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2020

Pan, S., Zhang, F., Cai, P., Wang, M., He, K., Luo, Y., . . . Chen, X. (2020). Mechanically interlocked hydrogel–elastomer hybrids for on-skin electronics. *Advanced Functional Materials*, 30(29), 1909540-. doi:10.1002/adfm.201909540

<https://hdl.handle.net/10356/142988>

<https://doi.org/10.1002/adfm.201909540>

This is the accepted version of the following article: Pan, S., Zhang, F., Cai, P., Wang, M., He, K., Luo, Y., . . . Chen, X. (2020). Mechanically interlocked hydrogel–elastomer hybrids for on-skin electronics. *Advanced Functional Materials*, 30(29), 1909540-, which has been published in final form at <http://doi.org.remotexs.ntu.edu.sg/10.1002/adfm.201909540>.

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Mechanically Interlocked Hydrogel-Elastomer Hybrids for On-Skin Electronics

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Keywords: mechanical interlock, hybrid electrodes, on-skin electronics, mechanical softness, electrophysiological signals

Abstract

Soft electronics that seamlessly interface with skin are of great interest in health monitoring and human-machine interfaces. However, achieving mechanical softness, skin adhesiveness, and high conductivity concurrently has always been a major challenge due to the difficulty in bonding dissimilar materials while retaining their respective properties. Herein, the mechanically interlocked hydrogel-elastomer hybrid is reported as a viable solution to this problem. Hydrogels with low moduli and high adhesiveness were employed as the substrate, while porous elastomer webs were used as matrices to load conductive films and lock the hydrogels through a mechanically interlocked structure. The bonding strength between hydrogel and elastomer in the interlocking hybrid structure was 14.3 times of that of physical stacking method. As a proof of concept, interlocking hybrids were used as on-skin electrodes for electrophysiological signals recording including electromyography and electrocardiogram. The robust hybrid electrodes still well detect signals after multiple cycles. The proposed

strategy not only is an effective approach to achieve interlocking structure, but also provides a new perspective for soft and stretchable electronics.

1. Introduction

Soft electronics are attracting tremendous attention for their application in health monitoring,^[1-13] human-machine interfaces,^[14-23] and soft robotics.^[24-29] Skin-attachable sensors are a popular form of stretchable electronics, which allow continuous recording of physiological signals in a noninvasive way.^[30-37] Mechanical matching of adhering electrodes with skin has been identified a critical design aspect.^[38,39] In particular, skin is a soft organ with Young's moduli in the range of 0.1-2 MPa.^[30] Soft electrodes of similar mechanical properties to skin can conformably adhere to curving skin, which ensure signal fidelity and wearing comfort. Polymers are the most suitable matrix for soft electrodes due to their low mechanical stiffness.^[40-42] Hydrogels, polymer networks able to contain a large amount of water, have aroused growing attention in bioelectronics due to extraordinary softness (1-100 kPa) and stretchability (up to 30 times of original length), as well as ionic conductivity and biocompatibility.^[43-46] Although ionic conductivity has been utilized for various electronics application,^[47-49] real-world application still requires electronic conduction to seamlessly wire with external equipment. Therefore, many efforts have been devoted to render hydrogels electronically conductive. For example, conductive polymers, metal-based nanowires, and carbon nanomaterials are incorporated into bulk hydrogels, forming conductive composites.^[50-57] Despite the success in bringing about conductivity, the mechanical properties of originally soft and stretchy hydrogels are unavoidably compromised due to volumetric loading of high-stiffness materials.^[51,57-59]

To achieve mechanical softness and electronic conductivity concurrently, the hydrogel and conductive material should maintain their bulk and film form respectively, only bonded at a single interface. In our body, soft tendon and hard bones are connected by an interface layer,

the tendon-bone insertion, the so-called enthesis. Enthesis allows soft tendon tissues and hard bone tissues to firmly bond together, and well retain their respective functions.^[60-63] Getting inspirations from this, we could introduce an interface layer, which interlocks with hydrogel and bonds tightly to conductive materials, to bridge the two (**Figure 1a**). For the choice of the interface material, elastomers with stable chemical property and reasonable adhesion with conductive materials are handy candidates as they are frequently used in flexible electrodes. In such a way, mechanical softness and high conductivity can be realized on a single hybrid electrode, where an elastomer serves as the interface material to load the conductive materials and integrate with hydrogel.

Here, we report robust hydrogel-elastomer hybrids via mechanical interlocking. The mechanical interlocking structure not only gives rise to stable bonding, but also achieves mechanically soft and highly conductive electrodes. The interlocking structure is realized by infiltration of hydrogel precursor into porous thermoplastic polyurethane (TPU) webs, followed by thermal curing. Conductivity is endowed by thermal evaporation of Au nanofilm on TPU webs before hydrogel precursor infiltration. The hybrid electrodes show mechanical softness and self-adhesiveness. The bond strength between the hydrogel and elastomer in mechanical interlocking hybrids reaches to 50.9 J/m^2 , 14.3 times of physically attached structures. As a proof of concept, we demonstrated that the hybrid electrodes can be used as on-skin electrodes for electrophysiological signals recording including electromyography (EMG) and electrocardiogram (ECG). The proposed strategy is an effective approach to realize mechanical softness and electronic conductivity in flexible electrodes, especially for materials like hydrogel that cannot be processed by conventional electronics processing techniques.

2. Results and Discussion

Electrospinning is the most popular method to fabricate porous structure due to its

versatility and facility.^[64-66] Here, TPU is used as the elastomeric candidate to obtain porous films and the detailed fabrication process is presented in the Experimental Section. Microfibers are successfully obtained and the porous structure is formed among these intertwined fibers, as indicated by the scanning electron microscopy (SEM) image (**Figure 2a**). The diameter is in the range of 1-3 μm . In addition, the junctions are naturally merged together, which is advantage to the mechanical property of membranes as previously reported.^[67] The morphology of fibers is kept intact after stretching, and the junctions are still connected after 50% stretching (Figure S1). The mechanical property of electrospun TPU fiber webs is different from TPU films due to the porous structure in the webs. Thickness greatly affects the mechanical property of TPU fiber webs (Figure 2d). The stress at rupture increases with increasing web thickness, and the maximum strain at rupture is 840% at a web thickness of 137 μm . The stress-strain curves of TPU webs in successive deformation were shown in Figure S2. The stress-strain curve shows good repeatability after the first cycle. The TPU webs have both elasticity and plasticity. We compare the Young's moduli of TPU fiber webs of different thickness. The Young's moduli are calculated from the initial linear region in stress-strain curves. It is interesting that the thinner the web is, the lower Young's moduli is; it decreases to 75 KPa for the web with a thickness of 31 μm , which is only 2.9% of the nonporous TPU film that is 2.55 MPa (Figure 2e). The Young's moduli of nonporous TPU film is obtained from Figure S3. The surface morphology of TPU fiber webs with different thicknesses was recorded (Figure S4). The thicker the web is, the denser the web is. For the thickest film, fibers more closely bond with neighboring fibers. The void in the thick film became less compared to the thin film. Furthermore, we also compare the density of these webs, and the density of web gradually increased with increasing web thickness (Figure S5). In other words, the mass of TPU per area increases with film thickness. Hence, the Young's moduli of webs gradually increased with increasing film thicknesses. In general, the fabricated TPU fiber webs are softer than the bulk film, which is suitable for on-skin

application.

Hydrogel is a network of polymer chains where water is the dispersion medium. The conductivity of hydrogel can be achieved by adding ionic salts. In addition, the self-adhesive hydrogels is a new and promising material for flexible and wearable electronics.^[68-71] Here, we chose the polyacrylamide/Ca-alginate hydrogels (PAM/Ca-Alg) as an example in our experiment due to its tough and soft properties.^[72,73] We synthesized the PAM/Ca-Alg hydrogel according to previous works, and detailed fabrication process is available in the Experimental Section. PAM/Ca-Alg hydrogel includes two types of crosslinked polymer: covalently crosslinked polyacrylamide and ionically crosslinked alginate. The alginate chains interpenetrate with the PAM network, and the alginate network is ionically crosslinked by calcium ion from calcium carbonate nanopowder. The covalent crosslinked and ionically crosslinked networks render the hydrogel high toughness. This tough hydrogel also shows mechanical softness and self-adhesiveness. The Young's moduli is around 5.3 KPa, and the hydrogel can stretch to 25 times of its original length (Figure S6). The PAM/Ca-Alg hydrogel shows ionic conductivity due to the existing calcium ion in hydrogel network. The ionic conductivity of PAM/Ca-Alg hydrogel is about 1.1 mS/cm (Figure S7).

Although elastomers and hydrogels have been widely used in soft and stretchable electrodes, they cannot be easily integrated into hybrid structures with reliable interfaces and keep their respective properties well. It is well known that an interpenetrating polymer network is a polymer combined two or more networks, and different polymers are interlocked with each other while keep their main properties. The interlocking function in interpenetrating polymer network mainly focuses on the molecule chain.^[74] Herein, we proposed a simple yet effective method, mechanical interlock, to assemble elastomers and hydrogels into hybrids. The fabrication process is shown in Figure 1b. In order to increase the hydrophilicity of the web, TPU fiber webs are first treated with oxygen plasma to become more hydrophilic, and the detailed fabrication process is available in the Experimental Section.

Then the fresh hydrogel precursor was cast onto TPU webs with the mould. Hydrogel precursor was filled into porous TPU webs by capillary action, and the hydrogel-TPU hybrid was obtained after thermal curing. The structure of hybrids were observed after freeze-drying, and the cross-sectional SEM image of hybrids were presented in Figures 2b and c. Homogeneous porous structure was observed in the hydrogel layer, which is typical in freeze-dried hydrogels. TPU fibers maintain their original structure very well in the interlocking layer. Meanwhile porous structure was also clearly observed in the enlarged image of this layer (Figure 2c), which indicates that hydrogel was successfully locked into TPU webs. We investigated the mechanical property of the hybrid structure, and Young's moduli of the hybrid is 11.5 KPa, calculated from the initial linear region in stress-strain curves (Figures 2f and S8). In the hybrid structure, the thickness of TPU web and hydrogel is 0.05 mm and 2 mm, respectively. Moreover, an inflection point was observed in the stress-strain curve. This is because the rigid TPU webs in hybrid were first ruptured during the stretching process, which dissipated large amounts of fracture energy. Hence, the maximum stress is 28.7 KPa at a strain of 557% for this hybrid.

In order to quantitatively evaluate the bonding strength of mechanically interlocked hydrogel-elastomer hybrids, we use the standard 90°-peeling test to measure the bonding strength between hydrogel and elastomer webs. The schematic illustration of test is presented in **Figure 3a**, and the detail process is available in Experimental Section. In a typical experiment, the bottom surface of TPU webs was fixed on the glass slide, while the top surface of the hydrogel was adhered to a thin stiff backing (polyimide, with a thickness of 90 μm), which prevented the elongation of hydrogels along the peeling direction. It can be found that hydrogels firmly anchored into the TPU webs in the interlocked hybrids (Figure 3b). As control experiments, hydrogel-TPU webs composites (HTWC) and hydrogel-TPU films composites (HTFC) were prepared by physical stacking method (details available in Experimental Section). The interfaces between hydrogel and TPU in these physical stacking

samples are clear, and hydrogel can not well adhere to these films (Figures 3c and d). We further quantitatively measure the bonding strength. As shown in Figures 3e and f, the bonding strength between hydrogel and TPU webs in interlocked hybrids was 50.9 J/m^2 . The bonding strength of the hydrogel and TPU in HTWC and HTFC are only 5.10 and 3.56 J/m^2 , respectively. So, the bonding strength between the hydrogel and TPU elastomer, via mechanically interlocked method, was greatly enhanced, which was 14.3 times of that of HTFC from physical stacking method. The enhanced bonding strength is ascribed to the interlocking structure. The bonding strength in the hybrid structures was investigated at different web thickness. For the thin webs, the bonding strength is relatively low. This may be ascribed to the mechanical softness and thin interlocked layer in the thin webs. The optimal bonding strength appeared around a thickness of $85 \mu\text{m}$.

Till now, metal nanowires have been widely used to fabrication of flexible and stretchable electrode due to their accessibility and high performance.^[28,75,76] Compared to these flexible electrodes based on metal nanowires, the thermally evaporated method not only endows polymer films with high conductivity, but also keeps physical property of these films, such as porous property of substrates. To endow the hybrids with high conductivity, gold nanofilm was thermally evaporated onto the TPU webs in advance. The gold/TPU web with 50 nm thick gold nanofilm has a sheet resistance of $40.9 \pm 6.3 \Omega/\text{sq}$ from four-point probe system. The resistance change is recorded under 10% applied strain for successive cycling (Figure S9). The resistance changes in the small scale from 20 to 90Ω , and this small variation is suitable for use in electrophysiological signals detection.^[77] The interlocked structure was achieved following the above-mentioned steps. The conductive TPU web was mechanically interlocked with hydrogel to obtain self-adhesive hybrid electrodes. Hence, the introduction of intermediate material, TPU webs, is an effective strategy to integrate dissimilar materials, such as gold nanofilm and hydrogel, into one composite while keep respective performance. This method may explore to bond other dissimilar materials together,

such as hydrophilic and hydrophobic materials, mechanically soft and hard materials. In the hybrid electrodes, the gold nanofilm side still retains high conductivity (Figure S10), and the hydrogel side gives ionic conductivity. The resistance change of hybrid was recorded under stretching. The resistance change is mild when the applied strain is smaller than 10%, and the resistance of hybrid electrodes gradually increases when the applied strain increases from 10% to 25%. The electrode loses its conductivity when the strain exceeds 25% (Figure S11). Similar phenomenon was also reported in other web-based electrodes.^[31] The stretchability of electrode could be improved by prestretching method. Detailedly, TPU webs were firstly prestretched by 15%, and then the gold nanofilm was thermally evaporated onto the prestretching webs. The electrodes based on prestretching method could sustain around 35% strain while reserving decent resistance (Figure S12), which is enough for the on-skin measurements that typically deformation up to around 30%.^[78] Due to high adhesiveness and mechanical softness, the hybrid electrode can easily adhere to skin. For example, a hybrid electrode firmly adhered to the wrist even if the volunteer bend the wrist inward and outward (**Figures 4a-c**). Some wrinkles appeared on the surface of hybrid electrodes during bending, which confirms that our hybrid electrodes are mechanically soft and highly skin-adhesive. The adhesion strength between the skin and hybrids electrodes was also measured (Figure S13), and it is around 30 N/m, which is comparable with the commercial polyimide tape.^[30]

We demonstrated that our interlocking hybrid electrodes can be used as on-skin electrodes for electrophysiological signals detection, such as EMG and ECG. The property of the interface between electrodes and skin affects the quality of signals.^[79,80] We first studied the interfacial impedance between interlocking hybrid electrodes and skin. Pairs of electrodes were placed onto the upper arm for measurement (Figure 4d). Our adhesive and conformal interlocking electrodes showed as low interfacial impedance with skin as commercial electrodes. This result further confirms that our hybrid electrodes have a conformal contact with skin. In contrast, the TPU/Au electrode cannot be conformably shaped and attached onto

the skin, and the interfacial impedance increased in one order of magnitude (Figure 4e). The EMG signal detected by hybrid electrodes has a signal-to-noise ratio of 43.03 dB, which is higher than that 17.8 dB of TPU/Au electrode (Figures 4f and g). The TPU/Au electrode was attached onto the skin with the help of commercial tape. Normally, most of dry electrodes for signal detection were mounted onto the human skin with the help of tape,^[81] which may bring uncomfortable wearing. In addition, our interlocking electrodes show durable performance after multiple cycles (Figure 4h). The SNR of EMG signal still kept well after multiple cycles (Figure 4i). Although some work based on web electrodes were used for signal detection, the reusability is not concerned and mentioned.^[31] In the ECG signal recording, pairs of electrodes were attached onto the volunteer's left and right forearms, respectively, with a third reference electrode attached on the abdomen. In the ECG signals, all of the P, Q, R, S, and T waves can be clearly identified (Figure S14), and these signals are crucial in determining heart rate and various cardiac arrhythmias. In addition, we have observed the skin reaction after wearing our electrode with different times. There is no skin irritation after using our hybrid electrodes for 60 min (Figure S15).

3. Conclusions

In summary, we reported mechanically interlocked hydrogel-elastomer hybrids with high electrical performance by assembling hydrogels with conductive elastomeric webs. The mechanically interlocked structure was realized by infiltration of hydrogel precursor into porous TPU webs, and then thermally cured to form hydrogel-TPU hybrids. The hybrids show high bonding strength between the hydrogel and TPU. Meanwhile the hybrid electrodes retain the mechanical softness of hydrogels and the high conductivity of TPU/Au webs, which enables low interfacial impedance with skin. The fabricated hybrid electrodes can be used as on-skin electrodes to reliably record EMG and ECG signals. The robust hybrid electrodes still well detect signals after multiple cycles. Our study provides a new perspective to achieve

soft and high-performance electrodes through interlocking interfacial layer that bridges soft and polymeric substrates and fragile conductive films. This strategy is expected to be generally applicable for flexible electronics. Furthermore, it could make new application in various fields by introducing an interlocking structure to merge distinctive yet complementary advantages of dissimilar materials together.

4. Experimental Section

Fabrication of TPU fiber webs: The electrospinning solution was made by adding TPU pellets (CP) (20 wt%) to a tetrahydrofuran/dimethyl formamide (3:1, w/w) mixed solvent then stirring at room temperature for 24 h. The TPU is chemically pure, and tetrahydrofuran and dimethyl formamide are anhydrous. The electrospinning was conducted at a volumetric flow rate of 1.0 mL/h with a tip-to-collect distance of 10 cm under an accelerated voltage of 20 kV by using a Nanon electrospinning apparatus (MECC Co., Ltd., Japan).

Synthesis of PAM/Ca-Alg hydrogel: The PAM/Ca-Alg hydrogel was synthesized by mixing 10 ml of a carefully degassed aqueous precursor solution of 12.5 wt% acrylamide, 0.0075 wt% N,N-methylenebisacrylamide, 1.56 wt% sodium alginate (Sigma-Aldrich, A0682), 0.117 wt% ammonium persulphate, 0.207 wt% calcium carbonate nanopowder, and 0.77 wt% tetramethyl-ethylenediamine. The degassed precursor was quickly injected into a mould and crosslinked at 50 °C for 2h.

Fabrication of mechanically interlocked hydrogel-TPU hybrid electrodes: First, a thin layer of gold film with a thickness of 50 nm was thermally evaporated onto one side of TPU fiber webs at an evaporation rate of 0.4 Å/s. Second, the other side of TPU webs without gold film was treated with oxygen plasma to turn hydrophilic. Third, the Au-coated side of TPU fiber webs was placed onto PDMS film, and the precursor was carefully cast onto the oxygen plasma-treated side. Finally, the hybrid electrodes are obtained by thermal curing of hydrogel at 50 °C for 2h. For the hydrogel-TPU hybrids, TPU fiber webs were directly used without

coating gold nanofilms.

Measurement of resistance properties of films: The sheet resistance of Au/TPU webs was measured by the four-point probe system (CMT-SR2000N). Data were collected from four samples. The resistance change of composite films was recorded by Keithley 4200A-SCS parameter analyzer. The successive deformation was conducted using MTS Criterion Model 42. Samples were stretched at a fixed speed of 12 mm/min.

Fabrication of control samples of HTWC and HTFC: HTWC was fabricated by physical stacking the hydrogel and TPU web into one sample. HTFC was fabricated by cast the hydrogel precursor to the TPU film with mould and then thermal curing.

Mechanical testing: The interfacial toughness of hydrogel-TPU hybrid was measured using the standard 90°-peeling test with mechanical testing machine (MTS C42). The bottom surface of TPU webs was fixed on the glass slide, while the top surface of the hydrogel was adhered to a thin stiff backing (polyimide, with a thickness of 90 μm). Cyanoacrylate adhesive was used to bond the polyimide film with hydrogel. The as-prepared samples were used to measure the mechanical performance. All tests were conducted in ambient air at room temperature.

Ionic conductivity measurement: The ionic conductivity of the hydrogel was tested by using electrochemical workstation (ZAHNER ZENNIUM) and obtained from the equation, $\sigma = \frac{L}{RA}$. In the formula, σ is the ionic conductivity; L is the film thickness; R is the bulk resistance obtained from Cole-Cole plot (Figure S7); A is the area of an electrode. The L, R, and A are 4 cm, 14.3 kΩ, 0.25 cm², respectively. Therefore, the ionic conductivity is about 1.1 mS/cm.

Impedance measurement and electrophysiological signals detection: The interfacial impedance was measured by attaching pairs of electrodes with a circle shape (diameter: 20 mm), and a pitch of 40 mm on upper arm. Interlocking hybrid electrodes and commercial gel

electrodes (Large muscle electrodes, Backyard Brains) were used. The interfacial impedance measurements were tested by using electrochemical workstation (ZAHNER ZENNIUM) from 10 Hz to 10^4 Hz with a voltage of 100 mV. In the EMG measurement, pairs of interlocking hybrid electrodes were attached on the upper arm, and the third reference electrode was placed onto the palm. EMG signals were detected while clenching the fist for 1-2 s and the signals were recorded by a toolkit for EMG recording (Muscle Spikerbox, Backyard Brain). The toolkit includes amplifier and 50/60 Hz filter. SNR were obtained from the equation, $SNR(dB) = 20\log_{10}(\frac{A_{signal}}{A_{noise}})$. Where A_{signal} and A_{noise} denote the amplitude of signal and background, respectively. In the ECG signal measurement, pairs of electrodes were attached onto the volunteer's left and right forearms, respectively, and a third reference electrode was attached on the abdomen. The signal was recorded by ECG Monitor PC-80A (Heal Force Bio-meditech Holdings Limited).

Supporting information

Supporting information is available from the author.

Acknowledgements

We thank the financial support from Singapore Ministry of Education (MOE2017-T2-2-107).

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Figure 1. Schematic of structure and fabrication process of mechanically interlocked electrodes. a) Schematic of mechanically interlocked electrodes. The hydrogel is locked in the conductive porous elastomer webs to form a hybrid structure. b) Schematic of fabrication process of hybrid electrodes based on mechanical interlock: I) Porous TPU webs were obtained by electrospinning of TPU. II) A layer of gold nanofilm was deposited onto the surface of TPU webs. III) Infiltration of hydrogel precursor into TPU/Au webs, and then thermal curing to achieve mechanically interlocked electrodes.

Figure 2. The morphology and mechanical property of TPU fiber webs and mechanically interlocked hybrids. a) SEM image of TPU fiber webs with a thickness of 55 μm from electrospinning. b) The cross-sectional SEM image of mechanically interlocked hydrogel-TPU hybrids. c) The enlarged cross-sectional SEM image of the interlocking layer. d) The stress-strain curves of TPU fiber webs with different thickness. e) Young's modulus of TPU fiber webs with different web thickness. f) The stress-strain curve of interlocked hybrid. In the hybrid structure, the thickness of TPU web and hydrogel is 0.05 mm and 2 mm, respectively. An inflection point at a strain of 557% appeared in the stress-strain curve. This is because the rigid TPU webs in hybrid were first ruptured, which dissipated large amounts of fracture energy.

Figure 3. a) Schematic illustration of the 90°-peeling test for bonding strength. b-d) The optical images of peeling process for interlocking hybrids (b), hydrogel-TPU webs composites (HTWC) (c), and hydrogel-TPU films composites (HTFC) (d). The thickness and width of hydrogel are 2 mm and 10 mm, respectively. e) The measured peeling forces per width of the hydrogel sheets for interlock hybrids, HTWC, and HTFC. The thickness of TPU webs is around 83 μm . f) The interfacial toughness performance of HTFC, HTWC, and interlock hybrids. g) The interfacial toughness performance of interlock hybrids with different TPU web thickness.

Figure 4. Demonstration of mechanically interlocked hybrid as on-skin electrodes for detecting EMG signals. a-c) The optical images of an interlocking hybrid electrode adhere onto wrist at resting state (a), inward bending state (b), and outward bending state (c); the electrode size is 25×10 mm (length $\times$ width). These results indicate that our interlocking hybrid electrodes are mechanically soft and highly skin-adhesive. d) An optical image of the EMG measurement setup using interlocking hybrid electrodes attached on the upper arm, and the diameter of electrode size is 20 mm. The third reference electrode was placed onto the palm. e) Comparison of impedance of the skin/interlocking electrodes, skin/TPU/Au electrodes, and skin/commercial electrodes. The testing is under same area of electrodes

(diameter: 20 mm) and a pitch of 40 mm. f) EMG signals detected by the interlocking electrodes and TPU/Au electrodes. g) Signal-noise-ratio (SNR) comparison of interlocking electrodes and TPU/Au electrodes. h) Durable performance of the interlocking electrode for detection of EMG signal. The electrode was repeatedly attached/detached from skin. i) SNR comparison of interlocking electrodes under different cycle numbers.

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The novel hydrogel-elastomer hybrid was developed by the strategy of mechanical interlock. Porous elastomer webs were used as matrices to load conductive materials and lock hydrogels through an interlocking structure to achieve mechanically soft and skin-adhesive electrodes. The interlocking hybrid was used as on-skin electrode for recording electrophysiological signals.

Mechanical interlock, hybrid electrodes, on-skin electronics, mechanical softness, electrophysiological signals

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Mechanically Interlocked Hydrogel-Elastomer Hybrids for On-Skin Electronics

ToC figure