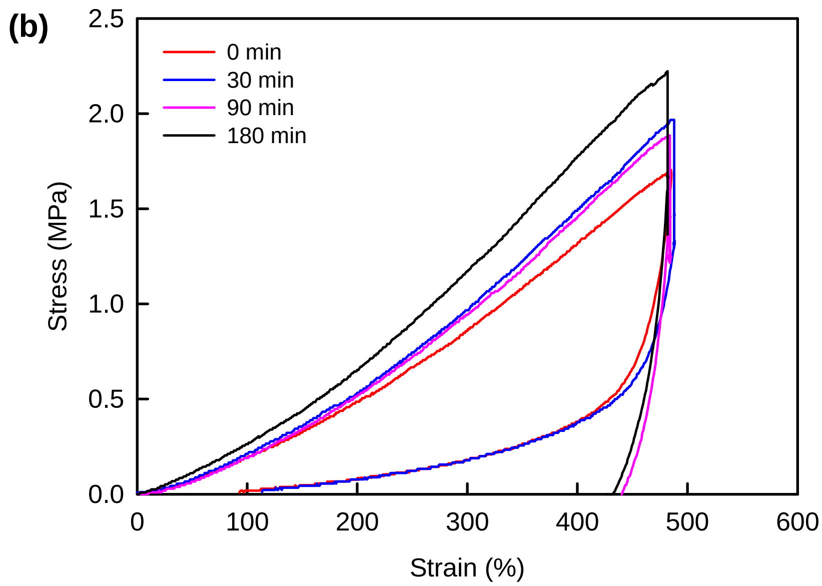


Figure S5. Stress-strain response of (a) films and (b) webs which were deformed in wet state at 192 %/min and fixed (dried) for different time durations at room temperature. Following the fixing step, all samples were unloaded at 192 %/min until the force dropped to zero.

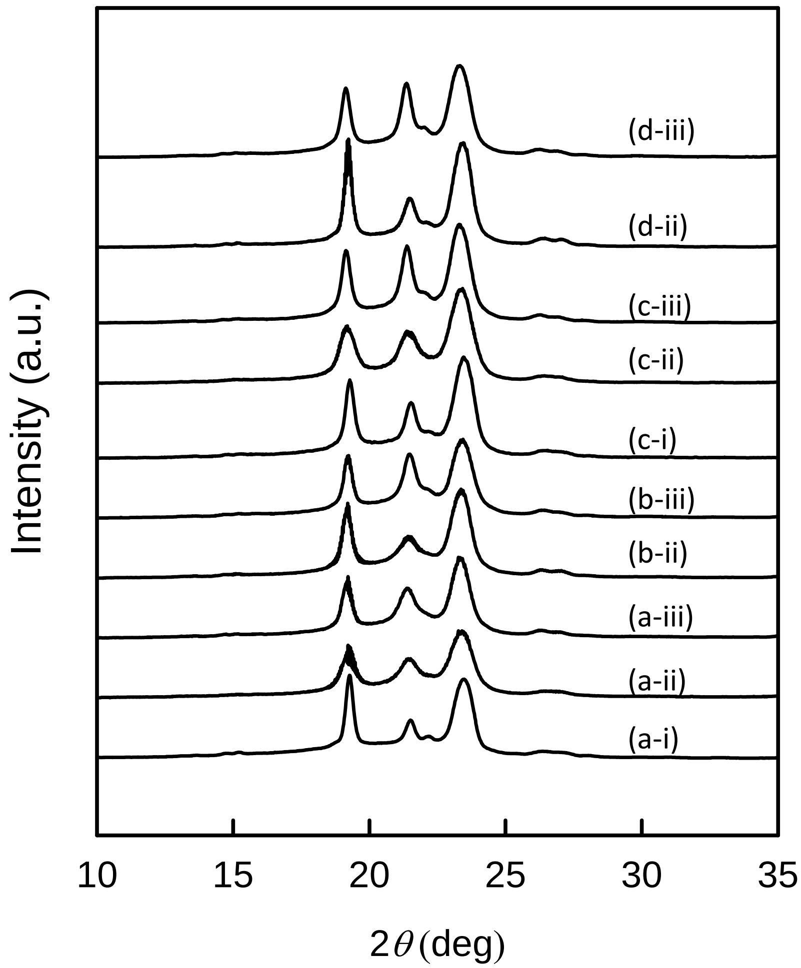


Figure S6. 1D WAXS profiles of (a) dry films, (b) wet films, (c) dry webs, and (d) wet webs. (i) original samples; (ii) samples which were deformed and fixed by Linkam (S/F); and (iii) samples which were deformed, fixed, water recovered and dried (S/F/R/D).

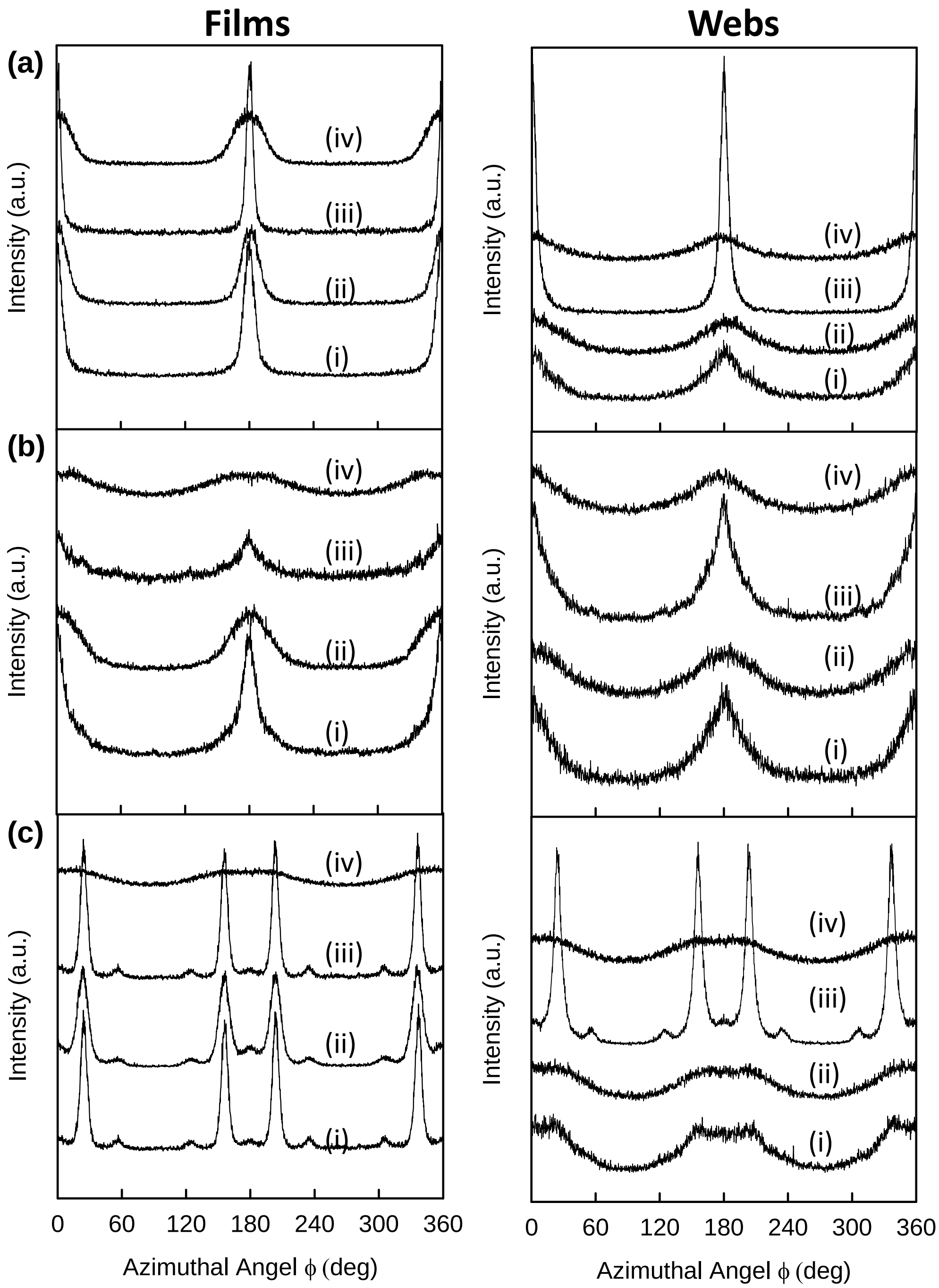


Figure S7. Intensity versus azimuth of (a) Peak 1: (120) reflection of PEG phase, (b) Peak 2: (110) reflection of PCL phase and (c) Peak 3: (200) reflection of PCL phase, and diverse planes of PEG phase of hot-pressed films and epsun webs. (i) dry film/web_S/F; (ii) dry film/web_S/F/R/D, (iii) wet film/web_S/F, and (iv) wet film/web_S/F/R/D. The corresponding 2D WAXS image is shown in Figure 8.

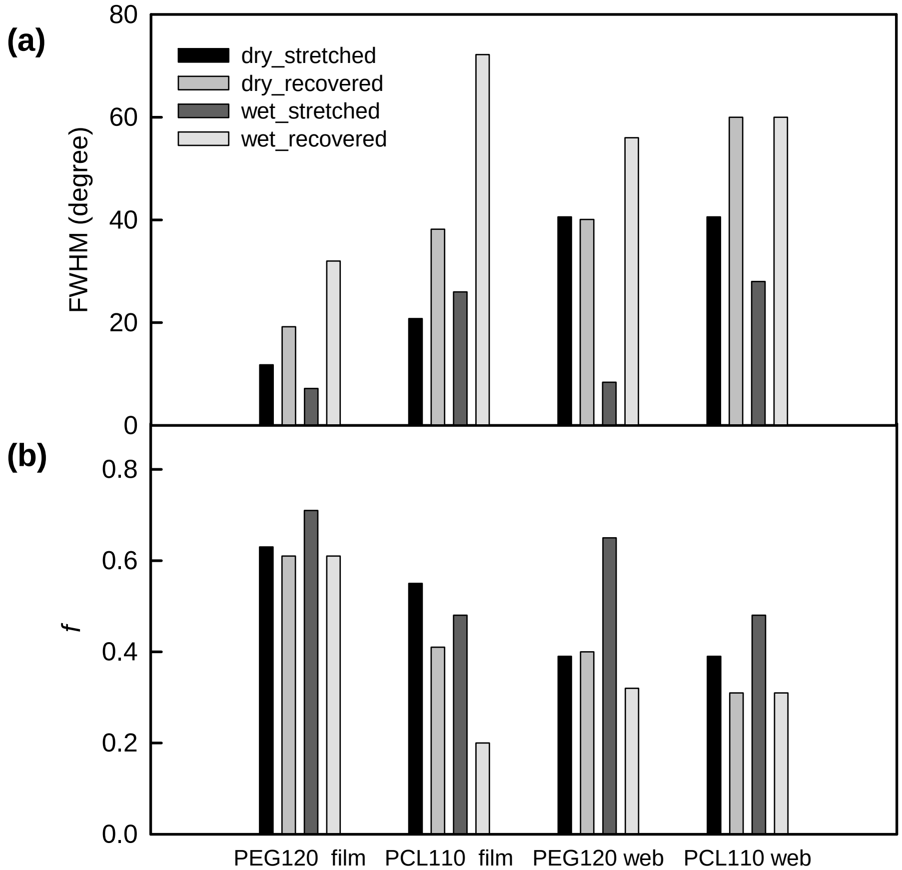


Figure S8. (a) Full-width at half maximum (FWHM) and (b) Herman's orientation function (*f*) of PEG(120), and PCL(110) reflection of hot-press films and e-spun webs which were deformed in dry state and wet state, respectively. The azimuthal scan data was fit using Curve Resolution Program for Windows software (Asai Company, Japan) and the values of FWHM for were obtained from the software. Herman's orientation function, *f*, is defined as: $f = \left(3\left\langle \cos^2 \varphi \right\rangle_{hkl} - 1\right)/2$. The average orientation, expressed as $\left\langle \cos^2 \phi_{hkl} \right\rangle$, was calculated by numerical integration using the following equation: $\left\langle \cos^2 \varphi_{hkl} \right\rangle = \left(\int_0^{\pi/2} I(\varphi) \cdot \cos^2 \varphi \cdot \sin \varphi \cdot d\varphi \right) / \left(\int_0^{\pi/2} I(\varphi) \cdot \sin \varphi \cdot d\varphi \right)$ where φ is the azimuthal angle and $I(\varphi)$ is the scattered intensity along the angle φ. It is noted that Peak 3 was not used to determine degree of crystal orientation since it is an overlap of several reflections described above.

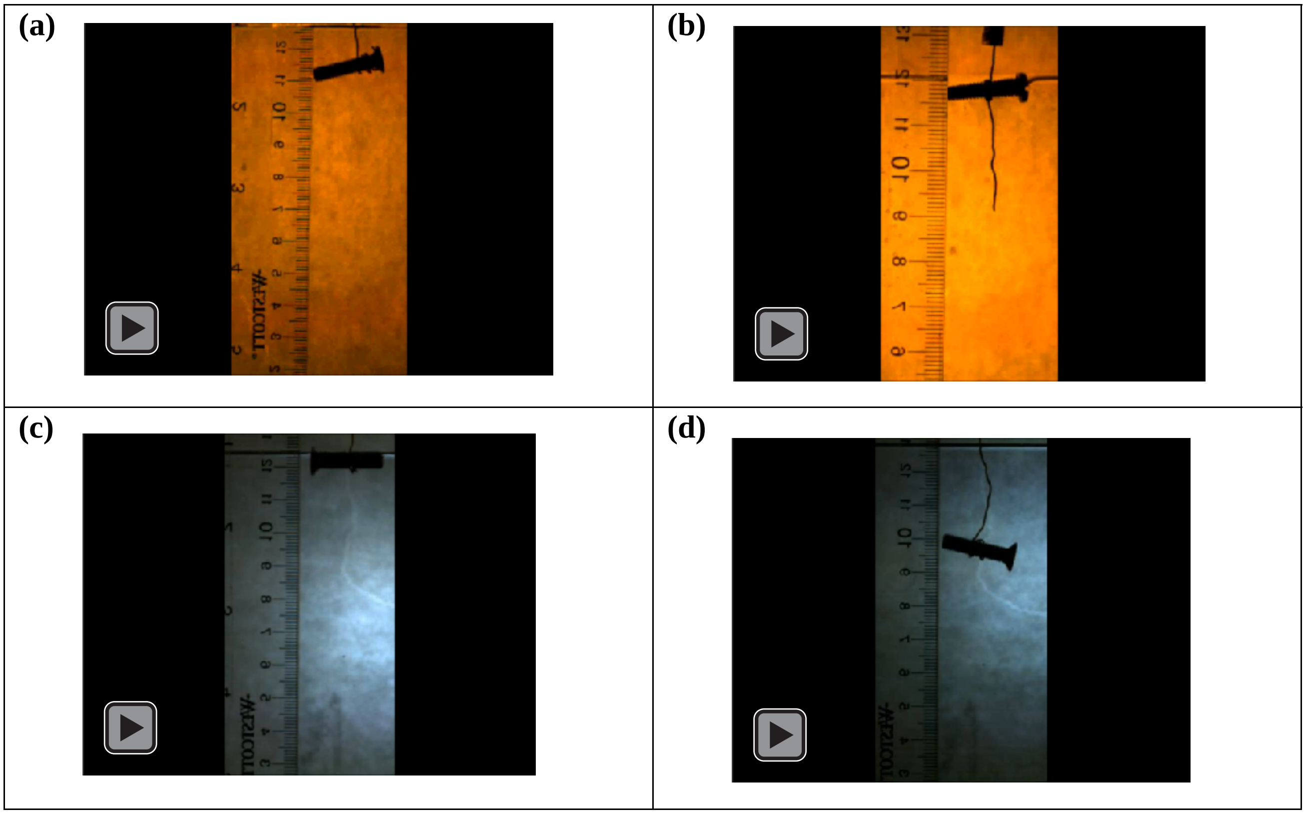


Figure S9: Movies showing water-triggered recovery of pre-deformed e-spun web and hot-press film at RT. (a) film_dry stretch with sampling rate 60 fps and play rate 240 fps, (b) web_dry stretch with sampling rate 250 fps and play rate 250 fps, (c) film_wet stretch with sampling rate 60 fps and play rate 480 fps, and (d) web_wet stretch with sampling rate 60 fps and play rate 240 fps.

Table S1: Comparison of mechanical properties of synthetic and natural hydrogels reported in the literature. For the ultimate stress and strain-at-break, the highest one was reported here if there are a series of values shown in the paper.

References	Hydrogel	Young's modulus (MPa)	Ultimate stress (MPa)	Strain at break (%)
Wan *et al., J Biomed Mater Res,* **2002**, 63:854	PVA hydrogels	0.2	1.0	80
Temenoff *et al., J Biomed Mater Res,* **2002**, 59:429	Oligo (PEG fumarate) + PEG-DA	0.02~0.08	0.02	80
Burdick *et al., Biomacromolecules,***2005**, 6:386	Hyaluronic acid	0.02~0.1	0.15	50
Normand *et al., Biomacromolecules,***2000**, 1:730	Agarose gel	0.08~3.7	0.6	45
Roeder *et al., J Biomech Eng,* **2002**, 124:214	Collagen	0.02	0.008	60
Drury *et al., Biomaterials,* **2004**, 25, 3187	Alginate hydrogels	0.05	0.03	100
Gu and Mather (current work)	PCL-PEG based hydrogel	0.2~1.1	2.8	742