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Nanoscale TEM visualization of polymer network rupture using mechanoradical indicators

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Polymer networks, such as elastomers and hydrogels, are widely used in various applications for their combination of elasticity, mechanical strength, and toughness. These properties arise from the network structure, which influences strand behavior and interactions. While significant progress has been made in understanding fracture mechanisms at larger scales, the nanoscale distribution of rupture events remains less understood.

Recent advances in mechanochemistry, including the use of mechanophores—molecules that change structure under mechanical force—have enabled the visualization of polymer rupture in hydrogels and elastomers. Similarly, mechanoradical polymerization has been applied to study polymer rupture in hydrogel networks with fluorescent probes. However, these methods are limited by the resolution of visible light (~400-800 nm), which cannot resolve rupture events in polymer networks with nanoscale mesh sizes (~1-100 nm). Mechanophores also introduce weak points, altering rupture behavior.

This study overcomes these challenges by combining mechanoradical polymerization with mineral staining. Mechanoradicals, generated when polymer strands are cleaved by mechanical stress, initiate the polymerization of marker polymers at rupture points. Mineral nanoparticles are then selectively mineralized onto these markers, serving as indicators for rupture locations. Transmission electron microscopy (TEM) provides high-resolution imaging of these nanoparticles, offering insights into fracture mechanisms at the molecular scale.

Double-network hydrogels (DN gels) and single-network hydrogels (SN gels) were synthesized, and TEM analysis revealed that nanoparticles were selectively mineralized on the marker polymers. This method enables the visualization of nanoscale rupture points and enhances our understanding of fracture behavior in polymer networks. Results on the relationship between tensile strain and fracture behaviors of DN and SN gels will be presented.

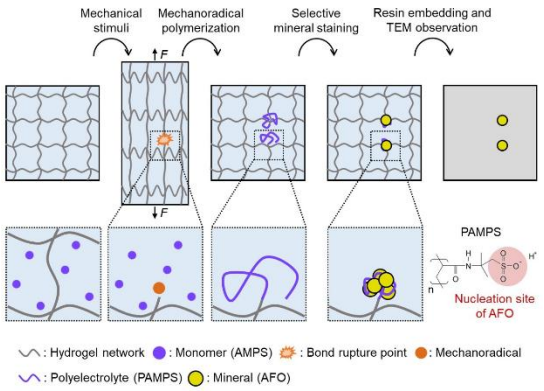

Figure: Schematic illustration of principle and sample preparation procedures to visualize ruptures of polymer strands in polymer network