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Ionic Tactile Sensors as promising biomaterials for Artificial Skin: review of latest advances and future perspectives

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Abstract:	Ionic tactile sensors (ITS) are an emerging subfield of wearable electronics, capable of mimicking the human skin, including not only the typical anisotropic structure, mechanical behaviour, and tactile functions but even the mechanosensitive ionic channels that are crucial for the human sense of touch. With the rapid development of intelligent technology, such bioinspired materials constitute the core foundation of intelligent systems and are a candidate to be the next generation e-skins, offering a more accurate and evolved biointerface. In the latest years, a wealth of novel ultra-stretchable ITS was proposed, progressively refining the choice of soft materials, including ion gels, ionic liquids and hydrogels, and fabrication techniques. Regardless of materials and methods adopted, all these tactile sensors can feel mechanical solicitations and external stimuli, thus behaving as – or even better than – human skin. In this review, an overview of the very latest advances in high-performance ITS applied in intelligent systems is reported. First, generality of ITS will be summarized. After, ion gel, ionic liquid, hydrogel, and elastomer ITS will be discussed focusing first on composition, fabrication, type and mode of sensing and then on their characteristics and application. In this perspective, the advantages that biomimetic approaches brought in terms of sensitivity, speed of response and multimodality of sensing will be highlighted, with a particular focus on the development of electrochromic, thermochromic, self-powered and self-healing devices. In conclusion, the prospects of tactile sensors for intelligent systems in biomedicine and robotics will be discussed, along with the possible strategies to overcome the current shortcomings, in terms of biocompatibility, durability, mechanical performance, adhesion to biological substrates, which represent the future challenges.
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Response to Reviewers:	

Dear Editor,

We are pleased to submit the revised version of the review paper entitled: “Ionic Tactile Sensors as promising biomaterials for Artificial Skin: review of latest advances and future perspectives”.

First, we are grateful to you all for the time spent for revising our paper, and we thank the Reviewers for their very positive feedbacks and, especially, for the invaluable suggestions that enabled us improving the quality of the State-of-Art of this paper.

Hence, we hope that this manuscript can be considered as suitable for publication.

Sincerely yours,

Roberto Scaffaro

Andrea Maio

Maria Clara Citarrella

Reviewer #1: The authors reviewed the very latest advances in high-performance ionic tactile sensors applied in intelligent systems. The overall idea of this manuscript is clear and the logic is reasonable. However, there are also some questions should be addressed. I recommend this manuscript can be accepted after a mandatory revision. The detailed comments are listed as follows,

R: We are grateful to the Reviewer for the positive feedback.

Q1. Different ionic tactile sensors have been introduced and compared, but what is the best for different application scenarios? Please give a clear answer.
R1: Dear Reviewer, due to the complexity of skin functionalities and features required, it is hard to select the best ionic tactile sensor. Unfortunately, to date no sensor fulfil all the prerequisites of human skin. Hence, given the fact that ITS research is an extremely emerging field, the perfect way to regenerate skin is far from being individuated. However, in the Conclusion section we highlighted advantages and drawbacks for each class of sensors, thus indicating the best class of sensors for each feature, according to your suggestions.

Q2. Sensors have been reported with other systems. The following paper need be cited:

1. Adv. Funct. Mater., 2020, 30, 2000398; Flower-like Bismuth Metal-Organic Frameworks Grown on Carbon Paper as a Free-Standing Electrode for Efficient Electrochemical Sensing of Cd2+ and Pb2+ in Water, Engineered Science, 2018, 3, 77-83;

2. Heterogeneous Iridium Oxide/Gold Nanocluster for Non-enzymatic Glucose Sensing and pH Probing, Engineered Science, 2019, 8, 46-53, https://dx.doi.org/10.30919/es8d512;

3. A Subcutaneously Injected SERS Nanosensor Enabled Long-term in Vivo Glucose Tracking, Engineered Science, https://dx.doi.org/10.30919/es8d1161;

4. Tunable Thermal-Response Shape Memory Bio-Polymer Hydrogels as Body Motion Sensors, Engineered Science, 2020, 9, 60-67;

5. Embeddable Piezoelectric Sensors for Strength Gain Monitoring of Cementitious Materials: The Influence of Coating Materials, Engineered Science, 2020, 11, 66-75;

6. Recent Progress on Thermo-electrical Properties of Conductive Polymer Composites and Their Application in Temperature Sensors, Engineered Science, 2020, 12, 13-22;

7. Thermo-Responsive and Shape-Adaptive Hydrogel Actuators from Fundamentals to Applications, Engineered Science, 2019, 6,111, https://dx.doi.org/10.30919/es8d788;

R2: The references were added. We thank the Reviewer for giving us the opportunity to enhance bibliography related to sensors.

Q3. In the ionic liquid part, the following papers need be cited:

8. Influence of Various Ionic Liquids Embedded Electrospun Polymer Membrane Electrolytes on the Photovoltaic Performance of DSSC, Engineered Science, 2018, 4, 44-51;

9. Ionic Liquids as "Green Solvent and/or Electrolyte" for Energy Interface, Engineered Science, 2020, 11, 3-18, https://dx.doi.org/10.30919/es8d0013;

10. Studies on ionic liquid incorporated polymer blend electrolytes for energy storage applications https://doi.org/10.1007/s42114-019-00102-x;

11. Facile synthesis of nanostructured polyaniline in ionic liquids for high solubility and enhanced electrochemical properties https://doi.org/10.1007/s42114-019-00103-w;

12. A review on synthesis and application of solvent-free nanofluids https://doi.org/10.1007/s42114-019-00125-4

R3: The references were added. We thank the Reviewer for giving us the opportunity to improve the state-of-art related to ionic liquids.

Q4. For the hydrogel part, the following papers should be cited:

13. Amino Carbon Nanotube Modified Reduced Graphene Oxide Aerogel for Oil/Water Separation, ES Materials & Manufacturing, 2019, 6, 68-74, https://dx.doi.org/10.30919/esmm5f611;

14. Fabrication of pH-electroactive Bacterial Cellulose/Polyaniline Hydrogel for the Development of a Controlled Drug Release System, ES Materials & Manufacturing, 2018, 1, 41-49, https://dx.doi.org/10.30919/esmm5f120;

15. Fast 4-nitrophenol Reduction Using Gelatin Hydrogel Containing Silver Nanoparticles, Engineered Science, 2019, 8, 19-24, https://dx.doi.org/10.30919/es8d504;

16. Highly Stretchable Self-Healing Nanocomposite Hydrogel Reinforced by 5 nm Particles, ES Materials & Manufacturing, 2018, 2, 16-23, https://dx.doi.org/10.30919/esmm5f158;

17. Thermo-Responsive and Shape-Adaptive Hydrogel Actuators from Fundamentals to Applications, Engineered Science, 2019, 6, 1-11, https://dx.doi.org/10.30919/es8d788;

18. Super-hydrophilic/oleophobic chitosan/acrylamide hydrogel: an efficient water/oil separation filter https://doi.org/10.1007/s42114-020-00150-8;

19. Synthesis and characterization of polyethylene oxide (PEO)—N,N-dimethylacrylamide (DMA) hydrogel by gamma radiation https://doi.org/10.1007/s42114-018-0058-x;

20. Reversible photo-controlled release of bovine serum albumin by azobenzene-containing cellulose nanofibrils-based hydrogel https://doi.org/10.1007/s42114-019-00112-9;

R4: The references were added. We thank the Reviewer for helping us to improve the state-of-art related to hydrogels.

Q5. The possible strategies to overcome the current shortcomings have been proposed in the review, what are the mechanisms of these strategies and why are the strategies not achieved now?

R5. The strategies proposed are suitable in the development of well-defined architectures, including graded or hierarchical structures, which are prerequisites of all biological tissues. Of course, since these strategies have only very recently been reported for the first time for "classical" systems, their implementation in the fabrication of ITS materials could reasonably take a few months or years.

Q6. The composites generally used as artificial skin can also be used to construct flexible electromagnetic materials. The authors are recommended to properly cite the references about electromagnetic function to further elaborate the potential applications:

21. Hierarchically porous Co/C nanocomposites for ultralight high-performance microwave absorption http://dx.doi.org/10.1007/s42114-020-00202-z;

22. Magnetic negative permittivity with dielectric resonance in random Fe3O4@graphene-phenolic resin composites https://doi.org/10.1007/s42114-017-0014-1;

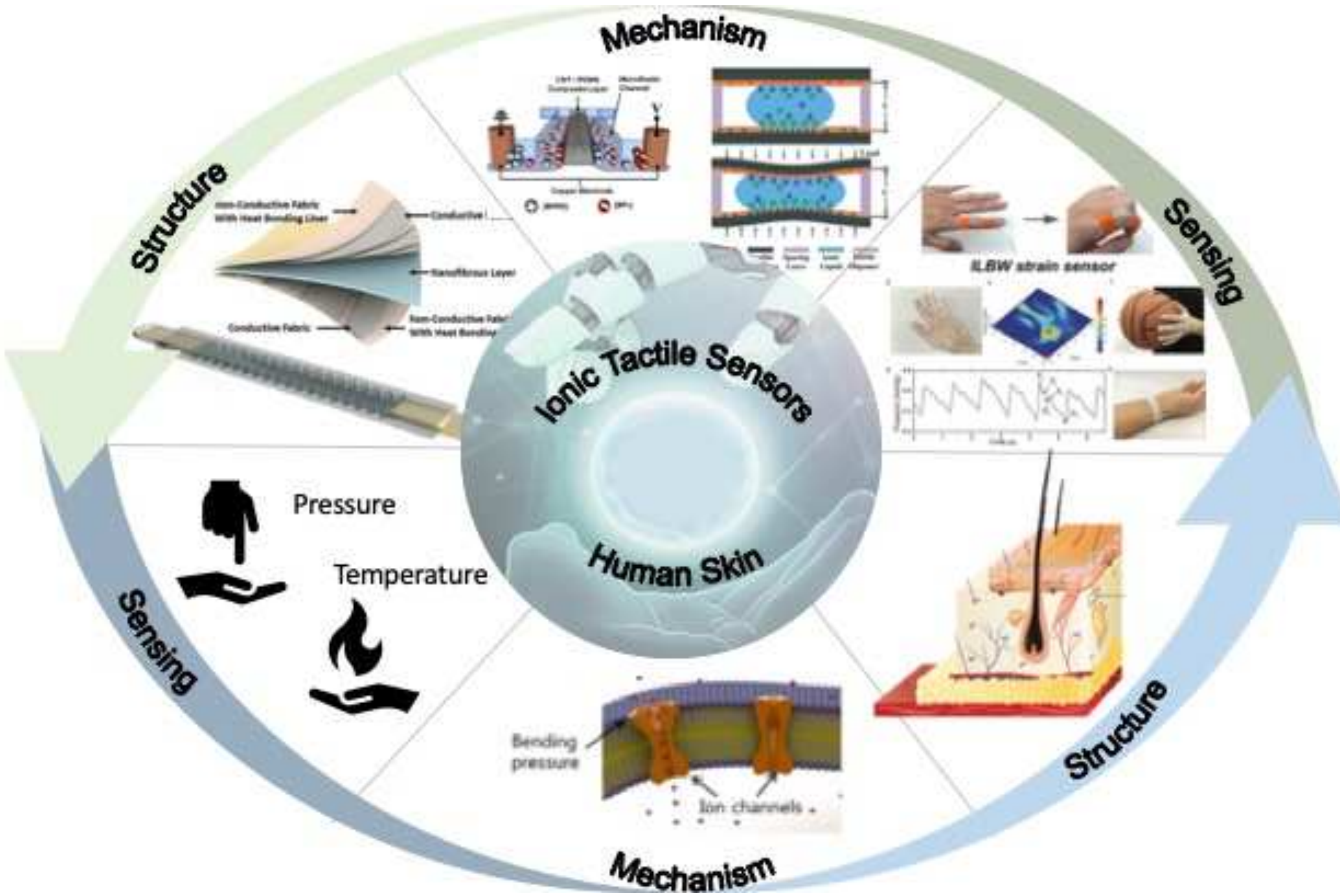
23. Recent Advances of Asymmetric Supercapacitors https://doi.org/10.1002/admi.202001710.

R6: We are grateful for this suggestion. Electromagnetic materials were included in the list of possible, next-generation materials for ITS application and the references were added.

Reviewer #2: The review paper is nice and well written. The topic is very interesting and nice.
R: We are grateful to the Reviewer for the positive feedback.

Graphical Abstract

Click here to access/download;Graphical Abstract;schema_rev (1).jpg



Ionic Tactile Sensors as promising biomaterials for Artificial Skin: review of latest advances and future perspectives

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ABSTACT: Ionic tactile sensors (ITS) are an emerging subfield of wearable electronics, capable of mimicking the human skin, including not only the typical anisotropic structure, mechanical behaviour, and tactile functions but even the mechanosensitive ionic channels that are crucial for the human sense of touch. With the rapid development of intelligent technology, such bioinspired materials constitute the core foundation of intelligent systems and are a candidate to be the next generation e-skins, offering a more accurate and evolved biointerface. In the latest years, a wealth of novel ultra-stretchable ITS was proposed, progressively refining the choice of soft materials, including ion gels, ionic liquids and hydrogels, and fabrication techniques. Regardless of materials and methods adopted, all these tactile sensors can feel mechanical solicitations and external stimuli, thus behaving as – or even better than – human skin.

In this review, an overview of the very latest advances in high-performance ITS applied in intelligent systems is reported. First, generality of ITS will be summarized. After, ion gel, ionic liquid, hydrogel, and elastomer ITS will be discussed focusing first on composition, fabrication, type and mode of sensing and then on their characteristics and application. In this perspective, the advantages that biomimetic approaches brought in terms of sensitivity, speed of response and multimodality of sensing will be highlighted, with a particular focus on the development of electrochromic, thermochromic, self-powered and self-healing devices. In conclusion, the prospects of tactile sensors for intelligent systems in biomedicine and robotics will be discussed, along with the possible strategies to overcome the current shortcomings, in terms of biocompatibility, durability, mechanical performance, adhesion to biological substrates, which represent the future challenges.

KEYWORDS: tactile sensor, stretchable sensor, strain sensor, pressure sensor, ionic liquid, ion gel, hydrogel

1 INTRODUCTION

Human skin is the largest organ of the integumentary system in our body and it exhibits a notable range of properties. It possesses a J-shaped strain-stiffening behavior, being soft and compliant at small strains, while becoming rapidly stiffer at higher strains to prevent tissue damage [1]. This behavior makes it sensitive enough to detect and distinguish differences in the texture of materials, but equally robust to protect the body against damage from mechanical shocks and bacterial infection.

Since skin represents the interface between the human body and the outside world, it is provided with complex tactile sensing functionality that allow to perceive the outside, thus facilitating many essential activities. Moreover, skin provides temperature sensing capabilities that help understand the surroundings and avoid damaging from extreme temperatures. Figure 1.1 shows the major biological signal sources in the skin anatomy specifying the correspondence between the various tissues that compose the organ and the type of sensing they allow.

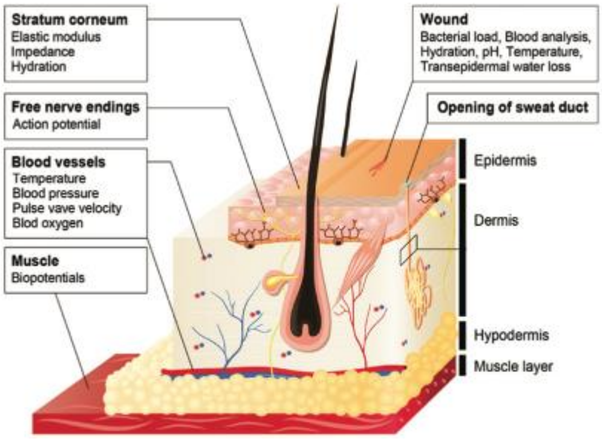

Figure 1.1 Description of human skin as a sensing platform for detecting various physiological signals [2].

The sense of touch, in particular, consists of a complex system of receptors distributed on the skin. As a response to pressure, the receptors produce electronic impulses that are transmitted to the brain that interprets the signal. The intensity of the pressure determines the frequency of the electrical impulses, the higher the pressure the larger the number of impulses per second.

During last years, sensors reached great achievements and hence attracted much interest as the next generation of artificial intelligence devices since they could be used in various application [3–9].

Artificial receptors mimic this process by coupling pressure sensors on sensitive materials with circuits capable of producing electrical impulses. The higher the pressure the greater the electricity that will flow to the sensors, which will produce electrical impulses more frequently.

In recent years, tactile sensors topic has reached much interest from the scientific community thanks to their possible implications in the development of artificial skin-like sensors for emerging human-interactive technologies, such as artificial skin, wearable or implantable devices and user-interactive ones. This tactile sensory capability of human skin has been emulated at first by deformable electronic materials for develop an electronic version of skin, named e-skin [10]. The development of e-skin allowed important advancements in robotics and medical devices fields, but the communications between these devices and biological systems poses a technological challenge as biological signalling is mediated by ions and molecules rather than electrons. For this reason, recently, ionic tactile sensors (ITS) have been developed. These sensors, composed by stretchable ionic materials, involve mobile ions. Thanks to these deformable ionic sensor devices that can sense pressure, strain, temperature, humidity, and even other external stimuli, it is possible to mimic the tactile sensing capability of human skin better than the e-skin can do. Miming the tactile perception of the human skin mechanism, in fact, ITS tactile sensing capability relies on the migration and redistribution of ions, modulated by external stimuli, which can bring to a more advanced biological interface for human-interactive platforms, when compared to conventional e-skin devices. In these regards, the develop of ITS will allow the use of synthetic skin in prosthetics, providing the touch ability and allowing to fell temperature for amputees and individuals with nerve damage. Moreover, these types of sensors are also capable of monitoring health parameters such as pulse waveforms and temperature distributions [11].

This review, after a brief general description of ITS, will be mainly focused on materials used to mimic the mechanical properties, tactile-sensing and temperature-sensing properties of human skin.

2 ITS GENERALITY

According to the working mechanism, tactile sensors are mainly based on piezoelectric, capacitive and resistive effects. Working mechanism of capacitive tactile sensors is based on the variation in the capacitance depending on the change in the relative position between the plates under an external pressure. The resistive tactile sensors are based on the piezoresistive effect, in which the conductivity varies under an external pressure. The latter one has the advantages of large detection, simple signal processing and strong anti-interference capability, if compared with the capacitive type.

What really makes difference in ITS fabrication is material selection and structure design. These aspects, in fact, play an important role in achieving good performance and various functions.

In order to enable accurate identification of position and direction of objects a *high resolution* is required in ITS. Moreover, to simulate human skin as much as possible to meet the needs of intelligent systems, the *stretchability* of tactile sensors is an indispensable condition. In addition, human skin can repair itself when exposed to external damage. So, an ideal tactile sensor should demonstrate a similar capability of repeatable *self-healing* that can greatly increase the lifetime of devices. Also, *self-powered* capability has great significance for future tactile sensors, in fact, devices powered by ordinary batteries need to be repeatedly recharged, which involves a great consumption of non-renewable energy. In addition, the large size, weight and hardness of batteries also restrain their application in micro-nano flexible electronic devices for intelligent systems. Therefore, collecting energy from nature and converting it into electrical energy is a relevant property for ITS [12].

Considering the medical field, sensors have been widely used as medical devices to monitor health or treat some diseases, such as arrhythmia and bradycardia. This means that the materials used must be *biocompatible*. Moreover, for diseases treatment, usually, the devices must work for a limited time, so, when devices are implanted in vivo, *biodegradability* is extremely important for avoid secondary surgery for device removal. This property will make the treatment of diseases safer, simpler, and more reliable [13].

3 ITS MATERIALS

To develop ITS, particular attention must be paid to human skin properties with the aim of emulating them. Taking this into account, to develop high-performance ITS materials that possess high flexibility, even deformability and low Young's modulus to allow conformability should be chosen. Moreover, the materials should be capable of ionic conduction under external electrical or mechanical stimuli [11].

In this regard, the most widespread materials for the development of high-performance ITS technologies have been reviewed. In **Table 1** different recently reported ITS materials have been summarized, in **Table 2** their characteristic and properties have been highlighted.

3.1 Ionic liquids

Ionic liquids (ILs) are defined as molten salts that are composed of organic cations and organic or inorganic anions with melting points below 100 °C. Moreover, ILs show interesting physicochemical properties such as high thermal, chemical, and electrochemical stability, low viscosity, non-volatility, and non-flammability. Furthermore, physical and chemical properties in ILs can be highly modified due to their numerous combinations of cations and anions. Owing to these unique properties, interest in ILs has grown considerably in recent years [14–18].

3.1.1 Composition, fabrication, type and mode of sensing of ILs ITS

The resistive strain sensors will be analysed first. *Keulemans et al.* fabricated a novel ionic liquid-based strain sensor composed of a tubular silicone micro channel filled with an ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][BTI] [19]. *Zhu et al.* reported the first application of a room temperature IL for a low cost, eco-friendly strain sensor. A low viscous and high conductive IL, 1-butyl-3-meth-ylimidazolium tetra-fluoroborate [BMIM][BF_4] was utilized as a piezoresistive gauge material [20]. *Chossat et al.* proposed a strain-sensitive sensor made of a solution of sodium chloride (NaCl) in water (H_2O) containing glycerol, where glycerol was used for increasing the viscosity of the solution [21]. *Wang et al.* reported the simple fabrication of a rubber ultra-stretchable ionic strain resistive sensor made of 1-Octyl-3-methylimidazolium chloride [OMIM][Cl]. The device was fabricated using a 3D printing technique [22]. *Yoon et al*. fabricated a highly stretchable and transparent micro-fluidic strain sensor (maximum strain up to 200%) with fast response, by utilizing a highly conductive binary mixture of ILs: 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfo-nyl)imide ([BMIM] [TFSI]) and 1-butyl-3-methy-limidazolium acetate ([BMIM][Ac]) filled in polydimethylsiloxane (PDMS) microchannels [23]. *Choi et al.* fabricated a resistive strain sensor based on the ionic liquid resulting from ethylene glycol (EG) and sodium chloride (NaCl). This latter was then encapsulated within a symmetric wavy channel in an Ecoflex matrix, previously obtained using a polytetrafluoroethylene (PTFE) mould and ametal template to attain the wavy structure [24]. *Zhang et al.* fabricated a highly sensitive, resistive ITS using a highly conductive IL, the 1-Ethyl-3-methy-limidazolium bis(trifluoromethylsulfonyl) imide ([EMIM][TFSI]), contained in an Ecoflex silicone elastomeric cover that could detect several physiological signals. The strain sensor was fabricated using a PDMS mould and simple sealing method [25].

Moving to the capacitive pressure sensor, *Nie et al.* used an aqueous-based electrolyte solution (NaCl) with high ionic concentration, mixed with glycerol to reduce evaporation, for developing the droplet-based interfacial capacitive sensor [26].

Table 1. *Summary of composition, type of materials, type of functions, mode of sensing and relevant characteristics of recently reported ITS materials.*

Composition	Structure	Types	Mode of sensing	Relevant Characteristics	Refs.
[BMP][BTI]	Ionic liquid	Resistive	Strain	Small-scale sensor	[19]
[BMIM][BF_4]	Ionic liquid	Resistive	Strain	Good repeatability	[20]
Glycerol, NaCl	Ionic liquid	Resistive	Strain	Microfluidic structure	[21]
[OMIM][Cl]	Ionic liquid	Resistive	Strain	Good performance in cycling, aging, and water tests	[22]
[BMIM][TFSI]	Ionic liquid	Resistive	Strain	Fast response	[23]
EG, NaCl	Ionic liquid	Resistive	Strain	Low degree of hysteresis	[24]
[EMIM][TFSI]	Ionic liquid	Resistive	Strain	Biological compatibility	[25]
Glycerol, NaCl	Ionic liquid	Capacitive	Pressure	High sensitivity	[26]
[BMIM] [BF_4]	Ionic liquid	Capacitive	Pressure	Temperature sensing	[27]
[EMIM][$C(CN)_3$]	Ionic liquid	Capacitive	Pressure	Small-scale sensor	[28]
[EMIM][TFSI] TPU	Ion gel	Resistive/ Capacitive	Multimodal (pressure, shear, torsion)	Arbitrary multiplex human touching	[29]
[EMIM][ESO_4], KCl, PANi	Ion gel	Resistive	Pressure	Insensitive other environmental factors	[30]
[EMIM][TCM], PEGDA	Ion gel	Capacitive	Pressure	Flexible, transparent, high sensitivity	[31]
[EMIM][TFSI] P(VDF-HFP)	Ion gel	Capacitive	Pressure	Micropatterned pyramidal structure	[32]
[EMIM][TFSI] P(VDF-HFP)	Ion gel	Capacitive	Pressure	Micro-dome structure	[33]
[EMIM][TFSI] TPU	Ion gel	Capacitive	Pressure	High sensitivity over a wide pressure range	[34]
[EMIM][TFSI] P(VDF-HFP)	Ion gel	Capacitive	Pressure	High sensitivity, and fast response	[35]
[EMIM][TRIFLATE] PVA	Ion gel	Capacitive	Pressure	Fast response, high linearity	[36]
[EMIM][TFSI] TPU	Ion gel	Capacitive	Pressure	Ionic textile based on sheath core micro yarn	[37]
[EMIM][TFSI] TPU	Ion gel	Capacitive	Pressure	Cone-like micro-structures inspired from Calathea zebrine leaf	[38]
[EMIM][TCM] PEGDA	Ion gel	Transistor	Pressure	Micropyramidal structured dielectric layer	[39]
(PTMB)/(NDDA)/ silicone elastomer	Ion gel/elastomer	Capacitive	Multimodal (pressure, strain)	-	[40]
H_2SO_4, NaOH, KOH, Nafion	Hydrogel	Resistive	Strain	High sensitivity, stability, and linearity	[41]
NaCl (PAAmv)	Hydrogel	Capacitive	Multimodal (pressure, strain)	Uniaxial sensing	[42]
LiCl (PAAm), NaCl (PAAm)	Hydrogel	Capacitive	Pressure	Ionic touch panel	[43]
NaCl (PAAmv)	Hydrogel	Capacitive	Multimodal (bend, strain, touch)	Multi touch, transparent	[44]
LiCl (PAAm)	Hydrogel	Capacitive	Pressure	Highly stretchable electroluminescent skin	[45]
[HEA][AA]	Hydrogel	Capacitive	Multimodal (pressure, strain)	Easily adhere to a wide variety of substrates but removable without any damage	[46]
PAA/Ag0	Hydrogel		Pressure	Ultrahigh sensitivity and excellent cycling reliability	[47]
PAM/DCS/PANI	Hydrogel		Strain	Good stability and reproducibility	[48]
GelMA	Hydrogel	Capacitive	Pressure	Transparent, excellent mechanical and electrical properties	[49]
PAA-Fe^{3+}-PVA/TPU	Hydrogel-elastomer hybrid	Resistive	Multimodal (pressure, strain)	Seamless dermis/epidermis interface, self-healing, simple and fast assembly, total recover of properties after damage and self-healing	[50]
PAAm/LiCl/(MBI)	Hydrogel	Resistive	Pressure	Electrochromic, chameleon-inspired, from yellow to red (due to MBI). Conductivity: 0.4 S/m (due to LiCl); stretchability: 1600%	[51]
PDMS/Chiral Nematic LCR	Hydrogel/liquid crystal	Capacitive	Multimodal (pressure, temperature)	thermochromic response (26–40 °C) and tactile sensing (up to 20 kPa)	[52]

Yoon and Chang utilized microfluidic approach to fabricate super-capacitive ITS capable of sensing normal and lateral pressures. This pressure sensor utilized a linear sensing element consisting of 1-Butyl-3- methylimidazolium tetrafluoroborate [BMIM] [BF_4] IL as an electrode in the microfluidic channels and carbon nanotubes-polydimethylsiloxane CNT/PDMS composite as a dielectric layer [27].

Nie et al. fabricated an ionotropic microdroplet array for flexible tactile sensing applications. The sensor uses as IL the 1-ethyl-3-meth-ylimidazolium tricyanometha-nide [EMIM][C(CN)$_3$] droplets, sandwiched between two patterned indium-tin-oxide (ITO) coated ITO–PET films [28].

3.1.2 Characteristics and application of ILs ITS

Keulemans et al. prepared a sensor which showed the highest sensitivity in the frequency range from 10 to 25 kHz, with a corresponding gauge factors (GF) between 2 and 2.5 for an elongation of 10% [19]. The IL composed of 1-butyl-3-meth-ylimidazolium tetrafluoroborate [BMIM] [BF$_4$], prepared by *Zhu et al.* demonstrated the capability of measuring strain up to 55% at room temperature [20]. *Chossat et al.* sensor proved to be hyper elastic with a withstanding strain of up to 100% and showed a gauge factor of 3.08, as shown in Figure 3.1 [21].

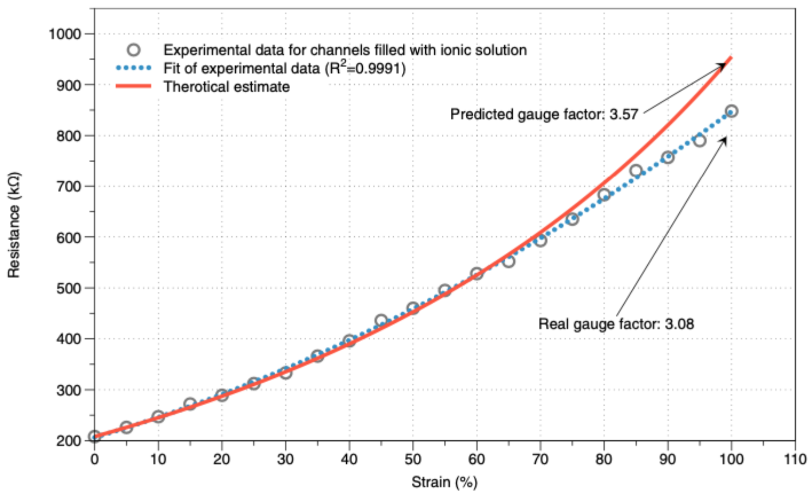

Figure 3.1 Variation of the resistance as a function of strain for the ionic solution strain sensor [21].

Wang et al. sensor showed excellent performance, including tuneable sensitivity, detection of a wide range of strains (0.1–500%), excellent long-term stability (>50 000 cycles), and high durability (after 6 months storage under ambient conditions) as is possible to notice from graphics in Figure 3.2.

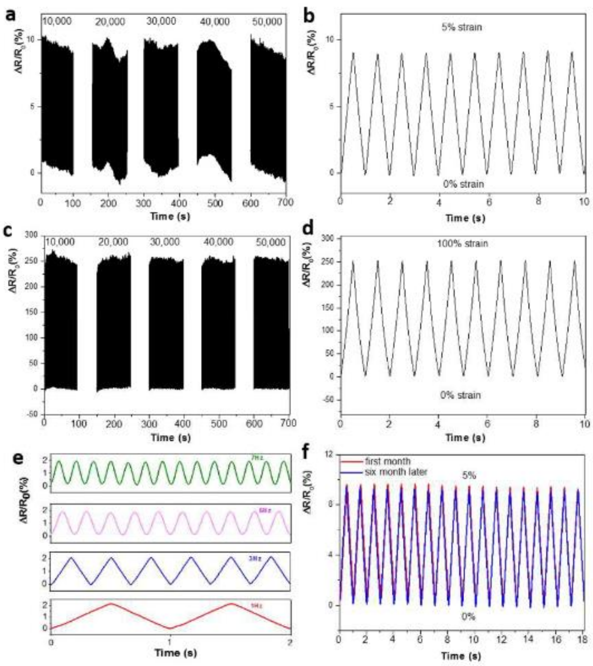

Figure 3.2 Durability and stability performance of IL based rubber band-like wearable sensors (input voltage: 3v). The 50,000 cycling test under 5% (a, b) and 100% (c, d) strains under a frequency of 1Hz. (e) Plots of resistance change under various frequencies of 1Hz. (e) Plots of resistance change under various frequencies of 1Hz to 7Hz under the strain of 1%. (f) Comparison of the resistance changes of the sensor before and after storing it under ambient conditions for 6 months (1 Hz frequency and 5% strain) [22].

After being woven with commercial rubber bands into a bracelet, the sensor enabled real-time monitoring of wrist pulses and different hand gestures. Owing to the inherent mechanical deformability of the liquid phase, IL-based strain sensors demonstrated excellent conformability, which is strongly required to achieve high-performance and highly deformable ITS [22].

Strain sensor of *Yoon et al*. exhibited a GF of 2 for the linear region (<50% strain) and GF of 40 at the maximum stretching of 200%. The sensor exhibited outstanding performance under a variety of deformations induced by stretching, bending, pressing, and twisting. In addition, transparency enables visually customizable ITS capable of monitoring a wide variety of human body motions in real time. The transparency of the device can be noticed in Figure 3.3.

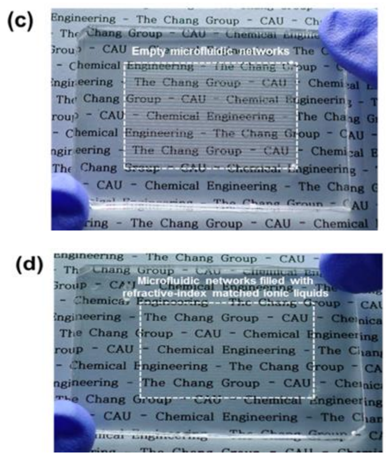

Figure 3.3 Optical characterization of the microfluidic strain sensor [23].

For large area tactile sensors (facial ones), scalable synthesis techniques are crucial to produce large-area, low-cost devices. Moreover, though some *in vivo* tests they monitored various human body motions in real time. In Figure 3.4 it is shown how electrical resistance changes as a function of time for the microfluidic strain sensor with a single linear channel in the PDMS elastomer at different finger bending motions. Electrical resistance also changes as a function of time for the PDMS microfluidic strain sensors with two linear channels at different wrist motions and at various movements of the arm. Photographs and diagram in Figure 3.4 are the corresponding motions of the forefinger (Figure 3.4 a) , wrist (Figure 3.4 b) and arm (Figure 3.4 c) attached with the strain sensors [23].

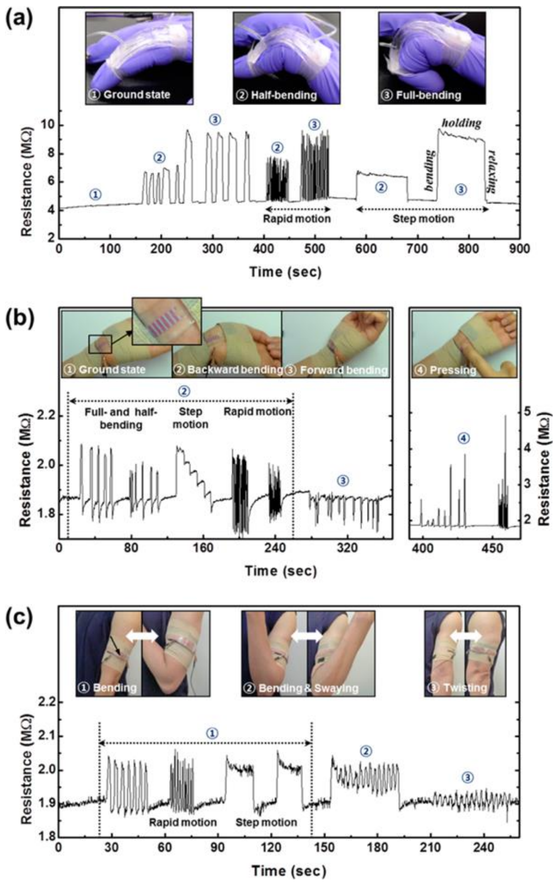

Figure 3.4 Monitoring of various human body motions in real time [23]

Table 2 *Summary of mechanical and other characteristics, sensing range, strain and sensitivities of recently reported ITS.*

Composition	Mechanical Characteristics	Other Characteristics	Sensing range	Strain	Sensitivity	Functional Tests	Refs.
[BMP][BTI]	-	-	-	<10%	2.5 G.F.	None	[19]
[BMIM][BF_4]	-	Low cost, environmentally friendly	-	<55%	-	None	[20]
Glycerol, NaCl	Hyperelastic	-	-	<100%	3.08 G.F.	Lab scale	[21]
[OMIM][Cl]	High durability (> 50,000 cycles), excellent long-term stability	Temperature sensitivity, scalable and low cost	-	500%	3 G.F. (strain 100%) 2 G.F. (strain (25%)	In vivo	[22]
[BMIM][TFSI]	High stretchability, flexibility	Sensitivity, long- term stability, high transparency	-	<200%	2 G.F. (strain <50%) 40 G.F. (strain <200%)	In vivo	[23]
EG, NaCl	Highly stretchable	Low-cost	-	300%	40 G.F. (strain 200%)	In vivo	[24]
[EMIM][TFSI]	Highly stretchable	Transparent	-	400%	7.9 G.F. (strain 5%) 1.7 G.F. (stain 100%)	In vivo	[25]
Glycerol, NaCl	A flexible and stretchable	Ultrahigh sensitivity, extreme flexibility	100 Pa-20 kPa	-	1.58 $nF\ kPa^{-1}$	In vivo	[26]
[BMIM] [BF_4]	-	Highly sensitive	<300 kPa	-	-	In vivo	[27]
[EMIM][$C(CN)_3$]	Highly elastic	Transparent	33 Pa–200 kPa	-	0.43 $nF\ kPa^{-1}$	In vivo	[28]
[EMIM][TFSI] TPU	-	Highly sensitive	<50 kPa	-	1.93 kPa^{-1}	Lab scale	[29]
[EMIM][ESO_4], KCl, PANi	High durability	High sensitivity, fast response time	<20 kPa	-	5.6 kPa^{-1}	In vivo	[30]
[EMIM][TCM], PEGDA	Flexible	-	1– 750 kPa	-	3.1 $nF\ kPa^{-1}$ (<5 kPa)	In vivo	[31]
[EMIM][TFSI] P(VDF-HFP)	Flexible	-	<50 kPa	-	41 kPa^{-1} (<400 Pa) 13 kPa^{-1} (0.5–5 kPa) 2 kPa^{-1} (<50 kPa)	In vivo	[32]
[EMIM][TFSI] P(VDF-HFP)	High stability	Excellent sensitivity	1.12 Pa– 32.35 kPa	-	131.5 kPa^{-1} (<1.5kPa) 11.73 kPa^{-1} (5-27.7kPa)	In vivo	[33]
[EMIM][TFSI] TPU	Flexible	-	<100 kPa	-	1.4 $nF\ kPa^{-1}$ (<10 kPa)	Lab scale	[34]
[EMIM][TFSI] P(VDF-HFP)	Flexible	Long-term wearability	0.018–80 mm Hg	-	114 $nF\ kPa^{-1}$	In vivo	[35]
[EMIM][TRIFLATE] PVA	Flexible	-	<100 kPa	-	10 $nF\ kPa^{-1}$	Lab scale	[36]
[EMIM][TFSI] TPU	High flexibility	High conductivity, high sensitivity	<150 kPa	-	0.68 $nF\ kPa^{-1}$ (<10 kPa) 0.12 $nF\ kPa^{-1}$ (>10 kPa)	In vivo	[37]
[EMIM][TFSI] TPU	Flexible	Low-cost, high sensitivity	0.1 Pa– 115 kPa	-	54.3 kPa^{-1} (<0.5 kPa) 1 kPa^{-1} (<115 Pa)	Lab scale	[38]
[EMIM][TCM] PEGDA	-	High sensitivity	5– 50 kPa	-	3.4 kPa^{-1} (0–8 kPa) 68 kPa^{-1} (8–20 kPa) 40.8 kPa^{-1} (20–50 kPa)	Lab scale	[39]
H_2SO_4, NaOH, KOH, Nafion	Highly cyclic stability	-	-	-	-	In vivo	[41]
NaCl (PAAmv)	Highly stretchable	-	-	-	-	In vivo	[42]
LiCl (PAAm), NaCl (PAAm)	Soft and stretchable	Transparent	-	1000%	-	In vivo	[43]
NaCl (PAAmv)	Stretchability	High transparency	-	-	-	In vivo	[44]

LiCl (PAAm)	Highly stretchable	Transparent	0.9–30.9 kPa	-	-	Lab scale	[45]
[HEA][AA]	Mechanical adaptability	High transparency, self-healing capability	-	200%	0.293 kPa^{-1}	In vivo	[46]
PAA/Ag0	Tissue-like mechanical property	Compatible with water environment	75–1500 Pa	-	171.4 kPa^{-1} (75–1500 Pa) 57.5 kPa^{-1} (<75 Pa)	In vivo	[47]
PAM/DCS/PANI	High degree of ductility and flexibility	-	-	0.3 MPa	15.9 G.F.	In vivo	[48]
GelMA	High durability	Excellent electrical properties	-	-	0.19 kPa^{-1}	In vivo	[49]
PAA-Fe^{3+}-PVA/TPU	High durability, total self-healing	Self-healable mechanical and electrical properties	-	90%	-	In vivo	[50]

Compared to IL-based flat strain sensors, *Choi et al.* wavy sensors show excellent stretchability (up to 250% strain) and improved hysteresis performance. The wavy structures were found to offer lower energy dissipation when compared to the flat structures under a given deformation. In a finger mounted skin-like sensor device, this sensor could successfully detect various activities of the human hand, as illustrated in Figure 3.5.

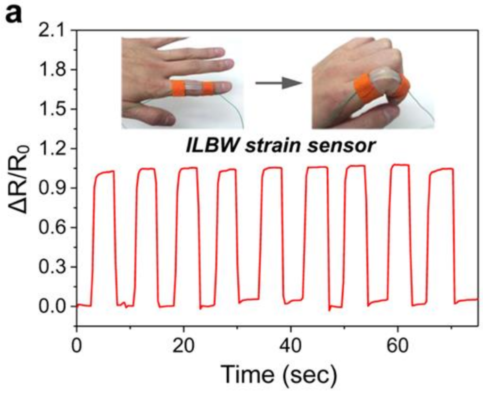

Figure 3.5 Monitoring of human joint motions in real time [24].

Even under the maximum strain of 300%, the response feature was rarely deteriorated after 3000 cycles, the sensor exhibiting excellent durability and a remarkable. gauge factor of 40 at 200% strain [24].
The high electrical conductivity of [EMIM][TFSI] allowed high signal-to-noise ratio in *Zhang et al.* sensor. This sensor exhibited a wide sensing range (0.1% to 400%) and high sensitivity with a GF of 7.9, which is much higher if compared with the previously discussed sensors. The sensor results to be flexible and stretchable. Moreover, the electrical signals of as-obtained sensors were found to depend on the ILs species and the channel size. Such wearable sensors were tested in vivo (Figure 3.6), exhibiting the capability of multiple deformation forms including strain, bending and pressure, which suggested their application in finger touching, wrist and elbow joint movement, throat muscle movement and pulse waveforms.

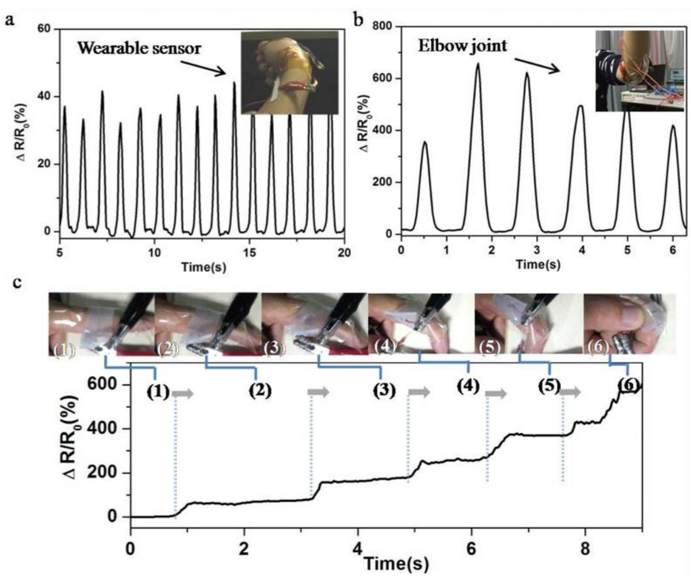

Figure 3.6 (a) The relative resistance change for monitoring of the wrist bending movement at input voltage of 4 V. Inset: the photograph of wearable sensor on the wrist joint. (b) The relative resistance change for monitoring of the elbow joint movement at input voltage of 4 V. Inset: the photograph of sensor on the elbow joint. (c) The relative resistance change of sensor monitoring the finger bending with different directions at input voltage of 4 V [25].

Noteworthy is the easy, low-cost, scalable fabrication strategy, that is supposed to set the stage for the practicable and widespread utilization as a wearable sensor [25].

Nie et al. presented a novel droplet-based pressure sensor that achieve ultrahigh mechanical-to-electrical sensitivity (1.58 $nF\ kPa^{-1}$) and resolution (1.8 Pa) with a simple device architecture. The simply constructed and mechanically flexible droplet sensor was successfully applied *in vivo* to detect minute blood pressure variations on the skin surface (with the maximum value equal to less than 100 Pa) throughout cardiovascular cycles [26].

Yoon and Chang microfluidic capacitive sensors showed good linear response and high-pressure sensitivity at pressure range of 100-300 kPa. Moreover, in vivo tests demonstrated that, when attached to human hand, such microfluidic ITS enabled the realization of skin-like multimodal sensor platforms for sensing different hand motions such as tapping, scratching and hand shaking [27]. *Nie et al.* sensor showed a pressure sensitivity of 0.43 $nF\ kPa^{-1}$, with a minimal pressure detection of 33 Pa. In addition, the low viscosity of the IL [EMIM][$C(CN)_3$] and the high contrast wettability control on the electrode surface enabled fast mechanical response and high durability over more than 20000 cycles of pressure loads. The high sensitivity and rapid response of the iontronic droplet sensor enabled cardiovascular pressure wave recording in a wearable wristband-type sensor device that was in vivo tested [28].

3.2 Ionic Gels

ILs have shown great potential in pressure and strain sensitive ITS owing to their interesting physiochemical properties. However, they also have weaknesses related to their "liquid" nature, which involves limitations such as poor durability, difficult handling, non-portability, and impossibility of miniaturization. For the fabrication of durable ITS, it is highly desirable that the ionic materials should have a polymer-like mechanical integrity, while retaining high ionic conductivity and good electrochemical stability. This can be achieved by developing ionic polymers or ionic gels. The concept of "polymer-in-salt" was introduced first by *Angell et al.* with the aim of doping polymers with salts for form the basis for the development of ionic polymers and ionic gels [11].

3.2.1 Composition, fabrication, type and mode of sensing of ion gels ITS

Pan at al. first demonstrated the use of ionic polymers as thin film-type super-capacitive sensing material, in order to realize a pressure-sensing ITS fabricated entirely of soft materials for wearable and health sensing applications. Poly(ethylene glycol) diacrylate (PEGDA) and 2-hydroxy-2-methylpropio-phenone (HOMPP) was dissolved in 1-ethyl-3-meth-ylimidazolium tricyano-methanide ([EMIM][TCM]) to obtain a flexible, transparent, and conductive ionic polymer matrix. For the fabrication of ITS, the ionic polymer film was sandwiched between two flexible indium-tin-oxide (ITO)-coated polyethylene terephthalate (PET) substrates with a spacer layer made of double-side tape [31]. Later, *Li et al.* reported a pressure-sensitive super-capacitive ITS composed by an electrospun ionic polymer nanofibrous layer as sensing matrix, sandwiched between two patterned conductive fabrics as shown in Figure 3.7. The ionic conductive material adopted in this study is a gel-based matrix on poly(vinylidene fluoride-co-hexafluoro-propylene) P(VDF-HFP), with its ionic component of 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][TFSI] [35].

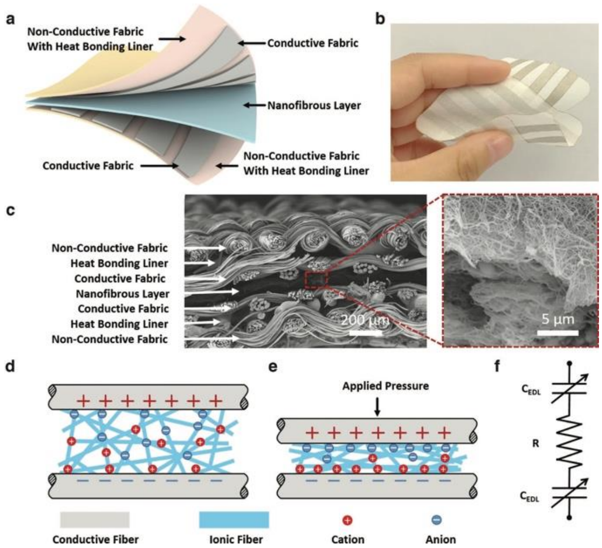

Figure 3.7 Schematic illustration of the all-fabric sensing matrix with a nanofibrous layer (a); SEM photos of the device in cross-section (b); views and operational principle of the nanofabric pressure sensor with the equivalent electrical circuit of the sensor (c) [35].

Recently, *Kim et al.* developed a highly conformable and reliable ionic textile (i-textile) based on sheath-core carbon nanotube (sc-CNT) microyarns and an ionic thermoplastic polyurethane polymer (i-TPU) to form a large area ITS array. The ionic polymer was fabricated by a noncovalent association of 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfoyl)imide [EMIM][TFSI] cation-anion pairs loaded in a TPU elastomeric matrix [37]. Very recently, *Li et al*. introduced an iontronic sensing paper by incorporating both ionic and conductive patterns to the classic paper substrates to develop all-in-one flexible sensing platform. The iontronic sensing paper can be structured into 2D or 3D pressure/force-sensitive devices only by paper specific manipulations, such as printing, cutting, folding, and gluing. Hydrophilic ionic liquid, 1-ethyl-3-methylimidazoliumtrifluoromethanesulfonate([EMIM][OTF]), is introduced to the pulp as the ionic donor in a polyvinyl alcohol (PVA) matrix as shown in Figure 3.8 [36].

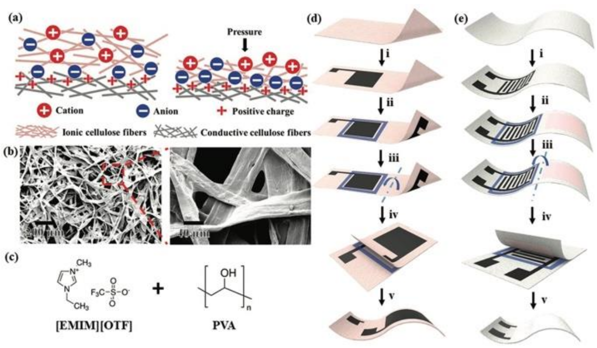

Figure 3.8 Iontronic pressure sensing paper (ISP) device in which the fibrous ionic fibers is used as the ionic region and the conductive fibers is used as the conductive region [36].

Cho et al. fabricated a pyramidal-shaped ionic gel prepared using a blended solution of P(VDF-HFP) as the structuring polymer and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMI][TFSA]) as the IL. Using anisotropic KOH etching on a photolithographically patterned Si wafer, they created moulds with pyramidal impressions in which ionic polymer blend was casted and cured to obtain micro-pyramidal structured ionic polymers (Figure 3.9) [32].

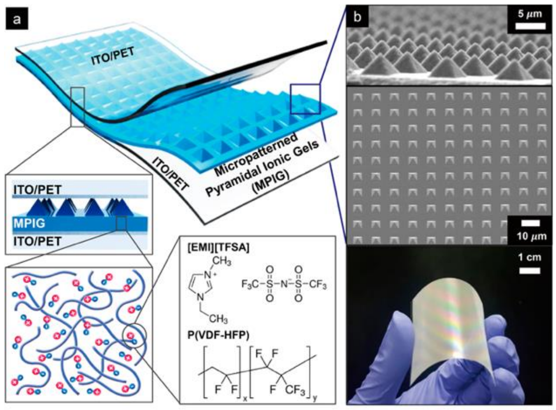

Figure 3.9 Micropyramidal structured ionic polymers [32].

In this regard, *Jang et al.* recently utilized a micro-structured deformable ionic polymer dielectric in an indium–gallium–zinc oxide (IGZO) based thin film transistor for develop a low-powered sensor. Using the silicon master moulding process, they created a micro-pyramidal pattern on ionic polymer 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]-TPU) that was casted and cured to obtain an i-TPU dielectric films with micro-pyramidal structures [39].

Chhetry et al. developed a super-capacitive ITS that resolves the issues of low sensitivity and high limit of detection (LOD) of the tactile sensors reported by *Cho et al.* [32]. The micro-structured iontronic film was fabricated by spin-coating the ionic gel-made of 1-ethyl-3-methylimidazolium bis-trifluoromethylsulfonylimide [EMIM][TFSI] and P(VDF-HFP), on silicon carbide abrasive in order to create the template. The capacitive sensor was fabricated by sandwiching micro-structured iontronic films between two identical AgNW/PDMS electrodes in such a way that microstructures were facing up [33].[20]

Bioinspired ITS involve sensory matrices whose structures, properties or functions directly mimic natural systems. The bioinspired strategy is a newly emerging interdisciplinary concept that has shown great success in e-skins to enhance sensitivity, detection range, selectivity and response time of tactile sensors [11]. According to that, *Qiu et al.* proposed a cost-effective approach to fabricate micro-structured ionic gel film. The *Calathea zebrina leaves* were used as templates to develop micro-cone-structured ionic gel (MIG) film (Figure 3.10). The ionic gel uses a blended solution of poly (vinylidenefluoride-co-hexafluoropropylene) (P(VDF-HFP)) as the structuring polymer and 1-ethyl-3-methylimida-zolium bis(trifluoromethylsulfonyl)imi-de ([EMIM][TFSI]) as the IL. This process provided an efficient and cost-effective route to fabricate micro-structured ionic polymer films compared to photolithographic processes [38].

In these regards, also *Chun et al.* developed a bioinspired ion channel pressure sensor that closely mimics the mechanotransduction features (ion transport mechanism) in biological ion channels. This bioinspired ion channel pressure sensor was fabricated by stacking structures utilizing polymers, electrolytes and nanopore membranes. The electrolytes, which included PANi, potassium chloride (KCl), and 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid (IL), were selected on the basis of their different ion mobility and ion conductivity [30].

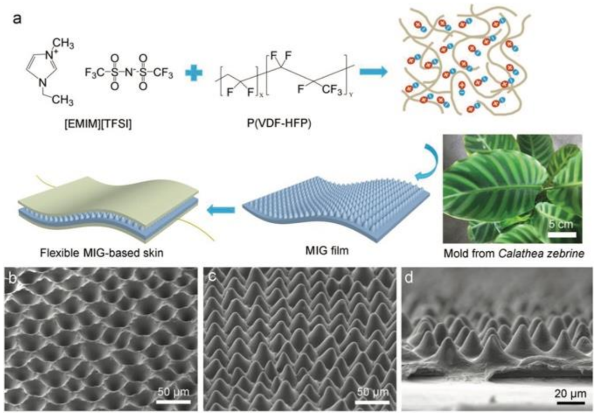

Figure 3.10 Fabrication of flexible MIG-based skin [38].

Jin et al. introduced a pillar shaped patterns that mimicked the papillary ridges of Merkel cells. In particular, a super capacitive ITS was designed in which an ionic thermoplastic polyurethane (i-TPU) film was prepared by the noncovalent association of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM] + [TFSI] − cation– anion pairs) loaded in a TPU matrix [34].

Choi et al. developed a pyramid-plug structure for highly sensitive tactile sensors that enables them to detect pressure, shear force, and torsion. The device is composed of pyramid-patterned ionic gel inspired by neural mechanoreceptors and engraved electrodes. Based on a pyramid-plug structure, the deformation mechanism differs between different types of external mechanical loadings [29].

3.2.2 Characteristics and application of ion gels ITS

The soft sensor proposed by *Pan at al.* offered an ultrahigh unit area capacitance (5.4 μF cm^{-2}) of the ionic sensor, leading to a high mechanical-to-capacitive sensitivity of 3.1 $nF\ kPa^{-1}$. In particular, this pressure sensitive ITS exhibited excellent mechanical stability (a variation of less than 3% even after deformation with various radii of curvatures) and high repeatability (30000 testing cycles) [31]. *Li et al.* fiber-based pressure-sensitive super-capacitive ITS offered an extraordinarily high sensitivity of 114 $nF\ kPa^{-1}$, with a pressure resolution of 2.4 Pa and a response time of 4.2 ms. High sensitivity and extended wearability of the nano-fabric sensor allowed ITS incorporation into several wearable pressure monitoring platforms that were in vivo tested as shown in Figure 3.11 [35].

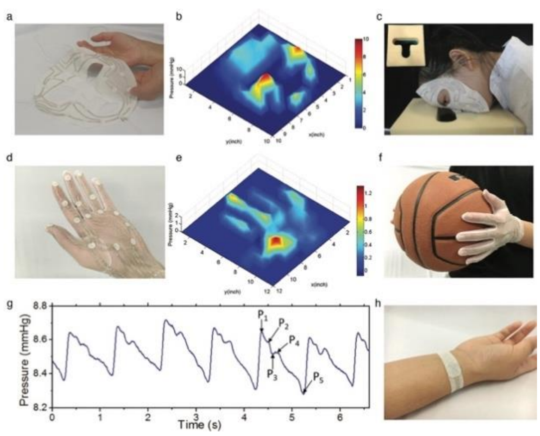

Figure 3.11 Supercapacitive all-fabric facemask with 20 pressure sensing units and a glove integrated with 16 all-fabric pressure sensing units [35].

Kim et al. ionic polymer demonstrated high stretchability and transparency, simultaneously. The sensor showed remarkable sensitivity of 0.68 $nF\ kPa^{-1}$ below 10 kPa and 0.12 $nF\ kPa^{-1}$over 10 kPa for more than 2000 cycles. In addition, based on this type of highly conformable and reliable i-textiles, forefinger motion before and after bending were detected in i-textile pressure sensor array [37].

Li et al. iontronic sensing paper exhibited a pressure sensitivity of 10 $nF\ kPa^{-1}$, a single-Pascal pressure resolution of 6.25 Pa, a single-millisecond response time, a high linearity (up to 25 kPa), and wide pressure sensing range up to 100 kPa. This iontronic sensing paper can be used as a simple ITS for the detection of various physiological signals such as continuous pulse wave monitoring of blood pressure, heart rates, respiratory rates, emotional stress and blood pressure variations. In vivo tests were performed as it is possible to see in Figure 3.12 [36].

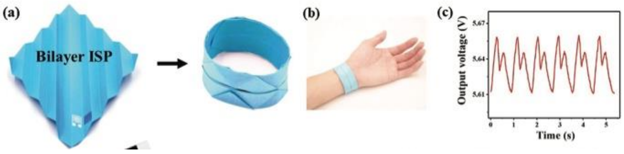

Figure 3.12 a) The preparation of the ISP origami bracelet using printing and folding; b) the ISP origami bracelet is wearable for pulse monitoring, c) the pulse wave signal collected by the ISP origami bracelet [36].

Cho et al. pyramidal ionic gel film exhibited improved mechanical properties such as low modulus, low surface attraction and low adhesion properties. This sensor demonstrated an ultrasensitive pressure detection (41 to 2 kPa^{-1}) and a broad sensing range (0–50 kPa), but a low sensitivity and high limit of detection (LOD). In vivo tests have shown that this ITS could efficiently detect a broad variety of pressure sources arising from sound, lightweight objects, jugular venous pulses, radial artery pulses, finger touch, and finger motion (Figure 3.13).

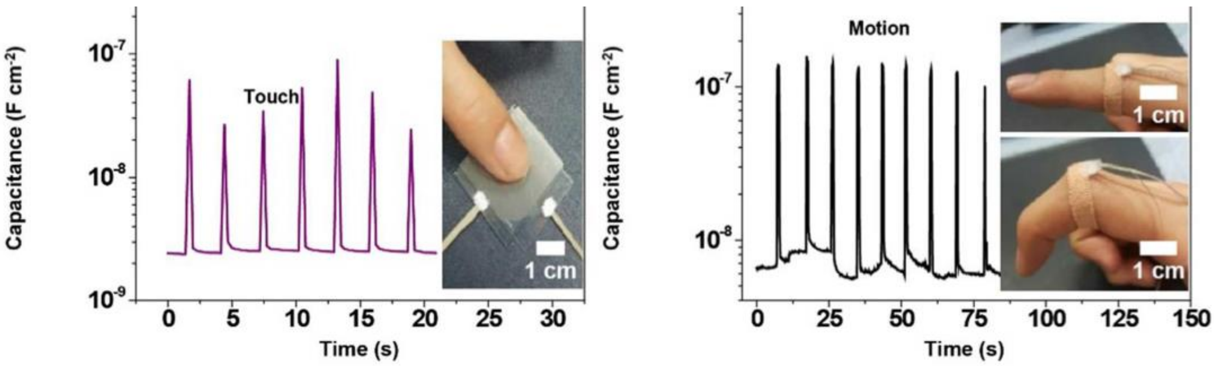

Figure 3.13 Real time monitoring of capacitance changes from pressure arising from finger touching and finger bending [32].

In general, transistor-type tactile sensors with micro-structured gate dielectrics show higher pressure sensitivity than micro-structured dielectric-based capacitive tactile sensors because small capacitance changes cause large alterations in the current channel [32].

Jang et al. transistor-type ITS exhibit ultrahigh sensitivity (43.6 kPa^{-1}) over a wide range of pressures from 5 to 50 kPa [39]. *Chhetry et al.* super-capacitive ITS has shown an ultrahigh pressure sensitivity of 131.5 kPa^{-1}, a low response time (43 ms), a LOD of 1.12 Pa, and a high stability over 7000 cycles was achieved. Furthermore, during the *in vivo* tests, the sensor exhibits excellent ability to detect physiological signals generated from the human wrist and the subtle human skin motion such as eye blinking Figure 3.14.

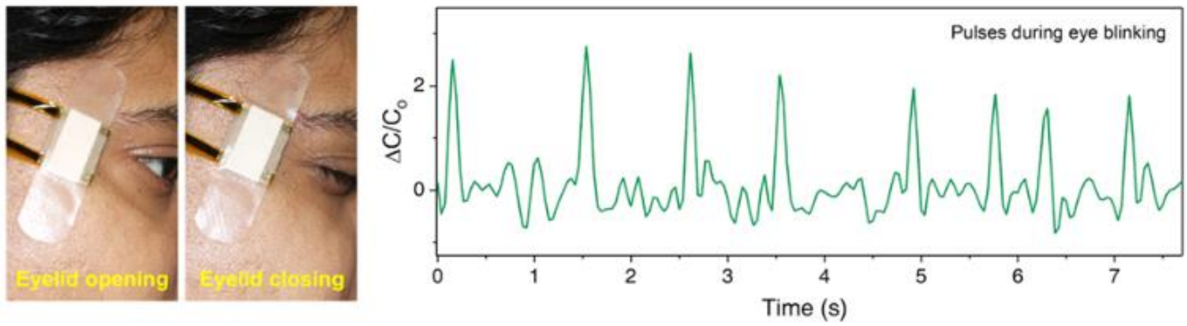

Figure 3.14 Photographs of the sensor attached to detect muscle movement during eyelid opening and closing. (h) Real-time capacitance response for the corresponding eye blinking movements [19].

The facile, low-cost fabrication, the excellent sensitivity along with low LOD demonstrate that this sensor is convenient for wearable electronics, e-skin, and human health status monitoring [33].

Qiu et al. ITS exhibited an ultralow LOD of 0.1 Pa, fast response time of 29 ms and high sensitivity of 54.3 kPa^{-1} (<0.5 kPa). With the aid of a simulation study of ionic-electronic contact area against external load, it was showed that local stress was concentrated at the cone tips to squeeze contacted cones. The contact area of the cone with the electrode increases as the area of each cone increases. As a result, the area significantly increased and capacitance of the sensor augmented accordingly [38].

Chun et al. bioinspired pressure-sensitive ITS that mimics ionic mechanotransduction, exhibited a sensitivity of 5.6 kPa^{-1} with a response time of 12 ms at a frequency of 1 Hz. In addition, the sensor was highly durable over 10000 loading cycles and could successfully detect blood pressure wave pulses when attached to a human wrist, as in vivo tests confirmed [30]. The emulation of ionic mechanotransduction mechanism in mammalian physiology proposed by *Jin et al.* led to an ultrahigh sensitivity over a wide range of mechanical stimuli (1.4 $nF\ kPa^{-1}$over 10 kPa) from subtle touch (10.2 Pa) to object manipulation tasks (100 kPa) even under an ultralow voltage of 1 mV [34].

Choi et al. sensor provides the high sensitivities of 1.93 kPa^{-1} and a wide range of detection for tactile daily activity. Moreover, this tactile sensor could work through either of the two transduction methods (capacitive transduction and piezoresistive transduction). It is shown that this tactile sensor can be used to monitor changes in electrical signals ranging from those caused by human breathing to those caused by arbitrary multiplex human touching [29].

4 Hydrogels

Hydrogels are 3D, cross-linked polymer networks extensively swollen with water. The polymer network endows the hydrogel with elastic properties, while the water molecules make it an ionic conductor. Hydrogels have been widely used for diversified applications, including biomedical ones such as drug delivery, tissue engineering, artificial burn dressings and cell cultures [53–60]. Recently, hydrogels have emerged as new ionic conductors with excellent stretchability, high transparency, modulable conductivity and biocompatibility, which enables new applications of hydrogels in soft electronics [11]. Relevant examples of that are discussed below.

4.1.1 Composition, fabrication, type and mode of sensing of hydrogels ITS

Sun et al. fabricated a strain-sensitive ITS utilizing a PAAm–NaCl hydrogel as a flexible ionic conductor [42]. *Kim et al.* developed a surface-capacitive ionic touch panel utilizing PAAm–LiCl hydrogels to sense position of touch point [43].

PAAm-LiCl hydrogels were even loaded with 1-methyl-4,4′-bipyridinium iodide (MBI) to endow the tactile sensors with chameleon-inspired electrochromic properties [51]. In fact, while PAAm hydrogel and LiCl granted, respectively, extreme stretchability (up to 1600% strain) and ionic conductivity (0.6 S/m), MBI provided the proposed e-skin with the additional ability to turn from light yellow to red as a function of pressure applied, as shown in Figure 4.1.

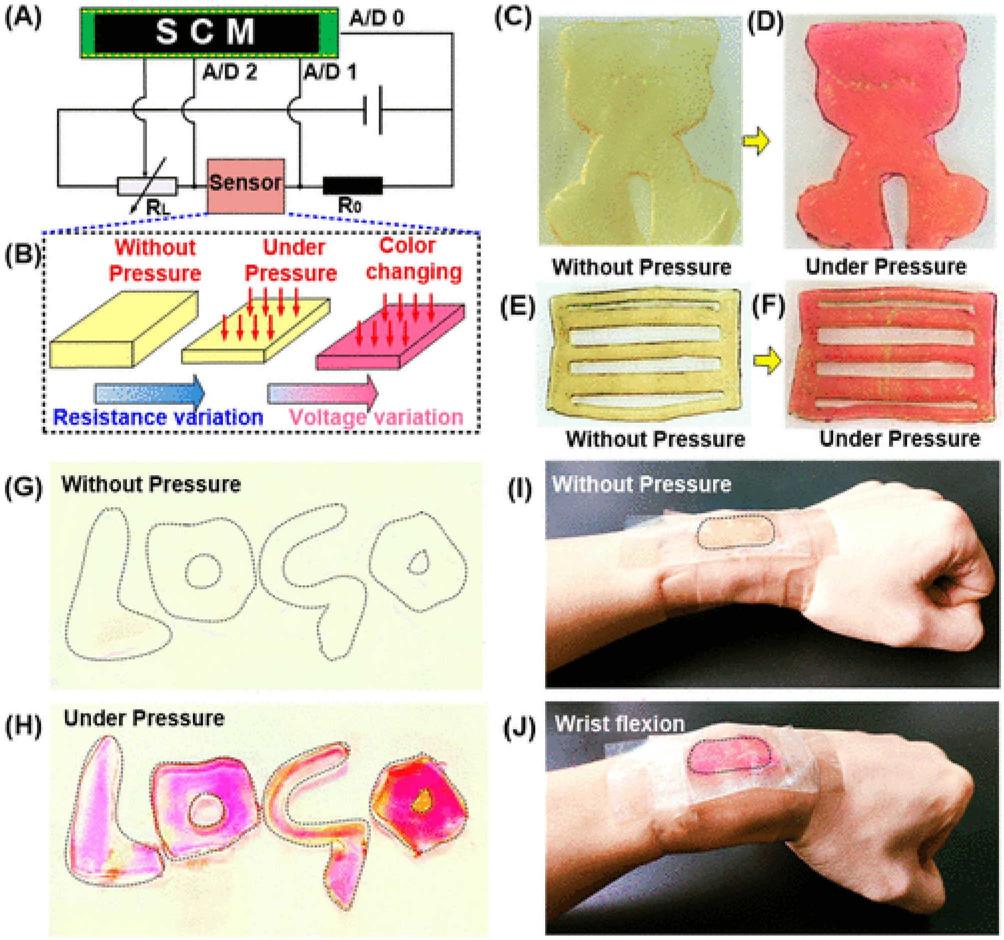

Figure 4.1 (A) The circuit diagram and (B) working mechanism of the tactile sensor for direct visualization of stresses. (C, D) The PAAm organogels with the patterns of a teddy bear and (E, F) bar code. (G) The PAAm organogel with BMI hidden in the PAAm organogel without BMI, which is visualized under pressure (H). (I, J) Interactive color changing controlled by wrist flexion via the PAAm organogel [51].

Nguyen et al. utilized a cross-grid array of PAAm–NaCl hydrogel electrodes to fabricate an ionic touch panel based on projected-capacitive touch sensing that enabled sensing of finger proximity and the multiple touch detection capabilities. A three-step fabrication process mould-bond-polymerize was used to fabricate cross-grid array of ionic hydrogels [44].

Han et al. fabricated a bioinspired, strain-sensitive ITS based on a single-ion conductor sandwiched between two vertically aligned carbon nanotubes (VA-CNT) array electrodes. In this study, Nafion was used as the polymeric ion conductor. Under compressive or tensile strain, the ions move to the expanded regions from the compressed regions as a result of stress gradient. This redistribution of ions generates an output potential in the
direction of the membrane thickness [41].

Larson et al. developed a hydrogel-based light-emitting device (LED) that provides both light-emitting and touch sensing capabilities, simultaneously. Layers of transparent PAAm–LiCl hydrogel electrodes sandwiched a ZnS phosphor-doped silicon elastomer layer. This device exhibited a change of illuminance and capacitance under deformation (Figure 4.2) [45].

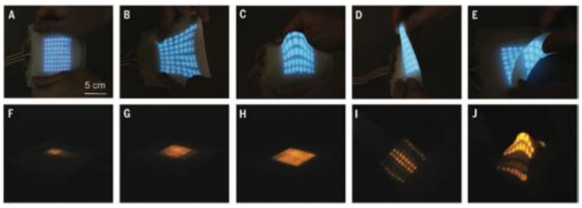

Figure 4.2 Multipixel electroluminescent displays fabricated via replica molding [45].

Zhang et al. synthesized a series of cross-linked organogels with high transparency, mechanical adaptability and adhesiveness to serve as dielectric layers for capacitive ionic skin by a simple yet versatile strategy. The organogels were assembled into a sandwich configuration with ionic conductive hydrogels to obtain a robust capacitive ionic sensor. The ionic conductive hydrogel was prepared using hydroxyethyl acrylate (HEA) and acrylic acid (AA) [46].

Ding et al. reported a novel type of ultrasensitive ionic-type tactile sensor based on a silver-nanoparticles (Ag NPs)-embedded hydrogel sandwiched by two copper electrodes named as asymmetric ionic sensing hydrogel (AISH). These sensors employ polyacrylic acid hydrogel with both silver nanoparticles and ions inside (PAA/Ag0 hydrogel) as the conducting channel, and copper foils as two electrodes. The hydrogel was fabricated in one step by the UV curing of the mixed aqueous solution of acrylic acid (AA) monomer, cross-linking agent N,N′-methelene-bisacrylamide (MBAA), photo-initiator α-ketoglutarate, and silver nitrate. In the mixed solution, negatively charged carboxy groups in AA monomers facilitate the dispersion of positively charged silver ions [47].

Xie et al. synthesized an hydrogel by free radical copolymerization: the double bond modified chitosan (DCS) was grafted onto the polyacrylamide (PAM). The PAM/DCS hydrogel containing aniline monomer was immersed in $FeCl_3$ solution, and aniline was oxidized in situ by Fe^{3+}. PANI network was formed in the hydrogel, converting the transparent hydrogel into dark green. Meanwhile, the DCS chains were physically cross-linked through chelating bonds between the CS chains and the Fe^{3+}/Fe^{2+} ions. As a result, the PAM/DCS/PANI hydrogel contained chemically and physically cross-linked interpenetrating network, which endowed the hydrogel with superior mechanical properties, high degree of ductility and flexibility. The morphology of PAM, PAM/DCS and PAM/DCS/PANI hydrogels was investigated by scanning electron microscopy (SEM). The images show that the hydrogels have a porous structure due to the loss of water in the process of freeze-drying. The pure PAM hydrogel exhibited a structure of a microporous sheet structure (Figure 4.3 a). The PAM/ DCS hydrogel had a denser structure than PAM hydrogel (Figure 4.3 b). After aniline was absorbed into the PAM/DCS hydrogel and polymerized in the presence of the FeCl3 solution, the hydrogel became more porous, which suggested that the PANI broke the dense cross-linking between the CS and Fe ions (Figure 4.3 c). The high-magnification micrograph showed that PANI nanofibers on the wall of the hydrogel micropores (Figure 4.3 d) [48].

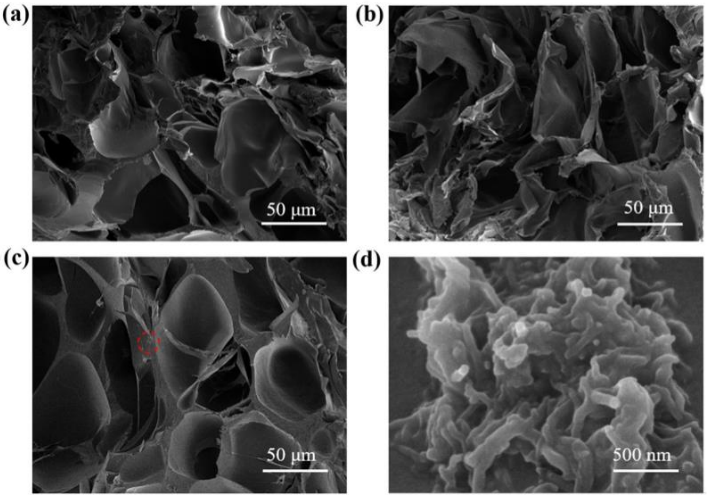

Figure 4.3 Morphology of the various hydrogels. a PAM hydrogel, b PAM/DCS hydrogel, c PAM/ DCS/PANI hydrogel and d magnified image of circle area in (c), showing that PANI nanorods embedded in the hydrogel [48].

Li et al. demonstrated the successful development of a GelMA-based wearable capacitive tactile sensors for monitoring human physiological signals. A processable and transparent GelMA-based pressure sensor structure was developed, with conducting polymer PEDOT:PSS as transparent electrodes and PDMS/GelMA/PDMS as dielectric layers. In this design, GelMA serves as the core dielectric layer; PDMS acts as an insulator between the GelMA dielectric layer and electrodes, and also as an encapsulation layer to prevent water evaporation of GelMA [49].

4.1.2 Characteristics and application of hydrogels ITS

Strain sensor prepared by *Sun et al.* has a large dynamic range and is stable over more than 1000 cycles (Figure 4.4).

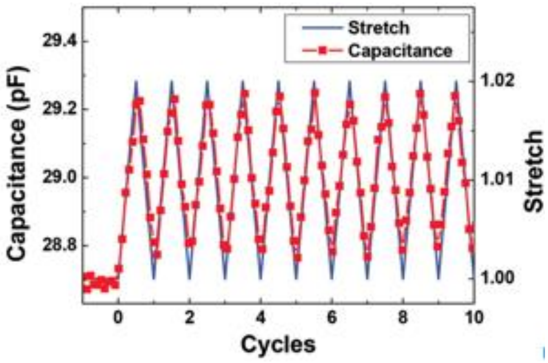

Figure 4.4 A uniaxial force loaded the strain sensor cyclically at a frequency of 1 Hz between the undeformed state and a stretch of 1.02 [42].

In vivo tests confirmed that the softness of ITS allowed it to conform readily with respect to curved surfaces like finger joints to detect bending and other motions (Figure 4.5) [42].

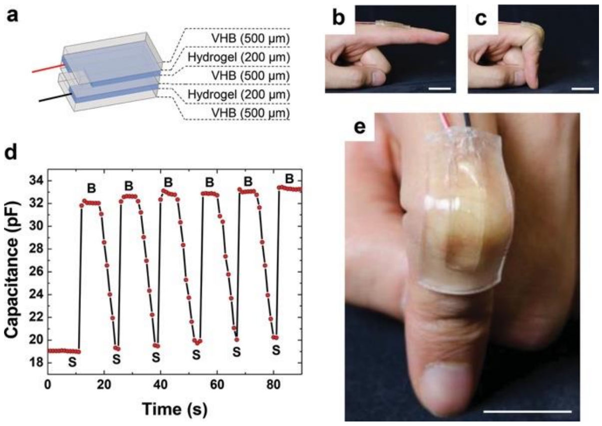

Figure 4.5 Characteristics and application of ion gels ITS [42].

Kim et al. fabricated a soft and stretchable panel, capable of sustaining large deformation. The panel can freely transmit light information because the hydrogel is transparent, with 98% transmittance for visible light. A surface-capacitive touch system was adopted to sense a touched position. The panel can be operated under more than 1000% areal strain without sacrificing its functionalities. Electromechanical stability was tested for the hydrogel through a cyclic loading test up to 100 cycles.

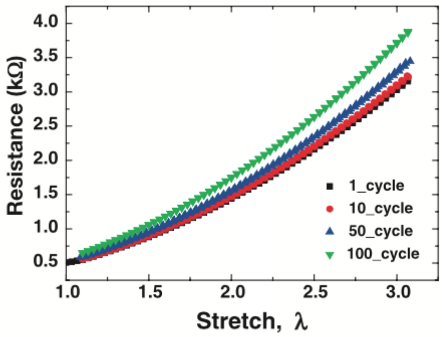

Figure 4.6 Measured resistance at various cycles is presented in Fig. 3H: 1, 10, 50, and 100 cycles.

As shown in Figure 4.6 the resistance slightly increased as the cycles increased. The increase in resistance during a cyclic test may originate from water evaporation in the gel. Epidermal touch panel use on skin was demonstrated by writing words, playing a piano and playing games [43].

The effect of touch of *Nguyen et al.* sensor is clearly visible even when the sensor is bent or stretched. In addition, the sensor is transparent (95% transmittance), resilient under repeated tensile strain, can withstand exposure to temperatures between −4 and 100°C without loss of performance and shows good shelf life [44].

Han et al. ITS showed excellent sensitivity (7.85 mV per 1% strain) with good cyclic stability: no obvious change in output potential was observed during the measurement of over 4000 bending per flat cycles (Figure 4.7).

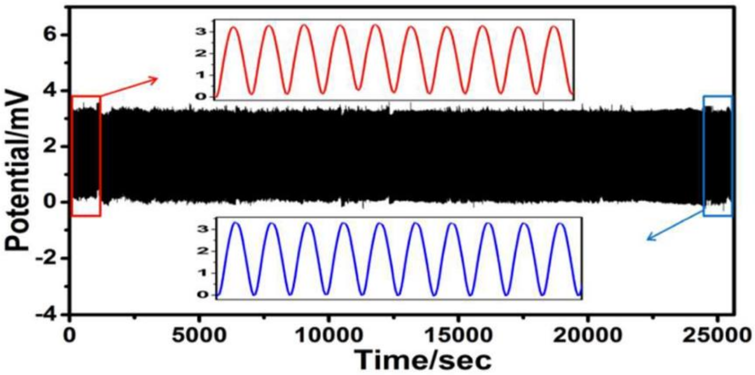

Figure 4.7 Real-time potential-time curves of the VA-CNTs electrodes based sensors for over 4000 bending/flat cycles [41].

In addition, when this strain-sensitive, bioinspired ITS was attached to human skin, it could detect various human physiological signals such as movement of muscles and pulse waveforms [41].
The low Young's modulus of *Larson et al.* hydrogel electrodes allowed excellent stretchability to the device without delaminating. The excellent transparency and the conductivity of PAAm–LiCl hydrogel electrodes even in the stretched state enabled the user-interactive visual response under various modes of deformation, including stretching, folding, rolling, and wrapping [45].
Through regulation of the chemical cross-linking density and network polymer contents, the. organogels synthesized by *Zhang et al* exhibited a wide spectrum of comprehensive properties, including high stretchability, compression fatigue resistance and adhesiveness. This ionic sensor exhibited high sensitivity (0.293 kPa^{-1}), thus being suitable to monitor various human motions such as finger stretching, wrist bending, and throat movement during chewing [46].
The tactile sensor reported by *Ding et al.* exhibits an ultrahigh sensitivity of 57.5 kPa^{-1} in the pressure range of 0–75 Pa and 171.4 kPa^{-1} in the range of 75–1500 Pa (Figure 4.8 a). The sensor still has a noticeable current change by ≈2% under an extreme subtle pressure of 0.075 Pa (Figure 4.8 b), or equally meaning a 0.75 mg object with an area of 1 cm^2 laid on the sensor (inset of Figure 4.8 b), which suggests that the sensor has an extremely low detection force. Cycling tests of the tactile sensor show that after a slight decay of the sensitivity during the initial 500 cycles, the performance of the sensor remains quite stable in the following 1000 cycles, revealing a good reliability (Figure 4.8 c).

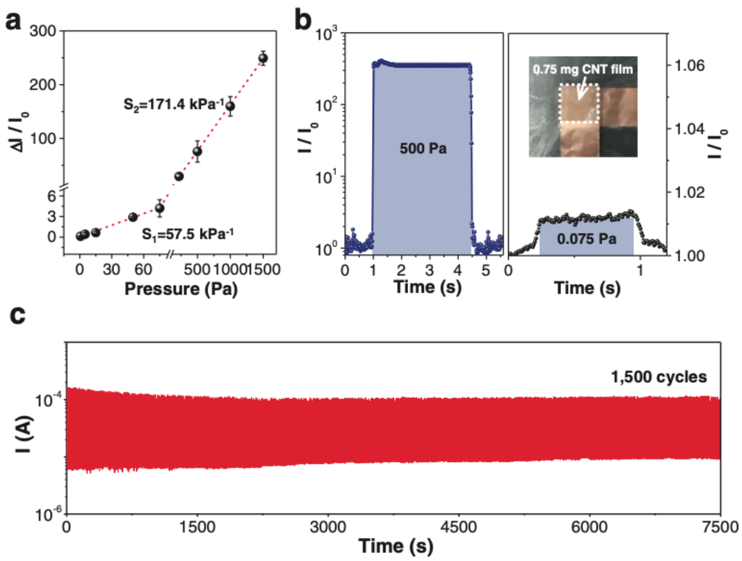

Figure 4.8 a) Change rates of current under different pressures. b) Typical electromechanical response of the tactile sensor at 500 Pa (left panel) and 0.075 Pa (right panel), respectively. The 0.075 Pa pressure is applied through a 0.75 mg CNT film with an area of 1 cm2 (inset of the right panel). c) Cyclic test of the sensor under applying and releasing of a pressure of 500 Pa at 0.2 Hz [47].

This tactile sensor was taped on human wrist to record the waveform of pulse vibration. Moreover, the compatibility of such materials with water environment, could pave the road for their use as ultra-sensitive vibration sensors that work underwater, thus enormously broadening the range of possible applications [47].

PAM/DCS/PANI hydrogel sensor proposed by *Xie et al.* can recover from repeated loading and unloading cycle quickly and effectively, showing excellent mechanical stability. The hydrogel exhibited high sensitivity (GF = 15.9) at low strain and excellent linearity at high strain. Moreover, as shown in Figure 4.9 it maintains good electrical stability during cyclic loading and unloading.

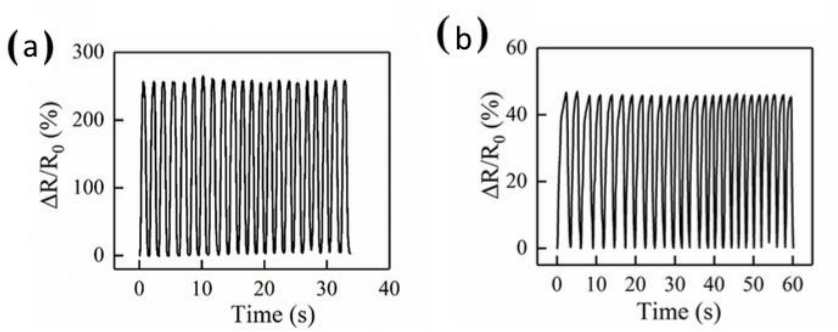

Figure 4.9. Resistance changes of hydrogels upon cyclic (a) tensile and (b) compression loading/unloading tests

As depicted in Figure 4.10 the PAM/DCS/PANI hydrogel was attached to the index finger by a conductive tape to monitor its gripping motion. During the grip holding process of the hand, the relative resistance of the hydrogel sensor was found to rapidly rise to a corresponding value as the degree of bending of the finger during the movement was different. When the hand was re-stretched, the relative resistance immediately returned to the original level. These results fully demonstrate the high strain sensitivity and ultra-fast response of hydrogel sensors, making them ideal for human health monitoring. [48].

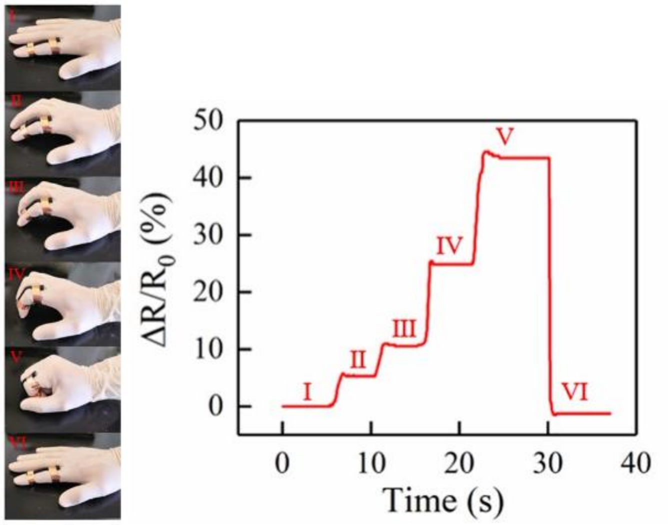

Figure 4.10 The PAM/DCS/PANI hydrogels as an electronic skin fixed on forefinger of a human hand to monitor its grasping motions, and its corresponding resistance variations. [48].

Li et al. GelMA-based pressure sensor showed a pressure sensitivity of 6.5 × 10−3 kPa^{-1} in the pressure range of 0–17 kPa, which was one order of magnitude higher than that of PDMS-based device. The sensitivity decreased to 8.7×10^{-4} kPa^{-1} in the pressure range of 25–84 kPa, which was attributable to the reduced deformability of GelMA hydrogels under high pressure. In order to demonstrate the potential of GelMA tactile sensor for practical applications, the sensor was tested under air blowing pressure and finger touch. The capacitance proved to increase immediately in the presence of air pressure (≈0.1 kPa) while returning to its original value in the absence of the air pressure (Figure 4.11 a). Moreover, the sensor was found to be responsive to a gentle finger touch with a pressure of ≈1 kPa (Figure 4.11 b). In both cases, the base capacitance remained stable after cyclic tests, demonstrating that the GelMA-based pressure sensors have great potential to monitor the subtle pressure as wearable sensors [49].

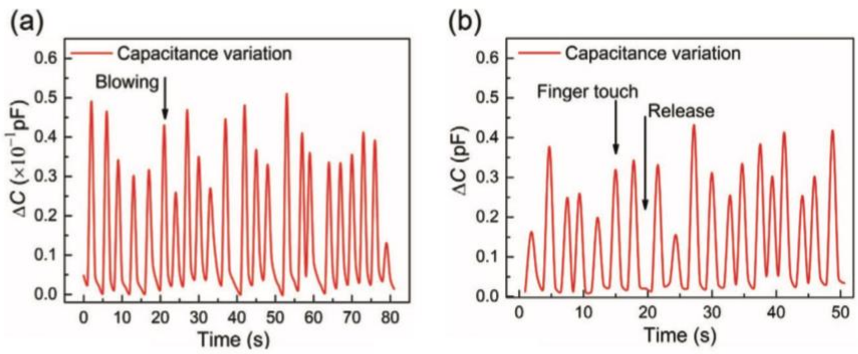

Figure 4.11 Applications of GelMA-based pressure sensors in monitoring of human physical or physiological signals. a) Detection of air blowing from a nitrogen gun. b) Sensing of finger touch force. c) Digital photo for set up of human wrist pulse monitoring. d) Results for wrist pulse detection. e) Schematic of the set up for carotid artery pulse measurement. f) Capacitance change with carotid artery pulse. g) Schematic of the set up for the vocal cord vibration detection. h) Capacitance change when swallowing. i) Capacitance variation when speaking letters, "U," "C," "L," and "A."

5 Hydrogel-Elastomer Hybrids

In the field of biomedical devices, combining epidermis-like elastomers and dermis-like hydrogels into a hybrid system is currently limited by assembly failures because of the weak interfacial bonding between heterogeneous materials. Furthermore, adhesion to wet and dynamic surfaces, such as biological tissues, although crucial, is still a challenging issue. In fact, the necessity to avoid the use of cytotoxic adhesives, together with the poor efficacy of existing adhesives in wet environments, currently hinders the possibility to mimic dermis-epidermis structure of the skin [61,62]. A bioinspired design of hybrid materials, capable of mimicking dermis-epidermis structure of human skin, was recently proposed by Shi et al. [50], who gathered a dermis-like hydrogel, for ion conductivity and an epidermis-like thermoplastic polyurethane (TPU) elastomer for protection, into a unique e-skin device. The hydrogel was prepared via interpenetrating polymer network strategy, involving the sequential chemical/ionic crosslinking of Fe^{3+}/poly(acrylic acid) (PAA) chains, and the physical crosslinking of poly(vinyl alcohol) chains. Such wholly "self-healable" material displayed a seamless interface with remarkably strong adhesion. Figure 5.1 depicts the damage-restoration-concept of a hybrid e-skin mimicking the human skin. As reported in Figure 5.2, not only mechanical and electrical properties, but even strain-sensing performances could be totally restored as original by simply recontacting the cut pieces at room temperature.

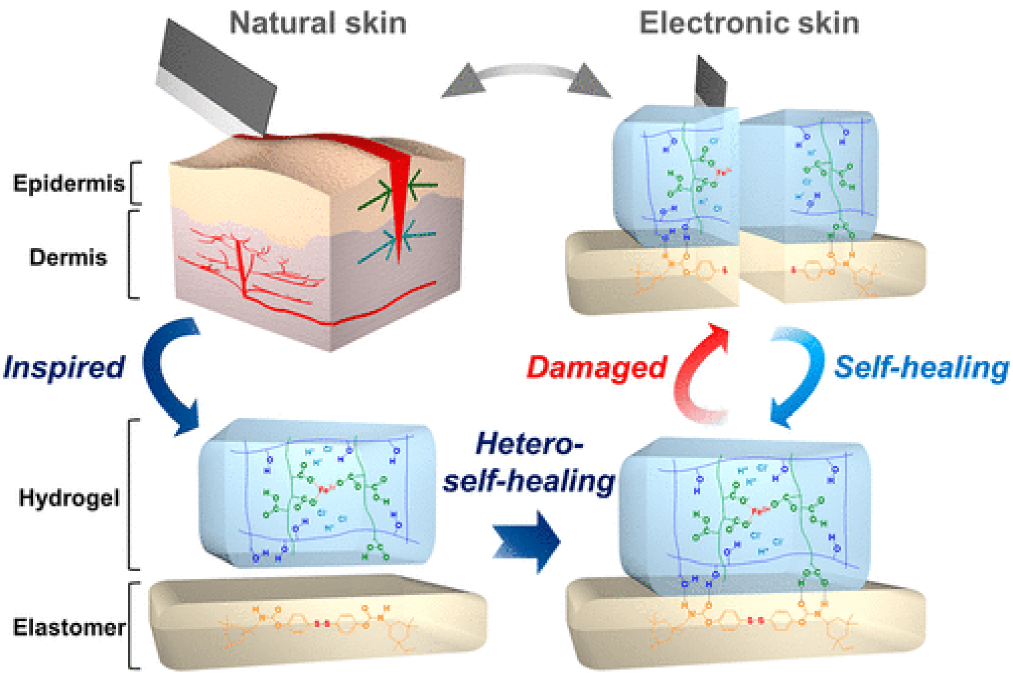

Figure 5.1 Concept of self-healing electronic skin (e-skin) mimicking natural human skin, made of hydrogel and elastomer. The schematic illustrations depict the formation of a seamless interface between the IPN hydrogel and disulfide TPU by heteroself-healing, as well as the concept of a wholly self-healing e-skin, respectively ([50]).

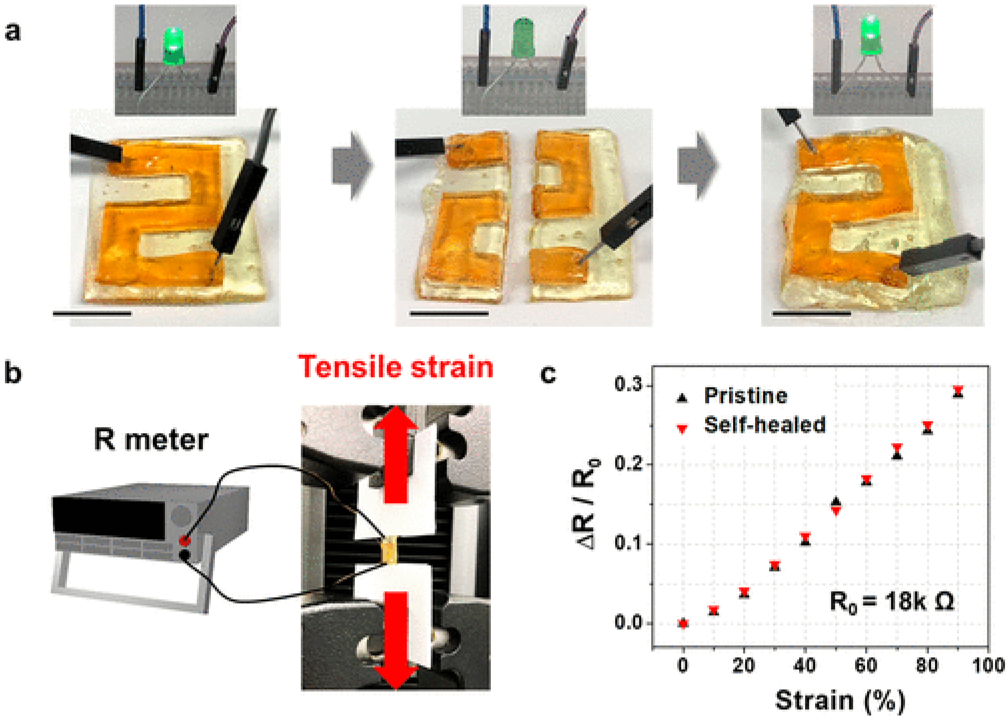

Figure 5.2 Electrical self-healing of an e-skin. (a) "S-shape"-patterned IPN hydrogel electrode on disulfide TPU (scale bar: 1 cm). (b) The tensile testing setup for self-healing of strain sensitivity and (c) the change in electrical resistance as the strain was applied on the pristine and self-healed devices (Adapted from [50]*).*

Charaya et al. fabricated a thermochromic ITS via the incorporation of a chiral nematic liquid crystal into a hydrogel/elastomer sandwich based on ion- containing polyampholyte hydrogel and PDMS. Such material showed intriguing capability of changing colour as a response to temperature changes in the range 26–40 °C, while being able to sense finger tap (≈20 kPa pressure), thus serving as a pressure sensor (Figure 5.3) [52].

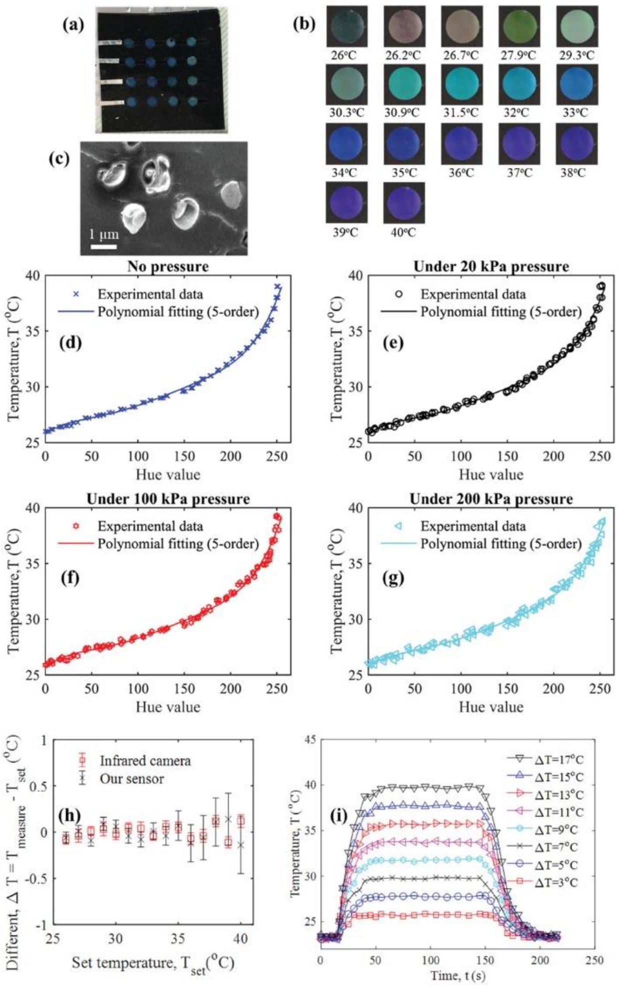

Figure 5.3 Digital image of a temperature sensing unit at different temperatures with gaussian filter. c) Scanning electron microscopy (SEM) image of the cross- section of the PDMS/TLC composite with microcapsules of TLC slurry. Hue–temperature calibration curve of PDMS–TLC composite material under d) no pressure, e) 20 kPa, f) 100 kPa, and g) 200 kPa. Black line is the fitted (five- order) polynomial curve. h) Comparison of PDMS/TLC and IR based temperature sensing in regarding to the same preset temperature stage for the sensor under less than 200 kPa. i) The real- time response of the temperature sensor with varying temperature difference between active surface and ambience [52].

Capacitive, extremely soft ITS can be prepared by embedding ion gels, constituted by pentaerythritiol tetrakis(3-mercaptobutylate) (PTMB) and 1,9-nonanediol diacrylate (NDDA), into a silicone elastomer matrix. Such materials, relying on the synergism of ion conductivity and stretchability, demonstrated outstanding sensing capabilities in a wide range of pressure and strain [40].

6 Conclusion and future perspectives

Recently, many efforts have been done to develop high-performance, human skin-like deformable ionic tactile sensors along with self-powered and self-healing capabilities. In this review, the recent advances in ITS and their potential applications for emerging human-interactive technologies have been reported. In particular, several ionic materials such as ILs, ionic polymers/gels, and hydrogels were reviewed as attractive candidates for realizing high-performance ITS to emulate the tactile sensory capability of human skin. The latest advances in ionic tactile sensors in terms of nature of materials, type of functions and pressure/strain sensitivities were analysed and discussed. From these comparisons, it is possible to deduce that sensitivity and sensing range of ITS could be extremely enhanced with the structural engineering of ionic materials. In addition, it could be highlighted that biomimetic approaches in ITS bring to the fabrication of sensors with a pressure sensing range that satisfies the specific requirements in various applications, such as robotics and prosthetics as well as skin-attachable health monitoring. Unfortunately, devices capable of sensing multiple forms of mechanical loads have not been fully developed. Most of the ionic devices, in fact, have been focused on the capability to perceive only a single type of mechanical stimulus. However, multimodal tactile sensing ability is essential to be able to create a sensor that perfectly reproduces the human sense of touch. In some cases, they have been also reported examples of ITS based on ion transport under external stimuli that not only replicate the tactile sensory topologies of human skin but also mimic tactile sensing mechanism. These significant advancements in the ITS make them a grate candidate for emerging human interactive technologies.

Because of the great conceptual similarity between human skin and ITS, these sensors are envisioned to be applied as implantable devices and advanced human–machine interfaces.

Considering the possible applications, materials used for the fabrication of these devices should have high biocompatibility. In general, among the classes of ITS herein discussed, hydrogels are the most bio-compatible ones, but suffer from long-term stability and durability. On the other hand, ionic materials such as ILs and ionic polymers/gels are comparatively stable but lack of biocompatibility.

Since the saline environment inside human body can cause unintended shorts or electrical leakage, if electronic components are exposed, proper encapsulation of the ITS is required to protect sensor components from water intrusion [11]. In this perspective, future developments in the field of ITS may involve strategies to prepare core-shell and/or hierarchical structures [63], granting excellent interfacial adhesion, including dry-jet-wet-electrospinning into active liquid collector [64], as well as the design of new, bioinspired non-cytotoxic adhesives capable of working in a wet environment [61,62].

From a mechanical standpoint, typical strain-stiffening behavior of skin can be mimicked by optimizing the integration of stiff structures with soft matrices. In this context, hydrophilic nanocarbons, including graphene oxide and oxidized carbon nanotubes, capable of imparting mechanical robustness and piezocapacitive/resistive properties to soft polymers could be considered, although their use could worsen the transparency of devices [65–73]. Moreover, the composites generally used to construct flexible electromagnetic materials can be also considered for fabricating artificial skin[74,75].

Today, there is no solution for restoration of a natural sense of touch for people using prosthetic limbs. Providing a natural sensation of touch could improve quality of life for amputees. The application of ITS on prosthetic limbs will improve the capacity to use the prosthesis in particular activities. In conclusion, the use of the ITS in emerging human-interactive robotics, medical devices and prosthetic limbs is expected to bring great innovation in these areas.

7 Reference

[1] D. Zhalmuratova, H.-J. Chung, Reinforced Gels and Elastomers for Biomedical and Soft Robotics Applications, ACS Applied Polymer Materials. (2020). https://doi.org/10.1021/acsapm.9b01078.

[2] H.R. Lim, H.S. Kim, R. Qazi, Y.T. Kwon, J.W. Jeong, W.H. Yeo, Advanced Soft Materials, Sensor Integrations, and Applications of Wearable Flexible Hybrid Electronics in Healthcare, Energy, and Environment, Advanced Materials. (2020). https://doi.org/10.1002/adma.201901924.

[3] X. Xiang, F. Pan, Y. Li, Flower-like Bismuth Metal-Organic Frameworks Grown on Carbon Paper as a Free-Standing Electrode for Efficient Electrochemical Sensing of Cd2+ and Pb2+ in Water, Engineered Science. (2018). https://doi.org/10.30919/es8d736.

[4] Q. Dong, X. Wang, H. Liu, H. Ryu, J. Zhao, B. Li, Y. Lei, Heterogeneous Iridium Oxide/Gold Nanocluster for Non-enzymatic Glucose Sensing and pH Probing, Engineered Science. (2019). https://doi.org/10.30919/es8d512.

[5] Y. Huang, Y. Luo, H. Liu, X. Lu, J. Zhao, Y. Lei, A Subcutaneously Injected SERS Nanosensor Enabled Long-term in Vivo Glucose Tracking, Engineered Science. (2020). https://doi.org/10.30919/es8d1161.

[6] H. Huang, L. Han, Y. Wang, Z. Yang, F. Zhu, M. Xu, Tunable Thermal-Response Shape Memory Bio-Polymer Hydrogels as Body Motion Sensors, Engineered Science. (2020). https://doi.org/10.30919/es8d812.

[7] Y.-F. Su, G. Han, Z. Kong, T. Nantung, N. Lu, Embeddable Piezoelectric Sensors for Strength Gain Monitoring of Cementitious Materials: The Influence of Coating Materials, Engineered Science. (2020). https://doi.org/10.30919/es8d1114.

[8] Chen Jianwen, Y. Zhu, Z. Guo, A.G. Nasibulin, Recent Progress on Thermo-electrical Properties of Conductive Polymer Composites and Their Application in Temperature Sensors, Engineered Science. 12 (2020) 13–22. https://doi.org/10.30919/es8d1129.

[9] Y. Zhang, S. Xie, D. Zhang, B. Ren, Y. Liu, L. Tang, Q. Chen, J. Yang, J. Wu, J. Tang, J. Zheng, Thermo-Responsive and Shape-Adaptive Hydrogel Actuators from Fundamentals to Applications, Engineered Science. (2019). https://doi.org/10.30919/es8d788.

[10] A. Chortos, Z. Bao, Skin-inspired electronic devices, Materials Today. (2014). https://doi.org/10.1016/j.mattod.2014.05.006.

[11] V. Amoli, J.S. Kim, S.Y. Kim, J. Koo, Y.S. Chung, H. Choi, D.H. Kim, Ionic Tactile Sensors for Emerging Human-Interactive Technologies: A Review of Recent Progress, Advanced Functional Materials. (2019). https://doi.org/10.1002/adfm.201904532.

[12] Z. Lei, P. Wu, Adaptable polyionic elastomers with multiple sensations and entropy-driven actuations for prosthetic skins and neuromuscular systems, Materials Horizons. (2019). https://doi.org/10.1039/c8mh01157e.

[13] Y. Liu, R. Bao, J. Tao, J. Li, M. Dong, C. Pan, Recent progress in tactile sensors and their applications in intelligent systems, Science Bulletin. (2020). https://doi.org/10.1016/j.scib.2019.10.021.

[14] S. Angaiah, V. Murugadoss, S. Arunachalam, P. Panneerselvam, S. Krishnan, Influence of Various Ionic Liquids Embedded Electrospun Polymer Membrane Electrolytes on the Photovoltaic Performance of DSSC, Engineered Science. (2018). https://doi.org/10.30919/es8d756.

[15] Wang Zhe, S. He, V. Nguyen, K.E. Riley, Ionic Liquids as “Green Solvent and/or Electrolyte” for Energy Interface, Engineered Science. 11 (2020) 3–18. https://doi.org/10.30919/es8d0013.

[16] S. Jayanthi, Studies on ionic liquid incorporated polymer blend electrolytes for energy storage applications, Advanced Composites and Hybrid Materials. (2019). https://doi.org/10.1007/s42114-019-00102-x.

[17] S. Li, C. Yang, S. Sarwar, A. Nautiyal, P. Zhang, H. Du, N. Liu, J. Yin, K. Deng, X. Zhang, Facile synthesis of nanostructured polyaniline in ionic liquids for high solubility and enhanced electrochemical properties, Advanced Composites and Hybrid Materials. (2019). https://doi.org/10.1007/s42114-019-00103-w.

[18] Y. Wang, D. Yao, Y. Zheng, A review on synthesis and application of solvent-free nanofluids, Advanced Composites and Hybrid Materials. (2019). https://doi.org/10.1007/s42114-019-00125-4.

[19] G. Keulemans, P. Pelgrims, M. Bakula, F. Ceyssens, R. Puers, An ionic liquid based strain sensor for large displacements, in: Procedia Engineering, 2014. https://doi.org/10.1016/j.proeng.2014.11.362.

[20] Y. Zhu, C. Chao, C.H. Cheng, W.W.F. Leung, A novel ionic-liquid strain sensor for large-strain applications, IEEE Electron Device Letters. (2009). https://doi.org/10.1109/LED.2009.2013884.

[21] J.B. Chossat, Y.L. Park, R.J. Wood, V. Duchaine, A soft strain sensor based on ionic and metal liquids, IEEE Sensors Journal. (2013). https://doi.org/10.1109/JSEN.2013.2263797.

[22] Y. Wang, S. Gong, S.J. Wang, G.P. Simon, W. Cheng, Volume-invariant ionic liquid microbands as highly durable wearable biomedical sensors, Materials Horizons. (2016). https://doi.org/10.1039/c5mh00284b.

[23] S.G. Yoon, H.J. Koo, S.T. Chang, Highly Stretchable and Transparent Microfluidic Strain Sensors for Monitoring Human Body Motions, ACS Applied Materials and Interfaces. (2015). https://doi.org/10.1021/acsami.5b08404.

[24] D.Y. Choi, M.H. Kim, Y.S. Oh, S.H. Jung, J.H. Jung, H.J. Sung, H.W. Lee, H.M. Lee, Highly stretchable, hysteresis-free ionic liquid-based strain sensor for precise human motion monitoring, ACS Applied Materials and Interfaces. (2017). https://doi.org/10.1021/acsami.6b12415.

[25] S.H. Zhang, F.X. Wang, J.J. Li, H.D. Peng, J.H. Yan, G.B. Pan, Wearable wide-range strain sensors based on ionic liquids and monitoring of human activities, Sensors (Switzerland). (2017). https://doi.org/10.3390/s17112621.

[26] B. Nie, S. Xing, J.D. Brandt, T. Pan, Droplet-based interfacial capacitive sensing, Lab on a Chip. (2012). https://doi.org/10.1039/c2lc21168h.

[27] S.G. Yoon, S.T. Chang, Microfluidic capacitive sensors with ionic liquid electrodes and CNT/PDMS nanocomposites for simultaneous sensing of pressure and temperature, Journal of Materials Chemistry C. (2017). https://doi.org/10.1039/c6tc03994d.

[28] B. Nie, R. Li, J.D. Brandt, T. Pan, Iontronic microdroplet array for flexible ultrasensitive tactile sensing, Lab on a Chip. (2014). https://doi.org/10.1039/c3lc50994j.

[29] D. Choi, S. Jang, J.S. Kim, H.J. Kim, D.H. Kim, J.Y. Kwon, A Highly Sensitive Tactile Sensor Using a Pyramid-Plug Structure for Detecting Pressure, Shear Force, and Torsion, Advanced Materials Technologies. (2019). https://doi.org/10.1002/admt.201800284.

[30] K.Y. Chun, Y.J. Son, C.S. Han, Highly Sensitive and Patchable Pressure Sensors Mimicking Ion-Channel-Engaged Sensory Organs, ACS Nano. (2016). https://doi.org/10.1021/acsnano.6b00582.

[31] B. Nie, R. Li, J. Cao, J.D. Brandt, T. Pan, Flexible Transparent Iontronic Film for Interfacial Capacitive Pressure Sensing, Advanced Materials. (2015). https://doi.org/10.1002/adma.201502556.

[32] S.H. Cho, S.W. Lee, S. Yu, H. Kim, S. Chang, D. Kang, I. Hwang, H.S. Kang, B. Jeong, E.H. Kim, S.M. Cho, K.L. Kim, H. Lee, W. Shim, C. Park, Micropatterned Pyramidal Ionic Gels for Sensing Broad-Range Pressures with High Sensitivity, ACS Applied Materials and Interfaces. (2017). https://doi.org/10.1021/acsami.7b00398.

[33] A. Chhetry, J. Kim, H. Yoon, J.Y. Park, Ultrasensitive Interfacial Capacitive Pressure Sensor Based on a Randomly Distributed Microstructured Iontronic Film for Wearable Applications, ACS Applied Materials and Interfaces. (2019). https://doi.org/10.1021/acsami.8b17765.

[34] M.L. Jin, S. Park, Y. Lee, J.H. Lee, J. Chung, J.S. Kim, J.S. Kim, S.Y. Kim, E. Jee, D.W. Kim, J.W. Chung, S.G. Lee, D. Choi, H.T. Jung, D.H. Kim, An Ultrasensitive, Visco-Poroelastic Artificial Mechanotransducer Skin Inspired by Piezo2 Protein in Mammalian Merkel Cells, Advanced Materials. (2017). https://doi.org/10.1002/adma.201605973.

[35] R. Li, Y. Si, Z. Zhu, Y. Guo, Y. Zhang, N. Pan, G. Sun, T. Pan, Supercapacitive Iontronic Nanofabric Sensing, Advanced Materials. (2017). https://doi.org/10.1002/adma.201700253.

[36] S. Li, N. Pan, Z. Zhu, R. Li, B. Li, J. Chu, G. Li, Y. Chang, T. Pan, All-in-One Iontronic Sensing Paper, Advanced Functional Materials. (2019). https://doi.org/10.1002/adfm.201807343.

[37] S.Y. Kim, E. Jee, J.S. Kim, D.H. Kim, Conformable and ionic textiles using sheath-core carbon nanotube microyarns for highly sensitive and reliable pressure sensors, RSC Advances. (2017). https://doi.org/10.1039/c7ra02215h.

[38] Z. Qiu, Y. Wan, W. Zhou, J. Yang, J. Yang, J. Huang, J. Zhang, Q. Liu, S. Huang, N. Bai, Z. Wu, W. Hong, H. Wang, C.F. Guo, Ionic Skin with Biomimetic Dielectric Layer Templated from Calathea Zebrine Leaf, Advanced Functional Materials. (2018). https://doi.org/10.1002/adfm.201802343.

[39] S. Jang, E. Jee, D. Choi, W. Kim, J.S. Kim, V. Amoli, T. Sung, D. Choi, D.H. Kim, J.Y. Kwon, Ultrasensitive, Low-Power Oxide Transistor-Based Mechanotransducer with Microstructured, Deformable Ionic Dielectrics, ACS Applied Materials and Interfaces. (2018). https://doi.org/10.1021/acsami.8b09840.

[40] Y. Hara, K. Yoshida, A. Khosla, M. Kawakami, K. Hosoda, H. Furukawa, Very Wide Sensing Range and Hysteresis Behaviors of Tactile Sensor Developed by Embedding Soft Ionic Gels in Soft Silicone Elastomers, ECS Journal of Solid State Science and Technology. (2020). https://doi.org/10.1149/2162-8777/aba913.

[41] S. Han, J. Zhao, D. Wang, C. Lu, W. Chen, Bionic ion channel and single-ion conductor design for artificial skin sensors, Journal of Materials Chemistry B. (2017). https://doi.org/10.1039/c7tb01760j.

[42] J.Y. Sun, C. Keplinger, G.M. Whitesides, Z. Suo, Ionic skin, Advanced Materials. (2014). https://doi.org/10.1002/adma.201403441.

[43] C.C. Kim, H.H. Lee, K.H. Oh, J.Y. Sun, Highly stretchable, transparent ionic touch panel, Science. (2016). https://doi.org/10.1126/science.aaf8810.

[44] N.T. Nguyen, M.S. Sarwar, C. Preston, A. le Goff, C. Plesse, F. Vidal, E. Cattan, J.D.W. Madden, Transparent stretchable capacitive touch sensor grid using ionic liquid electrodes, Extreme Mechanics Letters. (2019). https://doi.org/10.1016/j.eml.2019.100574.

[45] C. Larson, B. Peele, S. Li, S. Robinson, M. Totaro, L. Beccai, B. Mazzolai, R. Shepherd, Highly stretchable electroluminescent skin for optical signaling and tactile sensing, Science. (2016). https://doi.org/10.1126/science.aac5082.

[46] Z. Zhang, L. Wang, H. Yu, F. Zhang, L. Tang, Y. Feng, W. Feng, Highly Transparent, Self-Healable, and Adhesive Organogels for Bio-Inspired Intelligent Ionic Skins, ACS Applied Materials and Interfaces. (2020). https://doi.org/10.1021/acsami.9b22707.

[47] H. Ding, Z. Xin, Y. Yang, Y. Luo, K. Xia, B. Wang, Y. Sun, J. Wang, Y. Zhang, H. Wu, S. Fan, L. Zhang, K. Liu, Ultrasensitive, Low-Voltage Operational, and Asymmetric Ionic Sensing Hydrogel for Multipurpose Applications, Advanced Functional Materials. (2020). https://doi.org/10.1002/adfm.201909616.

[48] H. Xie, Q. Yu, J. Mao, S. Wang, Y. Hu, Z. Guo, A conductive polyacrylamide/double bond chitosan/polyaniline hydrogel for flexible sensing, Journal of Materials Science: Materials in Electronics. (2020). https://doi.org/10.1007/s10854-020-03585-3.

[49] Z. Li, S. Zhang, Y. Chen, H. Ling, L. Zhao, G. Luo, X. Wang, M.C. Hartel, H. Liu, Y. Xue, R. Haghniaz, K. Lee, W. Sun, H. Kim, J. Lee, Y. Zhao, Y. Zhao, S. Emaminejad, S. Ahadian, N. Ashammakhi, M.R. Dokmeci, Z. Jiang, A. Khademhosseini, Gelatin Methacryloyl-Based Tactile Sensors for Medical Wearables, Advanced Functional Materials. (2020). https://doi.org/10.1002/adfm.202003601.

[50] S.-H. Shin, S.-M. Kim, H. Jeon, S.Y. Hwang, D.X. Oh, J. Park, Skin-Inspired Hydrogel-Elastomer Hybrid Forms a Seamless Interface by Autonomous Hetero-Self-Healing, ACS Applied Polymer Materials. (2020). https://doi.org/10.1021/acsapm.0c00925.

[51] Y.F. Liu, Q. Liu, J.F. Long, F.L. Yi, Y.Q. Li, X.H. Lei, P. Huang, B. Du, N. Hu, S.Y. Fu, Bioinspired Color-Changeable Organogel Tactile Sensor with Excellent Overall Performance, ACS Applied Materials & Interfaces. (2020). https://doi.org/10.1021/acsami.0c12811.

[52] H. Charaya, T.G. La, J. Rieger, H.J. Chung, Thermochromic and Piezocapacitive Flexible Sensor Array by Combining Composite Elastomer Dielectrics and Transparent Ionic Hydrogel Electrodes, Advanced Materials Technologies. (2019). https://doi.org/10.1002/admt.201900327.

[53] J. Cai, J. Tian, H. Gu, Z. Guo, Amino Carbon Nanotube Modified Reduced Graphene Oxide Aerogel for Oil/Water Separation, ES Materials & Manufacturing. (2019). https://doi.org/10.30919/esmm5f611.

[54] M. Ul-Islam, J. Ali, W. Khan, A. Haider, N. Shah, Md.W. Ahmad, M.W. Ullah, G. Yang, Fast 4-nitrophenol Reduction Using Gelatin Hydrogel Containing Silver Nanoparticles, Engineered Science. (2020). https://doi.org/10.30919/es8d504.

[55] S. Li, A. Jasim, W. Zhao, L. Fu, M.W. Ullah, Z. Shi, G. Yang, Fabrication of pH-electroactive Bacterial Cellulose/Polyaniline Hydrogel for the Development of a Controlled Drug Release System, ES Materials & Manufacturing. (2018). https://doi.org/10.30919/esmm5f120.

[56] X. Hu, R. Liang, J. Li, Z. Liu, G. Sun, Highly Stretchable Self-Healing Nanocomposite Hydrogel Reinforced by 5 nm Particles, ES Materials & Manufacturing. (2018). https://doi.org/10.30919/esmm5f158.

[57] Y. Zhang, S. Xie, D. Zhang, B. Ren, Y. Liu, L. Tang, Q. Chen, J. Yang, J. Wu, J. Tang, J. Zheng, Thermo-Responsive and Shape-Adaptive Hydrogel Actuators from Fundamentals to Applications, Engineered Science. (2019). https://doi.org/10.30919/es8d788.

[58] S. Kordjazi, K. Kamyab, N. Hemmatinejad, Super-hydrophilic/oleophobic chitosan/acrylamide hydrogel: an efficient water/oil separation filter, Advanced Composites and Hybrid Materials. (2020). https://doi.org/10.1007/s42114-020-00150-8.

[59] S. Afroz, F. Afrose, A.K.M.M. Alam, R.A. Khan, Md.A. Alam, Synthesis and characterization of polyethylene oxide (PEO)—N,N-dimethylacrylamide (DMA) hydrogel by gamma radiation, Advanced Composites and Hybrid Materials. (2019). https://doi.org/10.1007/s42114-018-0058-x.

[60] L. Dai, J. Lu, F. Kong, K. Liu, H. Wei, C. Si, Reversible photo-controlled release of bovine serum albumin by azobenzene-containing cellulose nanofibrils-based hydrogel, Advanced Composites and Hybrid Materials. (2019). https://doi.org/10.1007/s42114-019-00112-9.

[61] J. Yang, R. Bai, B. Chen, Z. Suo, Hydrogel Adhesion: A Supramolecular Synergy of Chemistry, Topology, and Mechanics, Advanced Functional Materials. (2020). https://doi.org/10.1002/adfm.201901693.

[62] J. Li, A.D. Celiz, J. Yang, Q. Yang, I. Wamala, W. Whyte, B.R. Seo, N. v. Vasilyev, J.J. Vlassak, Z. Suo, D.J. Mooney, Tough adhesives for diverse wet surfaces, Science. (2017). https://doi.org/10.1126/science.aah6362.

[63] P. Xie, Y. Liu, M. Feng, M. Niu, C. Liu, N. Wu, K. Sui, R.R. Patil, D. Pan, Z. Guo, R. Fan, Hierarchically porous Co/C nanocomposites for ultralight high-performance microwave absorption, Advanced Composites and Hybrid Materials. (2021). https://doi.org/10.1007/s42114-020-00202-z.

[64] A. Maio, M. Gammino, E.F. Gulino, B. Megna, P. Fara, R. Scaffaro, Rapid One-Step Fabrication of Graphene Oxide-Decorated Polycaprolactone Three-Dimensional Templates for Water Treatment, ACS Applied Polymer Materials. (2020). https://doi.org/10.1021/acsapm.0c00852.

[65] R. Scaffaro, A. Maio, G. lo Re, A. Parisi, A. Busacca, Advanced piezoresistive sensor achieved by amphiphilic nanointerfaces of graphene oxide and biodegradable polymer blends, Composites Science and Technology. (2018). https://doi.org/10.1016/j.compscitech.2018.01.008.

[66] R. Scaffaro, A. Maio, Integrated ternary bionanocomposites with superior mechanical performance via the synergistic role of graphene and plasma treated carbon nanotubes, Composites Part B: Engineering. (2019). https://doi.org/10.1016/j.compositesb.2019.03.076.

[67] R. Scaffaro, A. Maio, F. Lopresti, D. Giallombardo, L. Botta, M.L. Bondì, S. Agnello, Synthesis and self-assembly of a PEGylated-graphene aerogel, Composites Science and Technology. (2016). https://doi.org/10.1016/j.compscitech.2016.03.030.

[68] R. Scaffaro, A. Maio, Optimization of two-step techniques engineered for the preparation of polyamide 6 graphene oxide nanocomposites, Composites Part B: Engineering. (2019). https://doi.org/10.1016/j.compositesb.2018.11.107.

[69] R. Scaffaro, A. Maio, Influence of oxidation level of graphene oxide on the mechanical performance and photo-oxidation resistance of a polyamide 6, Polymers. (2019). https://doi.org/10.3390/polym11050857.

[70] R. Scaffaro, A. Maio, F. Lopresti, L. Botta, Nanocarbons in electrospun polymeric nanomats for tissue engineering: A review, Polymers. (2017). https://doi.org/10.3390/polym9020076.

[71] R. Scaffaro, A. Maio, A green method to prepare nanosilica modified graphene oxide to inhibit nanoparticles re-aggregation during melt processing, Chemical Engineering Journal. (2017). https://doi.org/10.1016/j.cej.2016.09.131.

[72] R. Scaffaro, A. Maio, L. Botta, E.F. Gulino, D. Gulli, Tunable release of Chlorhexidine from Polycaprolactone-based filaments containing graphene nanoplatelets, European Polymer Journal. (2019). https://doi.org/10.1016/j.eurpolymj.2018.11.031.

[73] A. Maio, R. Scaffaro, L. Lentini, A. Palumbo Piccionello, I. Pibiri, Perfluorocarbons–graphene oxide nanoplatforms as biocompatible oxygen reservoirs, Chemical Engineering Journal. (2018). https://doi.org/10.1016/j.cej.2017.10.032.

[74] H. Wu, Y. Zhang, R. Yin, W. Zhao, X. Li, L. Qian, Magnetic negative permittivity with dielectric resonance in random Fe3O4@graphene-phenolic resin composites, Advanced Composites and Hybrid Materials. (2018). https://doi.org/10.1007/s42114-017-0014-1.

[75] N. Wu, X. Bai, D. Pan, B. Dong, R. Wei, N. Naik, R.R. Patil, Z. Guo, Recent Advances of Asymmetric Supercapacitors, Advanced Materials Interfaces. 8 (2021) 2001710. https://doi.org/https://doi.org/10.1002/admi.202001710.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: