

Rapid, pH-dependent self healing hydrogels

Ameya Phadke¹, Cheng-Chih Hsu², Chao Zhang¹, Gaurav Arya³, Michael Tauber², Shyni Varghese¹.

Departments of ¹Bioengineering, ²Chemistry and Biochemistry, ³NanoEngineering, University of California- San Diego, La Jolla, CA-92093

Statement of Purpose: An intriguing aspect of biological systems is their ability to undergo healing structural damage. Smart materials with the ability to undergo healing upon damage are being developed at a rapid pace. However, many of these approaches can't be employed to achieve healing of chemically crosslinked hydrogels due to the presence of water and irreversible chemical crosslinks. In this study, we describe the development and characterization of smart self-healing hydrogels, where two hydrogels pieces undergo reversible healing within seconds of contact in aqueous environment in response to changes in environmental pH. These rapid, reversible, self-healing hydrogels are polyanionic hydrogels derived from N-acryloyl amino acids having a unique balance of hydrophilic and hydrophobic interactions, where the accessibility of dangling side chains carrying terminal carboxyl groups facilitates intermolecular co-ordinated hydrogen bonding between two macroscopic hydrogels. Such easy-to-synthesize, cost-effective hydrogels represents a new class of smart, self-healing systems with applications in biology, materials science, and medicine.

Methods: N-acryloyl amino acids with 1, 3, 5, 7 and 10 CH₂ groups respectively were synthesized as specified previously. A 1M solution of each N-acryloyl amino acid was prepared in 1N NaOH and polymerized for 16 hrs at 37°C using redox initiators. Hydrogels were healed by bringing in contact with each other in low pH (≤ 3). Weld-line strength of the healed hydrogels was measured by determining the ability of the interface of healed hydrogels to withstand added known weight. The degree of crosslinking was varied by adding known amounts (0.1% to 0.5%, w/v) of N,N-methylene bisacrylamide (BisAm). Protonated and deprotonated samples were dried at 37°C for 24 hours and then characterized by Raman and FT-IR spectroscopy.

Results: Upon interfacial contact at pH 0.3, the hydrogels underwent healing within 1-2 seconds of contact, with a strong interfacial weld line (Fig. 1 (top)). This healing was found to be reversible; upon exposing the healed gels

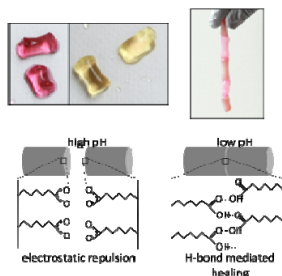


Figure 1: Schematic of healing mechanism

to pH ~ 13 , they were observed to separate at the interface. These separated gels underwent healing when re-introduced in low pH conditions and this healing-separating-rehealing cycle was repeated more than 12 times. Using the healing ability of these hydrogels, complex shapes can be assembled from simple units.

Healing was also highly pH dependent with strong healing observed below pH 3, weak healing at pH 4 and no healing above pH 4.5. This indicates that only highly protonated hydrogels are capable of healing. In addition to high pH buffers, the healed hydrogels were found to separate in a 30% solution of urea in water unlike healed hydrogels exposed to water; urea is known to disrupt hydrogen bonds. Moreover, healed hydrogels did not separate even in boiling water (100°C) further suggesting the role of extremely strong co-ordinated H-bonding. These findings along with spectroscopic (Raman and FT-IR) evidence suggest that the self-healing is due to intermolecular hydrogen bonding between the protonated terminal carboxyl groups of the pendant side chains across the interface (Figure 1 (bottom))

As anticipated, an increase in interfacial weld strength was observed with healing time from 10 seconds to 24 hours. On the contrary interfacial weld strength was found to decrease with an increase in cross-linking density (Figure 2a), possibly due to the decreased chain mobility due to increased presence of crosslinks- for hydrogels with no added BisAm, rupture was observed in the hydrogel interior, rather than the interfacial weldline. Furthermore, the pendant side chain length was found to have a non-monotonic effect of healing; only hydrogels with pendant side chains containing 5 CH₂ groups and to a lesser extent, 7 CH₂ groups, were capable of undergoing healing, suggesting that optimal accessibility is crucial for the formation of co-ordinated hydrogen bonds responsible for healing.

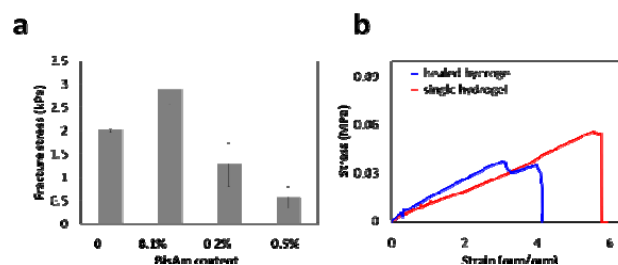


Figure 2: (a) Effect of crosslink density on weldline strength (b) Stress-Strain curve for 24 hour healed hydrogels

Conclusions: Crosslinked hydrogels derived from N-acryloyl 6-aminocaproic acid are capable of rapid, reversible pH-dependent self healing in aqueous solutions with $\text{pH} \leq 3$. This is due to the formation of intermolecular hydrogen bonds between the protonated terminal carboxyl groups of the pendant side chains across the interface. Weld line strength is dependent on healing time, pendant side chain length and degree of crosslinking.

References: 1. Badiger M. J Chem Phys. 1998;109 (3): 1175-1184
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