

Predicting Properties of Polymer Networks Using Analytical Theory and Data-Driven Approaches

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Polymer networks have important applications in commodity products like car tires, biomedical applications like drug delivery, and everyday items like contact lenses. Despite seminal advances in theories and experiments, predicting important properties of polymer networks based on chemistry and topology remains challenging. This thesis has two broad aims to predict the properties of polymer networks. The first aim introduces physics-based theories and tools to predict valuable mechanical properties of networks such as the swelling behavior, modulus, and tearing energy. These theories and tools consider topological defects in the structure of the material that affect the mechanical properties. The second aim presents algorithms to support the new language encoding polymers as strings called BigSMILES to enable searching for all polymers, including polymer networks.

The first aim successfully proves that incorporating knowledge of topological defects into network prediction models improves accuracy. In the first project, an update to the famous Flory-Rehner equation is derived to include topological defects to predict the equilibrium swelling behavior of the network. The Flory-Rehner theory is a venerable solution for predicting the swelling behavior of a polymer network but it does not consider topological defects. The updates proposed in this thesis assume defect contributions to the elasticity are linear and additive. Swelling experiments are performed on gels in which topological defect densities are known, and the revised swelling equations are more accurate than the Flory-Rehner equation.

In the second project of the first aim, a pipeline is introduced to connect the chemistry of a polymer network to its topology and mechanical properties, specifically the modulus and fracture behavior. Very few tools exist for polymer networks that connect chemistry to property. In this project, a tool called the Network Elasticity and Reaction Designer (NERD) has been devised to fill this gap. NERD has a drawing tool designed for polymers with BigSMILES strings automatically generated, a reaction prediction module that detects functional groups, a coarse-graining module that uses databases of Kuhn parameters, a kinetic Monte Carlo simulation module, and a property prediction module. Each module has been heavily validated.

The second aim presents algorithms to accelerate molecular search to improve knowledge discovery and innovation. Search algorithms for polymers are less developed than those for small molecules because polymer search generally relies on searching by name, which can be challenging; even simple polymers like poly(ethylene) can have multiple names! This project introduces a query language for polymers that extends BigSMILES called BigSMARTS, a graph generation algorithm inspired by finite state machines, and a graph traversal search algorithm that first identifies and searches cycles representing the repeat units, then searches the end groups, and then performs a depth-first search to match entire subgraphs. This algorithm can be implemented on web search engines.

However, subgraph search can be computationally expensive, whereas string-based matching is simpler. In order to search by string, the BigSMILES language for a single ensemble must be standardized: the same polymer can have multiple equally valid representations. In this project, an analogy is drawn between polymers and formal languages, and BigSMILES can be mapped onto finite state machines, which can then be standardized (determinized and minimized).

This standardized graph can then be converted into a standardized BigSMILES string, which can serve as a unique identifier on web search engines for string-based search.

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