Sustainable Materials from Renewable Protein Feedstock and Waste Rubber

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This thesis focuses on developing sustainable materials from underutilized feedstock, namely proteins and waste rubber from used car tires. Valorization of proteins for use in engineering plastics can reduce reliance on fossil fuels for materials manufacturing, as well as increase economic viability of agriculture and biorefinery processes. Strategies have been proposed to address challenges in formulating protein-based plastics, such as protein feedstock and functional group diversity, difficulties in material processing, and undesirable physical and mechanical properties. Methods to devulcanize and recycle used tire rubber, one of the largest polymer waste sources, are also described.

The first part of this thesis explores the use of proteins as reinforcing domains in thermoset elastomers. Copolymers were prepared by conjugating proteins to rubbery polymers, and the presence of both components had synergistic effects on material mechanical properties. These protein-based crosslinked materials were prepared using a two-step approach, both of which are versatile, and tolerant to the feedstock diversity and chemical functionality typical in protein biomass streams. Amine groups on protein were first reacted with methacrylic anhydride in water. The proteins were then mixed and randomly copolymerzed with a water-soluble (meth)acrylate comonomer that makes up the flexible soft segment. This grafting-through polymerization strategy was first demonstrated via a solution polymerization method with whey protein and water soluble monomers, and the resulting materials were demonstrated to have mechanical performance comparable to that of some biomass based polyurethanes. To eliminate the need for post-processing solvent evaporation, the method was further expanded to enable melt polymerization with hydrophobic monomers. Difficulties with thermoforming protein-based materials were addressed by using surfactants as plasticizers to lower softening points of proteins. The surfactants also functioned as compatibilizers, allowing protein blends and conjugates to be formulated with non-water soluble polymers, resulting in materials with lowered overall hydrophilicity. Screening studies showed that the protein-surfactant complexation and polymerization approaches are generalizable across many combinations of proteins, ionic surfactants, and vinyl monomers.

As proteins typically have multiple copies of reactive functional groups, efforts at developing protein-based commodity plastics have focused almost entirely on chemically crosslinked networks. Synthesis of a novel thermoplastic protein-copolymer elastomer is described. Diblock copolymers were prepared by site-selectively conjugating a RAFT agent to the protein N-terminus, followed by polymerization of the rubbery polymer segment via a grafting-from approach. The materials exhibited thermoplastic behavior, and were thermally reprocessable.

The last part of this thesis presents alternative feedstocks for manufacturing materials. First, an engineered protein expressed in high yields in *E. coli*, recombinant cyanophycin, was investigated. This zwitterionic protein was found to be brittle in the dry state, and demonstrates both upper and lower solution transition temperature type behavior in solution. The high charge density and thermoresponsiveness of cyanophycin could potentially be harnessed in material design. Lastly, methods to recycle waste rubber was explored to process ground vulcanized rubber particles into new rubber sheets. Sheets containing high fractions of recycled rubber were prepared using a bulk devulcanization approach. Ground rubber particles were melt mixed with nucleophiles that may selectively break sulfur crosslinking bonds, enabling the once-crosslinked rubber to be thermally processable. In addition, methods to increase the bond strength at the interfaces of virgin and once-cured rubber were shown to improve mechanical performance of rubber containing recycled material.