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

Huan Qin, Rachel E. Owyeung, Sameer R. Sonkusale, and Matthew J. Panzer*

*Corresponding author: matthew.panzer@tufts.edu

Experimental Methods and Details

Materials

All materials were used as received without further purification. Choline chloride (ChCl) was purchased from TCI Chemicals and gelatin from porcine skin (Type A, 175 g Bloom) was purchased from Sigma-Aldrich. Both ChCl and gelatin were stored in the dark prior to use. Ethylene glycol, EG, (anhydrous, 99.8%) was purchased from Sigma-Aldrich and stored in a recirculating N_2-filled glove box (O_2, $H_2O < 0.1$ ppm) to prevent water vapor absorption. VHB tape (0.5 mm thickness, 12.7 mm width) was purchased from 3M.

Preparation of DES Gels and Other Gels

The deep eutectic solvent (DES) was synthesized by mixing ChCl and EG at a molar ratio of 1:2 into a glass vial and stirring on a hotplate at 100 °C inside a N_2-filled glove box (O_2, $H_2O < 0.1$ ppm) until a homogeneous, colorless liquid was formed.[1,2] DES gel precursor solutions were prepared by weighing out the required amount of gelatin into a small vial using a balance located in a chemical fume hood, then transferring the vial into the inert atmosphere glove box and adding the desired amount of DES, measured volumetrically, to the vial. DES gel precursor solutions were stirred on a hotplate at 70 °C for one hour until a clear, homogeneous solution was formed. Subsequently, the DES gel precursors were poured into various molds to produce different gel dimensions. Molds used in this work included both patterned polydimethylsiloxane (PDMS) films in the bottom of a glass petri dish as well as cylindrical poly(tetrafluoroethylene) (PTFE) spacers (outer diameter 13.2 mm, inner diameter 6.44 mm, thickness 3.24 mm). Filled molds were then sealed with Parafilm® and refrigerated overnight at 4 °C. Hydrogels, EG gels and ChCl hydrogels were synthesized via the same procedure using deionized water, EG, and ChCl aqueous solution (4.2 M), respectively; all non-DES gel precursors were prepared inside a chemical fume hood. All gels were removed from the refrigerator and allowed to equilibrate at room temperature before their characterization or use in ionic skin devices.

Gel Characterization Methods

Electrical Characterization AC impedance spectroscopy was performed to measure DES gel ionic conductivity using a VersaSTAT 3 potentiostat with a built-in frequency response analyzer (Princeton Applied Research). Warm DES gel precursor solutions were poured into a custom-built Teflon cell array with gold-coated electrode pins and cooled *in situ* via refrigeration overnight at 4 °C in the array. Room temperature (22 °C) AC impedance spectroscopy measurements were performed inside the nitrogen-filled glove box over the frequency range of 1 Hz to 100 kHz using a sinusoidal voltage amplitude of 10 mV (with 0 V DC offset). The cell constant used to convert impedance at high frequency (~100 kHz) to ionic conductivity was determined by calibration using three different neat ionic liquid electrolytes with known conductivity values. At least three replicate DES gel samples at each gelatin concentration were tested, and average values were calculated to determine ionic conductivities.

Mechanical Characterization Gel mechanical characterization was performed by tensile or compression testing in free-extension mode using two different setups (BOX PRL PL SET 25MM for compression; TOOL TRSN RECT for tension) of a rheometer instrument (ARES-LS2, TA Instruments). Each DES gel sample prepared for compression testing was synthesized in the PTFE spacer described above and compressed at a rate of 0.01 mm s^{-1}. Gel samples for tensile testing were prepared using PDMS molds and shaped into thin rectangular slabs (L x W x H = 40 mm x 6 mm x 2.5 mm). The gel samples were clamped tightly at both ends to prevent slippage and stretched at a rate of 0.1 mm s^{-1}. Cyclic tensile testing to 50% strain data (500 cycles) were measured at a rate of 0.5 mm s^{-1}. It should be noted that all of the stresses reported are nominal stresses, which are calculated by the normal force divided by the original sample cross-sectional area. Gel toughness values were calculated from the numerically integrated area under each tensile stress-strain curve.

Thermogravimetric Analysis (TGA) TGA measurements were conducted with a TA Instruments Q500 Thermogravimetric Analyzer using a nitrogen gas flow of 50 mL min^{-1}.

Samples with a mass of ~10 mg were placed into the pan, heated to 40 °C at a heating rate of 5 °C, and held isothermally for one hour while the mass was recorded.

Wide Angle X-Ray Diffraction Spectroscopy Wide angle X-ray diffraction (WAXD) spectra were collected for lyophilized gel films, which were obtained by lyophilizing gel samples for 24 hours in a Labcono Lyophilizer under vacuum with a set pressure of 0.003 Torr. Samples were subsequently mounted on a single crystal <100> silicon wafer substrate and placed in a Phillips PW1830 X-ray diffractometer (Westborough, Massachusetts) operating at the wavelength of Cu-Ka radiation (λ = 0.154 nm). X-ray intensities were collected in $\theta/2\theta$ reflection mode (for θ the half-scattering angle, and $\lambda = 2d*\sin\theta$ relates θ to the atomic planes of spacing d). The scans were performed with a step scan interval of 0.02°/step, and a scan rate of 0.5 step/s.

Fabrication and Characterization of Ionic Skin Devices

A strain sensor was assembled by lamination of a piece of VHB tape between two identical pieces of 22 wt.% gelatin-supported DES gel (L x W x H = 4 cm x 6 mm x 2 mm). Two extra layers of VHB tape were attached to the top and bottom of the sensor to encapsulate the copper wires connected to the capacitance meter (Eucol U2818 Precision LCR Meter). Device capacitance was measured using a bias of 1 V at a frequency of 20 kHz while the strain sensor was stretched at a rate of 0.1 mm s^{-1} using the TA rheometer. The strain sensor was attached onto a finger joint to monitor the human motion and the capacitance was measured using the same method. Two identical circular DES gel films (diameter: 6 mm, thickness: 0.5 mm) were used to fabricate a pressure sensor with a layer of VHB tape sandwiched in between them. Capacitance was measured while compression was applied at a rate of 0.01 mm s^{-1} using the TA rheometer.

Visual Comparison of DES gel vs. Hydrogel Ambient Stability

Both a DES gel and a hydrogel (deionized H_2O), each containing 22 wt.% gelatin, were synthesized using cylindrical PTFE molds. After sitting out in ambient laboratory conditions for 10 days, the DES gel retained its original shape without any apparent loss of liquid, while the hydrogel volume was severely reduced after only 1 day (24 hours later). This demonstrates the superior nonvolatility of the DES gel compared to a hydrogel analogue in ambient conditions.

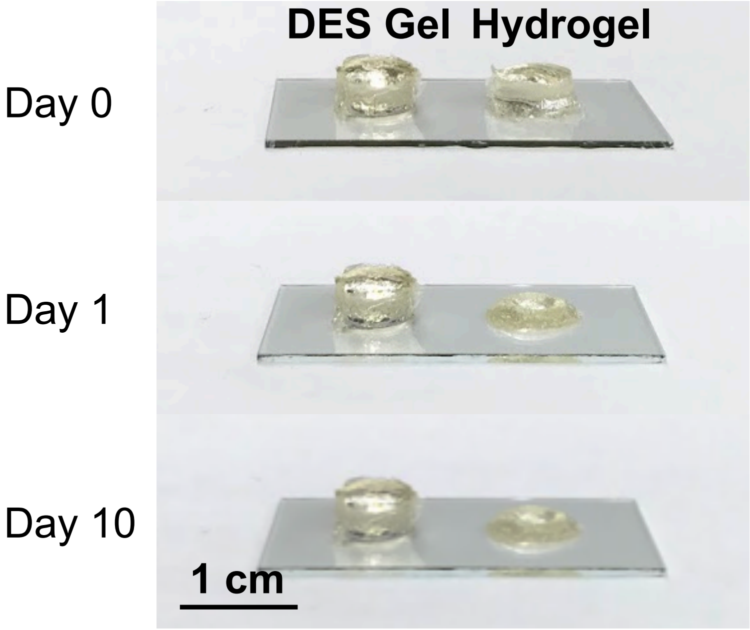

Figure S1. Photographs of a DES gel and a hydrogel, each containing 22 wt.% gelatin, allowed to sit out in ambient laboratory conditions for 10 days, taken on days 0, 1, and 10.

Gel Transparency Characterization

Two DES gel compositions were chosen to examine the transparency of DES gels. One contained 12 wt.% gelatin, which is the minimum gelatin content required to form a free-standing DES gel, while the other was the 22 wt.% gelatin DES gel, which is the highly stretchable DES gel composition used in all sensor prototype devices. Transmittance spectra of 0.5 mm thick DES gel films were recorded using a fiber optic spectrometer (USB-2000, Ocean Optics). Both DES gels films exhibited similarly high transparency values (~80-90%, Figure S2) across the entire range of visible light (400-800 nm), demonstrating the excellent transparency of gelatin-supported DES gels.

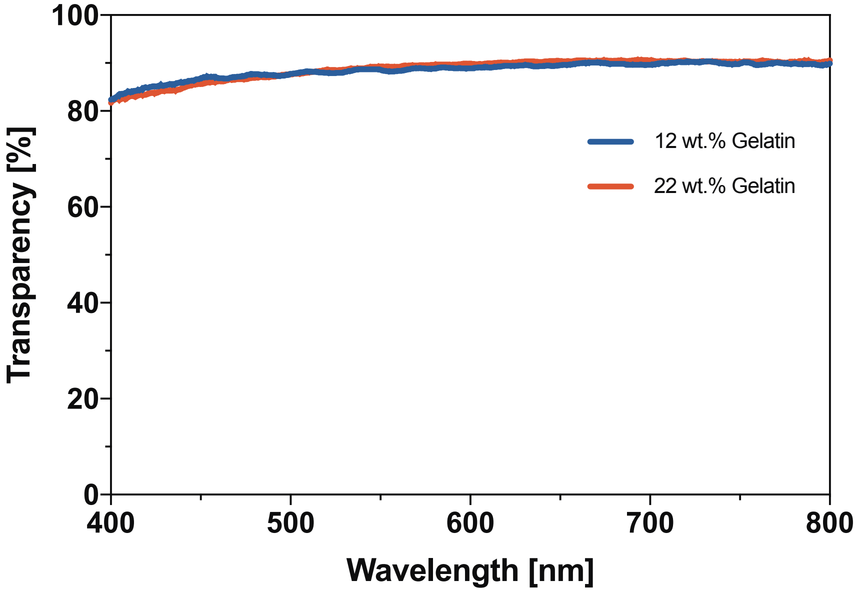

Figure S2. Transparency spectra measured for 12 wt.% and 22 wt.% gelatin-supported DES gels across the wavelength range of visible light.

Ionic Conductivity of Gelatin DES Gel Tested in Ambient Laboratory Conditions

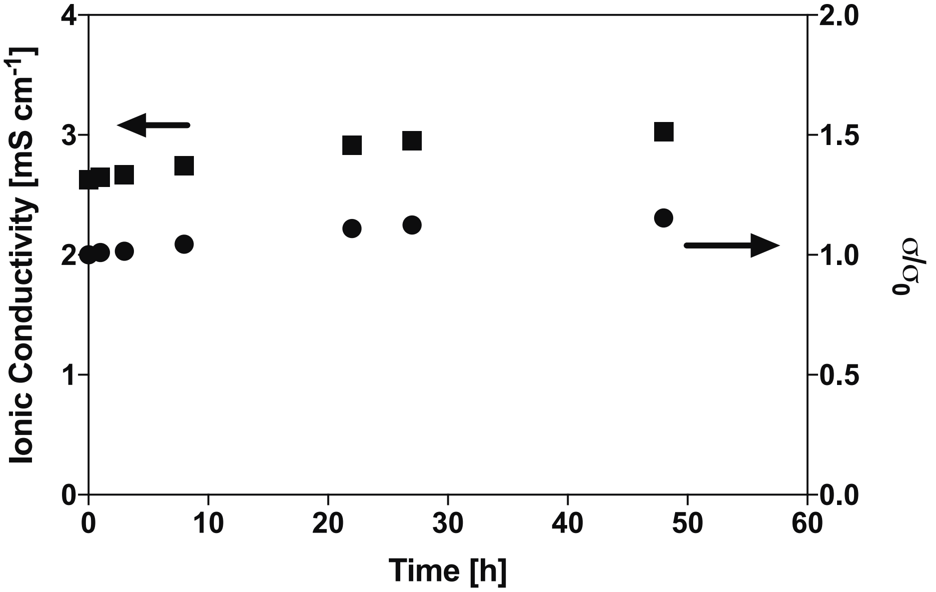

Figure S3. Ionic conductivity versus time of a 22 wt.% gelatin-supported DES gel measured via AC impedance spectroscopy for gel storage in ambient laboratory conditions (21 °C, 16% relative humidity) over a period of 48 hours. The small increase in ionic conductivity over this time period (~15%) is likely attributable to the absorption of moisture from air. Notably, the change in ionic conductivity is very modest (~4% increase) during the first 8 hours in air.

Additional Tensile Testing Data

DES gels could be also synthesized by adding greater than 22 wt.% gelatin into the precursor solutions. As shown in Figure S4, both 25 wt.% and 30 wt.% gelatin-supported DES gels exhibited increased ultimate tensile strengths compared to the 22 wt.% gelatin formulation, but the failure strains were lower by comparison.

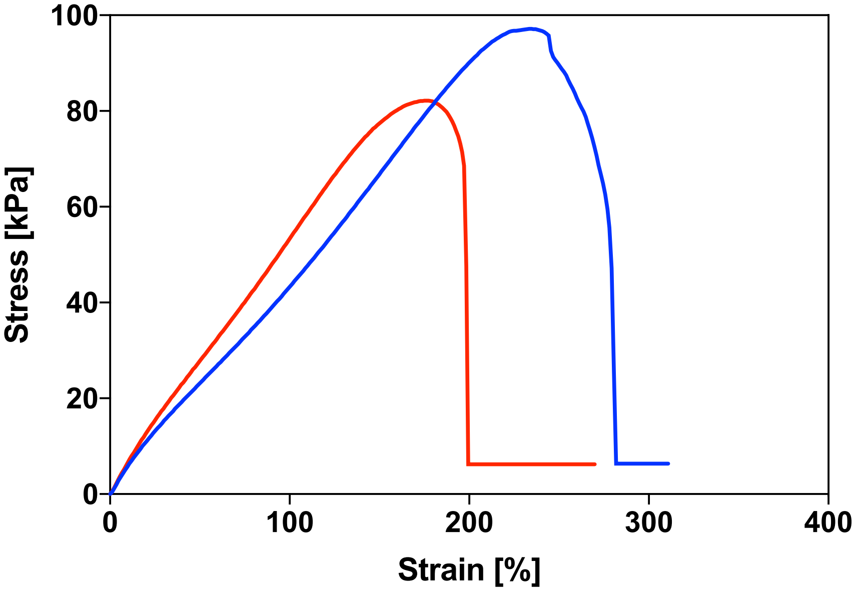

Figure S4. Representative tensile stress-strain curves for DES gels containing 25 wt.% (red) and 30 wt.% (blue) gelatin scaffolds.

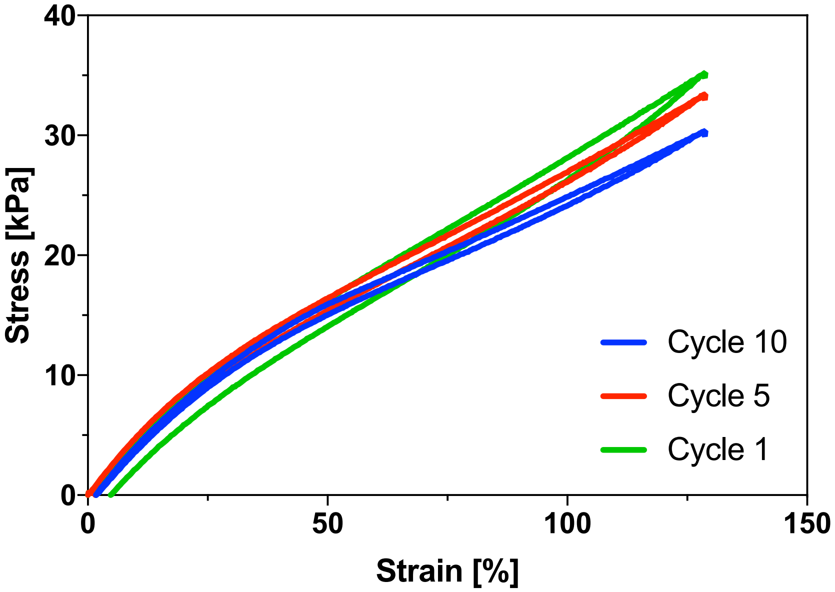

Figure S5. Representative tensile cycling stress-strain curves of a 22 wt.% gelatin-supported DES gel at a maximum strain of 125%.

WAXD Spectra of Lyophilized EG Gel vs. Hydrogel Films

Wide-angle X-ray diffraction (WAXD) was performed on lyophilized EG gel film and lyophilized hydrogel film samples (both gels contained 22 wt.% gelatin) in order to compare the triple helix content of both films by examination of the peak at $2\theta = 8°$, which represents the diameter of the triple helix.[3] A significant decrease in peak intensity and a shift of the peak position to lower 2θ were observed for the EG gel film in comparison to hydrogel film (Figure S6), which suggested that the EG gel contained not only a lower triple helix content, but that the triple helices formed in EG possess a larger diameter. The broad peak located at 20-22° corresponds to the spacing between amino acid residues along the gelatin backbone.[3,4]

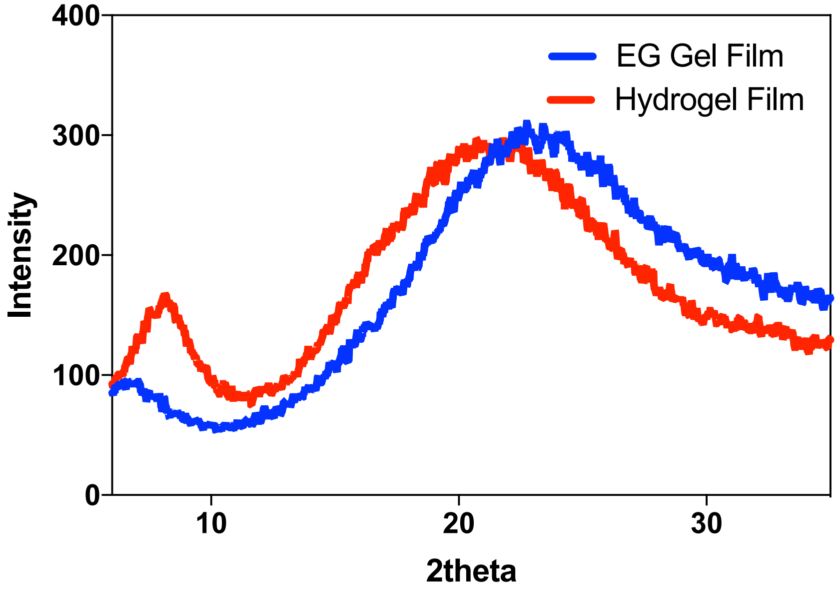

Figure S6. Wide angle X-ray diffraction patterns measured for lyophilized EG gel and hydrogel films obtained from 22 wt.% gelatin-supported gel samples.

Schematic Illustration of Gelatin Scaffold Assembly in Various Gels Investigated

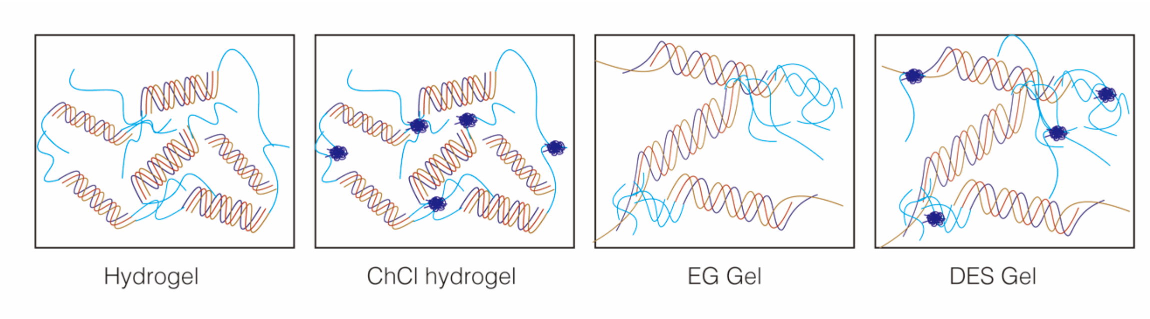

Figure S7. Illustration of gelatin-supported hydrogel, ChCl hydrogel, EG gel, and DES gel electrolytes, showing the proposed different extents of triple helix formation and gelatin chain bundling within the various liquid environments.

Fabrication and Characterization of 3 x 3 Sensor Array

Six thin, rectangular DES gel strips (L x W x H = 4 cm x 2 mm x 2 mm) were cut from a larger a DES gel film and used in order to maximize the spacing between each gel intersection point and decrease the crosstalk between taxels. Three DES gel strips were placed on one side of a plastic film (polyethylene, thickness = 65 μm) with a spacing of 2 cm and the other three gel strips were placed perpendicular to these on the opposite side (see Fig. S8). Another two layers of plastic film and regular Scotch tape were used to encapsulate the whole device and stabilize the copper wire connections, respectively. The capacitance of each taxel was measured point by point using the LCR meter after placing weight(s) on different taxel(s). The 200 g weight used was a standard cylindrical weight from Ohaus with a diameter of 3 cm and a height of 4 cm, which was placed atop a small cylindrical plastic lid (diameter = 1.5 cm) to create an approximate effective "touch" pressure of 11.1 kPa. (=[0.2 kg*9.8 m/s^2] / [π*(7.5x10^{-3} m)^2]). The 20 g weight was a hexagonal head screw/nut assembly, with a contact area of 1.06x10^{-4} m^2. This corresponded to an effective pressure of 1.8 kPa (=[0.02 kg*9.8 m/s^2] / [1.06x10^{-4} m^2]).

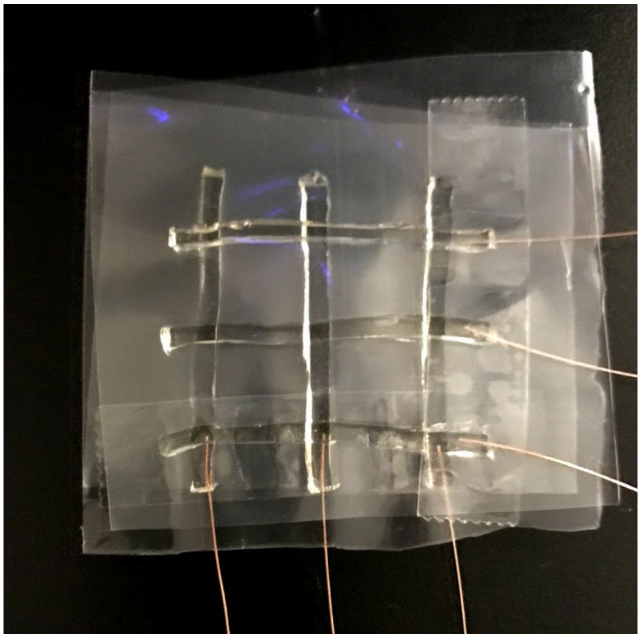

Figure S8. Photograph of a 3 x 3 capacitive pressure sensor array.

Supplementary References

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