

Synthesis, Characterization, and Theory of Polymer Gels to Elucidate Topology-Property Relationships

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Abstract

Crosslinked polymer networks and gels are pervasive in daily life, with applications ranging from tires to contact lenses to precision drug delivery. For any application, it is desirable to engineer the material based on fundamental principles and predictive theories *a priori* to synthesis or production. This is challenging because end-linked polymer gels are filled with defects, specifically loops, dangling ends, and unreacted chains that significantly impact the elasticity of the network. Many classical theories do not account for these defects and rely on untested molecular assumptions that lead to inaccurate predictions.

To address this gap, experiments were designed to relate gel topology to key properties: equilibrium swelling, gel point, chain conformation, and fracture toughness. Equilibrium swelling data demonstrated that gels with more loops reach a higher degree of swelling due to fewer elastic constraints, and led to a revised Flory-Rehner swelling theory which accurately captures this behavior. Gel points measured during both bond forming and bond breaking processes deviated as gels became more dilute, indicating a departure from truly random percolation and suggesting kinetic effects should be considered when modelling gelation. Small angle neutron scattering was used to measure single chain conformations within a gel, indicating that elastic chains stretch to create a space-spanning network, with increased stretching as gels become more dilute. Fracture toughness data showed that gels with more loops have a lower fracture toughness but a larger strain at break due to the effective extension of average chain length, which led to an update to the Lake Thomas fracture theory that accounted for defects.

A new conceptual understanding of fracture as a process guided by the intrinsic reactivity of the substituent strands was demonstrated, further validating the revised fracture theory. Weak and strong mechanophores were used as crosslinkers in an end-linked network where the tearing energy was shown to correlate directly to the force-coupled reactivity of the linker. Tearing energy of mixed reactivity network demonstrated that depercolation of the fracture zone was the necessary criterion for failure. These experiments collectively enabled quantitative improvements to classical network models, provided evidence to verify molecular assumptions, and deepened conceptual understanding of network properties, enhancing predictive material design capabilities. Finally, a theoretical model for crosslinking with side reactions was updated and experimentally validated, enabling the study of nonideal networks common in industrial applications.

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