JELLYFISH-LIKE HYDROGELS FOR TRANSPARENT, SELF-HEALING AND ULTRA-STRETCHABLE SENSORS AND ACTUATORS

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ABSTRACT
We present the synthesis and characterizations of jellyfish inspired biomimetic hydrogels for potential applications in transparent, self-healing, and ultra-stretchable sensors and actuators. Compared to the state-of-art, this work achieved five distinctive advancements: (1) highly transparent with ~85% transmittance within the visible light range; (2) ultra-stretchable without mechanical failure under more than 1100% applied strain; (3) excellent self-healing capability with broken pieces fully amended visually in 24 hours and piezoresistive gauge factor increased from 1.4 to 2.3; (4) highly adhesive with the self-bonding property, and (5) demonstrations of strain sensing and mechanical actuating for various potential applications.

KEYWORDS
Hydrogel; self-healing; stretchable; strain sensor; actuator

INTRODUCTION
Animal skins often possess both functions of sensing and actuation to detect external stimulations and to change shapes when needed, respectively. As such, biomimetic, skin-like materials have been widely investigated in recent years for wearable systems [1]. Many animals, such as jellyfish and leptocephalus (eel larvae) [2] have tissues that are transparent and ultra-stretchable, which are difficult to build in synthetic sensors and actuators. Specifically, these living skins have the self-healing property after being traumatized. On the contrary, electronic systems are often brittle and non-transparent. In the emerging field of flexible and stretchable electronic devices, unexpected mechanical damage is a main cause for device failures. One approach to address this mechanical failure issue is to learn and emulate living things in nature [3], [4] – such as the skin of jellyfish for the self-healing property to extend the service life of electronics.

MATERIAL PREPARATION
This bio-inspired hydrogel consists of two parts: LiCl for enhancing electrical conductivity and polymer backbone for self-healing and ultra-stretchable properties. Figure 2 shows the key chemistry of the material system and Figure 3a shows the polymer backbone structure, where free-radical polymerization is used in the synthesis process by adjusting the mass ratio of two monomers – acrylic acid (AA) and 3-dimethyl (methacryloyloxyethyl) ammonium propanesulfonate (DMAPS) as 2:1. The molar ratio of the cross-linker, N, N'-methylenebis(acrylamide) (MAA) is 2% in the prototype design. The synthesis process is initiated by ammonium persulfate (APS) with a molar ratio of 0.2% in 45wt% DI water at 50°C for 24 hours to solidify the hydrogel. In this experiment, the volume of DI water is 2.5 mL and the mixture solution is poured into a plastic petri dish with a diameter of 5 cm and the final hydrogel film thickness is around 1 mm. All chemicals were bought from Sigma-Aldrich and used as received without further treatment.

After the prototypes are constructed, the dynamic bonds between N’ (the red part) and -SO3- (the blue part) have ionization interactions, and -COOH (the green part) and -SO3- have hydrogen bond interactions to assist the self-healing process [5]. Specifically, after completely cutting and separating the synthesized material, covalent bonds suffer from irreversible damage at the cross-section. However, the two kinds of dynamic bonds can quickly recover after a period of time to heal the cutting damages. Both fixed covalent crosslinking (realized through MAA) and dynamic crosslinking (realized through the two kinds of aforementioned dynamic bonds) can enhance the mechanical stretchability. Under a very large stress, the dynamic bonds may break but they can be recovered.
when the stress is removed, while the covalent bonds help to prevent material failure at the same time.

The self-healing property is demonstrated by using two prototypes, which were dyed with titanium white and methyl blue as shown in Figure 3b. They were pressed together for a 24-hour waiting period under the room temperature environment without other stimulations and the two pieces were observed to be self-healed together. LiCl was added with monomers at the same time and well-dispersed to increase the electrical conductivity. Small crystals were observed after the freeze-drying process in Figure 3c (SEM, Hitachi TM-1000).

By changing the concentration of LiCl in the polymer, the conductivity of the hydrogel was adjusted as shown in Figure 4a, where the resistivity was measured by an electrochemical workstation (Gamry Reference 600), through electrochemical impedance spectroscopy (EIS). The resistivity was lowered to 44 ohm-cm as the LiCl concentration reached 4 mol/L. The addition of LiCl also helped to stabilize the material as shown in Figure 4b as LiCl lowered the vapor pressure to help keeping the water contents in the hydrogel [6]. Here, the concentration of 4 mol/L of LiCl was chosen in the prototype devices: (1) adding more LiCl didn’t enhance the conductivity; and (2) transparency degraded with high concentration of LiCl due to its insolubility in the polymer.

The combination of the polymer and LiCl helped to increase the electrical resistivity is much lower than that as compared to that of the traditional poly(vinyl alcohol) (PVA)-H3PO4 hydrogel [7] (Figure 5a). After healing at room temperature for 6 hours, the resistivity is only 2% higher than the original value (Figure 5b) [8]. The high conductivity of the hydrogel may be attributed to abundant charge carriers, including Li⁺ and Cl⁻, and H⁺.

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**Figure 3**: (a) Chemical structure of the polymer backbone. (b) Optical photos for the self-healing tests: the two hydrogel samples were dyed with titanium white and methyl blue and pressed together for 24 hours to become a single inseparable piece. (c) SEM image of the hydrogel showing the formation of small LiCl crystals.

**Figure 4**: The influences of LiCl contents for: (a) resistivity; (b) resistance vs time of the Jellyfish-inspired hydrogel.

**Figure 5**: (a) Resistivity comparison of traditional PVA-H3PO4 and the Jellyfish-inspired hydrogel; (b) Resistivity change of the Jellyfish-inspired hydrogel before and after healing under room temperature for 6 hours.
released from the carboxyl groups. During the self-healing process, the covalent bonds cannot be established again while they have little influence on charge carrier movements such that the electrical property can be restored nicely.

PROPERTIES

Transparency
The transparency of the Jellyfish-inspired hydrogel is characterized by Cary 5000 UV-Vis-NIR. The optical transmittance under the visible light range (400 nm-700 nm) for the material is ~85% as shown in Figure 6. The insert is a photograph showing a piece of hydrogel (about 2 ×0.5×0.1 cm³) on a paper with the “MEMES 2020 VANCOUVER CANADA” logo. The blue dash line is used to mark the hydrogel position to show good transparency of the hydrogel.

![Figure 6: Transmittance test showing ~85% transparency of the prototype hydrogel in the visible light range.](image)

Ultra-stretchability
Under the mechanical stress and strain test (strain rate was 1% per second performed on Instron and data was recorded by Bluehill software), it is observed that the film is ultra-stretchable and only fractures as the applied strain reached 1100% (Figure 7). For example, a piece of hydrogel with the original length of 1.4 cm can be stretched to a new length of 11.4 cm[8]. When the applied strain is less than 1100%, the dynamic bonds inside the hydrogel may break up first but they can be recovered when the applied stress is removed. However, for high strain-level more than 1100%, covalent bonds break up to result in the separation of the film.

Adhesive ability
Another interesting feature of the prototype material is its capability to adhere to human skin tightly. For example, Figure 8 is a photograph of the hydrogel which was peeled off from the human finger. It is observed that this hydrogel has a strong adhesive force to the finger which could be attributed to its abundant dynamic bonds[9] to form multiple connections with proteins and/or fats on the skin. This property makes it possible to attach prototype devices onto various surfaces easily.

APPLICATIONS

Strain sensor
Animal skin can sense the external stimulations by acting like a strain sensor. The prototype hydrogel devices also can act like a strain sensor as their electrical resistances were found to increase under a tensile strain.

![Figure 7: The stress-strain mechanical testing result showing the ultra-stretchable property of the prototype without failure up to 1100% applied strain.](image)

![Figure 8: An optical photo showing the prototype hydrogel was peeled off from the human finger with strong adhesive force to the skin.](image)

Qualitatively, under a tensile strain, the length of the hydrogel increases and the cross-section area decreases to reduce the transportation of ions (Li⁺, H⁺, and Cl⁻) such that electrical resistance increases. Quantitative testing results as a strain sensor (prototype device of 2×0.5×0.1 cm³) in Figure 9 shows the gauge factor (GF) of the sensor was 1.4. After the sensor was separated apart and self-healed (as described in Figures 3b), the GF increased to 2.4. One possible reason for the increase of GF is the micro-defects generated from the unrecoverable damages due to the cutting process. These defects are more sensitive to the outside stress to cause the increase of sensitivity.

Actuator
Another possible application is in the area of actuator. Using a polyethylene terephthalate (PET) film of 2×0.5×0.06 cm³ as the substrate with 1mm-thick hydrogel on top, the actuation function of the hydrogel is demonstrated. As the hydrogel absorbs or loses water, its volume expands or shrinks, respectively; while the volume of PET doesn’t change easily to induce the actuation of the whole structure. Figure 10a shows the simulation results of the process by finite element analysis (FEA). Qualitatively, under the dehydration/hydration process (a heated hot plate of 60 °C is utilized for the process control), the hydrogel volume will shrink/expand, respectively. The
The curvature of the actuator vs time on top of a hot plate is recorded in Figure 10b and the curvature reduced to 2 cm⁻¹ after 30 mins (the film was without LiCl to enhance the dehydration speed). Figure 10c shows an example of the actuator mimicking blooming process of a flower as the demonstration of an actuator, which is reversible during hydration and dehydration cycles.

CONCLUSIONS

In this work, we successfully designed and synthesized a hydrogel material system with high conductivity (44 ohm/m), high transparency (about 85% within the visible light range), ultra-stretchability (maximum strain of 1100%), self-healing ability (without external stimulation to recover 98% of conductivity after a 6-hour-long healing process in the ambient environment), and good adhesive capability. The hydrogel consists of polymer and LiCl to increase the electrical conductivity and water-retaining capability. Possible applications include strain sensing (measured GFs of 1.4 and 2.3 before and after the self-healing process for a prototype device) and the actuating function (the flower blooming process).

ABBREVIATIONS AND ACRONYMS

AA: acrylic acid;  
DMAPS: 3-dimethyl (methacryloyloxyethyl) ammonium propanesulfonate;  
MAA: N,N'-methylenebis(acrylamide);  
APS: ammonium persulfate;  
EIS: electrochemical impedance spectroscopy;  
DI water: deionized water;  
PVA: poly(vinyl alcohol);  
GF: gauge factor;  
PET: polyethylene terephthalate;  
FEA: finite element analysis.

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REFERENCES


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