nature portfolio

Peer Review File

Self-healing electronic skin with high fracture strength and toughness

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors reported an approach of mechanically tough and self-healable elastomers, conductors, and sensors in this work, and then integrated these self-healable materials into a soft robotic system with exteroceptive, nociceptive, and proprioceptive functionalities. This topic is interesting and promising. However, considering a vast of similar work about self-healable materials, the novelty involved in this work is not enough and should not be published in Nature Communications. Here are the detailed comments:

1. There are numbers of work about self-healing materials for soft gripper, Soft robotics: 2020, 7(6): 711-723, IEEE Robotics & Automation Magazine, 2020, 27(4): 44-55, ACS Appl. Mater. Interfaces 2019, 11, 10, 10328–10336, Adv. Mater. 2013, 25, 6709, Sci. Rob. 2017, 2, eaan4268; as well as about self-healing sensors for soft grippers: Materials Today Electronics, 2022, 1: 100003, Science Advances, 2022, 8(49): eabq2104, Applied Materials Today, 2022, 29: 101638. Moreover, the authors also had some similar work: Nature Communications, 2023, 14(1): 5026, Science, 2020, 370(6519): 961-965.

2. In this article, there are 3 main synthesized polymers, SHP-1, SHP-2 and SHP-3. But the ratios of DS and UPy are only 2 types, DS0.6-UPy0.4 and DS0.8-UPy0.2. What is the optimal ratio? Is there any other ratio performing better than SHP-1? Similarly, SHIC contains 5wt% of ILs, what is the reason for choosing 5%?

3. The authors emphasized self-healing materials for both actuators and sensors, corresponding videos (sensors, actuators, and the soft robotic system with sensing abilities) should be included to make it more convincing and easier to understand.

4. In Fig. 3g, the resistance of bending sensor decreased when increasing bending angle. However, the sensor is located at the back of the finger, which is likely to be stretched along with the angle increase. Then, the resistance should increase at the same time. Why the resistance decreases? In other words, why the compression effect dominates the elongation effect? Also, what is the method to fix the bending sensor? Please elaborate.

5. In Fig. 4d, how long time is needed for healing the scar? Is there any external force or other method to assist this healing process? Is the actuation air maintaining or stopped in this healing process?

6. In Fig. 4f, what is the signal of pressure? Is there any pressure sensor in this system? where is it and how to make it? In Fig. 4e, what is the blue dot? Please elaborate.

7. What is the full name of HU-PDMS? Or what is the meaning of ‘HU’?

8. Bending angle was measured in several figures of the paper, and this approach was illustrated in SFig. 23. Is this a standard approach for bending angle measurement?

Reviewer #2 (Remarks to the Author):

This work demonstrates soft robotics systems using novel, tough, self-healing polymers. The PCL-based polymer employs two kinds of dynamic bonds, namely DS-bond and UPy bond, where the DS bond facilitates self-healing and the UPy bond improves elasticity. Furthermore, the polymer can be functionalized by mixing with various conducting fillers. When mixed with an ionic liquid, the composite works as a multimodal sensing layer without losing its high mechanical properties. When mixed with silver flakes, it works as a stretchable electrode. When mixed with nickel powder, it works as a strain sensor. The importance of self-healability and sensing ability is clearly demonstrated in the pneumatic soft robotic system, which has never been reported. Therefore, I recommend the publication in Nature Communications. I recommend the authors revise the following points before the publication.

1. The current abstract has too much explanation on receptors and is too application-oriented. I recommend including more materials design aspects to properly address the readers.

2. The operation mechanism of nociceptor is not clear. In addition, how do the authors differentiate sensing of damage and strain? The output can be similar.

3. The nociceptor, proprioceptor, and exteroceptor are all sensing strain, and all the components seem to be replaced by the exteroceptor. What is the principle of designing these sensors separately?

4. The authors should show the sensing performance of proprioceptors against cyclic pressure loadings.

5. Supplementary figure 20a uses proprioceptor for describing nociceptor.

Reviewer #3 (Remarks to the Author):

Overall, the authors of this paper prepared tough self-healing elastomers using conventional methods, which did not reflect the innovation of the materials and preparation methods. The work did not show significant advantage in terms of sensing of soft robots. I strongly recommend the authors to carefully survey on the previous reports published in open literatures and add new scientific discoveries or technical advance. I regret that I could not be more positive in this study.

1. The title of the manuscript is confusing, what does “artificial multimodal receptors” mean? It appears only once in the manuscript, and it is in the title.

2. In the introduction part, the newest advances in synthesis of tough self-healing elastomers are not carefully introduced.

3. The polymer was not carefully characterized. (1) What’s the molecular weight? (2) The origin of self-healing lacks evidence, FTIR is necessary. (3) The origin of tough mechanical properties lacks evidence, What’s the degree of crystallinity?

4. what’s the ionic conductivity value of SHIC?

Point-to-Point Responses to Reviewers' Comments

Reviewer #1

The authors reported an approach of mechanically tough and self-healable elastomers, conductors, and sensors in this work, and then integrated these self-healable materials into a soft robotic system with exteroceptive, nociceptive, and proprioceptive functionalities. This topic is interesting and promising. However, considering a vast of similar work about self-healable materials, the novelty involved in this work is not enough and should not be published in Nature Communications. Here are the detailed comments:

=> We thank the reviewer for the suggestion and comment. We have now completely revised our manuscript as we believe it did not adequately highlight the unique aspects of our research in the previous version. We hope this revised manuscript more effectively conveys the strengths of our study.

Comment #1: There are numbers of work about self-healing materials for soft gripper, Soft robotics: 2020, 7(6): 711-723, IEEE Robotics & Automation Magazine, 2020, 27(4): 44-55, ACS Appl. Mater. Interfaces 2019, 11, 10, 10328–10336, Adv. Mater. 2013, 25, 6709, Sci. Rob. 2017, 2, eaan4268; as well as about self-healing sensors for soft grippers: Materials Today Electronics, 2022, 1: 100003, Science Advances, 2022, 8(49): eabq2104, Applied Materials Today, 2022, 29: 101638. Moreover, the authors also had some similar work: Nature Communications, 2023, 14(1): 5026, Science, 2020, 370(6519): 961-965.

=> We thank the reviewer for this suggestion and comment. Our research has unique advantages compared to each of the papers mentioned. I would like to elucidate how our study differs from the ones. Our materials are designed to be used for soft grippers and sensors with high fracture strength, high fracture toughness, and even efficient self-healability at room

temperature like human skin.

Many self-healing and tough materials have been reported. However, when ionic additives are introduced, the bonding between polymers inevitably weakens, leading to a reduction in mechanical properties. As a result, ion gels typically exhibit significantly reduced mechanical properties. In contrast, our developed SHIC maintains very high mechanical properties even in the ion gel state while also being capable of self-healing at room temperature. This unique characteristic is due to the UPy units, which provide robust network anchoring and crosslink the disulfide-based self-healing polymer. This approach is a key advantage of our material.

- Soft robotics: 2020, 7(6): 711-723. → The materials used in this research are based on the Diels-Alder reaction, which typically requires heating to 90 °C for self-healing. However, our materials can self-heal autonomously at room temperature. Additionally, materials based on Diels-Alder reactions are generally very stiff and tend to tear easily due to their low fracture toughness.

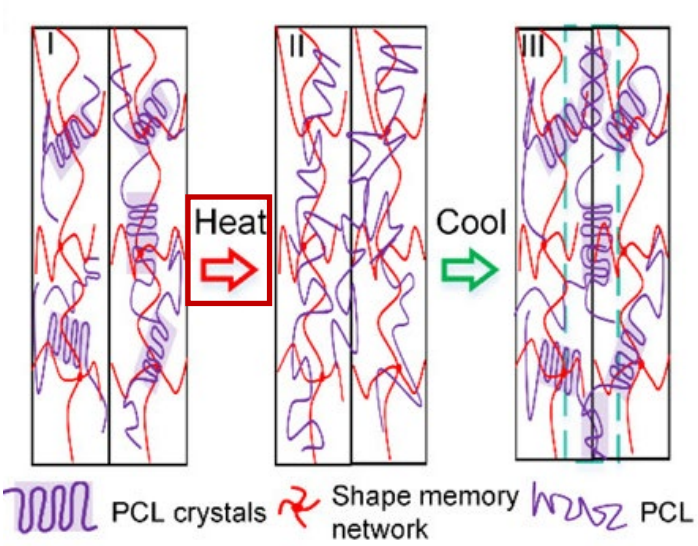
- IEEE Robotics & Automation Magazine, 2020, 27(4): 44-55. → Although the materials used in this paper can be self-healed at room temperature, the self-healing process is considerably time-consuming (7 days) and the mechanical properties are very poor (Maximum stress: 0.1 MPa). These weaknesses render this material impractical for soft robot application. In contrast, our self-healing materials (SHP-1, SHIC-1) can heal relatively quickly at room temperature (100% self-healing efficiency within 48 hours) and our SHIC has record-high mechanical strength and toughness (Maximum stress > 30 MPa), making them highly suitable for self-healing soft robot applications.

Reversible Reaction	Institution	E (MPa)	σ (Maximum) (MPa)	ε (Maximum) (%)	η at 25 °C (%)
Hydrogen	SupraPolix [18]	0.8	0.35	250	90 (24 h)
	ESPCI Paris [17]	0.25	3	550	90 (3 h)
	UC [21]	17	1.94	780	90 (24 h)
Metal ligand	SU [22]	0.5	0.25	4,500	90 (48 h)
Exchange	Cidetec [23]	0.05	0.5	3,000	97 (24 h)
DA	VUB	0.12	0.1	245	80–97 (Seven to 14 days)

UC: University of California; VUB: Vrije Universiteit Brussel; SU: Stanford University.

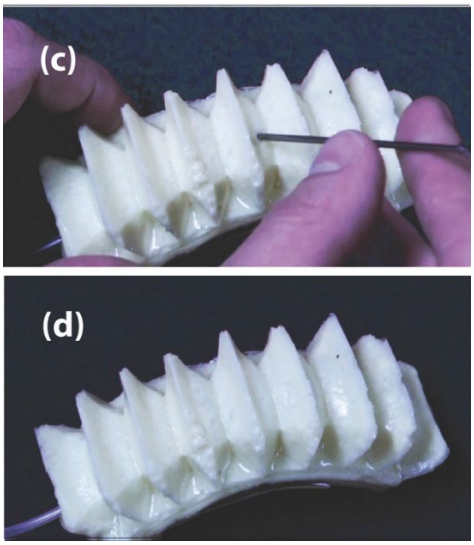
IEEE Robotics & Automation Magazine. **27**, 44-55 (2020).

- ACS Appl. Mater. Interfaces 2019, 11, 10, 10328–10336. → In this study, PCL was utilized as the self-healing agent in shape memory polymer. Consequently, this material can be self-healed at 80 °C above the T_m of PCL. In contrast, our materials (SHP-1, SHIC-1) are capable of self-healing autonomously at room temperature.



ACS Appl. Mater. Interfaces. **11**, 10328-10336 (2019).

- Adv. Mater. 2013, 25, 6709. → In this study, the material is a composite of PDMS (Ecoflex) with added polyaramid fibers, serving solely for the self-sealing process. While self-sealing materials are effective for sealing small holes or penetrations, their efficiency significantly decrease for large damages or cracks compared to self-healing materials. Furthermore, repeated punctures or damages can degrade the material's self-sealing capabilities over time. In contrast, our tough, self-healing materials (SHP-1. SHIC-1), capable of self-healing at room temperature not only effectively repair minor holes or penetrations but also heal large damages or cracks (Fig. 4e).



Adv. Mater. **25**, 6709 (2013).

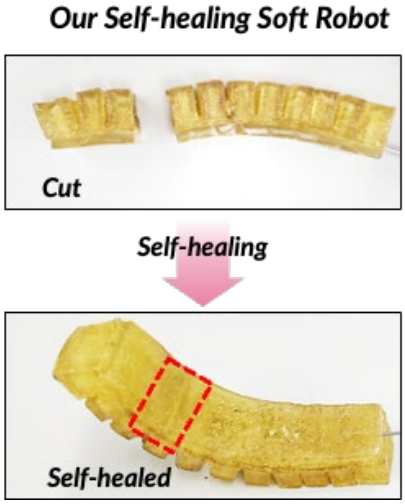
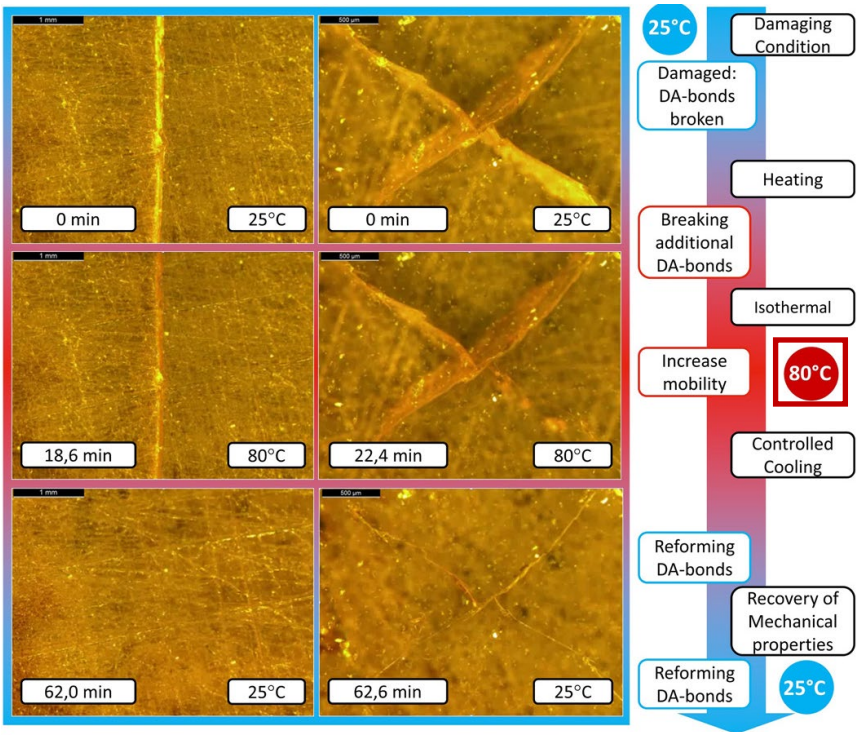


Fig. 4e| Photographs of self-healing soft gripper. After cutting the gripper in half, grippers were attached each other. After some time, self-healed gripper could be actuated well.

- Sci. Rob. 2017, 2, eaan4268. → The materials used in this research are based on the Diels-Alder reaction, which typically requires heating to 80 °C for self-healing. However, our materials can self-heal autonomously at room temperature. Additionally, materials based on Diels-Alder reactions are generally very stiff and tend to tear easily due to their low fracture toughness.



Sci.Rob. **2**, eaan4268 (2017).

- Materials Today Electronics, 2022, 1: 100003. → In this study, the self-healing polymer used for the self-healing sensor can be self-healed at 80 °C through Diels-Alder reaction. In contrast, our self-healing ionic conductors for sensors are capable of self-healing at room temperature through disulfide metathesis.

80 °C, 40 min	**Matrix**			**Composite**		
	pristine	after healing	efficiency	pristine	after healing	efficiency
Fracture strain (%)	183.5±12.1	181.3±9.4	96 %	86.7±29.6	79.6±21.7	92 %
Ultimate stress (MPa)	0.37±0.02	0.35±0.01	99 %	3.08±0.80	3.04±0.59	98 %
Young's modulus (MPa)	0.65±0.02 %	0.60±0.01	90 %	8.42±0.86	9.59±0.49	113 %

Table A.1: Mechanical properties of the pristine and healed materials used in this work: matrix DPBM-FT5000-R0.5 and composite DPBM FT5000-r0.6 + 20wt %CB260 + 1 wt% C15A.

Materials Today Electronics. **1**, 100003 (2022).

- Science Advances, 2022, 8(49): eabq2104. → In this study, the researchers fabricated a self-healing waveguide that transmits optical signals by attaching LEDs and photodiodes to a self-healing polymer. However, the flexible PCBs used to receive and recognize these signals are not capable of self-healing. Additionally, the pneumatic actuators are made from a composite of PDMS (Ecoflex) with added polyaramid fibers, serving solely for self-sealing. While self-sealing materials are effective for sealing minor holes or penetrations, their performance significantly decreases for larger

damages or cracks when compared to self-healing materials. In contrast, the entire robot system is capable of self-healing at room temperature because our soft gripper and stretchable sensors for soft robots are fabricated from our tough, self-healing polymer.

- Applied Materials Today, 2022, 29: 101638. → As introduced in this paper, numerous types of self-healing sensors have been extensively reported. However, research on the mechanical properties of these self-healing sensors has not been reported. Typically, self-healing sensors are fabricated by adding conductive fillers to self-healing polymers. During this process, the conductive fillers can interfere with the interactions between polymers, resulting in a decrease in mechanical properties (Response Fig. 1). In our study, disulfide moiety imparts self-healability and UPy moiety gives robust mechanical properties. Additionally, even with the addition of ionic liquid, the UPy group can maintain strong quadruple H-bonding, allowing the self-healing sensor to possess robust mechanical properties.

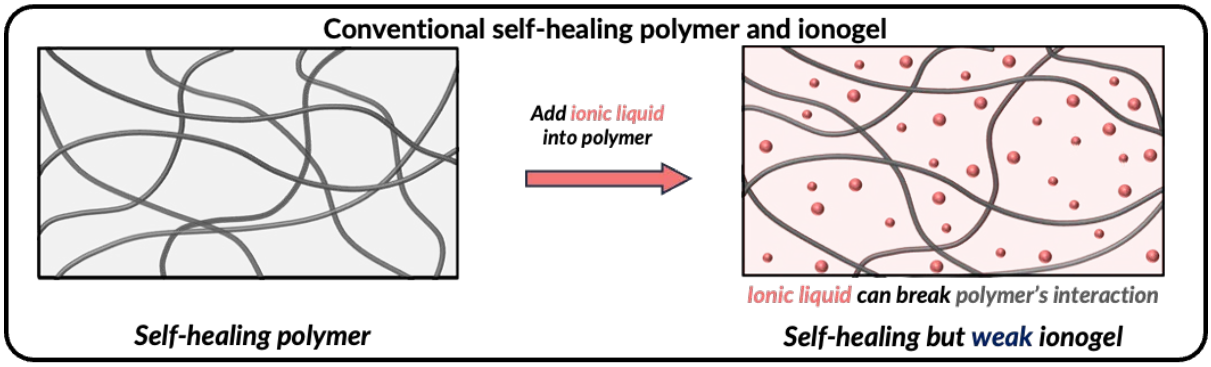


Fig. r1| Schematic illustration of the conventional self-healing polymer and ionogel. Conventional self-healing polymers exhibit weakened mechanical properties when ionic liquid is added because the ionic liquid disrupts the interactions between polymer chains.

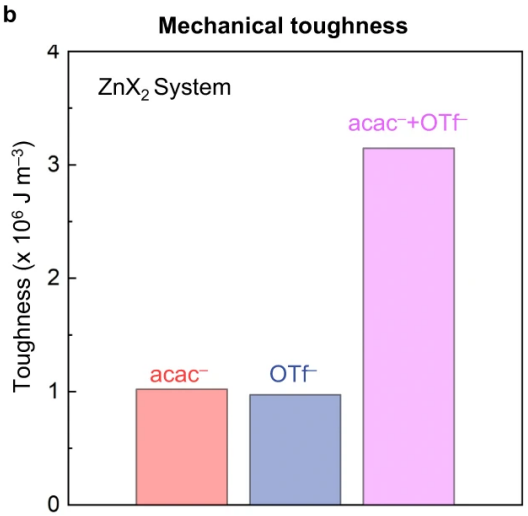
- Nature Communications, 2023, 14(1): 5026 → This study analyzed the changes in mechanical and dynamic properties according to the type of counter anions in the metal-ligand polymer. It reported the novel finding that introducing two different types of counter anions achieves mechanical

toughening and self-healing efficiency simultaneously.

In contrast, our tough, self-healing polymer has two dynamic bonds. One is disulfide moiety which enables efficient self-healing at room temperature and the other bond is UPy moiety which can enhance the mechanical properties. This approach not only allows the polymer to be tough and self-healable but also enables ionogel to maintain high mechanical properties and self-healing abilities.

Although both papers have similarities in possessing self-healing efficiency and mechanical toughening simultaneously, the mechanisms are different. Additionally, the extent of their mechanical properties is different. Compared to the material in the previous study, our tough, self-healing materials (SHP-1, SHIC-1) have approximately 30 times higher toughness than metal-ligand polymer using acac- + OTf- anions (Fig. 2d).

In addition, the materials used in the previous study utilized hydrophobic PDMS as the main polymer, resulting in poor miscibility with the ionic liquid and thus inducing consequent phase separation when fabricating ionogels. In contrast, SHP-1 employs hydrophilic polycaprolactone as the main polymer, facilitating excellent mixing with the ionic liquid and thus ensuring high ionic conductivity (Response Fig. 2).



Nat. Comm. **14**, 5026 (2023).

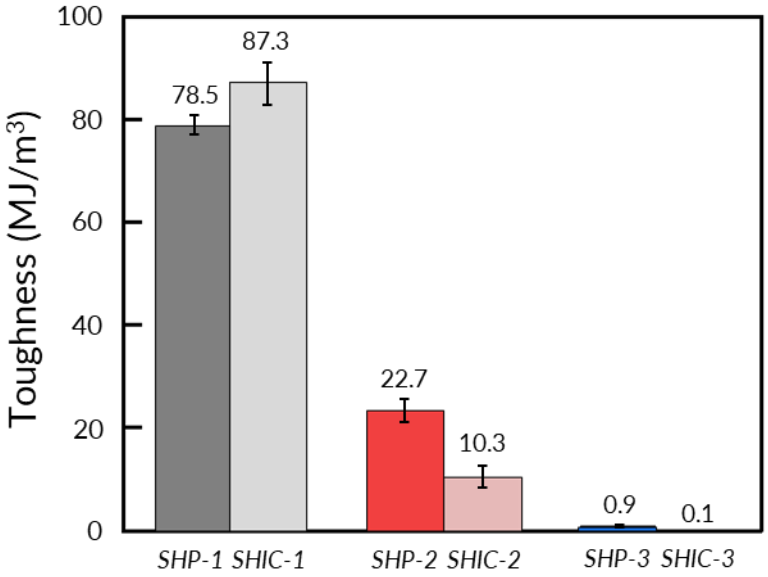


Fig. 2d| Photographs of self-healing soft gripper. Graph comparing toughness of materials. The data plotted represents the mean and standard deviation (n=3, n means number of independent experiment).

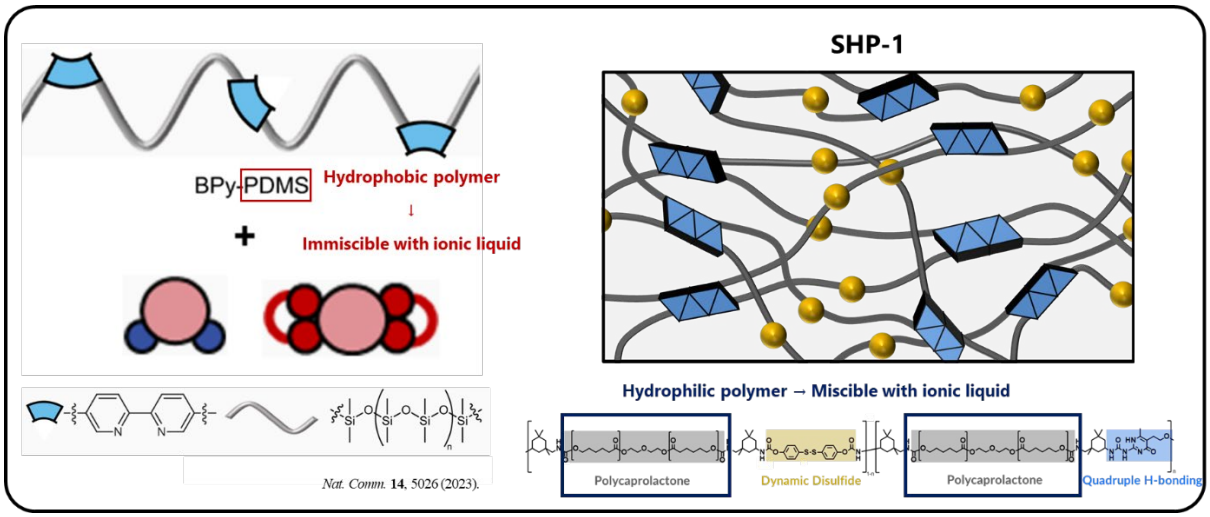


Fig. r2| Diagram illustrating the structural differences between the materials from the previous study and SHP-1.

- Science, 2020, 370(6519): 961-965 → The design of the artificial multimodal sensor used in this study is identical to that of the self-healing multimodal sensor employed in our research. However, there is a big difference in the polymers used for the fabrication of the sensors, The

sensor's active layer in the previous research utilized PVDF_HFP polymer with ionic liquid (EMIMTFSI). PVDF-HFP exhibits lower mechanical properties compared to polymers possessing hydrogen bonding. Furthermore, the addition of ionic liquid further reduces mechanical properties leading to a short lifespan of the sensor.

In contrast, the SHIC used for our multimodal sensor has sensitivity, self-healability, and high mechanical properties through novel polymer design at the molecular level.

Comment #2: In this article, there are 3 main synthesized polymers, SHP-1, SHP-2 and SHP-3. But the ratios of DS and UPy are only 2 types, DS0.6-UPy0.4 and DS0.8-UPy0.2. What is the optimal ratio? Is there any other ratio performing better than SHP-1?

=> We thank the reviewer for this suggestion and comment. To synthesize materials that concurrently exhibit self-healing properties and high mechanical strength, finding an optimal ratio of disulfide and UPy is very important. Disulfide moiety enhances the self-healing efficiency of the material but at the cost of diminished mechanical properties. Conversely, a higher proportion of UPy moiety improves mechanical strength but at too high concentrations of UPy moiety, the mobility of the polymer chains becomes restricted, resulting in lower self-healing efficiency. Notably, our additional measurements of $S_{0.4}$-$U_{0.6}$ revealed a marked decline in self-healing efficiency at room temperature (Supplementary Fig. 13b). Considering this observation, we have determined that SHP-1 ($S_{0.6}$-$U_{0.4}$) serves as the optimal balance, effectively harmonizing the self-healing and mechanical properties (Supplementary Fig. 13c).

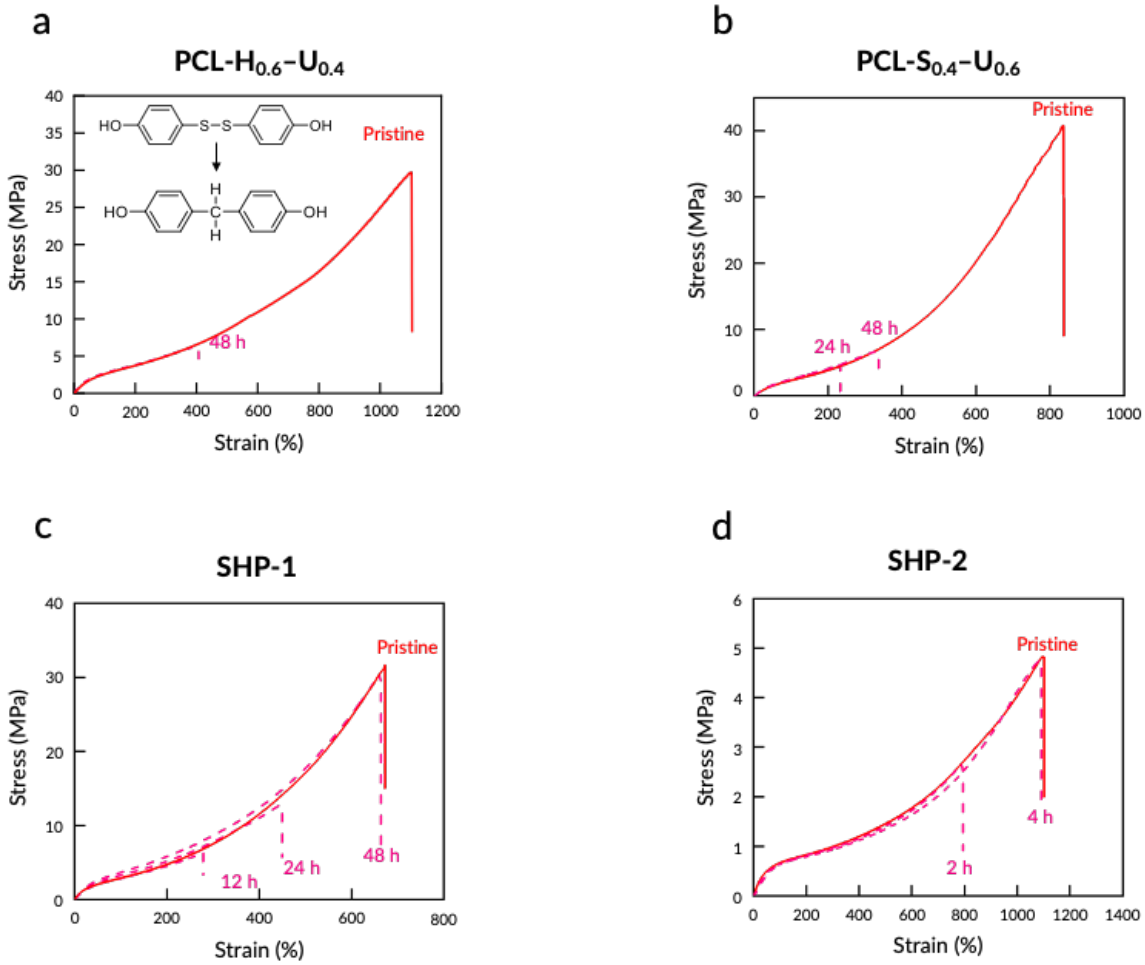
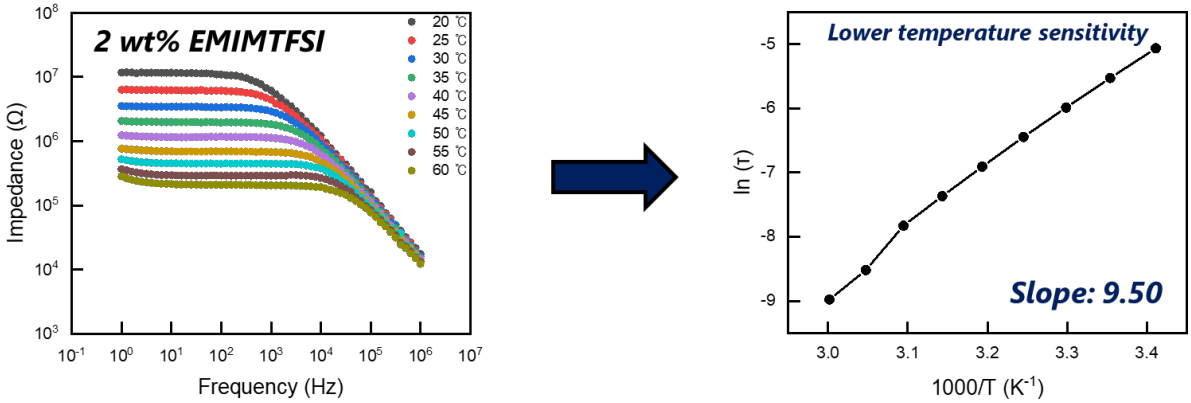


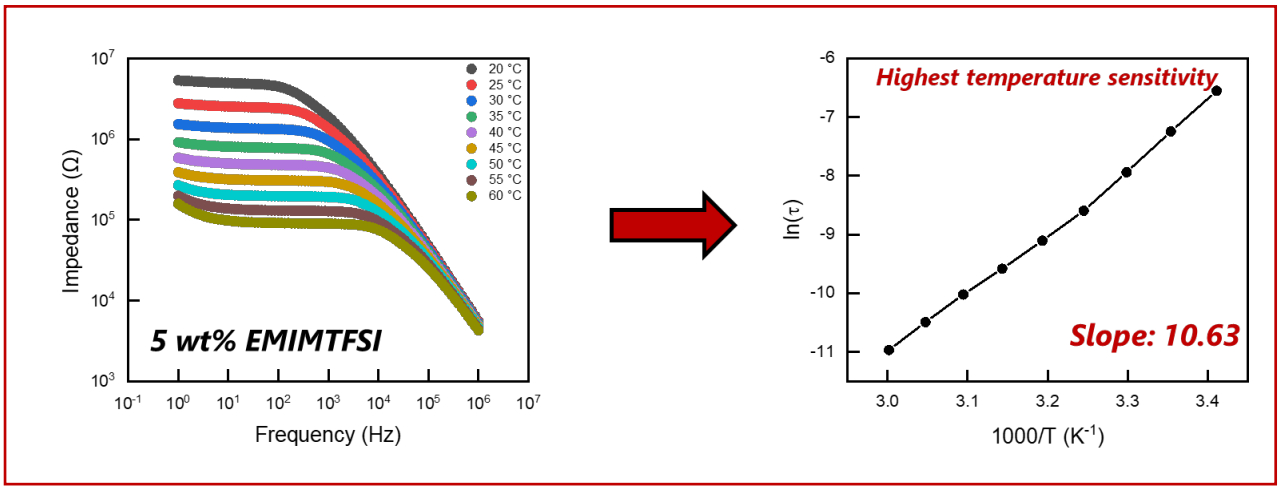
Fig S13| Self-healing tests of materials. Self-healing dog bone was cut into two pieces and then put any two pieces into contact. **a**, When 4,4'-dihydroxydiphenylmethane was used instead of bis(4-hydroxyphenyl) disulfide, the polymer was self-healed only 35% after 48 hours, indicating that disulfide imparts the self-healing properties of SHPs. **b**, PCL-$S_{0.4}$–$U_{0.6}$ was self-healed only 30% because strong because of restricted chain mobility for self-healing. **c**, However, appropriate ratio of aromatic disulfide and UPy made complete self-healing. **d**, And SHP-2, which had a higher ratio of disulfide, was self-healed in a faster time.

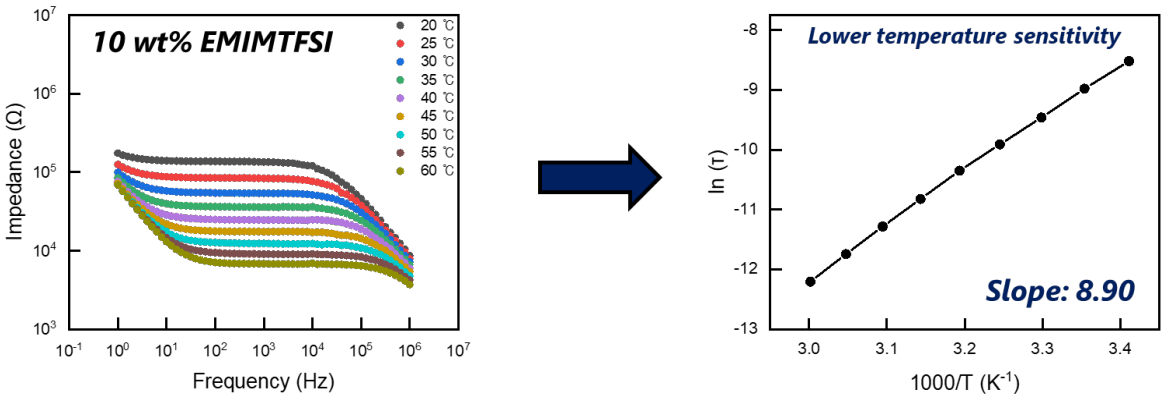
Similarly, SHIC contains 5wt% of ILs, what is the reason for choosing 5%?

=> We thank the reviewer for this suggestion and comment. We compared the temperature sensitivity using various concentrations of ionic liquid SHIC-1 as the active layer. Among them,

it was confirmed that 5 wt% EMIMTFSI SHIC-1 exhibited the highest temperature sensitivity, thus it was selected. The following data represent the Bode plot and temperature sensitivity according to the concentration of EMIMTFSI (Supplementary Fig. 18).







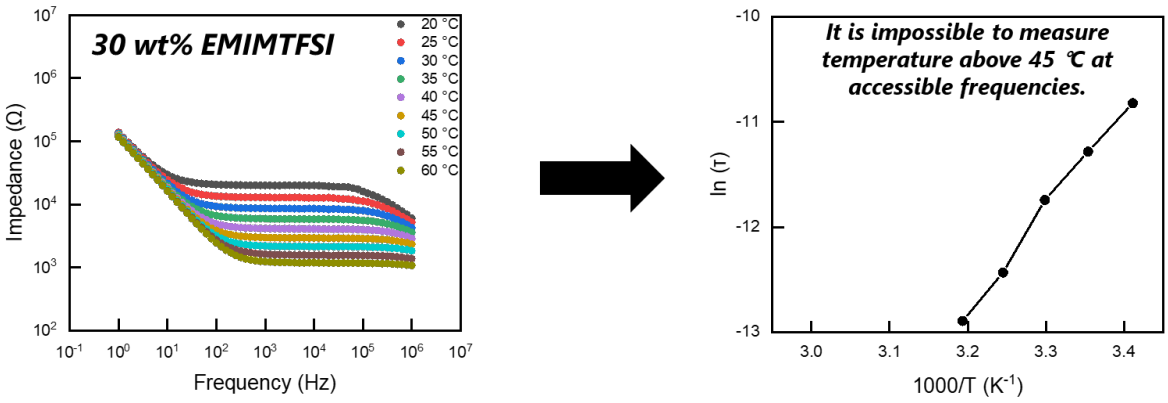


Fig. S18| Comparison of the temperature sensitivity of the multimodal sensor based on the amount of EMIMTFSI in the SHIC-1 active layer. a, Bode plot for the multimodal sensor of SHIC-1 with 2 wt% EMIMTFSI used as the active layer. **b**, Bode plot for the multimodal sensor of SHIC-1 with 5 wt% EMIMTFSI used as the active layer. **c**, Bode plot for the multimodal sensor of SHIC-1 with 10 wt% EMIMTFSI used as the active layer. **d**, Bode plot for the multimodal sensor of SHIC-1 with 30 wt% EMIMTFSI used as the active layer.

SHIC-1 with 5 wt% EMIMTFSI exhibited the highest temperature sensitivity, thus this SHIC-1 was selected as the active layer.

Comment #3: The authors emphasized self-healing materials for both actuators and sensors, corresponding videos (sensors, actuators, and the soft robotic system with sensing abilities) should be included to make it more convincing and easier to understand.

=> We thank the reviewer for this suggestion and comment. We have included supplementary videos demonstrating the sensors and gripper in operation when the soft robot grasps an object.

Comment #4: In Fig. 3g, the resistance of bending sensor decreased when increasing bending angle. However, the sensor is located at the back of the finger, which is likely to be stretched along with the angle increase. Then, the resistance should increase at the same time. Why the resistance

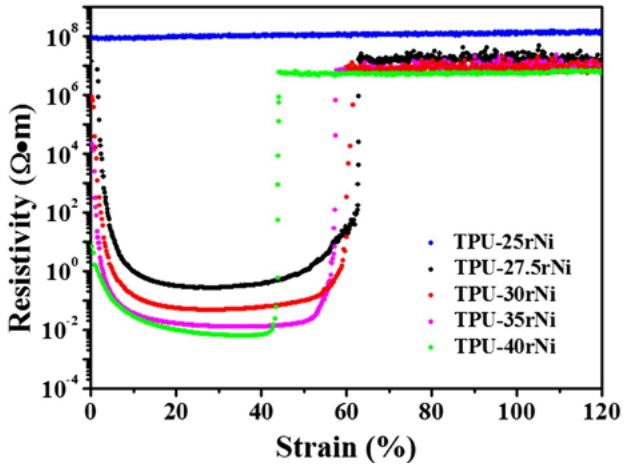
decreases? In other words, why the compression effect dominates the elongation effect?

=> We thank the reviewer for this suggestion and comment. As the reviewer suggested, it is indeed true that elongation effect predominantly occurs on the back of the finger. At low levels of strain, micro-Ni particles of the flexion sensor (proprioceptor) form a conductive network, leading to a sharp decrease in resistance (I). Then, beyond a certain threshold of strain, the conductive network is disrupted, resulting in a rapid increase in resistance (II), ultimately a high resistance value (III) (Supplementary Fig. 25). Consequently, when a soft gripper is actuated, a small strain is applied to the flexion sensor (proprioceptor), causing a dramatic decrease in resistance. We have included a reference figure from reference paper and a graph depicting the resistance change in our flexion sensors (proprioceptors) in response to strain. Additionally, we have revised the text in the manuscript accordingly to reflect these points. We appreciate the reviewer's insightful feedback.

Main text

'The final self-healing sensor is the flexion sensor., responsible for perceiving actuation. The flexion sensor is composed of conductive nickel particles embedded in SHP-3.[31] An experiment was conducted by applying strain to the sensor and measuring the change in resistance (Supplementary Fig. 25). At low levels of strain, micro-Ni particles of the flexion sensor form a conductive network, leading to a sharp decrease in resistance.[32] Therefore, when the flexion sensor is positioned on the outside of the gripper, a small strain is applied to gripper during actuation, resulting in a change in resistance. As a result, by measuring resistance, the sensor can provide feedback to enable reliable operation of pneumatic actuators. Fig. 3g illustrates the flexion sensor's response to increased small strain applied to the actuator, leading to an increase in bending angle and a decrease in resistance due to small strain. Additionally, the flexion sensor demonstrated reliable resistance changes corresponding to the bending angle, even with

repeated actuations of the gripper (Supplementary Fig. 26).'



Composites Part A: Applied Science and Manufacturing. **130**, 105757 (2020).

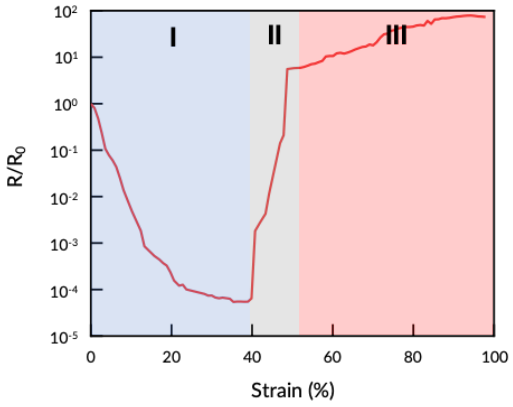


Fig. S25| Changes of resistance of flexion sensor as a function of strain. At low levels of strain, micro-Ni particles of the flexion sensor form a conductive network, leading to a sharp decrease in resistance (I). Then, beyond a certain threshold of strain, the conductive network is disrupted, resulting in a rapid increase in resistance (II), ultimately a high resistance value (III). Consequently, when a soft gripper is actuated, a small strain is applied to the flexion sensor, causing a dramatical decrease in resistance.

Also, what is the method to fix the bending sensor? Please elaborate.

=> We thank the reviewer for this suggestion and comment. First, thin SHP-2 film was attached between the two gripper fingers where bending occurs most effectively. Next two wire leads

were then attached, followed by the placement of a flexion sensor (proprioceptor) on top (Response Fig. 3). During each attachment process, localized heat was applied to enhance adhesion. Because all the gripper and the flexion sensor (proprioceptor) were made of same polymer composition, they exhibited excellent adhesive properties.

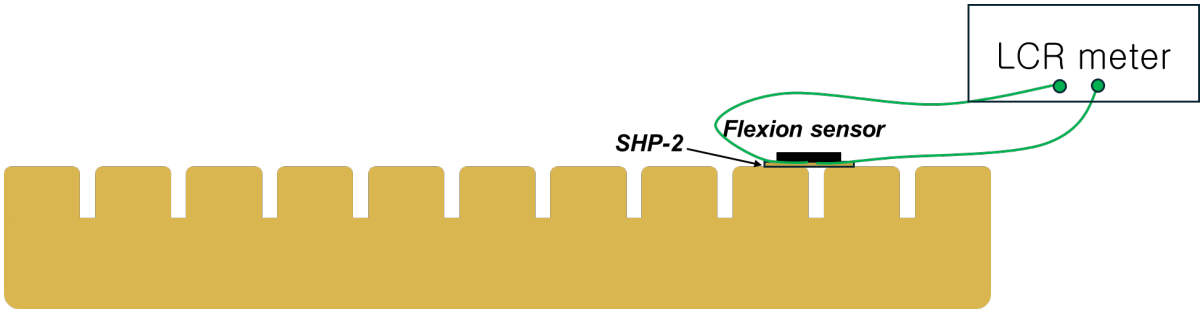


Fig. r3| Schematic illustration of the flexion sensor on the soft gripper.

Comment #5: In Fig. 4d, how long time is needed for healing the scar? Is there any external force or other method to assist this healing process? Is the actuation air maintaining or stopped in this healing process?

=> We thank the reviewer for this suggestion and comment. Normal operation was restored after 12 hours at room temperature. Additionally, applying heat enables self-healing within few minutes. When the damage sensor (nociceptor) recognize damage, we stopped operation for a period to allow for efficient self-healing, and then resumed operation.

Comment #6: In Fig. 4f, what is the signal of pressure? Is there any pressure sensor in this system? where is it and how to make it? In Fig. 4e, what is the blue dot? Please elaborate.

=> We thank the reviewer for this suggestion and comment. The pressure value refers to the pneumatic pressure applied to the soft gripper via syringe pump, and there is no pressure sensor

in sensing system. The blue dot also represents data including the actual pneumatic pressure applied using the syringe pump (Fig. 4g).

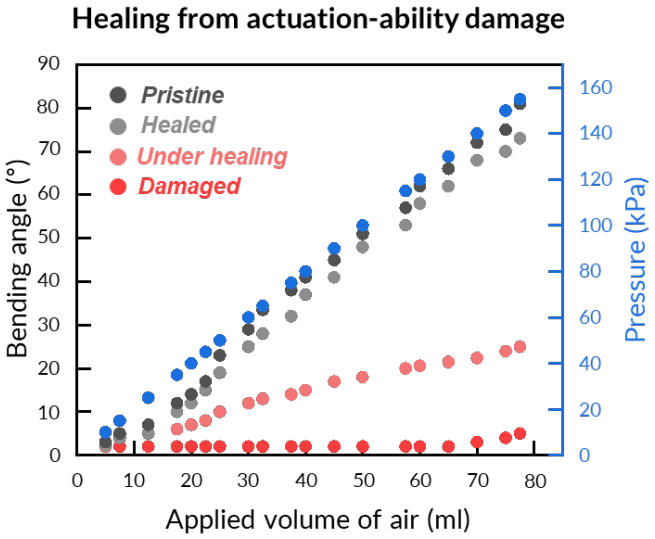


Fig. 4g| Graph showing the recovery of actuation ability after damage.

Comment #7: What is the full name of HU-PDMS? Or what is the meaning of 'HU'?

=> We thank the reviewer for this suggestion and comment. Hexamethylene Urea-PDMS is the full name of HU-PDMS. SHIC-1 which constitutes the active layer of the multimodal sensor is composed of hydrophilic PCL. In contrast, HU-PDMS composite with silver flake for self-healing electrode is relatively hydrophobic. This hydrophobic nature of electrode inhibits ion diffusion from active layer to the electrode, thereby preserving the sensing performance for long time (Supplementary Fig. 17).

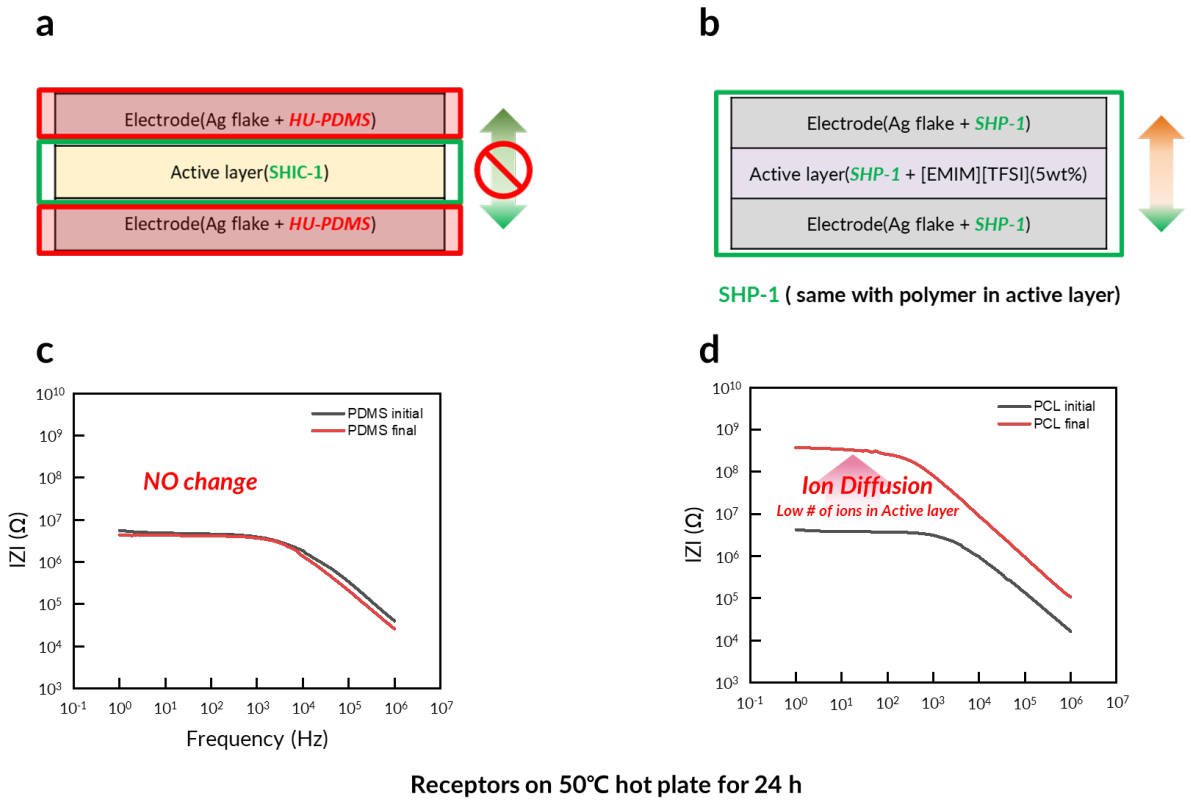
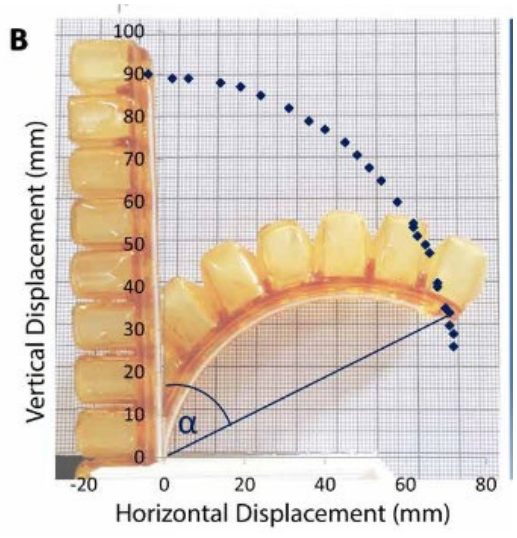


Figure S17| A comparison between self-healing artificial multimodal sensors with different active layers. a, Schematic illustration of self-healing artificial multimodal sensor with electrodes composed of HU-PDMS and Ag. **b,** Schematic illustration of self-healing artificial multimodal sensor with electrodes composed of SHP-1 and Ag. **c,** Because HU-PDMS was hydrophobic while PCL was hydrophilic, there was no significant change of impedance, after the sensors had been on 50 °C hot plate for 24 h. **d,** However, the recpetor consisting of same polymer (PCL) showed dramatic change of impedance after the same process. So, the HU-PDMS with Ag flake was chosen for self-healing stretchable electrodes.

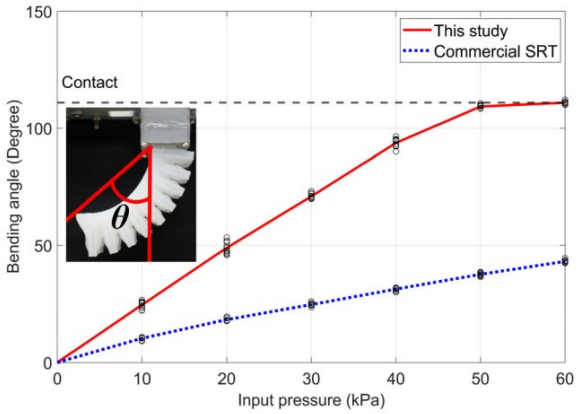
Comment #8: Bending angle was measured in several figures of the paper, and this approach was illustrated in Fig. S23. Is this a standard approach for bending angle measurement.

=> We thank the reviewer for this suggestion and comment. In the literature on soft grippers,

there are two main approaches to measure the bending angle: one directly measures the bending angle (θ) as we do, and the other measures the bending angle (2θ) by different method. In our study, we have chosen the method that is easier to measure. Below are examples that measure the bending angle in the same manner as our approach.



*Sci. Robot.***2**, eaan4268(2017).



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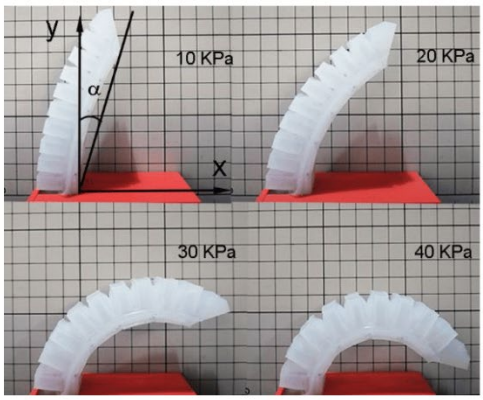
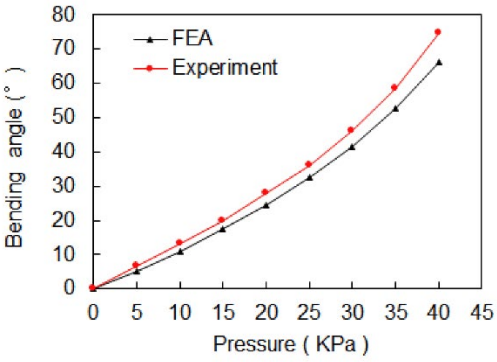


(a)



(b)

*Actuators.***11**, 246 (2022).

Reviewer #2

This work demonstrates soft robotics systems using novel, tough, self-healing polymers. The PCL-based polymer employs two kinds of dynamic bonds, namely DS-bond and UPy bond, where the DS bond facilitates self-healing and the UPy bond improves elasticity. Furthermore, the polymer can be functionalized by mixing with various conducting fillers. When mixed with an ionic liquid, the composite works as a multimodal sensing layer without losing its high mechanical properties. When mixed with silver flakes, it works as a stretchable electrode. When mixed with nickel powder, it works as a strain sensor. The importance of self-healability and sensing ability is clearly demonstrated in the pneumatic soft robotic system, which has never been reported. Therefore, I recommend the publication in Nature Communications. I recommend the authors revise the following points before the publication.

=> We appreciate these highly encouraging comments.

=> We have now carefully revised the manuscript according to the reviewer's comments and suggestions.

Comment #1: The current abstract has too much explanation on receptors and is too application-oriented. I recommend including more materials design aspects to properly address the readers.

=> We thank the reviewer for this suggestion and comment. As the reviewer recommended, we have revised the initial and middle sections of the abstract as follows.

'In physiology, the somatosensory system is vital for human perception, encompassing haptic, thermal, proprioceptive, and pain-sensing functions. Its resilient systems have inspired the development of stretchable, self-healing sensors. Self-healing ionogels, polymers swollen with ionic liquids, are promising but often suffer from weak mechanical properties. Here, we present a molecular design for mechanical tough and self-healable polymers and ionic conductors to develop a comprehensive artificial somatosensory system. Our polymer incorporates dynamic aromatic disulfide bonds (DS) and 2-ureido-4-pyrimidone (UPy) moieties, offering autonomous self-healing and high mechanical toughness. As a result, our self-healing ionic conductor (SHIC) demonstrates exceptional stretchability (850%), fracture strength (30 MPa), and toughness (87.3 MPa), the highest value among reported self-healing ionogels to the best of our knowledge.'

Comment #2: The operation mechanism of nociceptor is not clear. In addition, how do the authors differentiate sensing of damage and strain? The output can be similar.

=> We thank the reviewer for this suggestion and comment. When gripper grabs an object, relatively weak compressive force is applied to the damage sensor (nociceptor), resulting in a negligible decrease in resistance. Therefore, the damage sensor does not interpret the action of grabbing something as damage. However, when damaged by a sharp object, a sudden interruption in the electrical path leads to a large increase in resistance as observed (Supplementary Fig. 32). By assessing whether resistance increases or decreases, we can

differentiate between damage and strain. The following photos and data illustrate the difference in resistance changes when grabbing an object and when damage is inflicted by a sharp object.

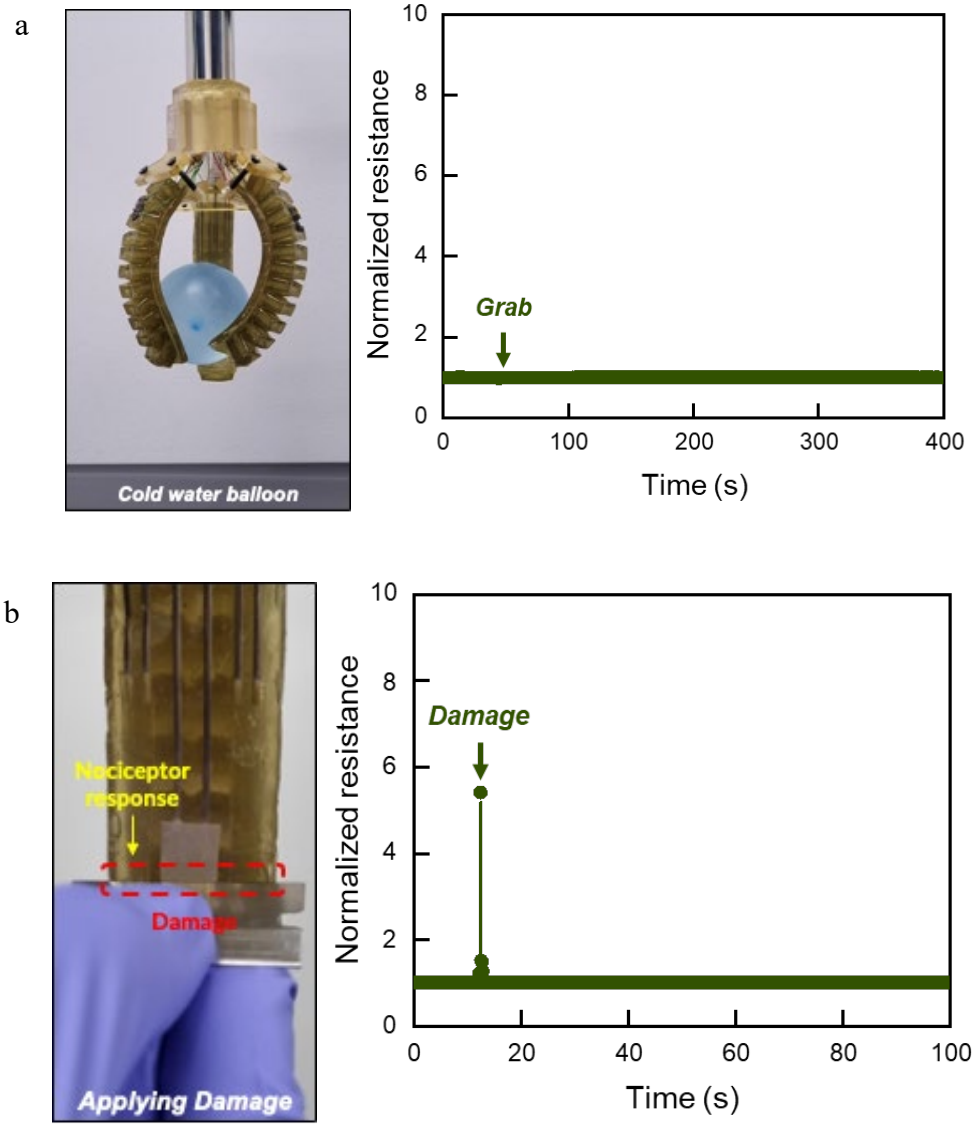


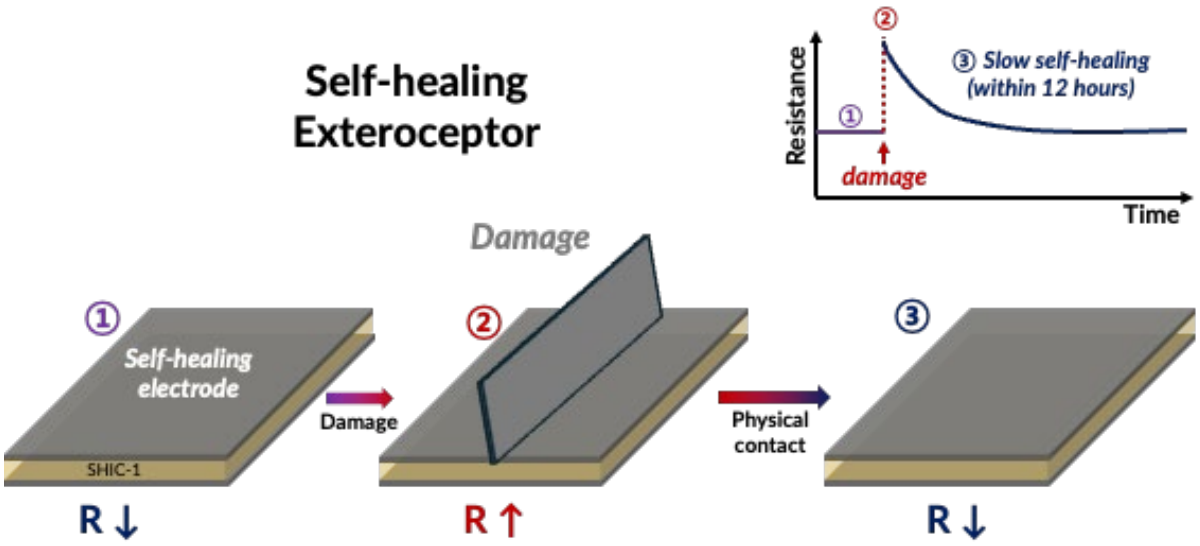
Figure S32| Difference in resistance change of the self-healing damage sensor when grabbing an object versus when damage is inflicted. a, When performing the action of grabbing an object, the resistance of the damage sensor remains almost unchanged. **b,** In contrast, when damage is inflicted, a significant resistance peak is observed. This experiment confirms that the damage sensor is responsive exclusively to damage.

Comment #3: The nociceptor, proprioceptor, and exteroceptor are all sensing strain, and all the

components seem to be replaced by the exteroceptor. What is the principle of designing these sensors separately?

=> We thank the reviewer for this suggestion and comment. For strain sensing (flexion sensor; proprioceptor), high sensitivity is required since the strain applied to the outer surface of the sensor is about 20%. The multimodal sensor (exteroceptor) is less sensitive to strain compared to flexion sensor. Therefore, to achieve more accurate sensing of bending angle, we have fabricated flexion sensor (proprioceptor) by incorporating SHP-3 and micro-Ni particles.

If the multimodal sensor (exteroceptor) is used as a damage sensor, we can't measure the extent of damage and just speculate occurrence of damage from the operational failure. Additionally, multimodal sensor (exteroceptor) needs to undergo self-healing, resulting in a longer time for electrical self-healing. In contrast, the self-healing damage sensor, composed solely of SHIC-1, achieves self-healing more easily through physical contact. Consequently, it is necessary to use only SHIC-1 (30 wt% ionic liquid) to measure damage.



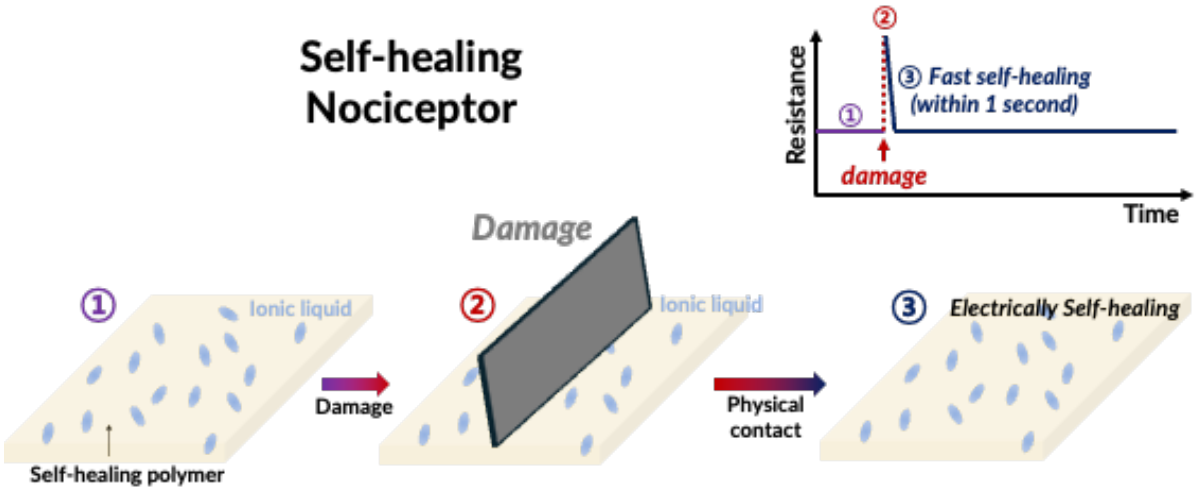


Figure S24| Difference in self-healing speed between the self-healing multimodal sensor and the self-healing damage sensor. a, In the case of the self-healing multimodal sensor, both the electrode and the active layer (SHIC with 5 wt% EMIMTFSI) need to undergo self-healing, resulting in a longer time for electrical self-healing. **b,** In contrast, the self-healing damage sensor, composed solely of SHIC-1, achieves self-healing more easily through physical contact. Additionally, due to the high concentration of ionic liquid (30 wt% EMIMTFSI), the self-healing speed is significantly faster.

Comment #4: The authors should show the sensing performance of proprioceptors against cyclic pressure loadings.

=> We thank the reviewer for this suggestion and comment. We confirmed that flexion sensors (proprioceptors) can sense bending angle accurately against cyclic pressure loadings (Supplementary Fig. 26).

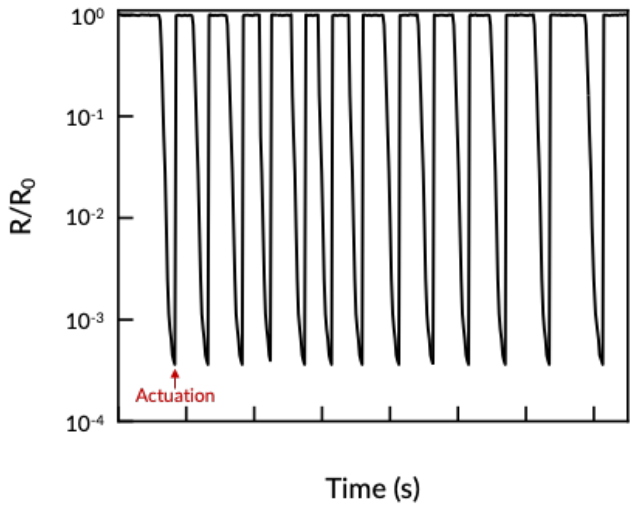


Figure S26| Cyclic test of the flexion sensor. It was confirmed that the flexion sensor exhibited consistent resistance changes when the soft gripper was actuated repeatedly.

Comment #5: Supplementary figure 20a uses proprioceptor for describing nociceptor.

=> Thank you for pointing out the typo. As the reviewer commented, we have corrected the mistake. We appreciate the reviewer's attention to detail.

Reviewer #3

Overall, the authors of this paper prepared tough self-healing elastomers using conventional methods, which did not reflect the innovation of the materials and preparation methods. The work did not show significant advantage in terms of sensing of soft robots. I strongly recommend the authors to carefully survey on the previous reports published in open literatures and add new scientific discoveries or technical advance. I regret that I could not be more positive in this study.

=> We thank the reviewer for the suggestion and comment. We have now completely revised our manuscript as we believe it did not adequately highlight the unique aspects of our research in the previous version. We hope this revised manuscript more effectively conveys the

strengths of our study.

Comment #1: The title of the manuscript is confusing, what does “artificial multimodal receptors” mean? It appears only once in the manuscript, and it is in the title.

=> We thank the reviewer for the suggestion and comment. The term ‘artificial multimodal receptor’ refers to an ‘exteroceptor’ capable of accurately sensing both temperature and strain simultaneously. To avoid any confusion, we have standardized the terminology to a single term ‘artificial multimodal sensor’.

Comment #2: In the introduction part, the newest advances in synthesis of tough self-healing elastomers are not carefully introduced.

=> We thank the reviewer for the suggestion and comment. As the reviewer correctly pointed out, reports on tough, self-healing elastomer have emerged recently. However, our material maintains its strong mechanical properties even with the addition of ionic liquid, resulting in the creation of a tough, self-healing ionogel. To the best of our knowledge, our self-healing ionogel possesses the highest mechanical properties among the reported self-healing ionogels. We have incorporated content into the main script as follow.

‘Fortunately, several studies have been reported to design and synthesize tough, self-healing polymers trying to solve trade-off relationship between self-healing capabilities and the mechanical properties of materials.[19,20,21,22,23] However, the self-healing ionic conductors designed for stretchable self-healing sensors exhibit significantly weaker mechanical properties when compared to their original self-healing polymers. This is attributed to the disruptive nature of ionic liquid used for electrical properties on the dynamic bonds. For these reasons, no studies have developed an approach for simultaneously realizing stretchable, mechanically tough and self-healing ionic conductor for stretchable self-healing sensors to the

best of our knowledge.'

Comment #3: The polymer was not carefully characterized. (1) What's the molecular weight? (2) The origin of self-healing lacks evidence, FTIR is necessary. (3) The origin of tough mechanical properties lacks evidence, What's the degree of crystallinity?

=> (1) We thank the reviewer for the suggestion and comment. The molecular weights of the materials we fabricated are as follows.

- PCL-$S_{0.4}$-$U_{0.6}$: M_n=24920 g/mol, M_w=102100 g/mol

- SHP-1: M_n=14190 g/mol, M_w= 52380 g/mol

- SHP-2: M_n=15150 g/mol, M_w=39530 g/mol

- SHP-3: M_n=12170 g/mol, M_w=25430 g/mol

As the UPy ratio increases, there is a tendency for the PDI to increase. This phenomenon is attributed to the strong bonds formed between UPy units, which do not easily break down in GPC solvents (THF), leading to the formation of domains within the solvent.

=> (2) We thank the reviewer for the suggestion and comment. Polymers containing aromatic disulfide groups can undergo disulfide exchange at room temperature.[11,12] Consequently, even in the absence of applied damage, a continuous disulfide exchange can occur at room temperature, making it challenging to detect self-healing process via disulfide exchange using FTIR spectroscopy due to this ongoing process. We only confirmed that polymer contains disulfide bonds through FTIR spectroscopy (Response Fig. 3).

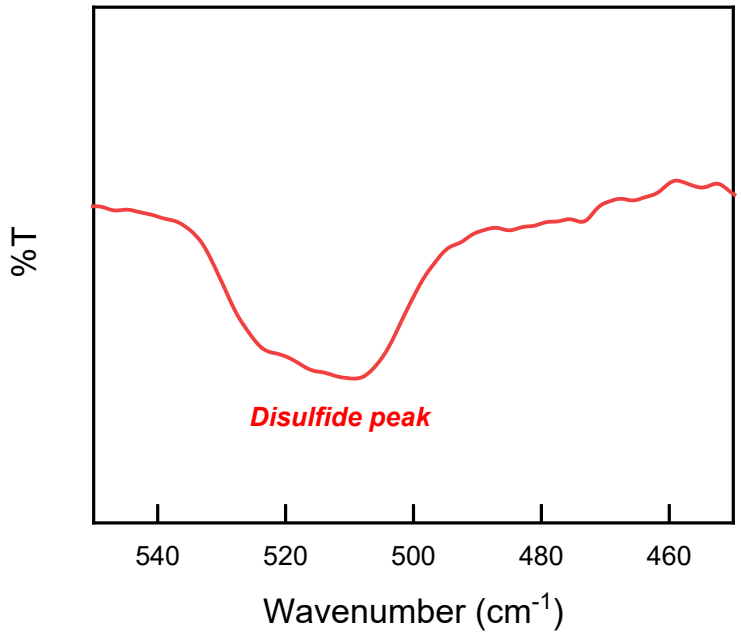


Fig. r3| Disulfide peak in the FTIR measurement of SHP-1.

To verify that self-healing primarily occurs through disulfide exchange, we synthesized PCL-$H_{0.6}$-$U_{0.4}$ using Bis(4-hydroxypheniyl) methane, which contains an alkyl group, as the dynamic bond instead of bis(4-hydroxyphenyl) disulfide, which contains disulfide groups, and compared its self-healing properties with SHP-1 (PCL-$DS_{0.6}$-$U_{0.4}$). Our findings show that our SHP-1 exhibited nearly 100% self-healing efficiency after 48 hours, whereas PCL-$H_{0.6}$-$U_{0.4}$ showed only about 35% efficiency (Supplementary Fig 13). These control tests indicate that disulfide exchange plays a significantly more crucial role in self-healing of our polymer system than hydrogen bonding.

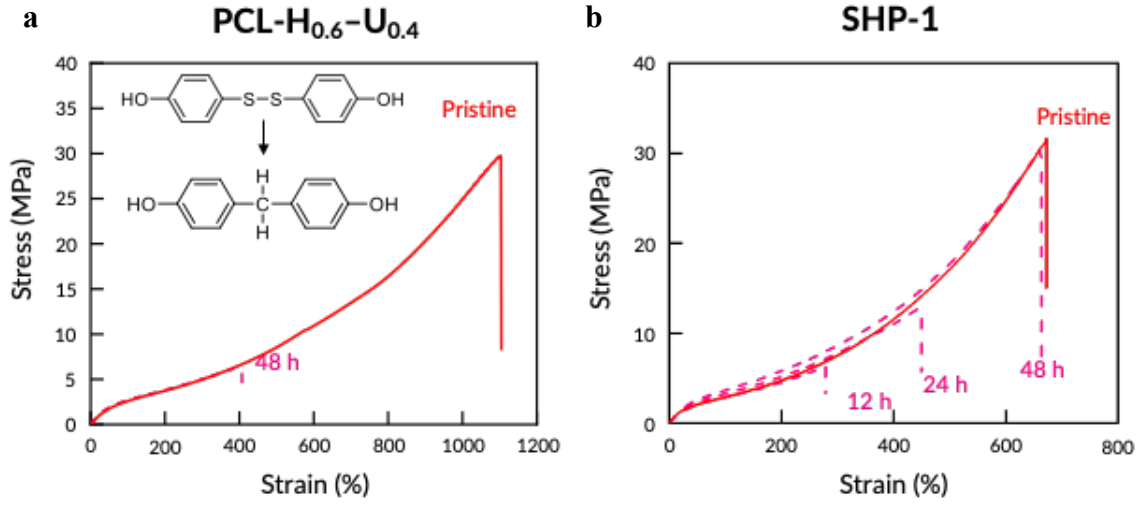


Fig. S13| Self-healing tests of materials. Self-healing dog bone was cut into two pieces and then put any two pieces into contact. **a,** When 4,4'-dihydroxydiphenylmethane was used instead of bis(4-hydroxyphenyl) disulfide, the polymer was self-healed only 35% after 48 hours, indicating that disulfide imparts the self-healing properties of SHPs. **b,** PCL-$S_{0.4}$–$U_{0.6}$ was self-healed only 30% because strong because of restricted chain mobility for self-healing.

=> (3) We thank the reviewer for the suggestion and comment. Due to our material being an amorphous polymer, they do not exhibit peaks indicating specific crystallinity in the SAXS (Small-Angle X-ray Scattering) data (Response Fig. 4).

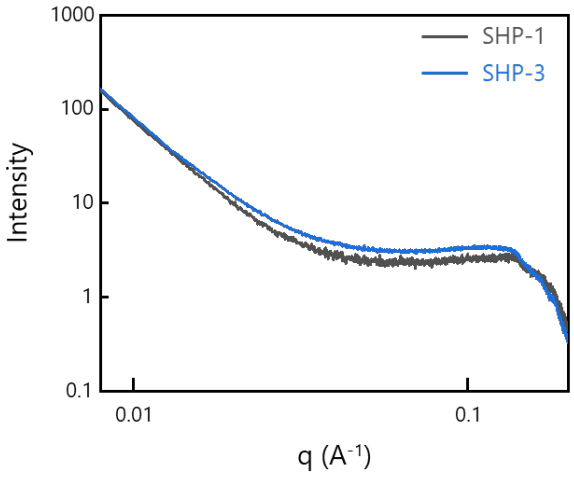


Fig. r4| SAXS data of SHP-1 and SHP-3.

The superior mechanical properties of our materials stem from the chain rigidity induced by strong hydrogen bonding between UPy-urea units. This level of chain rigidity can be inferred from the T_g (glass transition temperature); for example, it is evident that SHP-1, which contains UPy, exhibits a higher T_g than SHP-3, which doesn't have UPy. Moreover, upon the addition of ionic liquid, the extent to which T_g decreases is significantly smaller for SHIC-1, indicating that the strong UPy bonds are maintained even in the ionogel state (Supplementary Fig. 8).

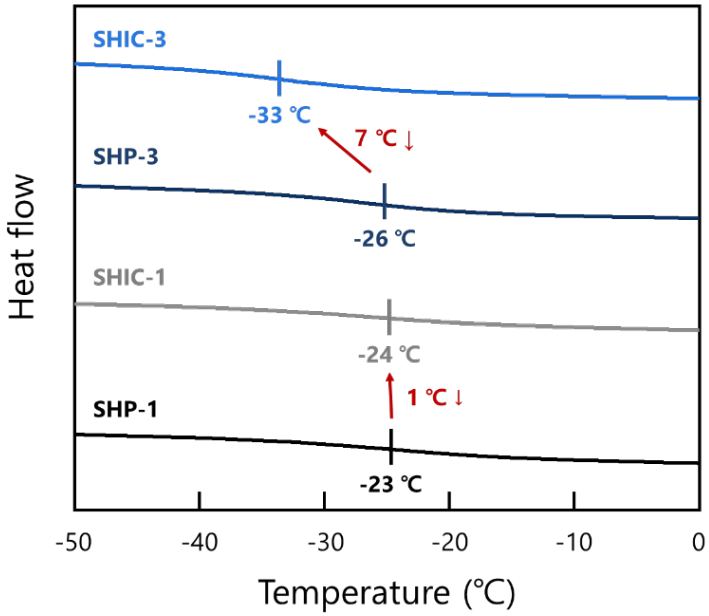


Fig. S8| DSC data of self-healing materials. In the case of SHP-1 containing UPy moiety, the addition of ionic liquid does not significantly affect the chain mobility, resulting in little to no change in the glass transition temperature (T_g). In contrast, for SHP-3 lacking the UPy moiety, the addition of ionic liquid disrupts the inter-chain interactions, thereby increasing chain mobility and leading to a decrease in the T_g value.

Furthermore, the chain rigidity due to strong UPy bonding can be verified through rheological measurements (Supplementary Fig. 7). Analyzing the frequency at which the crossover points of G' and G'' occurs provides insights into the material properties. If the crossover point occurs at a higher frequency, it indicates that the material exhibits a more

liquid-like property. In the case of SHP-1, which possesses UPy, it is observed that neither the polymer nor the ionogel exhibits a crossover point. However, for SHP-3, doesn't have UPy, both the polymer and ionic conductor show crossover points, with the ionic conductor having a crossover point at approximately 10 times higher frequency than the polymer. These results confirm that the strong UPy bonding contributes to the high mechanical properties of both polymer and ionogel.

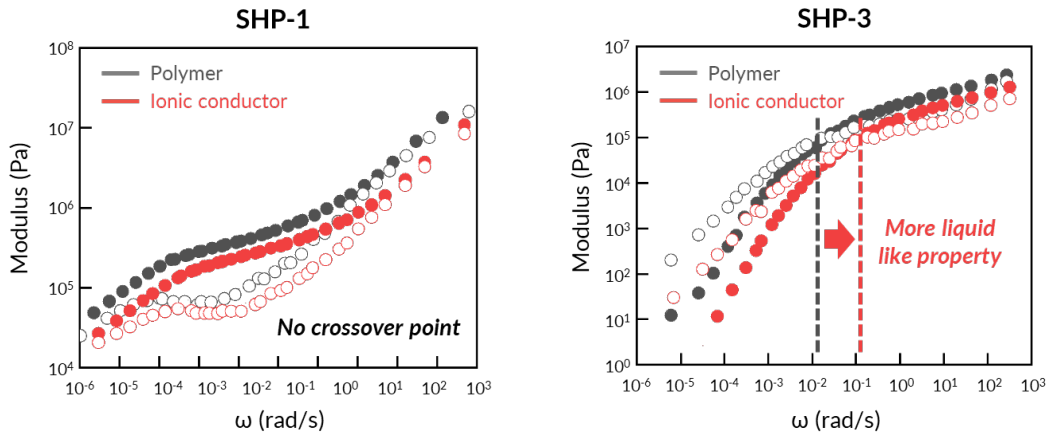


Fig. S7| Master curves of self-healing materials. b, Master curves of SHP-1 and SHIC-1. **d,** Master curves of SHP-3 and SHIC-3.

Comment #4: what's the ionic conductivity value of SHIC?

=> We thank the reviewer for the suggestion and comment. Our SHIC-1 serves as the active layer in the sensor, with the highest temperature sensitivity achieved by incorporating 5 wt% EMIM TFSI. The ion conductivity is measured at 3.04×10^{-6} S/cm. However, to utilized SHIC as an electrode, an ionic conductivity of 10^{-5} S/cm or higher is essential. When adding 30 wt% of EMIM TFSI, it was observed that ionic conductor exhibits a remarkable ionic conductivity of 2.30×10^{-4} S/cm, along with robust mechanical properties (Supplementary Fig. 12). Among the reported self-healing ionogels, SHIC-1 exhibits notably high mechanical properties within our current understanding (Supplementary Table. 1).

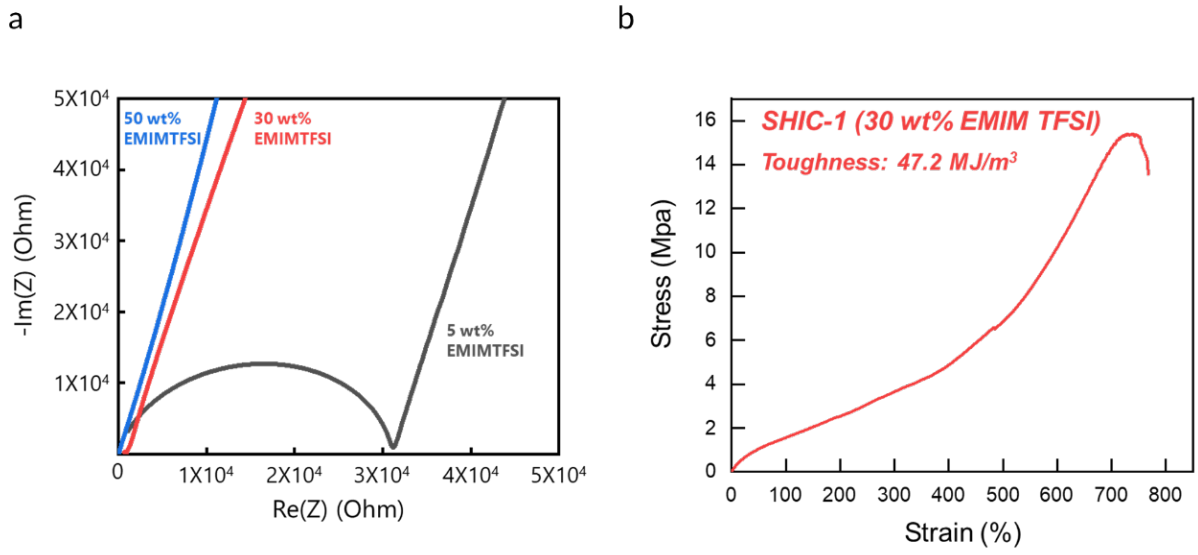
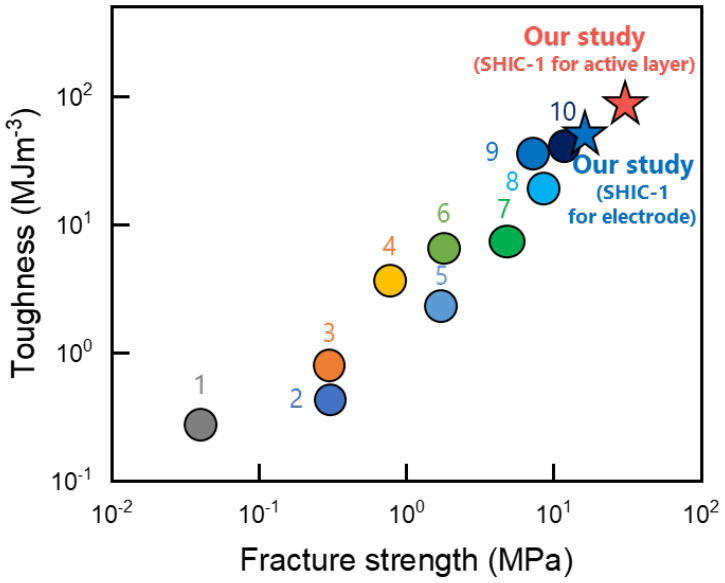


Fig. S12| Nyquist plot for SHIC-1 as a function of the amount of ionic liquid and the stress-strain curve (S-S curve) for SHIC-1 with 30 wt% EMIMTFSI. a, The ionic conductivity value increased with the amount of added ionic liquid. SHIC with 5 wt% EMIMTFSI: 3.04×10^{-6} S/cm, SHIC with 30 wt% EMIMTFSI: 2.30×10^{-4} S/cm, SHIC with 50 wt% EMIMTFSI: 3.20×10^{-3} S/cm. **b,** SHIC with 30 wt% EMIMTFSI show tough mechanical property.



	Toughness	Fracture strength	Ionic conductivity	Application

1	0.04 MPa	0.28 MJ/m^3	10^{-3} S/cm	Strain sensor
2	0.3 MPa	0.45 MJ/m^3	-	-
3	0.3 MPa	0.8 MJ/m^3	1.2×10^{-3} S/cm	-
4	0.7 MPa	3.66 MJ/m^3	3.49×10^{-4} S/cm	Wearable sensor
5	1.6 MPa	2.4 MJ/m^3	4×10^{-3} S/cm	Strain sensor
6	1.75 MPa	6 MJ/m^3	10^{-4} S/cm	Flexible keyboard
7	5 MPa	7.5 MJ/m^3	2×10^{-3} S/cm	Strain sensor
8	8 MPa	20 MJ/m^3	4×10^{-5} S/cm	Triboelectric nanogenerator
9	7.5 MPa	35 MJ/m^3	10^{-4} S/cm	Strain sensor
10	12.6 MPa	45 MJ/m^3	-	-
SHIC-1 (active layer)	30 MPa	87.3 MJ/m^3	3×10^{-6} S/cm	Self-healing artificial multimodal sensor
SHIC-1 (Electrode)	15 MPa	47.2 MJ/m^3	2.3×10^{-4} S/cm	Damage sensor

Table. S1| Comparison of the ionic conductivity and mechanical toughness of ionic conductors mentioned in the references.

References

1. Zhang, L. et al. Self-Healing, Adhesive, and Highly Stretchable Ionogel as a Strain Sensor for Extremely Large Deformation. *Small.* **15**, 1804651 (2019).

2. Kaimo, E., Yasui, T., Iida, Y., Gong, J. & Matsuyama, H. Inorganic / Organic Double-Network Gels Containing Ionic Liquids. *Adv. Mater.* **29**, 1704118 (2017).

3. Tamate, R. et al. Self-Healing Micellar Ion Gels Based on Multiple Hydrogen Bonding. *Adv. Mater.* **30**, 1802792 (2018).

4. Xu, L. et al. A transparent, Highly Stretchable, Solvent-Resistant, Recyclable Multifunctional Ionogel with Underwater Self-healing and Adhesion for Reliable Strain Sensors. *Adv. Mater.* **33**, 2105306 (2021).

5. Xu, J., Wang, H., Du, X., Cheng, X., Du, Z. & Wang, H. Self-healing, anti-freezing and highly stretchable polyurethane ionogel as ionic skin for wireless strain sensing. *Chemical Engineering Journal.* **426**, 130724 (2021).

6. Yang, L. et al. Mechanically Robust and Room Temperature Self-healing Ionogel Based on Ionic Liquid Inhibited Reversible Reaction of Disulfide Bonds. *Adv. Sci.* **10**, 2207527 (2023).

7. Xu, J., Wang, H., Wen, X., Wang, S. & Wang, H. Mechanically Strong, Wet Adhesive, and Self-Healing Polyurethane Ionogel Enhanced with a Semi-interpenetrating Network for Underwater Motion Detection. ACS. *Appl. Mater. Interfaces.* **14**, 54203-54214 (2022).

8. Li, H., Xu, F., Guan, T., Li, Y. & Sun, J. Mechanically and environmentally stable triboelectric nanogenerator based on high-strength and anti-compression self-healing ionogel. *Nano Energy.* **90**, 106645 (2021).

9. Zhang, M. et al. Self-healing, mechanically robust, 3D printable ionogel for highly sensitive and long-term reliable ionotronics. J. Mater. Chem. A. 10, 12005-12015 (2022).

10. Wang, M et al. Tough and stretchable ionogels by in situ phase separation. *Nat. Mater.* **21**, 359-365 (2022).

11. Azcune, I., Odriozola, I. Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more. *European Polymer Journal*. **84**, 147-160 (2016).

12. Kim, SM et al. Superior Toughness and Fast Self-healing at Room Temperature Engineered by Transparent Elastomer. *Adv. Mater.* **30**, 1705145 (2018).

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

[Note from the Editor: Reviewer #2 was asked to look also over the response given to Reviewer #1]

The authors fully revised the manuscript with the help of reviewers' comments.

Although Reviewer 1 mainly criticized the novelty of the self-healing polymer for soft robotics applications, the authors gave a thorough comparison of their work with the previous reports.

This criticism comes from the previous introduction with too much discussion on the receptors, which was also my concern and was fully revised in the current manuscript.

The current manuscript has much more discussion on the material and clearly addresses the novelty.

I recommend the publication.

Reviewer #3 (Remarks to the Author):

The revised manuscript have addressed all of the questions I raised before, I suggest the manuscripte be accepted.