

# Characterization, deconstruction, and valorization of natural and synthetic crosslinked polymers

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Plastics are ubiquitous in almost every aspect of modern life, from food packaging to healthcare to electronics. The linear lifecycle of most plastics, in which they are produced, used, and then discarded, emits a significant amount of greenhouse gases and contributes to a global waste crisis, necessitating a transition to a more circular plastics economy. This dissertation focuses on the lifecycle of two specific crosslinked polymers: lignin and crosslinked polyethylene (XLPE). Lignin is a major constituent of lignocellulosic biomass (LCB) whose valorization is critical to achieve industrially viable biorefineries. XLPE is a commercially abundant material whose excellent performance properties make it uniquely suited for applications such as cable insulation or piping. Crosslinking endows both lignin and XLPE with desirable properties, but inherently challenges their deconstruction for the generation of valuable products. Herein, strategies to characterize, deconstruct, and valorize these crosslinked polymers were developed to improve sustainability throughout the materials lifecycle. First, informed harvest optimization and feedstock selection strategies were established for forestry residues, as a major hurdle for LCB valorization is the compositional variability among feedstocks. Structural carbohydrate quantities, lignin content, and reductive catalytic fractionation deconstruction yields were analyzed to identify across residue types-, species-, and phenophase-level trends. A forest residue biorefinery concept was modeled, and techno-economic analysis and life-cycle assessment were performed to demonstrate that biomass composition shapes the economics and emissions of biorefineries. Second, after exhibiting the power of informing biorefinery optimization using biomass composition, a higher-throughput biomass characterization approach that leverages thermogravimetric analysis was developed. This method achieved comparable accuracy and repeatability to the standard wet chemistry method with significant reductions in time, sample, and reagent requirements. Third, considering the end of the materials lifecycle for XLPE, catalytic hydroconversion strategies were established to efficiently deconstruct commercially relevant classes of XLPE into potentially valuable liquid and gaseous hydrocarbon products. Overall, the strategies presented herein for lignin and XLPE have the potential to enhance plastics sustainability throughout the materials lifecycle.