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Highly Stretchable and Nonvolatile Gelatin-Supported Deep Eutectic Solvent Gel Electrolyte-Based Ionic Skins for Strain and Pressure Sensing

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Abstract

There is a growing demand for devices that exhibit human skin-like sensory capabilities due to their broad applications in soft robotics and healthcare. Ionically conductive hydrogels have long been studied for wearable, flexible sensor applications; however, the volatility of water inevitably leads to dehydration issues that can limit the long-term use of hydrogel-based devices. In this report, highly stretchable, gelatin biopolymer-supported deep eutectic solvent (DES) gel electrolytes are presented as a promising nonvolatile alternative to hydrogels for ionic skin applications. The DES gel containing 22 wt.% gelatin exhibited high stretchability (fracture strain >300%) and a room temperature ionic conductivity of 2.5 mS cm^{-1}. Capacitive-type pressure and strain sensors fabricated using gelatin-supported DES gel electrolytes provided linear responses over a wide range; an applied pressure as low as 1 kPa could be detected using a 1 V bias. A 3 x 3 sensor array was also constructed, which exhibited excellent performance for identifying the (multi)touch location(s) of applied pressure. These characteristics not only demonstrate the suitability of gelatin-supported DES gels for ionic skin applications, but also present a new class of materials for developing future nonvolatile sensors.

1. Introduction

Skin is the largest organ of the human body, integrated with a variety of stretchable sensors possessing the ability to sensitively detect multiple stimuli, such as mechanical force and temperature changes. Artificial skin devices with human-like sensory abilities have been intensively investigated in the past decade due to their broad applications in soft robotics, human motion monitoring, and prosthetic devices.[1] A myriad of conductive nanomaterial/polymer composites having low elastic modulus and good stretchability have been developed to realize the function of artificial skin devices using carbon grease, carbon nanotubes, silver nanowires, etc.[2–5] These electronically conducting materials can meet the essential demands for conductivity and stretchability, but their lack of biocompatibility and transparency limits their applications in biosensors and optical devices, respectively. Hydrogels, which consist of crosslinked polymer networks dispersed in aqueous solutions, are a promising class of *ionically* conducting materials for soft sensor applications because they are often biocompatible and environmentally friendly while possessing sufficient stretchability that can be realized via different approaches.[6,7] Sun et al. proposed the concept of an “ionic skin” and designed a capacitive sensor prototype using two hydrogel films to sandwich a thin dielectric layer.[8] This device demonstrated a high stretchability (>500% strain) along with a good pressure sensing capability as low as 1 kPa. However, hydrogels are susceptible to dehydration due to evaporation in the ambient environment, so the long-lasting performance of hydrogel-based devices always requires an extra sealing process.[9] On the other hand, ionogels, endowed with nonvolatility and an ion-dense nature by substituting ionic liquids (ILs) for aqueous solutions, provide an ideal remedy to address the volatility issue of hydrogels in sensing applications.[10] However, the widespread use of ionogels is often challenged considering their toxicity and high manufacturing cost. Deep eutectic solvents (DESs), typically formed by mixing a quaternary ammonium salt with a hydrogen bond donor in an appropriate molar ratio to obtain a low-melting eutectic mixture, represent an emerging subclass of ILs with similar physicochemical properties, such as an ion-dense nature, low volatility, and moderate ionic conductivity.[11,12] Moreover, the tremendous potential of DESs as more cost-effective, greener alternatives to conventional ILs can be more readily realized due to their inexpensive and environmentally-friendly nature.[13,14]

The utilization of biopolymers as supporting scaffolds in gel electrolytes offers an appealing way to advance gel biocompatibility and exploit self-assembly strategies (*e.g.* H-bonding) designed by nature. Although several manifestations of biopolymers have been employed to synthesize ionogels using ILs or IL/water mixtures, such as cellulose,[15] starch,[16] chitosan,[17] and gelatin,[18] very little work has been performed to date in demonstrating biopolymer-supported DES gels. Commonly-employed biopolymers typically have large molecular weights, which makes them difficult to dissolve in ILs/DESs without special functionalization of the polymer chains. Recently, Singh et al. reported gelatin-supported ionogels featuring a water-miscible IL, 1-ethyl-3-methylimidazolium ethylsulfate.[19] Unlike the low solubility of many polysaccharides in ILs/DESs, the presence of a variety of charged amino acid residues in gelatin facilitates the formation of dynamic interactions such as hydrogen bonding, as well as hydrophobic and electrostatic interactions,[20] resulting in the potential for higher compatibility with many ILs/DESs. Indeed, Mano and coworkers recently described the successful formation of electrospun fibers of a gelatin-encapsulated therapeutic DES as a fast-dissolving drug delivery vehicle.[21]

In this report, we present a highly stretchable, gelatin biopolymer-supported DES gel electrolyte and demonstrate its feasibility as a flexible, nonvolatile, and optically transparent ion conductor for ionic skin applications. The well-studied DES based on choline chloride (ChCl) and ethylene glycol (EG) (1:2 molar ratio of ChCl:EG)[22] has been employed. Gelatin-supported DES gels have been synthesized in a facile manner using the thermally modulated coil-helix transition process of gelatin[23] induced by heating and subsequently cooling the gelatin/DES mixture. The DES gel containing 22 wt.% gelatin demonstrated a large stretchability, exceeding 300% strain, together with a relatively high room temperature ionic conductivity of 2.5 mS cm^{-1} compared to other DES gels.[24]

Multiple ionic skin device prototypes were fabricated to demonstrate the ability of gelatin-supported DES gel electrolytes to be integrated into sensors. The fabricated pressure and strain sensors consistently provided linear responses over a wide range; an applied pressure as low as 1 kPa could be detected using a 1 V bias. Additionally, a 3 x 3 sensor array was constructed, which exhibited excellent performance for identifying the location(s) of applied pressure. Such characteristics not only prove the suitability of gelatin-supported DES gels for ionic skin applications, but also offer a new class of DES-based materials for developing nonvolatile sensors in the future.

2. Results and Discussion

One of the most important advantages of replacing hydrogels with DES gels/ionogels is their superior thermal stability and ultralow volatility, so that devices can last longer in ambient conditions without any extra sealing or encapsulation steps. Figure 1a compares the weight loss of the neat DES, a gelatin-supported DES gel, and a hydrogel (both gels contained 22 wt.% gelatin) measured using a thermogravimetric analyzer over a period of one hour with each sample held at 40 °C, which was picked as an extreme temperature of the human body. As seen in Figure 1a, the hydrogel lost more than half of its water content within one hour, while there was no obvious weight loss for either the neat DES or the gelatin-supported DES gel. This is not only indicative of the superior nonvolatility of the DES, but it also provides evidence of good compatibility between the DES and the gelatin scaffold. It was also observed that the DES gel retained its shape even after storage in ambient laboratory conditions for ten days without any cover, while the hydrogel lost essentially all of its water within just one day (see Fig. S1 in the ESI). This excellent stability of the gelatin-supported DES gel and its ability to retain the liquid DES paves the way for long-term performance of a DES gel electrolyte-based ionic skin device operating in ambient conditions.

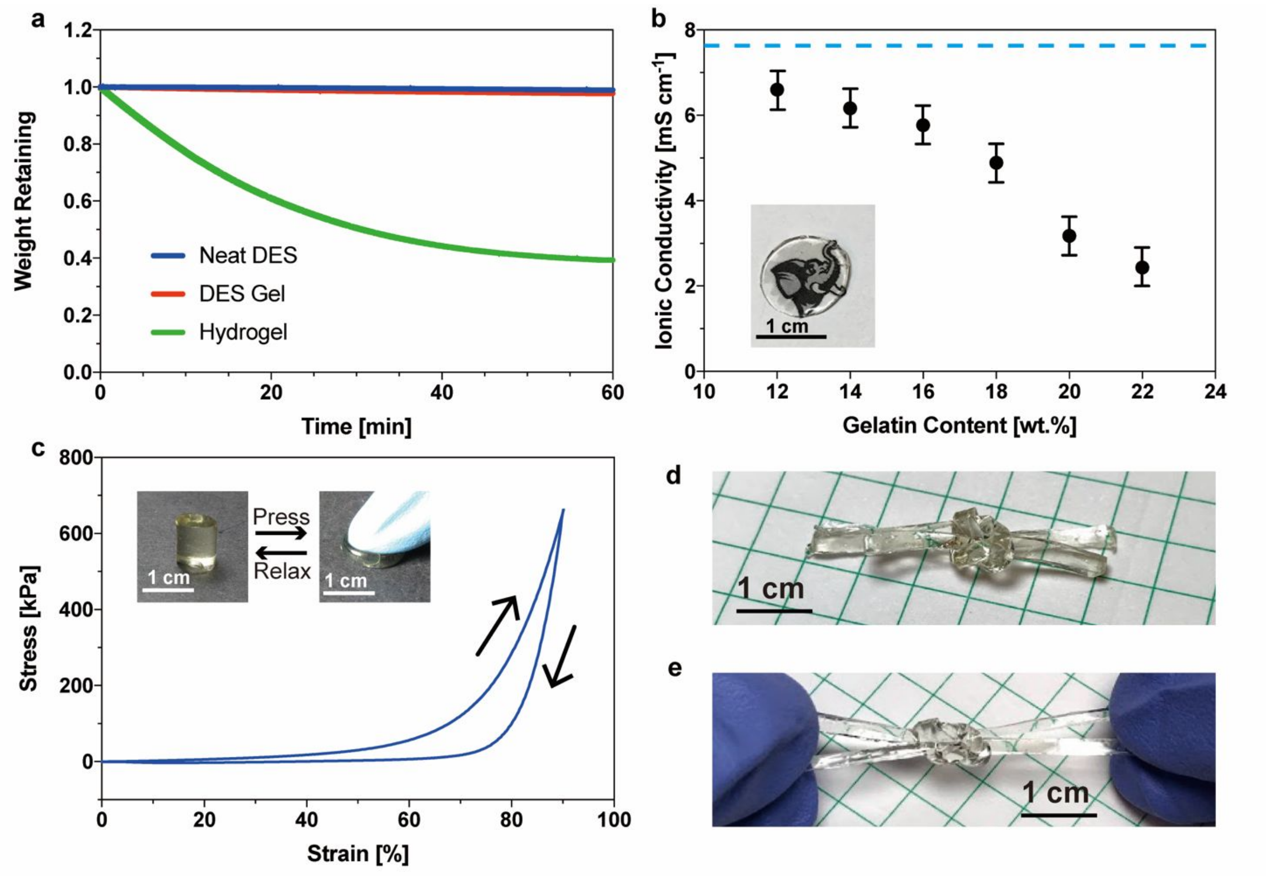

Fig. 1 (a) Normalized weight retention curves for the neat DES, a DES gel and a hydrogel (both gels contain 22 wt.% gelatin) isothermally held at 40 °C. (b) Room temperature DES gel ionic conductivity values; the dashed line indicates the neat DES value (7.6 mS cm^{-1}) and the inset shows a photograph of a thin circular DES gel film (22 wt.% gelatin) on top of a printed logo. (c) Compressive loading-unloading curve of a 22 wt.% gelatin-supported DES gel up to 90% strain; insets show photographs of a cylindrical DES gel before and during compression by a finger. (d) Photograph of a square knot created by tying two long, rectangular DES gel strips (22 wt.% gelatin) together; (e) the square knot being stretched by hand.

DES gels, like ionogels, can provide a large space for electrolyte material design due to the high tunability of both their mechanical and ion conductive properties obtained at different polymer scaffold contents. Here, the DES consisting of ChCl:EG (1:2 molar ratio) was selected because it offers one of the highest room temperature ionic conductivities among known DESs[11] and an eco-friendly nature.[12] Gelatin-supported DES gels having high optical transparency (see Fig. S2, ESI) could be synthesized via a facile three-step process: (1) mixing gelatin into the DES under ambient conditions, using a gelatin content between 12 wt.% (minimum required to obtain gelation) and 40 wt.% (observed solubility limit), (2) heating the solution to 70 °C to obtain unentangled gelatin coils and pouring the warm precursor solution into a mold of the desired shape; for example, the DES gel shown in the inset of Fig. 1b was cast as a thin circular film, and (3) cooling the solution in the mold overnight at 4 °C to facilitate gelatin scaffold self-assembly (*i.e.* triple helix formation, chain entanglement). The ionic conductivity values of DES gels with different gelatin contents were measured by AC impedance spectroscopy at room temperature inside a nitrogen-filled glove box (Fig. 1b). A high room temperature ionic conductivity of 6.5 mS cm^{-1} was obtained for the DES gel sample containing 12 wt.% gelatin, which compares favorably to that of the DES itself (7.6 mS cm^{-1}). Gel ionic conductivity was observed to decrease monotonically from 6.5 mS cm^{-1} to 2.5 mS cm^{-1} with an increase in gelatin content from 12 wt.% to 22 wt.% due to a reduction in the ion concentration (*i.e.* lower DES fraction) and hindered ion mobility, which is consistent with other polymer-supported ionogels/DES gels.[12,25,26] The ionic conductivity of a 22 wt.% gelatin-supported DES gel was also measured in ambient laboratory conditions over a period of 48 hours and was found to be relatively stable (see Fig. S3, ESI). It should be mentioned that the ionic conductivity of DES gels containing greater than 22 wt.% gelatin could not be measured via the experimental setup employed here because of the extremely high viscosity of the precursor solutions. Importantly, the ionic conductivity values obtained for the gelatin-supported DES gel electrolytes are on the same order of magnitude as that of a NaCl-containing hydrogel previously employed for an ionic skin device,[8] which suggests these DES gels to be promising candidates for ionic skin applications.

Remarkably, the gelatin-supported DES gels exhibited superior mechanical properties and stretchability compared to their hydrogel analogues (*vide infra*). Figure 1c shows a compressive stress-strain curve of a DES gel containing 22 wt.% gelatin. It was clearly observed that the DES gel could be compressed up to 90% strain without any irreversible damage. The DES gel recovered to its original cylindrical shape immediately after releasing the pressure (see the inset to Fig. 1c and Movie S1 in the ESI). Moreover, two long strip-shaped DES gels could tolerate being tied into a square knot (Fig. 1d) and the knot was very stretchable (Fig. 1e). DES gels could even be braided into a three-strand braid without any damage to the gels (Movie S1 in the ESI). It was observed that all of the gels recovered to their original shapes after untying the knot and unraveling the braid.

Tensile tests were conducted to systematically evaluate the mechanical properties of the DES gels. Figure 2a depicts representative tensile stress-strain curves obtained for DES gels with various gelatin contents. The ultimate tensile strength and fracture strain increase dramatically from 0.8 kPa and 54% to 67 kPa and 320%, respectively, as the gelatin content increased from 12 wt.% to 22 wt.%. It should be noted that there were no obvious cracks observed even when the gel was stretched close to its fracture strain (Fig. 2b), which is consistent with a homogeneous polymer network formed throughout the DES gel. Although the ultimate tensile strength of the DES gels could be further boosted by increasing the gelatin content above 22 wt.% (see Fig. S4, ESI), the fracture strain was invariably smaller than that of the 22 wt.% gelatin DES gel. Moreover, it is wholly expected that the ionic conductivity values of DES gels containing greater than 22 wt.% gelatin would also be lower, following the trend seen in Fig. 1b. Therefore, the 22 wt.% gelatin DES gel was adopted as our optimal composition for further study. The ultimate tensile strength of 67 kPa for the 22 wt.% gelatin-supported DES gel is lower than for chemically-functionalized biopolymer-supported hydrogels (1 MPa-50 MPa),[27] but higher than that of some double network-based hydrogels (4 kPa).[7] The fracture strain of 320% obtained from the DES gel containing 22 wt.% gelatin exceeds those of some recently reported stretchable ionogels (~150%)[28,29] and approaches that of the poly(acrylamide)-based hydrogel used in the first ionic skin device (500%).[8] The relatively low Young's modulus (~30 kPa, Fig. 2) and high fracture strain of the 22 wt.% gelatin DES gel is desirable for ionic skin devices because the gels would be highly compliant when applied to or worn on the human body. Figure 2c displays the hysteresis behavior observed for the 22 wt.% gelatin DES gel under loading-unloading cycles with varying maximum strains. The gel demonstrated negligible hysteresis loops until it was stretched up to ~150%. However, even the hysteresis behavior observed at 150% strain is significantly smaller than those of typical stretchable hydrogels,[7,30] which suggests that the physical crosslinks within the gelatin gel do not dissociate at this level of strain, such that the gel experiences primarily elastic deformation. We then conducted 500 successive tensile loading-unloading tests to a maximum strain of 50% to evaluate the antifatigue properties of the DES gel (Fig. 2d). The results indicated that there was no substantial plastic deformation occurring, and it demonstrated the excellent antifatigue and shape-recovery ability of the 22 wt.% gelatin-supported DES gel electrolyte. Cyclic tensile tests performed to a larger maximum strain (125%) also indicated a relatively stable gel response (see Fig. S5, ESI).

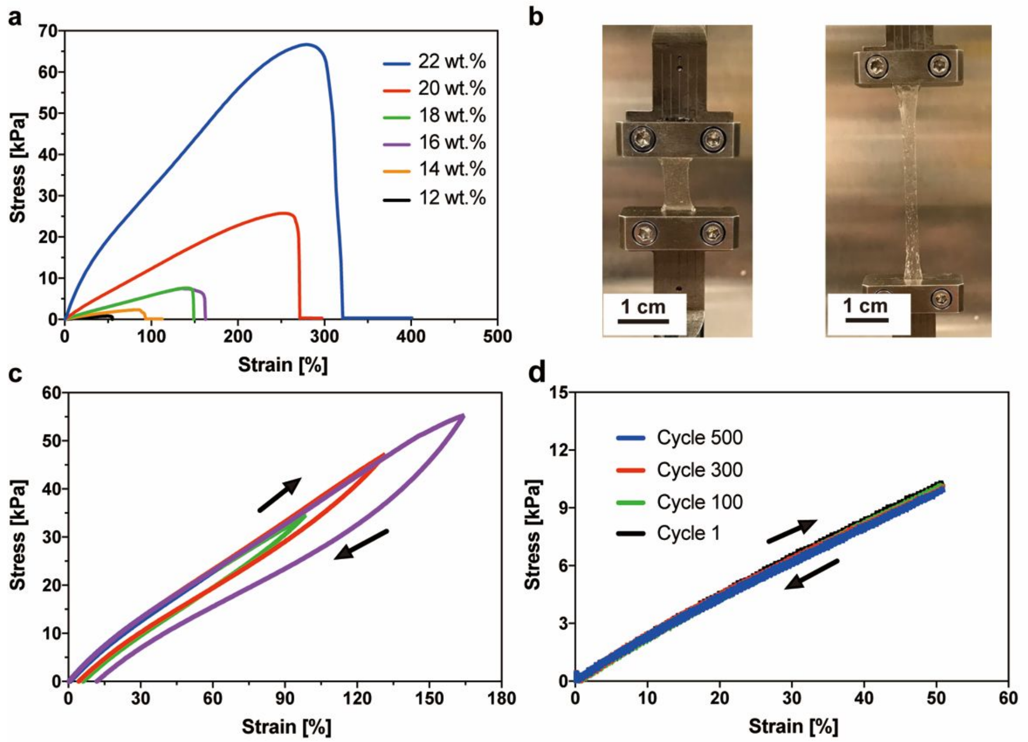

Fig. 2 (a) Representative tensile stress-strain curves of DES gels with various gelatin contents. (b) Photographs of a typical 22 wt.% gelatin-supported DES gel being stretched to ~300% strain. (c) Tensile loading-unloading stress-strain curves of a 22 wt.% gelatin-

supported DES gel taken to different maximum strain values, ranging from 65% to 165%. (d) Representative tensile cycling stress-strain curves of a 22 wt.% gelatin-supported DES gel at a maximum strain of 50%.

We observed that gelatin-supported DES gels possessed exceptional mechanical properties compared to their hydrogel analogues, which we fabricated using deionized water with the same procedure (see Movie S2 in the ESI). Therefore, we sought to elucidate the fundamental difference in the gelatin network structure obtained between DES gels and hydrogels by separately investigating the effects of the two DES components (ChCl and EG) on gelatin scaffold formation. Therefore, two additional gel samples were synthesized for comparison. The first one was an organogel formed using 22 wt.% gelatin in pure EG, and the other was a high ionic strength hydrogel synthesized using 22 wt.% gelatin in an aqueous solution having the same effective ChCl concentration as that of the DES (4.2 M), which were denoted as EG gel and ChCl hydrogel, respectively. Figure 3a displays representative tensile stress-strain curves of all four gels, each containing 22 wt.% gelatin, and Fig. 3b shows the toughness calculated for each gel sample (*i.e.* the numerically integrated area under each curve). The 22 wt.% gelatin-supported DES gel exhibited the largest stretchability (320% fracture strain) and highest toughness (133 kJ m^{-3}) among all four gel samples. In hydrogels, water molecules are known to reinforce the triple helices by establishing hydrogen bonds between two adjacent gelatin chains.[20,31] The 22 wt.% gelatin-supported hydrogel exhibited the lowest stretchability (~40% fracture strain) and lowest toughness (2.1 kJ m^{-3}) among all four gels, likely due to the highest relative extent of triple helix formation between gelatin chains and strong noncovalent interactions within these helices when assembled in DI water. However, the presence of an ionizable salt (ChCl) at 4.2 M concentration endowed the ChCl hydrogel with a much larger stretchability (~140% fracture strain) and a higher toughness (95 kJ m^{-3}) compared to the salt-free hydrogel (Fig. 3a). This can be understood by a reduction in the electrostatic interactions between gelatin chains in the ChCl hydrogel due to charge screening by the high ion density, which facilitates the formation of additional noncovalent, dynamic crosslinks between gelatin strands (chain bundling) due to hydrophobic interactions.[30] It should be noted that the kosmotropic nature of choline chloride as a solute[32] is important in promoting these enhanced hydrophobic gelatin interactions, since our attempts to create a 22 wt.% gelatin-supported NaCl (4.2 M) hydrogel were not successful due to the weakly chaotropic nature of NaCl.[33] In addition, we observed that the EG gel was nearly as stretchable as the ChCl hydrogel (~120% fracture strain), while its toughness (28 kJ m^{-3}) was much lower (Fig. 3). Within the nonaqueous environment of the EG gel, gelatin self-assembly into triple helix crosslinks is unsurprisingly impacted; wide-angle X-ray diffraction of a lyophilized EG gel film revealed a reduction in intensity and a shift in the scattering angle of the peak associated with the triple helix diameter compared to a lyophilized hydrogel film (see Fig. S6, ESI). Therefore, we suggest that both DES components contributed in their own ways to the outstanding stretchability of gelatin-supported DES gels. EG promotes the formation of fewer gelatin triple helices, which have larger diameters and presumably a more dynamic nature compared to those formed in water, while ChCl drives the assembly of additional chain bundles as dynamic crosslinks due to its kosmotropic character (see Fig. S7, ESI).

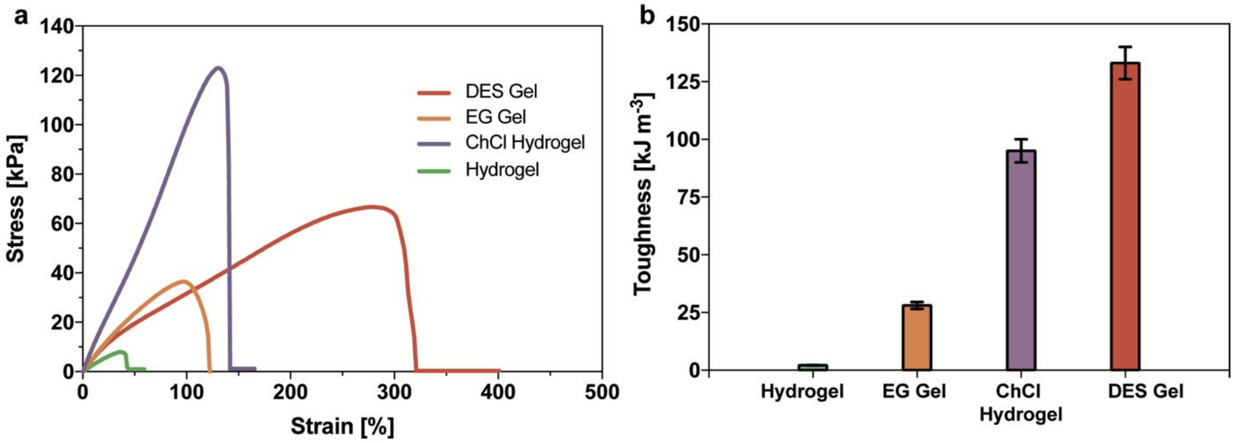

Fig. 3 (a) Representative tensile stress-strain curves for a DES gel, EG gel, ChCl hydrogel, and pure hydrogel, all containing 22 wt.% gelatin. (b) Toughness of each gel calculated from the stress-strain curves shown in panel (a).

Several types of ionically conductive hydrogels have been incorporated into capacitive-type strain sensors since the structure of the ionic skin was first proposed.[8,34,35] Here, we followed the commonly-employed device structure, constructing our ionic skin sensors by sandwiching a piece of VHB tape as the dielectric layer between two identical DES gel films, which made contact to external testing electronics via metallic wires. The whole device was encapsulated by two additional layers of tape in order to prevent direct contact of the DES gel layers with the metal clamps of the stress-strain testing apparatus (Fig. 4a). The overall device capacitance measured between the two wires is dominated by the capacitance of the dielectric layer because the electrical double layers formed within the gel electrolyte layers possessed a much larger capacitance.[8] A strain sensor was fabricated using two identical rectangular 22 wt.% gelatin-supported DES gel strips (4 cm x 6 mm x 2 mm) and stretched by a mechanical testing apparatus. Capacitance values were measured while the sensor was actively being stretched (Fig 4b). The ionic skin strain sensor could be stretched up to 125% strain with a linear increase of capacitance, which is highly desirable because nonlinearity would make the calibration process for applications more difficult. A gauge factor ($\frac{\Delta C}{C_0}/\varepsilon$) of approximately 0.5 was obtained from this strain sensor, which was comparable to other recently reported capacitive-type sensors.[2] A pressure sensor was also fabricated to demonstrate the pressure sensing ability of an ionic skin device containing DES gels. Two identical circular DES gel films having a diameter of 6 mm and a thickness of 0.5 mm were incorporated into the same structure shown in Fig. 4a to build a pressure sensor. The capacitance of the pressure sensor was also observed to increase approximately linearly with applied pressure (Fig. 4c). Notably, the pressure sensor exhibited good linearity in its response even at very small applied pressures, with a sensitivity of ~1% kPa^{-1} below 2 kPa (Fig. 4d).

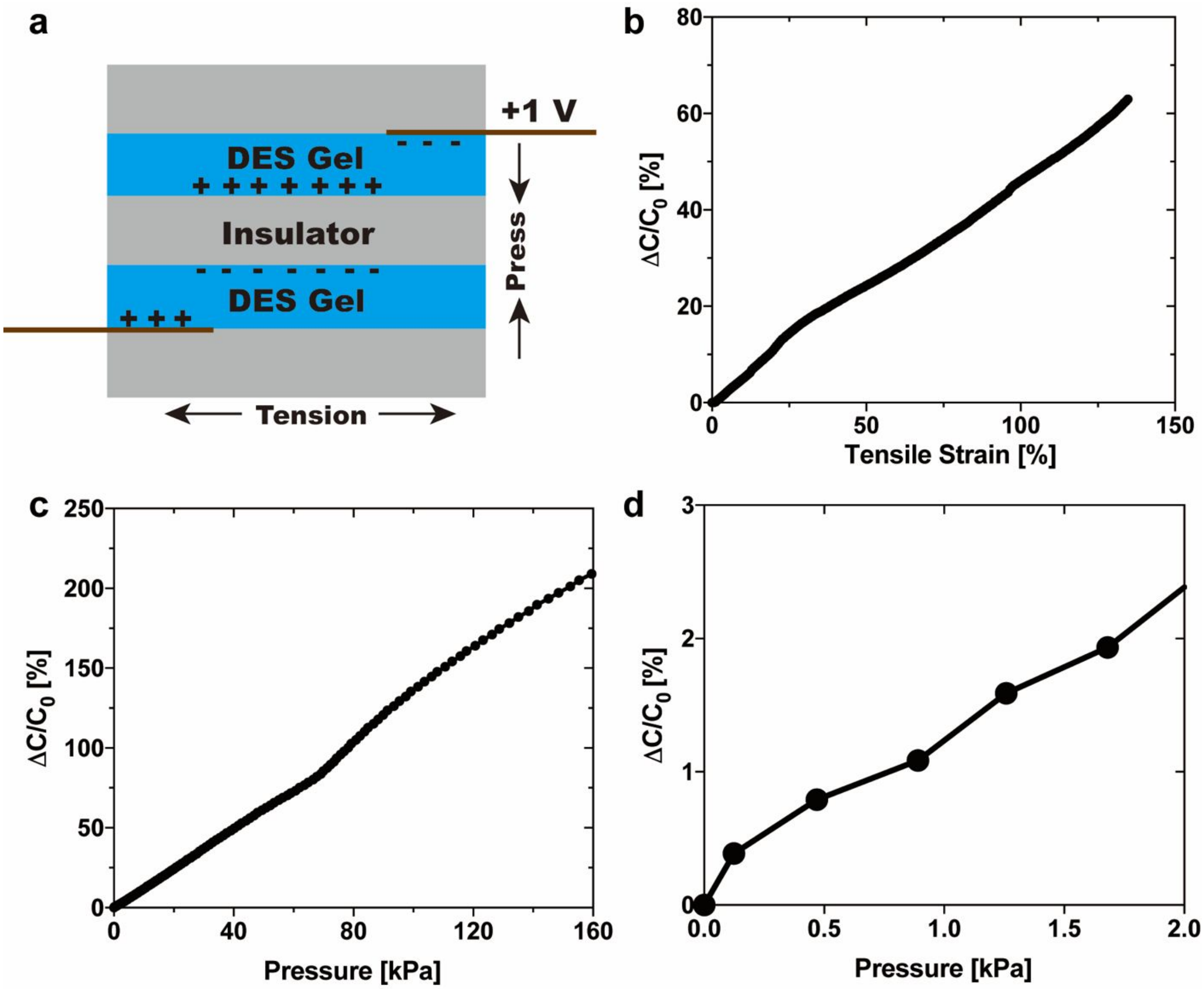

Fig. 4 (a) Cross-sectional schematic structure and operating principle of an ionic skin sensor device (not to scale). Application of a bias across the two metal wires contacting the electrolyte layers (here, DES gels) polarizes the middle insulator layer via capacitive coupling through the electrolytes. Tension or compression (directions shown) result in capacitance changes in strain and pressure sensor applications, respectively. (b) Relative capacitance change-strain curve of a strain sensor incorporating 22 wt.% gelatin-supported DES gels (C_0 = 21 pF). (c) Relative capacitance change-pressure curve of a pressure sensor incorporating 22 wt.% gelatin-supported DES gels (C_0 = 5.1 pF). (d) Zoomed-in portion of the data shown in panel (c) at very low pressures, indicating the high sensitivity of the pressure sensor.

The softness and the flexibility of the ionic skin devices allow them to conform readily to curved surfaces. We attached a DES gel-based strain sensor onto an extended human finger

(Fig. 5a) and the sensor was stretched by the joint as the finger was bent (Fig. 5b). The relative capacitance change was measured as the finger was repeatedly bent and extended; a substantial relative capacitance change of ~30% was obtained in each cycle (Fig. 5c). This demonstration of detecting finger bending using the ionic skin device suggests its great potential for detecting many other types of human motion.

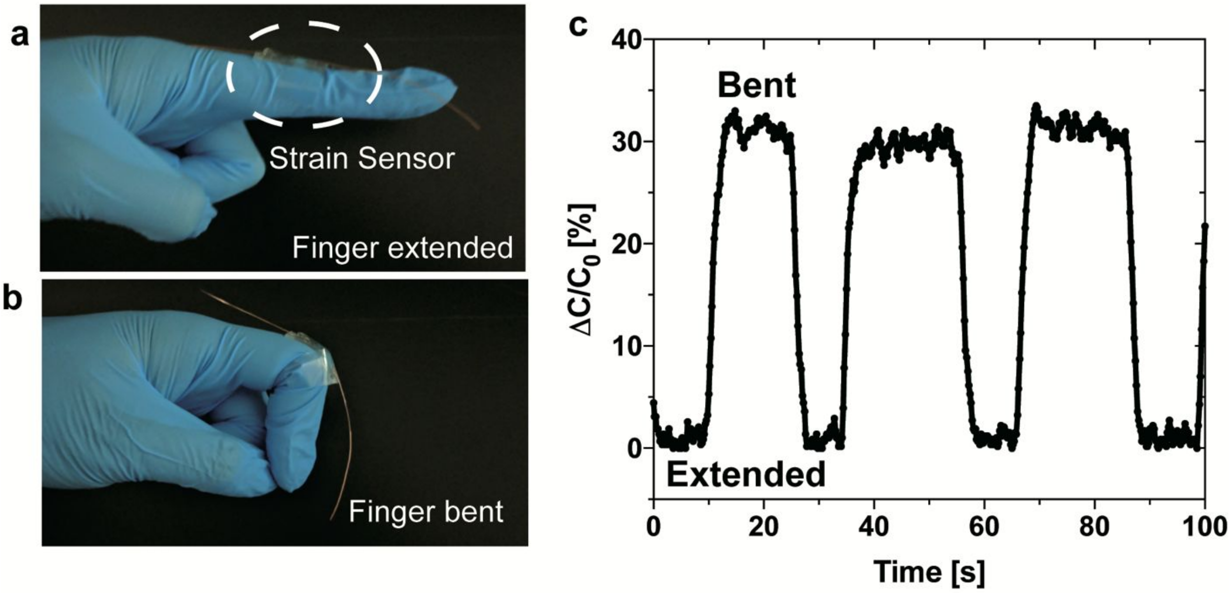

Fig. 5 DES gel-based ionic skin strain sensor used to detect finger bending. (a) Photograph of the strain sensor attached to an extended finger. (b) Photograph of the bent finger stretching the strain sensor. (c) Relative capacitance change measured while the finger was cyclically bent and extended (C_0 = 11 pF).

Finally, we designed and fabricated a 3 x 3 sensor array to demonstrate the capability of detecting both the location and pressure of touches, inspired by previous hydrogel sensor works.[8,36,37] Six rectangular DES gel strips (4 cm x 2 mm x 2 mm) were cut from a larger piece of a 22 wt.% gelatin-supported DES gel film using a razor blade. Three strips were arranged on one side of a plastic film (polyethylene, 65 μm thick) with a spacing between strips of 2 cm and the others were placed perpendicular to these on the opposite side of the film (Fig. 6a, see also Fig. S8 in the ESI). Each overlapping DES gel intersection point could be considered as an individual capacitive-type sensor and the capacitance of each tactile pixel (taxel) was measured to determine the location and the pressure of a single- or multitouch stimulus. The typical taxel initial capacitance value was 5.2 pF. Figure 6b shows the result of a heavy weight (200 g, 11.1 kPa pressure) placed on one of the taxels (position C3) of the sensor array; the sensor array indicated a dramatic change in relative capacitance at position C3 without any substantial crosstalk recorded. Next, a lighter weight (20 g, 1.8 kPa pressure) was placed on the center taxel (position B2). The relative capacitance change signal from position B2 was distinct and at least three times larger compared to those of the other taxels (Fig. 6c), which was indicative of the high sensitivity of the sensor. Multitouch capability was also demonstrated by placing two weights (20 g each) on the taxels at positions B3 and C1. Figure 6d displays the clear and independent responses measured at these two positions, which is highly desirable in a multitouch device application perspective. Collectively, these preliminary device demonstrations reinforce the notion that our gelatin-supported DES gel electrolyte represents a feasible and promising nonvolatile alternative to hydrogels for ionic skin applications.

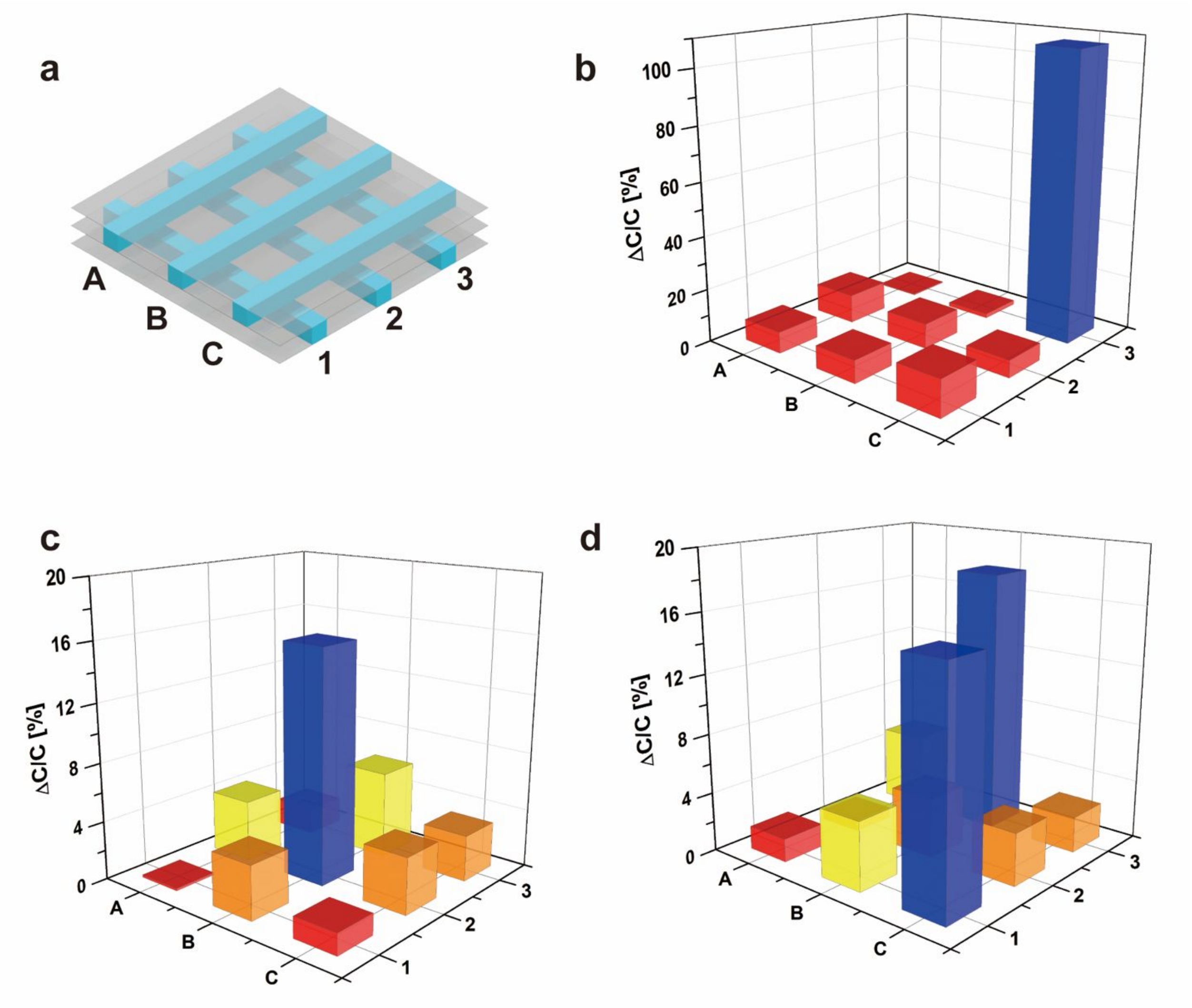

Fig. 6 Pressure sensor array prototype demonstration. (a) Schematic diagram of the constructed 3 x 3 sensor array. (b) Relative capacitance changes for the sensor array with a 200 g weight placed on position C3. (c) Relative capacitance changes for the sensor array with a 20 g weight placed on position B2. (d) Relative capacitance changes for the sensor array with two 20 g weights placed on positions B3 and C1, indicating its multitouch measurement capability.

3. Conclusion

This work describes a new class of stretchable, fully biopolymer-supported DES gel electrolytes and demonstrate their potential application in ionic skin devices. The transparent, nonvolatile and ionically conductive DES gels are readily synthesized by mixing gelatin into the DES, following by simple heating and cooling steps. Remarkably, the DES gel containing 22 wt.% gelatin exhibited a high stretchability, exceeding 300% strain, which can be attributed to intermolecular interactions of both DES components (EG and ChCl) with the gelatin scaffold that modify the biopolymer scaffold assembly compared to its hydrogel analogue. Furthermore, several ionic skin prototype sensor devices featuring gelatin-supported DES gels were fabricated with promising performance observed. A DES gel-based strain sensor exhibited good linearity in its response and a gauge factor of ~0.5, while a pressure sensor prototype could sensitively measure pressures as low as 1 kPa. These capabilities allowed DES gel-containing ionic skin devices to accurately monitor human finger bending and multitouch stimuli on a 3 x 3 sensor array. The results not only confirm the feasibility of gelatin-supported DES gel electrolytes for ionic skins, but also suggest that such DES gels could be considered as an ideal substitute for ionically conductive hydrogels in many applications due to their superior nonvolatility.

Conflicts of interest

There are no conflicts to declare.

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TOC Entry

Gelatin biopolymer-supported deep eutectic solvent gels offer greatly enhanced mechanical properties and nonvolatility compared to their hydrogel analogues for devices that utilize ionically conducting soft materials.