SYNTHESIS AND CHARACTERIZATION OF BIO-BASED VITRIMERS

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Polymers obtained from renewable resources have been increasingly investigated to reduce dependence on fossil feedstocks that generate a vast range of environmental impacts and attract remarkably attention due to their numerous advantages, such as biocompatibility, renewability, environmental friendliness and chemical functionality that promotes modifications for advanced materials and extraction [1,2]. Vitrimers are associative covalent adaptable networks (CANs) featuring dynamic crosslinks that enable exchange reactions at elevated temperatures, allowing network rearrangement at constant crosslink density and resulting in recyclability, repairability, self-healing, and malleability [3].

In this work, vitrimer networks were generated through photopolymerization of resin formulations incorporating bio-based monomers, with ethyl(2,4,6-trimethylbenzoyl) phenylphosphinate serving as the photoinitiator. Photocuring behavior was monitored by real-time photorheometry to assess curing kinetics and monomer-content effects. Structural verification of the vitrimers was achieved through FT-IR spectroscopy and Soxhlet extraction, whereas their thermal and mechanical performance was characterized using thermogravimetric analysis, dynamic thermomechanical analysis, and tensile testing.

The results indicated that photocuring behavior and the rheological, thermal, and mechanical properties of the vitrimers depended on the initial resin composition. Photocuring kinetics showed that higher monomer ratios in the formulations promoted longer induction periods and gelation times while simultaneously lowering viscosity, with minimal influence on the storage modulus. Vitrimers synthesized using aromatic ring containing monomers exhibited enhanced stiffness, reflecting changes in network structure and increased crosslink density. The improvement in mechanical properties after self-welding with increasing temperature highlights the repairability of vitrimers, as elevated temperatures activate dynamic bond exchange that enables network rearrangement and mechanical recovery. Moreover, the selected vitrimer displayed effective shape-memory performance, characterized by temporary shape stability and full recovery of the original shape upon heating.

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Keywords: bio-based, photopolymerization, vitrimers, repairability, shape-memory

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