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.

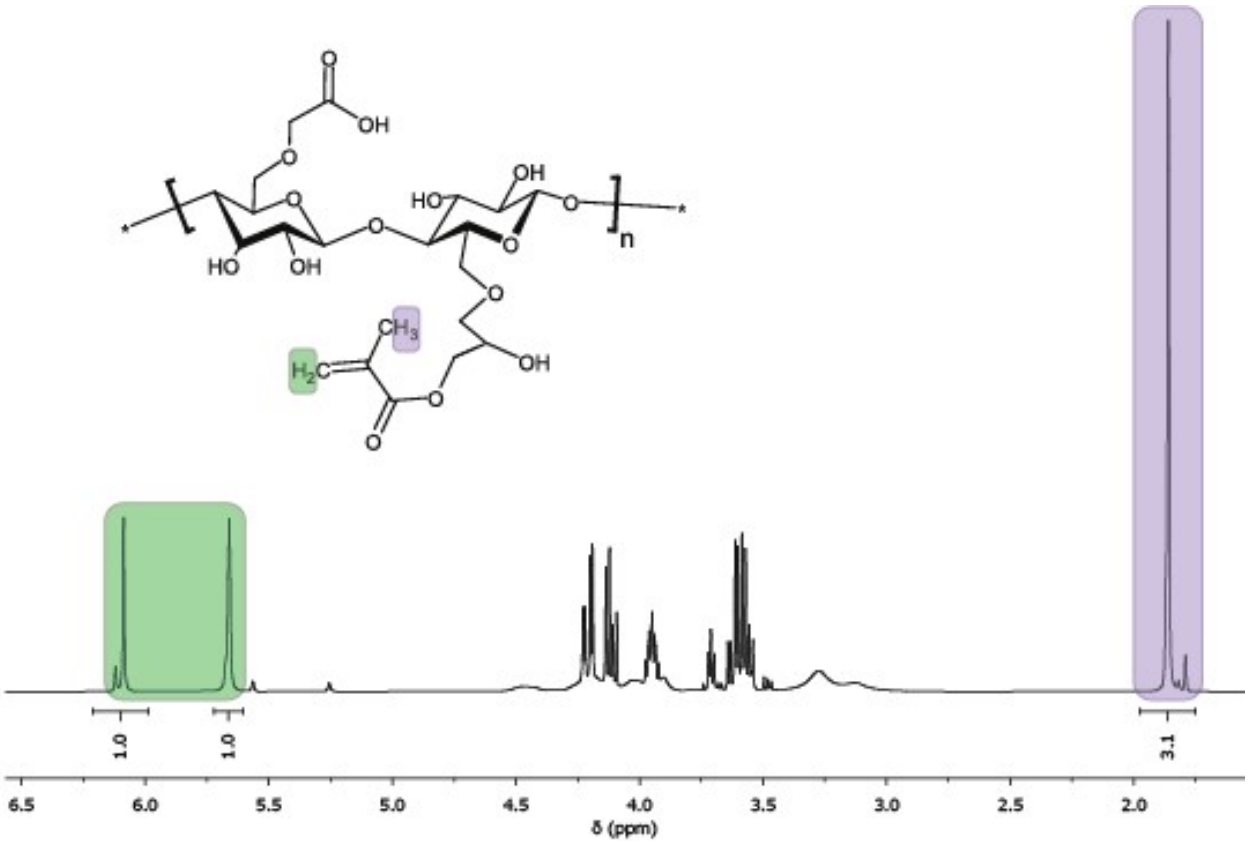

Figure S1. ^{1}H-NMR measurement of CellMA in D_2O. ^{1}H-NMR (400 MHz, Deuterium Oxide) δ 6.09 (s, 1H), 5.66 (s, 1H), 1.86 (s, 3H). The successful grafting of methacrylate groups onto cellulose is shown by the appearance of the peaks at 6.09, 5.66, and 1.86 ppm.

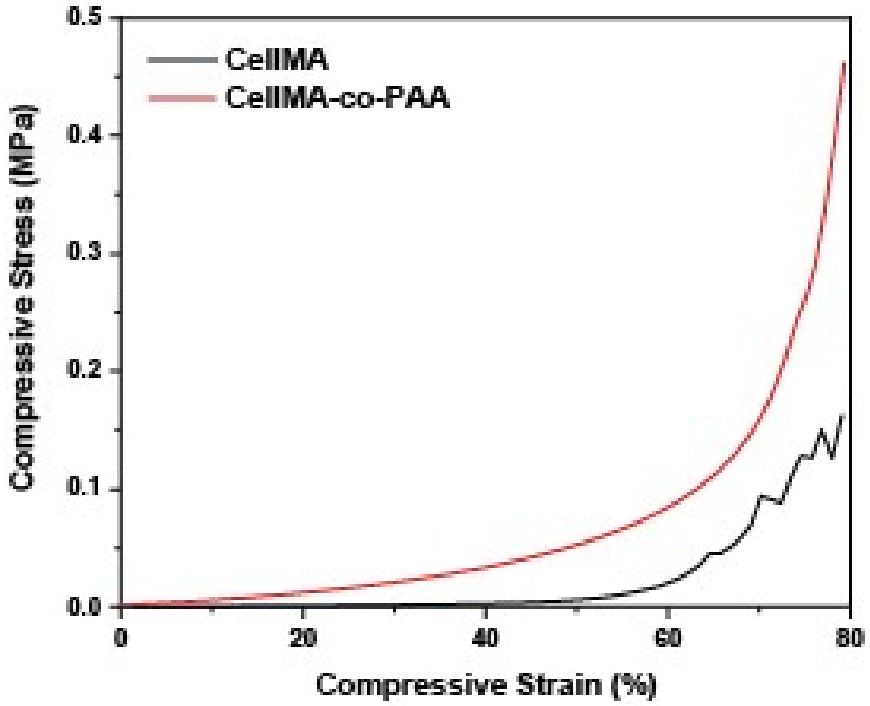

Figure S2. Compressive curves of CellMA and CellMA-PAA hydrogels. The curves show a clear toughening of the sample when CellMA is crosslinked with acrylic acid.

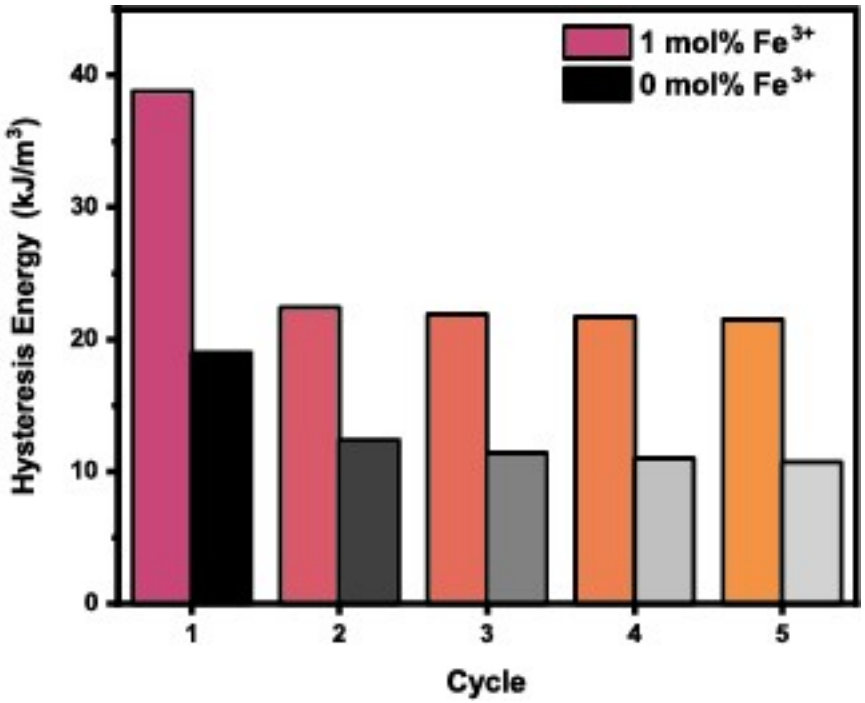

Figure S3. Hysteresis energies for CellMA-PAA and CellMA-PAA-Fe. Extracted hysteresis of CellMA-PAA hydrogels prepared in a one-pot approach crosslinked with 0, and 1 mol% Fe^{3+}. Values are calculated from 5 repeated compressive cycles. The sample reinforced with 1 mol% Fe^{3+} displays a 2-fold higher hysteresis energy than the non-reinforced counterpart.

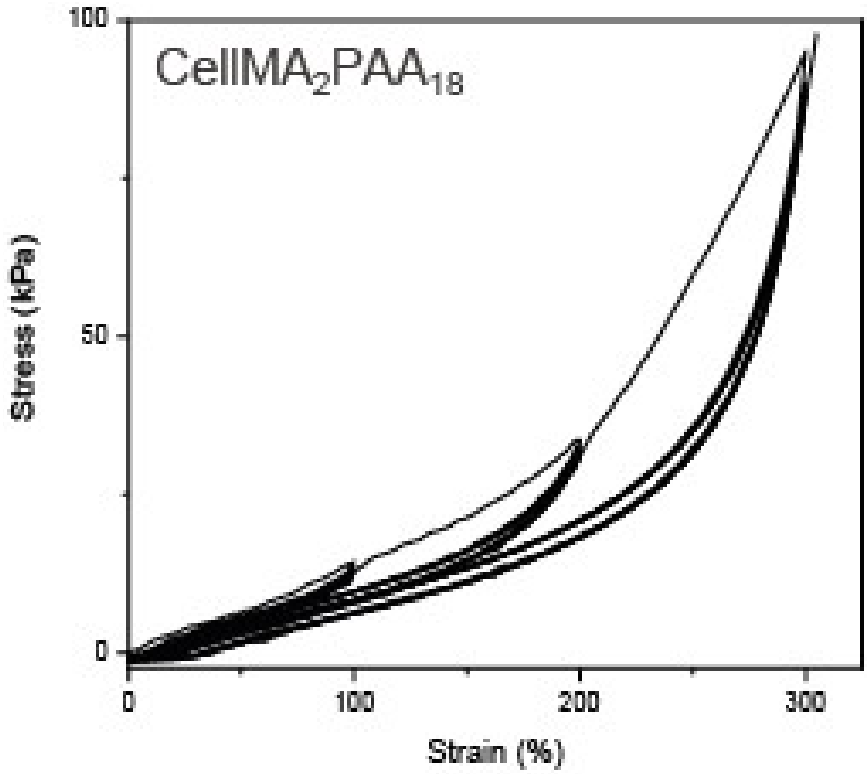

Figure S4. Cyclic tensile measurement of CellMA-PAA. Cyclic tensile loading reveals a Mullin's behavior of the hydrogel. Upon a first cycle, a hysteresis loop is present due to the irreversible deformation of the network. the following cycles that are performed to the same maximum elongation display a purely elastic behavior.

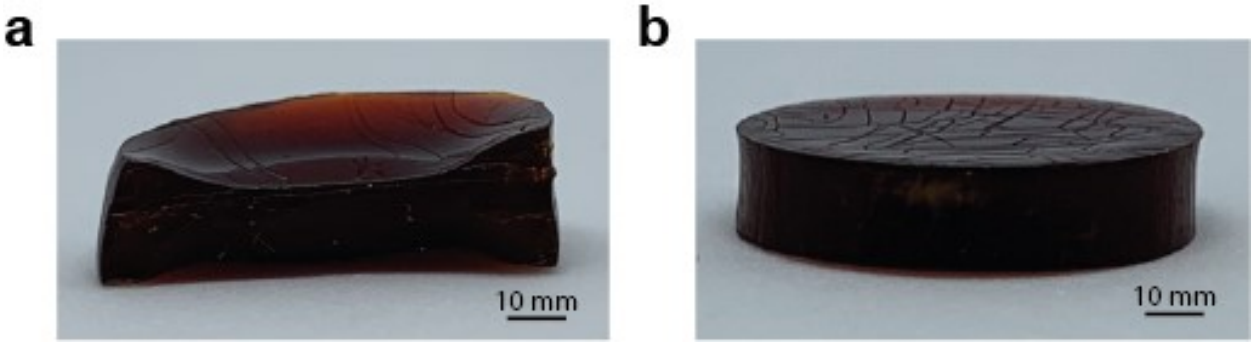

Figure S5. Optical photograph of CellMA-PAA-Fe hydrogels. Photographs of CellMA-PAA hydrogels reinforced with 1 mol% Fe^{3+} in the presence of 1.5 mol% (**a**), and 3 mol% (**b**) CA. At lower CA concentrations, the Fe^{3+} concentration is heterogeneous, creating an osmotic pressure that deforms the sample.

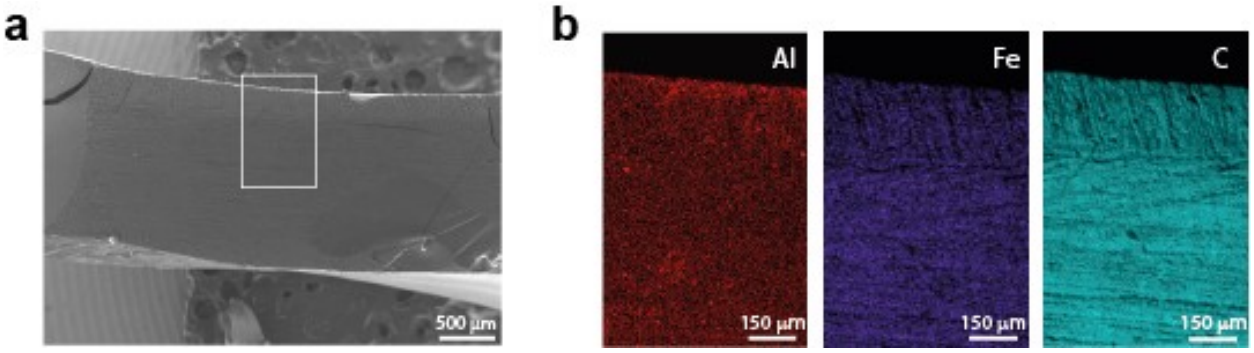

Figure S6. SEM and EDX micrographs. a, SEM micrograph of a core-shell CellMA-PAA hydrogel and the corresponding EDX area (white box). **b,** 2D EDX maps displaying the distribution of Al, Fe, and C respectively.