Chemical Engineering Dissertation Defense

Dual Pathways to Advance Polymer Sustainability: Reactive Melt Extrusion Deconstruction and Aqueous Latex 3D Printing

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Abstract

Crosslinked polyurethane networks (XPUs) and high molecular weight (MW) thermoplastics pose two distinct processing challenges: crosslinks prevent melt flow, while chain entanglements raise viscosities beyond the processing window compatible with vat photopolymerization (VPP). This Dissertation develops chemical and processing strategies to overcome both limitations by upcycling polyurethane (PU) waste into value-added materials and enabling high-MW 3D printing through waterborne latexes. First, this work established reactive melt extrusion deconstruction (RMED), a continuous, solvent-free process that rapidly deconstructs and functionalizes XPUs within legacy twin-screw extrusion infrastructure. During RMED, carbamate exchange reactions between XPUs and low-MW, carbamate-containing decrosslinkers (DXs) install DX-derived functional chain ends in the melt, withe DX concentration controlling gel content, MW, and melt viscosity. RMED's modularity tolerates diverse feedstocks, including aliphatic XPUs, highly filled composites, and commercial open-cell PU foams. Altering DX O- and N-functionality elucidated fundamental structure-property relationships in model XPUs, while meticulous DX design leveraging inexpensive, commercially available monomers directs deconstructed PUs toward targeted applications, such as 3D printing resins, stimuli-responsive materials, crosslinked adhesives, and waterborne PU dispersions (PUDs). Upon heating under vacuum, ethanol-blocked carbamate chain ends from MDI-ethyl regenerate isocyanates, empowering PU melt recrosslinking into hot-melt adhesives without extraneous catalysts or crosslinkers. The sulfonate salt-containing DX 2HESS NPC produced ion-functionalized PUs that readily form PUDs, enabling PU separation and recovery from composite fillers without organic solvents.

The second research thrust employed aqueous latexes for VPP, which confine high-MW polymers within discrete particles to uncouple polymer MW from formulation viscosity. Upon UV irradiation, a water-soluble scaffold polymerizes and crosslinks to define the greenbody, while drying and annealing coalesce the latex particles into an interpenetrating polymer network (IPN). In poly(styrene-b-isoprene-b-styrene) IPNs, substituting 2-hydroxyethyl acrylate for N-vinylpyrrolidone in the scaffold significantly altered 3D printing and final IPN thermomechanical performance. Adding a polystyrene (PS) latex to a synthetic isoprene rubber (SIR) latex produced polymer blend IPNs with distinct glassy, rubbery, and crosslinked scaffold phases, yielding 3D printed high impact PS analogues. Altogether, this Dissertation positions synergistic chemical and processing design as a versatile approach to sustainable polymer synthesis, manufacturing, upcycling, and end-of-life management.

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