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Electronic Supplementary Information for

Humidity-sensitive Polymer Xerogel Actuators Prepared by Biaxial Pre-stretching and Drying †

10 Jie Zhou,^a Chu Wu,^a Dongbei Wu^{*, a}, Qigang Wanga^{*, a} and Yonggui Chen^b

a. School of Chemical Science and Engineering, Shanghai Key Lab of Chemical Assessment and Sustainability, Tongji University, Shanghai 200092, PR China

b. Department of Geotechnical Engineering, Tongji University, Shanghai 200092, PR China

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Contents

	Index	Page
	1. Materials & Methods	2
	2. Pre-treatments and characterizations	2
20	3. Test of the energy conversion efficiency	4
	4. Experimental instrument for humidity sensitive tests ²	5
	5. Test of ionic conductivity of xerogel film	5
	6. Figures	6
	7. Tables	10
25	8 References	12

1. Materials & Methods

Materials: Polyethylene glycol methacrylate-200 (PEGMA-200, average M_n 200) and acrylamide (AAM) were purchased from Sigma-Aldrich Reagent Company. Organic photoimitator 2, 2-diethoxyacetonphenone (DEAP) was bought from Shanghai Energy Chemical Co.,

5 Ltd, Shanghai, China. Methylene blue, acetone, ethanol N-hexane, ethylene glycol, chloroform, LiCl and all other common laboratory reagents were obtained from Aladdin Reagent Co. Ltd., Shanghai, China. All chemicals were of analytical reagent grade and used as received.

Methods: We fabricated PAAM xerogel film using a three-step process. First, thin PAAM bulk hydrogel was prepared *via* a simple, photo-induced radical polymerization process. Unless

- 10 specified elsewhere, the mass ratio of monomeric AAM, the chemical cross-linker PEGMA-200, the photo-initiator DEAP, and water was maintained at 33: 100: 0.5: 0.5. Briefly, 0.19 g AAm, 3.0 μL PEGDA-200, and 3.0 uL DEAP were successively added to distilled water to form a 0.8 g precursor solution. Solution homogeneity was achieved by gentle stirring at room temperature for 15 min, after which the PAAM precursor solution was poured into a specially-
- 15 shaped organic glass mold (2bdf.0 cm \times 2.0 cm \times 0.5 cm). The mold was subjected to UV light irradiation for 3 min, after which the hydrogel had a thickness of approximately 0.2 cm. The prepared hydrogel was then successively confined in axial pre-stretching until it reached a length of 8.0 cm and a width of 8.0 cm. The final hydrogel had a thickness of approximately 40 µm. Finally, it was oven-dried at 50°C for 2 h to remove any remaining water. The final film
- 20 thickness was approximately 10 μm. Using the same composition ratio and procedure, xerogel films with other thicknesses (e.g., 1150 μm, 280 μm, and 80 μm) were made by adjusting the pre-stretching ratio of the initial hydrogel. Comparatively, xerogel films of varying thicknesses (e.g., 20 μm, 30 μm, and 40 μm) were also made by changing the volume of the precursor solution.
- 25

2. Pre-treatments and characterizations

Pre-treatment of SEM samples

The hydrogel samples for SEM analysis were cut into cubes of about 2×2×2 mm³ from the inner parts of hydrogels. The samples were rapidly quenched into liquid nitrogen, and then 30 freeze-dried for 48 h. A thin layer of gold (about 5 nm) was sputter-coated before scanning with a field emission SEM (Hitachi S 4800) at an accelerating voltage of 3 kV.

Tensile experiments

Initial hydrogel and the resulting xerogel films using a universal tensile-compressive tester (CMT 6503, SANS, China) with a GB/T 1040.3-2006 Standard. The rectangular hydrogels (5 mm thick and 15 mm wide) and films (10 - 40 mm thick and 15 mm wide) were investigated at a strain rate of 5 mm min⁻¹. The Young's modulus was evaluated from the initial linear region of the stress strain surge. All results are the surges of three independent superiments.

5 of the stress-strain curve. All results are the average of three independent experiments.

Biaxial stretching experiments

In-plane biaxial tension experiments were performed with the biaxial testing system (IPBF-300, CARE Measurement & Control Co., Ltd.).¹

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A three-step process was used to prepare xerogel film: A piece of hydrogel (2 cm \times 2 cm \times 0.2 cm) was firstly fixed by clamp of Y-direction,

stretched to a 400 % strain along Y-direction at 5 mm min⁻¹. Secondly, it was fixed by clamp

15 of X-direction and stretched to a 400 % strain by along X-direction at 5 mm min⁻¹. Finally, in case of uneven thickness of xerogel film, we utilized the middle part of the film to do follow-up test.

Water content q experiments

20 The xerogel films content q, was calculated according to the following equation: q = 1- (W_m / W_d), where W_m and W_d are the masses of monomer and dried state, respectively. the masses was got through analytical balance.

Polarizing optical microscopy experiments

25 The microcrystalline structures of the xerogel films were tested by polarizing optical microscopy (XPF-300, China) at room temperature.

2D wide-angle X-ray diffraction (WAXD) measurements

2D wide-angle X-ray diffraction (WAXD) measurements were obtained using a Bruker 30 Smart APEX II single-crystal four-circle diffractometer (SEA#107) that was operated at 40 kV and 0.65 mA with a Cu anode via the Debye-Scherer method. The distance between the chargecoupled device 4K detector and sample was 50 mm with aan exposure time of 60 s. The X-ray bean was focused on the horizontal middle of the sample during the exposure.

5 Small Angle X-ray scattering (SAXS) measurements

Small Angle X-ray scattering (SAXS) measurements were performed using a Xeuss 2.0 instrument (Xenocs, France). Spot size and exposure time was 0.7×0.7 mm and 600 s, respectively. Gel film thickness was examined using a digital stereo microscope (VH-Z100R, Keyence Corporation).

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Curvature equation ²

The curvature was calculated according to the following equation (1)

$$Curvature (k) = \frac{deflection \ angel \times \pi \div 180}{L}$$
(1)

Where *L* is the film-free bending length.

15 **3. Test of the energy conversion efficiency**

The total strain energy density W_{def} was the mechanical energy used to deform the hydrogel.³ It is related to the area under the load (unload) strain-stress curve, and was estimated according to the following equation under uniaxial tensile conditions:

20

Where γ is the strain defined as the ratio between current and initial length and σ is the nominal stress. When a hysteresis appears, the dissipated mechanical energy W_{hyst} over one cycle was calculated as follows:

$$W_{hyst} = W_{def}^{load} - W_{def}^{unload}$$

A three-step process was used to evaluate the energy storage of the xerogel film: A piece of fresh hydrogel was first pre-stretched to a 400 % strain using a tensile machine, followed by oven-drying at 50°C for 2 h to produce a xerogel film. After spraying a set amount of water, the xerogel film was replaced back into the tensile machine to determine its upload strain-stress curve. Energy storage was determined from the area under the unloaded strain-stress curve for

(3)

both the hydrogel and xerogel film. The energy conversion efficiency (P %) of the xerogel to the initial hydrogel was defined by equation (4):

4

$$P\% = \frac{W_{def}^{unload}(xerogel film)}{W_{def}^{unload}(hygrogel)} \times 100$$

5 4. Experimental instrument for humidity sensitive tests²



10 5. Test of ionic conductivity of xerogel film

The instrument was mainly composed of a conductivity meter, a piece of xerogel film and a bottle of saturated salt solution. The function of saturated salt solution is to provide a stable humidity atmosphere. ³



5 6. Figures



Figure S1. Characterization of xerogel film. (a) POM images of the xerogel film showing nematic liquid crystals. Scale bar, 2µm. (b) Small-angle X-ray scatter
(SAXS) images of the xerogel film. (c) 2D wide-angle X-ray diffraction (WAXD) of the xerogel film.



Figure S2. Loading test for the xerogel film



Figure S3. (a-d) The mechanical properties of the xerogel film with different AAm concentration and pre-stretching ratio as well as drying temperature and drying time.

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As shown above, as the pre-stretching ratio increased from 0% to 400%, the fracture stress and Young's modulus increased from 24.3 MPa to 35.8 MPa, and from 136.2 MPa to 297.9 MPa, respectively. However, the fracture strain decreased slightly from 17.8 % to 12.0 %.

- The thickness of the xerogel film was also strongly dependent on the pre-stretching ratio. With 10 increasing pre-stretching ratios from 0% to 400%, the thickness of the xerogel film decreased sharply from 2.0 mm to 13 µm. This finding indicated that xerogel film thickness was tunable and could be adjusted by changing the prestretching ratio of the initial hydrogel. Fig. S3c shows that increasing drying temperatures from 298 K to 373 K resulted in a significant increase in the mechanical strength of the xerogel film. However, the thickness of the xerogel film was
- 15 almost unchanged and water loss was significant. Therefore, it is logical that the water content of the xerogel film could be tuned by adjusting its drying temperature. The data from Fig. S3d shows that increasing drying time from 30 min to 180 min resulted in a rapid increase of Young's modulus from 145.1 MPa to 373.5 MPa, a rapid decrease of fracture strain from 18.5 % to 9.39 %, and decreased water loss from 35% to 14%.



Figure S4. Strain-stress curve of the xerogel and the initial hydrogel

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Figure S5. Loading test for the shrinked hydrogel



Figure S6. FTIR experiments of PAAM xerogel film in the different humidity. FTIR experiments were conducted to investigate the interactions between the PAAM xerogel film and water. As shown above , the peaks at 3337 cm⁻¹, 1651 cm⁻¹, and 1613 cm⁻¹ were

- 5 assigned to the stretching vibrations of the free –NH2 band, amide I band (C=O), and the bending vibrations of the amide II band (N-H), respectively ⁴. After adsorbing water, the absorption peaks at 3337 cm⁻¹, 1651 cm⁻¹, and 1631 cm⁻¹ shifted to 3350 cm⁻¹, 1660 cm⁻¹, and 1617 cm⁻¹, respectively, revealing the existence of H-bands between the PAAM chains and the surrounding water molecules. Given this, we propose that our xerogel film is water-specific and
- 10 may be used for the detection of water molecules.

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7. Tables

Table S1. Mechanical properties and water contents of xerogel under different conditions. Date are presented as average value with standard deviation from three measurements.

Sample	Variable	Condition	Young's modulus, (MPa)	Stress, (MPa)	Strain, (%)	Work of extension, (MJ· m ⁻³)	Water (wt %)	Thickness (µm)
Initial hydrogel		0.14	0.13	502	0.55	65	2000	
without prestretchin g		C _{AAM} =53% T = 323 K t = 120 min	136.2	24.3	17.8	2.79	30	1700
400 % prestretchin g			297.9	35.8	12.0	2.96	12	19
	Monomer concentration (%)	33	158.6	28.9	18.2	3.40	15	10
		43	220.7	33.4	15.1	3.42	13	14
	Prestretching Ratio (%)	25	151.3	25.7	17.0	2.85	18	1150
Resultant		50	164.6	26.3	16.1	2.74	15	280
xerogel with		100	208.0	29.2	14.0	2.79	14	80
prestretchin g	Drying temperature (K)	298	220.4	31.8	14.4	3.16	14	12
		373	297.9	35.8	12.0	2.43	10	12
	Drying time (min)	30	145.1	26.8	18.5	3.16	35	13
		60	236.7	33.3	14.0	3.18	15	14
		180	373.5	35.1	9.39	2.27	14	13

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Material		Stimulations	Lays	Strain (%)	Tensile strength (MPa)	Water specificity	Ref.
graphene oxide fibers		Humidity	One	2.8	100	Yes	11
Chitin Films		None ^{a)}	One	12	226	No	12
Cellulose hydrogel film		None ^{a)}	One	50	55	No	6
	PVDF/PVA ^{b)}	Acetone vapor	Two	25	20	No	13
Polymer	PEG-DA ^{c)}	Humidity	One	9	2.5	Yes	14
film	Poly(NIPAM) ^{d)}	Temperature	Two	4	16	No	15
	PAA-Clay ^{e)}	рН	Two	2000	4	No	16
	DHIR/PU ^{f)}	Temperature	Two	800	5	No	17
Hydrogel film	Polyelectrolyte ^{g)}	Electric field	Two	3000	0.06	No	18
	PU-PAA ^{h)}	рН	Two	900	2	No	19
	poly(NIPAM-co-AAM) ⁱ⁾	Temperature	Two	600	4.5	No	20
Xerogel film	РААМ	Humidity	One	12	36	Yes	This Work

Table S2. Comparison with the mechanical performance of other materials.

a) none of actuation performance reported

5 b) photopolymerization of poly(ethylene glycol) diacrylate polyvinylidene fluoride (PVDF) and polyvinyl alcohol

- c) poly(ethylene glycol) diacrylate
- d) poly (N-isopropyl acrylamide)
- e) poly(acrylic acid) (PAA)-Clay hydrogels
- 10 f) polyurethane/dipole-dipole and H-bonding interaction reinforced hydrogels
 - g) The anionic p(AAm-co-AMPS)/MMT nanocomposite hydrogels(SAM) and cationic
 - p(AAm-co-DMC)/MMT nanocomposite hydrogels (DAM)
 - h) polyether-based polyurethane and poly(acrylic acid) hydrogels
 - i) poly(N-isopropylacrylamide-co-acrylamide) hydrogels

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