Mechanochemical generation of redox species in Polyacrylamide hydrogels due to osmotic swelling

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In this talk, we report the mechanochemical production of free radicals in swelling polyacrylamide hydrogels.Osmotic swelling of hydrogels can lead to significant chain strain due to opposite forces of solvation and network integrity, resulting in bond scission at crosslink sites. We first investigated the swelling induced production of H_2O_2 due to crosslink breakage. By tuning the nature and loading of crosslinker employed in thin square hydrogels, mechano-scission of crosslink sites and subsequent production of free radicals was observed. Production of OH● radicals and the resultant combination to H_2O_2 was observed via colorimetric assay analysis. The assay consisting of Horseradish peroxidase and Amplex ultrared reported H_2O_2 concentrations from 5-28 μM depending on crosslinker strength in both weak (disulfide) and strong (PEG) linkages. H2O2 concentration was enhanced by swelling constrained gels, which is known to introduce significant biaxial stresses.
Next, we report contact separation induced radical formation of a hydrogel-glass interface to fluorescently tag the network at sites of interfacial damage. Weakly tethered hydrogels can undergo edge failure due to solvent ingress. Here, thin circular amine-doped hydrogels were swollen in aqueous solutions of a novel ketone containing fluorophore to initiate radical-mediated reductive amination between the dye and the hydrogel. After swelling and washing, fluorescent edge patterns were observed, enabling a post-swelling analysis of interfacial damage.Failure was tuned by varying monomer/crosslinker loading, swelling conditions and thickness to reveal variable fluorescent patterns. Higher crosslinker loading led to more radial penetration and higher area fraction of delamination across monomer loadings, while the length scale of delamination scaled directly with gel thickness. Currently, we are investigating the dual capability of redox specie generation to initiate versatile reactions. We also aim to control these pathways with scavengers/promoters, to design specific applications such as reductive generation of antibacterial gold nanoparticles and oxidative activation of a latent fluorophore.