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Preparation and characterization of PVA/PVP conductive hydrogels formed by freeze–thaw processes as a promising material for sensor applications

Ying Yi[1,2] , Mu Chiao[3], Khaled A. Mahmoud[4], Lidong Wu[5], and Bo Wang[2,*]

[1] *School of Mechanical Engineering and Electronic Information, China University of Geosciences, Wuhan, China*
[2] *Division of Information and Computing Technology, College of Science and Engineering, Hamad Bin Khalifa University, Doha, Qatar*
[3] *Department of Mechanical Engineering, University of British Columbia, Vancouver, BC, Canada*
[4] *Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University, Doha, Qatar*
[5] *Chinese Academy of Fishery Sciences, Beijing, China*

ABSTRACT

Biocompatible and multifunctional stretchable hydrogels have attracted growing interests for applications including electronic skin and soft robotics. This paper presents a conductive and humidity sensitive hydrogel formed by poly (vinyl alcohol) (PVA) and poly (vinylpyrrolidone) (PVP). Different from previous approaches where microwave-assisted aldol condensation reactions are needed to form the material, in this work, we demonstrate forming the hydrogel through only freeze–thaw process. The resulting hydrogel features a gauge factor ($\sim$ 0.8), which is higher than that of the strain sensor fabricated through traditional approach during the strain range up to 40%. Furthermore, the structural, elastic, thermal and electrical properties of the polymer blend are evaluated so the operating environment can be identified. Our experimental results show that elasticity of the blend reduces in air due to drying that cannot be completely restored. Moreover, the conductivity of the hydrogel changes with different ambient temperatures and humidity. Finally, the hydrogel is explored as a humidity sensor.

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Introduction

Flexible sensors using soft materials attracted great interests in the fields of electronic skin, soft robotics, dosage monitoring, human–machine interaction and displacement detection [1–6]. As a soft material, hydrogel has been widely studied for its three-dimensional (3D) macromolecular structures. It can maintain a large amount of water or ionic liquid while not dissolving in physiological conditions and is excellent in stretchability, surface compliance and biocompatibility [7, 8]. Although chemical crosslinking is a mature technique in fabricating hydrogels, a growing research interests are switching to physical treatments for their safer approaches concerning biomedical applications [9]. Popular physical crosslinking methods include freezing/thawing [10, 11], heating/ cooling [12], UV exposure [13] and a combination of different crosslinking methods [14].

Polyvinyl alcohol (PVA) is often used for hydrogel formation due to biocompatibility and easy preparation [15, 16]. Although PVA-based hydrogel is attractive, it structurally degrades into smaller crystallites over time, and undergoes calcification if exposed to body fluids [14]. To tackle these issues, a second polymer can be added to form a new network of hydrogel. Polyvinylpyrrolidone (PVP), an amorphous polymer, is a well-known additive to form pores in hydrogel. It possesses properties, such as high hydrophilicity and biocompatibility [16, 18]. Moreover, it has cryo- and lyoprotectant properties [19, 20], such that it can be used to prevent aggregation of nanoscale particles. PVP and PVA are highly compatible; therefore, it is often used to mix with PVA hydrogel to improve its physical properties such as transparency and refractive index [21, 22]. PVA/PVP polymer blend can be formed via the hydrogen bond interactions between the carbonyl groups in PVP and hydroxyl groups in PVA [16], and it can be tailored according to the specific application requirements, which may not be achieved by the PVA polymer alone.

The properties of PVA/PVP polymer blend have been studied, including its miscibility [23], friction [24] and swelling performance [25]. In this work, PVA/PVP polymer blend is explored as a flexible substrate for piezoresistive strain sensors. Full research attention is currently gained on the piezoresistive sensors due to their merits of simple structures, compatibility with many readout approaches, easy processing and direct measurement of dynamometric and geometric parameters [26–28], While, the other sensing mechanism, for example, the piezoelectric sensing mechanisms [29] can only detect transient/dynamic deformation because of the intermittence nature of piezoelectric effects [28]. Synthesizing the PVA/PVP hydrogel using different methods result in different performance in terms of viscoelasticity and piezoresistivity. In previous studies, physical treatment using freezing/ thawing was used to fabricate the blend [11]. It requires an extra microwave-assisted aldol condensation reaction; however, this reduces the piezoresistivity during a strain range up to 40% [11]. In this paper, we propose a method of using only the freezing/thawing processes and sulfuric acid catalysis to prepare the PVA/PVP hydrogel without using the microwave. The resulted hydrogel exhibits a detectable gauge factor (0.8) for a wide strain range up to 48%. Besides potential application as a strain sensor, the structural properties and elasticity of the hydrogel between its initial and recovered states were compared in order to clarify the hydrogel's preferred application environment, and the sensitivity to humidity was also evaluated to reveal its humidity sensing application.

Materials and methods

Figure 1a shows the photographs of hydrogel preparation process. Following an optimized mixture ratio of the PVA and PVP [11], 1.8 g of PVA powder (Mw ∼ 94 k, Sigma-Aldrich Co.) was dissolved in 11.4 mL of deionized (DI) water and stirred using a magnetic stirrer at 90 °C until a clear solution was formed, the stirring process took about one hour. Similarly, 0.3 g of PVP powder (Mw ∼ 40 k, Sigma-Aldrich Co.) was dissolved in 1.5 mL of DI water at room temperature (∼ 22 °C) in 5 min with manual stirring. Afterward, a drop (∼ 0.5 mL) of sulfuric acid was added in the PVP solution and then was stirred for another 1 ∼ 2 min to ensure a complete interaction between the sulfuric acid and PVP. The above two solutions were mixed at room temperature and stirred for one hour. Under the acid catalysis, the polymer chains of PVA and PVP interacted upon the rearrangement of the special side groups (PVA−OH
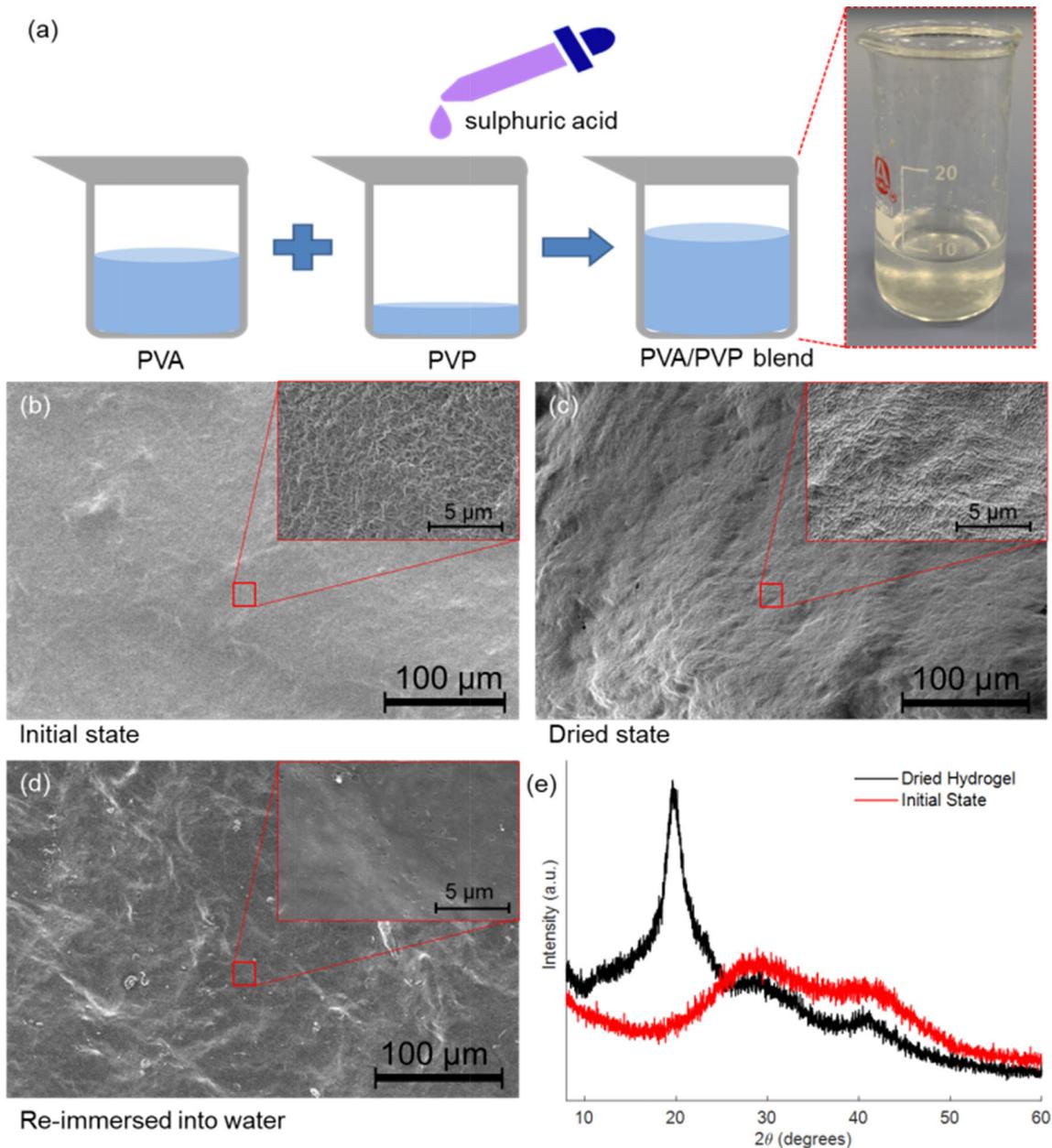
Figure 1 **a** Photographs of the components (PVA, PVP) and fabrication process of the hydrogel catalyzed by sulfuric acid. SEM images of the PVA/PVP hydrogel at **b** initial state; **c** dried state; and **d** recovered state; **e** XRD patterns of PVA/PVP hydrogel at different states.

and PVP−C=O) to form a homogeneous network [30].

The PVA/PVP blend solution was clear after a standard degassing process. It was poured into different plastic containers for different property testing. These containers were placed in a refrigerator at −20 °C for 12 h and then thawed at room temperature for 5 h. Such a freezing/thawing process was repeated three times to achieve an optimized mechanical behavior [11, 31]. PVA/PVP hydrogel was formed

after the polymer blend was frozen and thawed to change the randomly curled PVA chains into locally ordered nanocrystalline domains. Consequently, mechanical strength of the formed PVA/PVP hydrogel can be improved due to the formed crystal segments [32].

Surface morphology of the PVA/PVP hydrogel was studied by the scanning electron microscopy (SEM). As shown in Fig. 1b, Pristine PVA/PVP blend had smooth and homogeneous surface [33], however,

the magnification of the surface illustrates a three-dimensional porous structure formed during the gelation via the freeze/thawing procedure. The size of the pores increases with an increasing ratio of the PVP to the PVA [21]. When the hydrogel was dried in air in about 2 days due to water evaporation, the surface of the hydrogel became compact and rough, as illustrated by Fig. 1c. The dried hydrogel sample was immersed into water, it can be seen that the surface restored to its original smooth state after soaking. However, by comparing Fig. 1b and d, surface morphologies of the PVA/PVP hydrogel between its initial and recovered states are different, implying that the three dimensional macrostructure of the hydrogel was affected after it was dried. The X-Ray diffraction (XRD) patterns of the PVA/PVP hydrogel with different states were also studied, as shown in Fig. 1e. When the hydrogel was newly prepared, it had broad peaks in intensity because of a large amount of water content in the amorphous region. However, for dried hydrogel, its peak intensity increased. The peak locates at about 19.6°, which agrees with previously reported studies [33]. This is because water loss increases the crystalline fraction of the hydrogel [34], as a result, the peak in the intensity increases. The SEM and XRD can clarify the formation of the hydrogel, while the Fourier transform infrared spectroscopy (FTIR) and laser Raman spectroscopy that investigate the ion–polymer interaction and molecular structure of the hydrogel [35] is out of the research demand of this work.

Results and discussion

Mechanical properties of the PVA/PVP hydrogel

To demonstrate the toughness of the as-fabricated PVA/PVP hydrogel, high-level deformations were performed. As shown in Fig. 2, the hydrogel was highly flexible and robust to be stretched, curled, folded and poked. The hydrogel can recover to its initial state immediately after external force was removed, indicating an excellent resilience. Moreover, the hydrogel was robust to accommodate local stress concentration, as in Fig. 2d, when the hydrogel was stretched under biaxial tension, a plastic cone cannot pierce it within a given stretching level. This reveals that the hydrogel has an excellent puncture

resistance and it can withstand an inhomogeneous deformation. In Fig. 2e, the rectangular shaped hydrogel can withstand a load of 100 g without breakage or crack, showing toughness of the hydrogel.

Tensile testing was performed to evaluate the mechanical property of the PVA/PVP hydrogel. First, the hydrogel was synthesized following our proposed three-cycle freezing/thawing scheme. It is then naturally thawed in air, and its stress–strain property was measured at different thawing time. The thawing time must be more than 4 h; otherwise, the hydrogel will be too fragile to undergo any tension or compression. A dynamical mechanical analyzer (DMA Q8000) was used for the tensile testing. As shown in Fig. 3a, the tensile stress enhanced with an increasing thawing time, because the hydrogel continuously losses water molecule and gets dried eventually in air, which results in a reduced elasticity.

During the slow water evaporation in air, the hydrogel gradually shrank, as indicated in Fig. 3b. The initial thickness of the hydrogel sample was 0.15 mm. After exposed in air for about 2 days, its thickness reduced to 0.07 mm. The dried hydrogel loses elasticity and became quite fragile. Soaking the dried hydrogel in water can partially restore its flexibility. In our testing, the dried sample expanded when soaking it in the water; and its thickness recovered to 0.12 mm, still losing $\sim 20\%$ of its original thickness. For our synthesized hydrogel, it exhibits a certain degree of adhesion due to an existence of a large numbers of hydrophilic groups in the polymer matrix. Consequently, the hydrogel can be tightly attached to the object's surface, which brings a potential application for wearable sensors and devices.

To further investigate the tensile performance of the hydrogel film at its initial and recovered states, the same hydrogel sample was tested when it was newly prepared and after the soaking. First, after 4 h of the thawing in air, the hydrogel was immersed in the water bath of the DMA machine, its stress–strain curves were recorded, as shown in Fig. 3c. After the as-mentioned drying and soaking process, the stress–strain curve of the sample is shown in Fig. 3d. Herein, the reason for keeping the tested sample in the water bath was to avoid negative influence caused by the water evaporated in air and maintain its moist state. It can be observed that the stress enhances after the natural drying and soaking
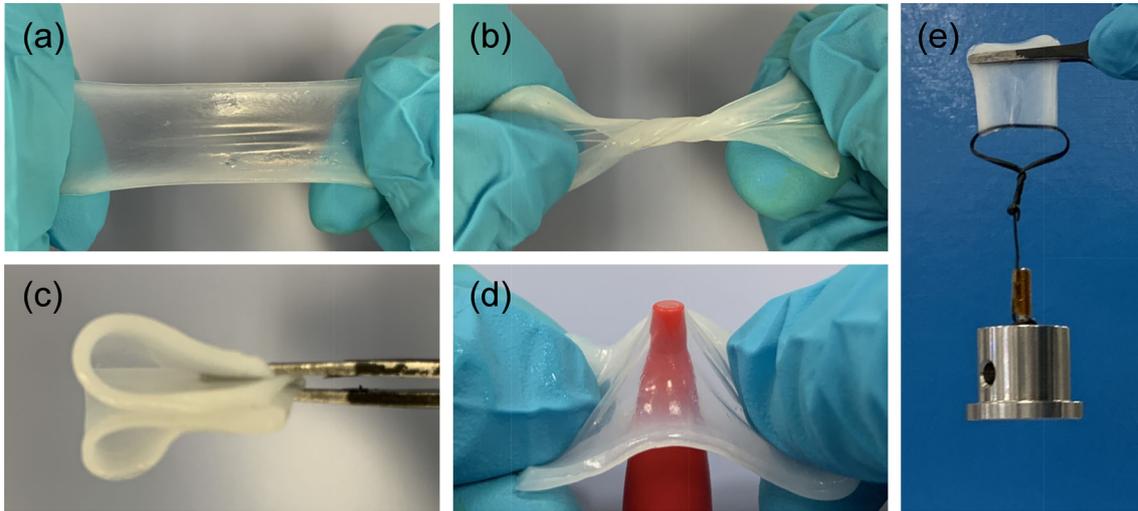
Figure 2 Photographs show a freestanding polymer blend film being **a** stretched; **b** twisted; **c** folded; **d** poked; **e** loaded.

Figure 3 a Stress–strain curves of the PVA/PVP hydrogel at different time during the thawing; **b** Photographs of the hydrogel at different states; **c**, **d** Stress–strain comparison of the hydrogel tested in the water bath between initial and recovered states.
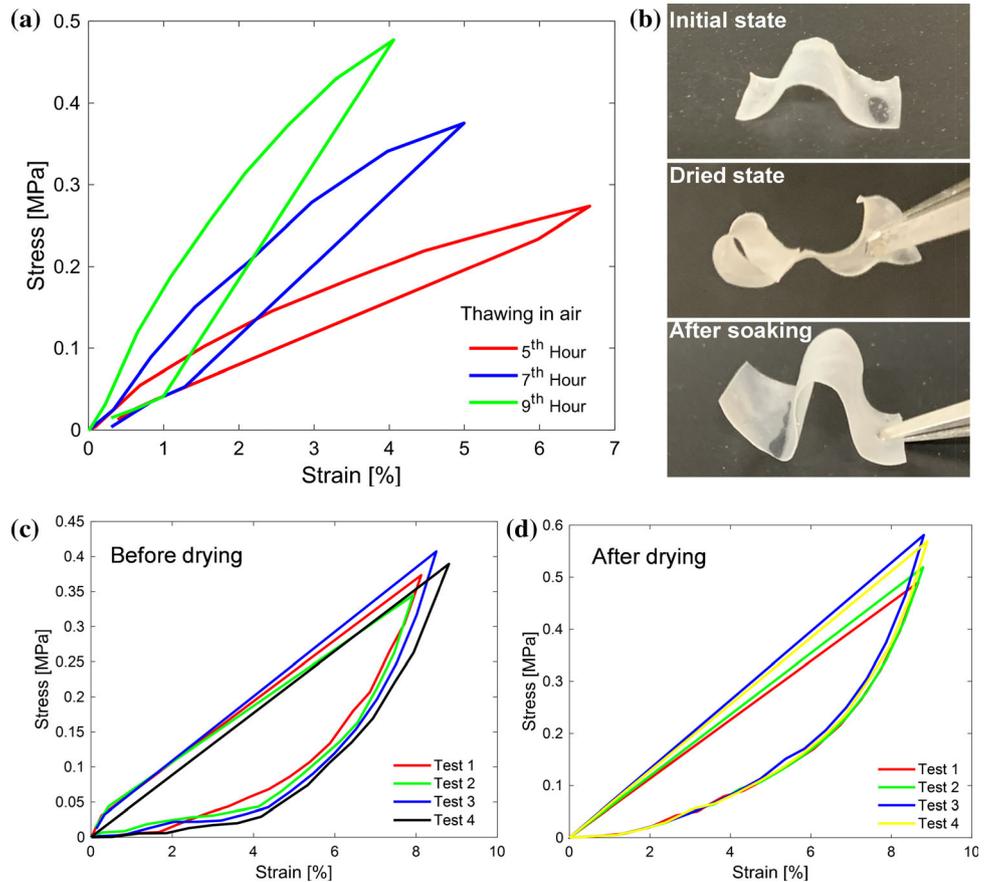
process, which means the hydrogel partially losses its elasticity if it has changed its initial moist state.

Electrical properties of the PVA/PVP hydrogel

To characterize the conductivity of the PVA/PVP hydrogel in different environments, its resistance was

measured when immersed in aqueous and exposed in air. As shown in Fig. 4, resistance of the sample tested was 19.18 KΩ ± 0.96% in liquid during a testing time of 16 min, this implies that the hydrogel can maintain a stable resistance level as long as its water content is stable. The hydrogel is conductive due to the formation of the polymer containing sulfuric acid and the effect of hydrogen ions in the water content of the hydrogel [36]. When the hydrogel was exposed in air, the resistance increased with time because the conductive links were eventually blocked during the water evaporation of the hydrogel. In the test, the hydrogel complete lost conductivity when it was dried. However, it was experimentally observed that the conductivity and volume of the hydrogel gradually recovered with soaking the dried hydrogel in the water. This property allows the PVA/PVP hydrogel to be used as a humidity sensor.

Furthermore, another variable causes the variation in resistance of the hydrogel is ambient temperature. The sample was placed in a water bath to only evaluate the temperature influence. As shown in Fig. 5, the resistance of the hydrogel sharply decreases with temperature increase from 20 °C to 43 °C, it has a temperature coefficient of ~ -0.79 KΩ/°C. This result provides a preliminary temperature calibration for the sensor application. While, a constant ambient liquid temperature can lead to a stable resistance level. Worthy mention that the hydrogel has a maximum temperature limit, in our experiments, the hydrogel cannot be heated over 45 °C, otherwise, the PVA-PVP hydrogel would dissolve in the liquid.
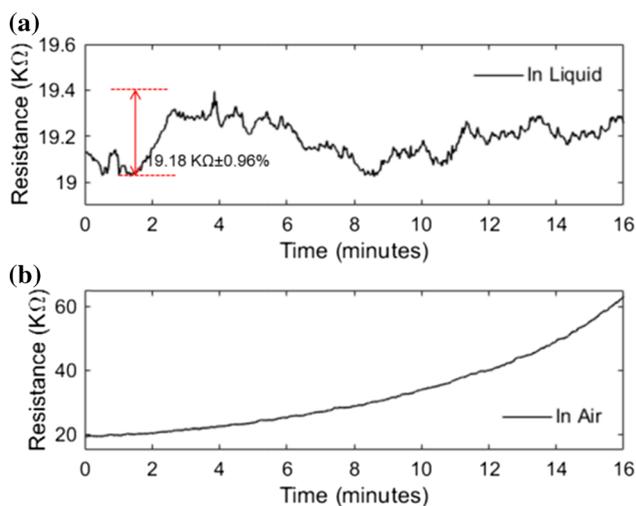

Figure 4 Resistance measurement of the MXene composited hydrogels in different ambient environments: **a** liquid; **b** air.
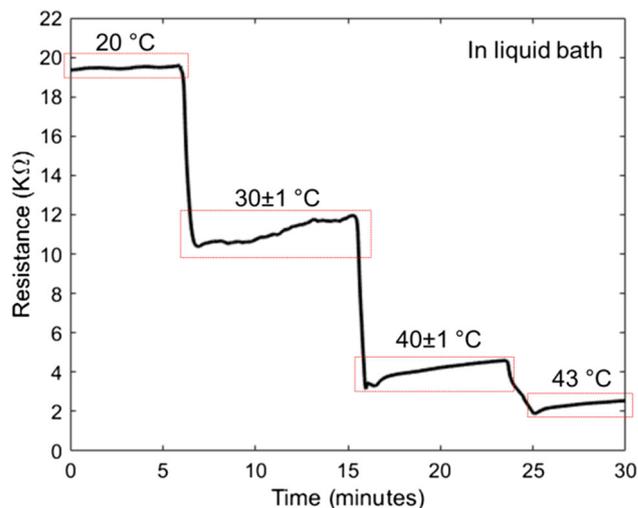

Figure 5 Resistance of the hydrogel measured at different water temperatures.

Therefore, the hydrogel sensor is not allowed to use in a hot environment (e.g., ~ 43 °C is the limit for the developed sensor).

PVA/PVP hydrogel-based piezoresistive property

The gauge factor (GF) defined as GF = $(\Delta R/R)/\varepsilon$ is used to demonstrate the piezoresistivity of the PVA/PVP hydrogel, where $\Delta R = R_s - R_r$, R_s and R_r are the resistance with and without applied strain ε, respectively. First, the hydrogel film was manually stretched to its maximum achievable strain of 48%, as shown in Fig. 6a, in which a smooth surface without breakage and crack was displayed. Then, tensile test was performed to investigate the sensor's sensitivity to different levels of strains. Four hydrogel samples with identical size were stretched under the strain from 12 to 48% with an increasing strain step of 12%, accordingly, the $\Delta R/R$ of the sample was recorded for each stretching test, as depicted by Fig. 6b. As expected, the $\Delta R/R$ increased with an increasing strain, an average $\Delta R/R$ of 38.8% was achieved at strain of 48%, giving a gauge factor of 0.8 for the testing. The $\Delta R/R$ increased with the stretching of hydrogel because the effective conductive path extended in accordance with the prolongation of the sample. This result reveals that the fabrication without using microwave may lead to an improved piezoresistivity, as no resistance change responding to strain up to 40% was observed for the PVA/PVP hydrogel fabricated following microwave-assisted

Figure 6 The electromechanical performances of the hydrogel-based strain sensor. **a** Illustration of prolongation of the PVA/PVP hydrogel sample under a maximum strain of 48%; **b** ΔR/R curve within a maximum strain range up to 48%.
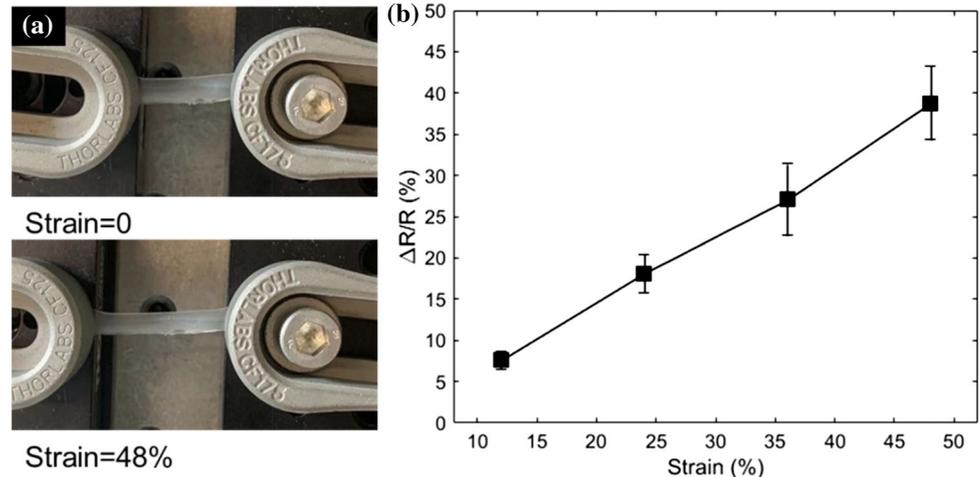
procedures [11]. The $\Delta R/R$ of the hydrogel may change at different ambient temperatures even the same strain is applied because the ion mobility inside the hydrogel is different with the different temperatures [37]. Even though the tensile test under different ambient temperatures is worthy of exploring, this is out of the research interest of this work.

Repeatability test of the PVA/PVP hydrogel was performed using the DMA. The sample was placed in the water bath of the DMA to avoid the negative influence of the natural water evaporation, the stretching and releasing were cyclically performed 160 times, no crack or damage was observed after the test, this implies that the sample can undergo more cycles [38]. The corresponding $\Delta R/R$s to the stretching and releasing were recorded as in Fig. 7. The $\Delta R/R$ increases with the applied strain over consecutive
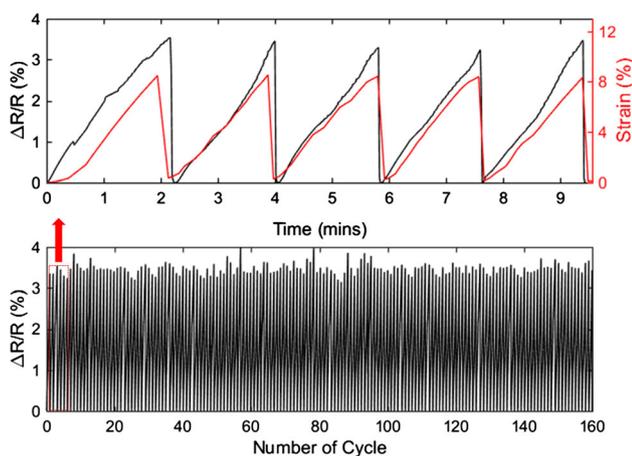

Figure 7 The repeatability test of the PVA/PVP hydrogel including: electromechanical hysteresis, piezoresistive sensitivity, and durability.

time, and drops corresponding to the releasing of the hydrogel. Electromechanical hysteresis is not obviously observed for our device. The result suggests that the hydrogel can reliably monitor its stretching and releasing processes. During the repeated stretching and releasing operation, an average $\Delta R/R$ of 3.6% ± 0.13% can be achieved for the maximum strain of 8.48% ± 0.07%. The strain variation is acceptable due to inevitable mechanical vibration of the DMA.

Example application of our hydrogel

Herein, we demonstrate a humidity/moisture sensor using our PVA/PVP hydrogel. A simple circuit was designed, as depicted in Fig. 8. An LED and our PVA/PVP hydrogel sensor were electrically connected in series, which was driven by a constant voltage input of 10 V. The LED can display different brightness caused by a varying resistance of the hydrogel if its surrounding humidity changed. We used a commercial humidifier to change the humidity of the environment surround the sensor. As mentioned previously, the dried hydrogel complete lost its conductivity, however, it gradually restored its moist state with a working humidifier. Consequently, the resistance of the dried hydrogel sample decreased, which was reflected by an increasing brightness of the LED light.

When a balance between the humidity of the surround environment and the moist level of the hydrogel itself was achieved, no more water can be sucked into the hydrogel. As a result, its resistance

Figure 8 **a** The resistance change of the red color-LED expressed by the dynamic process of brightness response (time 1–3), **b** to different humidity conditions applied on the PVA/PVP hydrogel sensor.
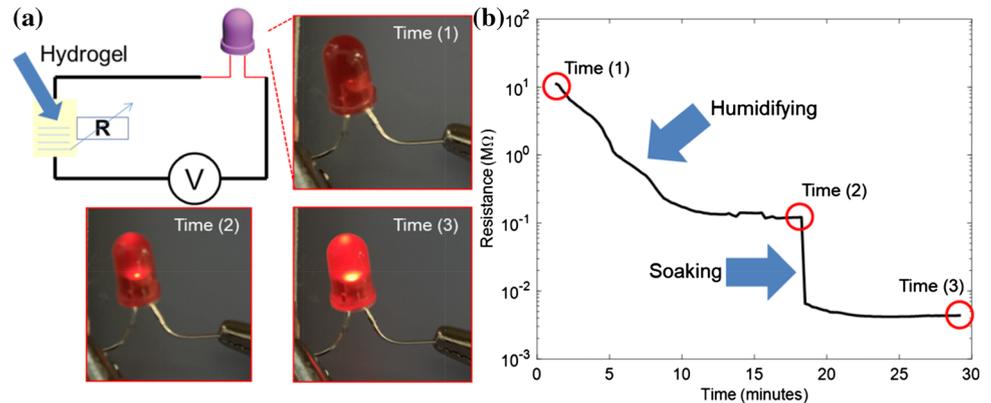
became stable, as illustrated by the time slot of 15 to 18 min of Fig. 8. However, directly immersing the hydrogel sensor in a drop of water caused further expansion of the hydrogel toward its original volume, which resulted in a sharp resistance decrease. This work proves the resistance variation of hydrogel sensor in response to the humidity of the environment, exhibiting potential applications in the field of humidity/moisture sensor or water leakage detection, etc. However, the PVA/PVP hydrogel is not practical for the detection of conductive liquid leakage, because it is hard to recognize the resistance change of the hydrogel coming from its wetting processes or the actual resistance of the liquid itself.

Conclusion

In this paper, physical hydrogel was synthesized using a mixture of PVA and PVP solutions with our proposed three-cycle freezing/thawing scheme. Our sample shows a high piezoresistivity of 38.8% for a strain up to 48%. Moreover, the amorphous nature and crystallites of the PVA/PVP blend was confirmed by XRD analysis. The structural, mechanical and piezoresistive properties of the hydrogel between its newly prepared and recovered states are compared, showing in-reversible performance degradation if it undergoes complete drying. The sensitivities to the ambient temperature and humidity are also studied, the results reveal that the resistance monotonously increases with the water loss of the hydrogel, and an increasing ambient temperature causes a resistance decrease. The durability and repeatability of the as-fabricated hydrogel were evaluated. Finally, an exemplary humidity/moisture sensor using our device was demonstrated. This new

hydrogel could find dosage monitoring applications in implantable drug delivery device which is deployed in a body liquid environment with consistent temperature, such that the output signal corresponds to the displacement of the hydrogel diaphragm alone.

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Declarations

Conflict of interest The authors declare that they have no competing financial interest.

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