Quantifying Topology-Property Relationships in Polymer Networks: From Kinetics and Fracture Mechanics to Data-Driven Design

Devosmita Sen

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Abstract

Polymer networks are ubiquitous, with wide applications ranging from commodity rubbers and adhesives to sophisticated drug delivery and soft robotics. These materials have a complex interconnected topology consisting of loops and dangling ends, which make accurate property prediction extremely challenging. Fundamentally understanding the relationships between molecular-scale details and macroscopic properties is crucial for precise material design.

This thesis aims to advance the predictive modelling of polymer networks by investigating the quantitative interplay between network topology, kinetics and fracture mechanics, and by developing foundational frameworks for data-driven design. A computationally efficient algorithm is developed to quantify higher order cyclic topology based on the mathematical framework of 3D-nets. Comparison of networks formed by different simulation algorithms, using a topology-based distance metric, identifies distinct topological classes and reveals that polymer networks possess a fundamental cycle size governed by the topological proximity of crosslinkers during bond formation. The kinetics of polymer network formation are further investigated using kinetic Monte Carlo simulations and experimental validation, demonstrating that incorporation of dynamic bond rearrangements can enhance both modulus and network connectivity.

A generalized theoretical framework is developed to investigate fracture mechanisms in end-linked and side-linked networks, which, in combination with coarse-grained fracture simulations, reveals a narrow regime of molecular parameters that gives rise to preferential toughening of side-linked networks over their end-linked counterparts. A quantitative relationship between higher ordered cyclic topology and mechanical properties is investigated by studying fracture behavior of networks with ideal 3D-net-based topologies. The non-linear strain stiffening behavior is found to be strongly correlated with the chain orientations and pre-strain within the network, both of which are dictated by the underlying cyclic topology. A coarse-grained framework for incorporating excluded volume interactions within fracture simulations is developed, enabling more physically consistent modeling of crack propagation at the molecular level. Finally, the foundation is laid for mechanistically informed data-driven models by developing a computational workflow for the estimation of polymer solution interaction parameters, which is benchmarked against a large experimental dataset, enabling high-throughput prediction of network swelling for novel material design.

Thesis supervisor: Bradley D. Olsen, Alexander and I. Michael (1960) Kasser Professor of Chemical Engineering