ENGINEERING DYNAMIC HYDROPHOBIC DOMAINS IN BIOREINFORCED IONIC HYDROGELS FOR ROBUST AND TRANSPARENT SOFT ELECTRONICS

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Keywords: Conductive hydrogels, hydrophobic association, gelatin reinforcement.

Introduction

Conductive hydrogels have emerged as versatile material platforms for flexible bioelectronics, soft robotics, human-machine interfaces, and wearable health monitoring devices. Reliable real-time motion detection requires materials that seamlessly combine high stretchability, mechanical resilience, optical clarity, and stable electrical signal transduction. However, conventional chemically cross-linked hydrogels exhibit low fatigue resistance due to irreversible rupture of covalent bonds under cyclic loading. Although double-network hydrogels address mechanical strength, stress concentration and permanent damage in sacrificial networks frequently induce performance degradation. Furthermore, high-performance conductive hydrogels often rely on conductive nanofillers or complex multinetwork architectures that impair structural transparency, increase process complexity, and restrict scalable manufacturing.

To overcome these inherent limitations, engineering dynamic physical networks governed by dynamic noncovalent interactions presents an appealing filler-free alternative. Hydrophobic associations mediated by surfactant micelles act as reversible cross-linking nodes capable of dynamic dissociation and reassociation during deformation, providing efficient energy dissipation and rapid elastic recovery. Incorporating bio-derived macromolecules like gelatin rich in hydrogen-bonding functional groups into a micelle-mediated poly(acrylamide) network establishes a cooperative dual physically cross-linked matrix. The objective of this study was to construct a transparent, bioreinforced, filler-free ionic hydrogel strain sensor with exceptional stretchability, high fracture stress, low mechanical hysteresis, and superior electromechanical stability across broad strain ranges.

Material and Methods

Gelatin (type B, bovine skin), stearyl methacrylate (SMA), acrylamide (AAm, ≥99%), sodium chloride (NaCl, 99%), sodium dodecyl sulfate (SDS, ≥90%), ammonium persulfate (APS, ~97.5%), and N,N,N',N'-tetramethylethylenediamine (TEMED, 99%) were used as received. Hydrogels were synthesized via a one-pot free-radical polymerization. SDS (0.7 g) and NaCl (0.3 g) were dissolved in 9.90 mL of deionized water at 40 °C. Gelatin was added at varied masses (0.05, 0.10, 0.15, 0.20, and 0.30 g; denoted as GT0.05 to GT0.3, alongside a pristine

Pure control) and stirred for 2 h. SMA (100 µL) was incorporated to form micellar domains, followed by AAm (2.5 g). Polymerization was initiated by APS (0.05 g) and TEMED (10 µL) at 60 °C for 90 min in sealed molds. Samples were thoroughly washed in distilled water to remove unreacted monomers.

Chemical interactions were confirmed by FTIR spectroscopy (Shimadzu, 4000–500 cm^{-1}), and surface morphology was examined by SEM (JEOL JSM-6610LV) on gold-sputtered freeze-dried samples. Optical transmittance (400–800 nm) was measured using a UV-vis spectrophotometer (PerkinElmer Lambda 25). Mechanical properties were evaluated in uniaxial tensile and cyclic loading-unloading modes using a universal testing machine (Biopdi MBIO-1, 50 mm min^{-1} crosshead speed). Ionic conductivity was determined via electrochemical impedance spectroscopy (CompactStat, 1 MHz–0.1 Hz, 10 mV AC amplitude) in a two-electrode cell. Strain sensitivity, gauge factors (GF), and real-time motion detection (finger, wrist, laryngeal speech, facial expressions, and touchscreen interaction) were recorded using a potentiostat (Metrohm Autolab PGSTAT302N) under chronoamperometric mode at 1 V.

The gelatin-reinforced hydrogels were prepared via a one-pot free-radical polymerization process. First, SDS (0.7 g) and NaCl (0.3 g) were dissolved in 9.90 mL of deionized water at 40°C under magnetic stirring. Gelatin was added at various contents (0 to 0.30 g), and the mixture was stirred at 40°C for 2 h to ensure complete dissolution. Subsequently, SMA monomer (100 µL) was introduced, followed by stirring at 40°C for 2 h to achieve uniform micellar solubilization. Acrylamide (AAm, 2.5 g) was then added and homogenized for 30 min. Free-radical polymerization was initiated by sequentially adding APS (0.05 g) and TEMED (10 µL), and the precursor solution was cured in a mold at 60°C for 90 min. The resulting hydrogels were thoroughly washed in distilled water to remove residual monomers and surfactants. Samples were encoded as Pure (without gelatin) and GTx, where x represents the mass of gelatin (Table 1). The hydrogels were characterized using FTIR, SEM, tensile mechanical tests, and electrochemical analyses. Their strain-sensing performance was evaluated through ionic conductivity, gauge factor, cyclic stability, and response/recovery measurements.

Results and Discussion

FTIR analysis confirmed successful dual physical cross-linking. Characteristic C-H alkyl stretching bands (2851 and 2924 cm^{-1}) demonstrated retention of micellar SMA hydrophobic domains. Upon gelatin incorporation, the C=O stretching band shifted from 1680 to 1653 cm^{-1}, proving enhanced hydrogen bonding with the P(SMA-co-AAm) backbone. SEM imaging revealed that while the Pure hydrogel exhibited a rough surface with microcracks, the GT0.15 sample possessed a uniform, highly interconnected porous morphology due to cooperative gelatin-polymer cohesion. High gelatin contents (GT0.2) led to localized aggregation and structural heterogeneity.

Mechanical testing demonstrated significant synergistic reinforcement in GT0.15. The Pure hydrogel exhibited a fracture stress of 0.15 MPa and fracture strain of 1512%. Incorporation of 0.15 g gelatin enhanced the fracture stress to 0.31 MPa (+107.3%) and fracture strain to 2420%, alongside a toughness increase from 79.7 to 267.1 kJ m^{-3} and Young's modulus from 0.094 to 0.6 kPa. This simultaneous gain in strength and extensibility stems from reversible

hydrogen bonding and salting-out effects induced by gelatin and NaCl, which stabilize SDS/SMA micellar cross-links. Optical transmittance of GT0.15 reached ~85.9% across visible wavelengths, whereas GT0.2 dropped to ~50% due to light scattering from aggregated domains.

Cyclic mechanical testing of GT0.15 displayed strain-dependent energy dissipation (1.91 kJ m^{-3} at 100% strain to 19.76 kJ m^{-3} at 500% strain). Across five consecutive 500% strain cycles without rest, dissipated energy stabilized at ~17.60 kJ m^{-3} with negligible decay, proving excellent fatigue resistance. Electrochemical impedance verified stable ionic conductivity up to 0.042 S m^{-1} for GT0.15. Electromechanical characterization revealed broad strain responsiveness (0.5%–650%) with three distinct linear sensing regimes: Gauge factor (GF) = 6.32 (0–200%), GF = 10.16 (201–500%), and a maximum GF = 12.08 (501–650%). The sensor exhibited rapid response (135 ms) and recovery times (124 ms), and sustained >1000 continuous loading-unloading cycles at 200% strain without signal drift. Epidermal application demonstrated accurate tracking of large joint motions (finger, wrist, knee) and subtle physiological signals, including silent speech laryngeal vibrations, frowning, breathing, handwriting recognition, and capacitive touchscreen operation.

Conclusions

A bioreinforced, filler-free ionic conductive hydrogel was successfully developed through a simple one-pot micelle-mediated strategy. By combining dynamic hydrophobic associations of SMA/SDS micelles with extensive hydrogen bonding from gelatin, the optimized GT0.15 hydrogel achieved exceptional stretchability (2420%), enhanced fracture stress (0.31 MPa), high optical transparency (85.9%), and robust fatigue resistance. The embedded ionic pathways enabled high strain sensitivity (maximum GF of 12.08 over 0.5–650% strain) and rapid electromechanical response times (135/124 ms). Practical epidermal sensing successfully captured both large human joint movements and subtle physiological signals (silent speech, laryngeal articulation, breathing), as well as interactive capacitive touchscreen inputs. This design establishes a scalable pathway for high-performance, transparent soft bioelectronics.

Acknowledgments

The authors acknowledge CNPq (Process 303125/2022-5) and CAPES (Finance Code 001) for financial support and fellowship grants.

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