Load-Bearing Hydrogels Ionically Reinforced Through Competitive Ligand Exchanges

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CellMA-PAA-Fe Hydrogel Preparation and Characterization

Acrylate-modified carboxymethyl cellulose (CMC) is prepared via an epoxy ring opening reaction with glycidyl methacrylate (GMA). To test the synthesis outcome, $^1$H-NMR is performed on a freeze-dried sample of CellMA (Figure S1). The functionalization renders CellMA compatible with conventional free-radical polymerization. However, the hydrogel shows poor mechanics when covalently crosslinked. Its mechanical properties are significantly improved if acrylic acid is added as a crosslinker (Figure S2).

CellMA-PAA hydrogels are prepared through a one-pot synthesis in the presence of 0, 0.5, 1, 2, and 4 mol% Fe$^{3+}$. Under compression, the reinforcement of CellMA-PAA hydrogels with Fe$^{3+}$ increases their stiffness and toughness until the Fe$^{3+}$ concentration exceeds 1 mol%. The hysteresis of CellMA-PAA hydrogels increases 2-fold if they are reinforced with 1 mol% Fe$^{3+}$ (Figure S3). To circumvent the detrimental interaction of Fe$^{3+}$ with the radical polymerization reaction that is observed at Fe$^{3+}$ concentrations higher than 1 mol%, a two-step approach is implemented. This new procedure allows to temporally decouple the formation of the covalent network from the ionic reinforcement. As a result, CellMA-PAA hydrogels can be produced via a UV-induced
polymerization. The resulting CellMA-PAA hydrogels reveal a Mullin’s behavior that is attributed to the progressive fracture of CellMA chains under applied stress (Figure S4).

CellMA-PAA hydrogels can be made stronger by soaking them in aqueous solutions containing various amounts of Fe$^{3+}$ and CA (Figure S5). Moreover, the dynamic nature of competitive ligand exchange can be used to selectively remove Fe$^{3+}$ ions from the surface of CellMA-PAA-Fe hydrogels, thus making it accessible for further ionic crosslink with Al$^{3+}$ ions, yielding a core-shell structure (Figure S6).

**Movie M1.** Process flow for the fabrication of CellMA-PAA-Fe reversible joints. Briefly, a hydrogel beam is immersed in a 1 mol% Fe$^{3+}$ and 1.5 mol% CA solution. The infiltrated beam is strong enough to withstand a load of 0.03 MPa.
Figure S1. $^1$H-NMR measurement of CellMA in $\text{D}_2\text{O}$. $^1$H-NMR (400 MHz, Deuterium Oxide) δ 6.09 (s, 1H), 5.66 (s, 1H), 1.86 (s, 3H). The successful grafting of methacrylate groups onto cellulose is shown by the appearance of the peaks at 6.09, 5.66, and 1.86 ppm.
Figure S2. Compressive curves of CellMA and CellMA-PAA hydrogels. The curves show a clear toughening of the sample when CellMA is crosslinked with acrylic acid.
Figure S3. Hysteresis energies for CellMA-PAA and CellMA-PAA-Fe. Extracted hysteresis of CellMA-PAA hydrogels prepared in a one-pot approach crosslinked with 0, and 1 mol% Fe$^{3+}$. Values are calculated from 5 repeated compressive cycles. The sample reinforced with 1 mol% Fe$^{3+}$ displays a 2-fold higher hysteresis energy than the non-reinforced counterpart.
Figure S4. Cyclic tensile measurement of CellMA-PAA. Cyclic tensile loading reveals a Mullin’s behavior of the hydrogel. Upon a first cycle, a hysteresis loop is present due to the irreversible deformation of the network. The following cycles that are performed to the same maximum elongation display a purely elastic behavior.
Figure S5. Optical photograph of CellMA-PAA-Fe hydrogels. Photographs of CellMA-PAA hydrogels reinforced with 1 mol% Fe$^{3+}$ in the presence of 1.5 mol% (a), and 3 mol% (b) CA. At lower CA concentrations, the Fe$^{3+}$ concentration is heterogeneous, creating an osmotic pressure that deforms the sample.

Figure S6. SEM and EDX micrographs. a, SEM micrograph of a core-shell CellMA-PAA hydrogel and the corresponding EDX area (white box). b, 2D EDX maps displaying the distribution of Al, Fe, and C respectively.