Structure-architecture-property Relationships of Lignin-derivable Acrylate Networks Toward High-performance Materials

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Lignin-derivable building blocks present a promising avenue for addressing critical sustainability and performance challenges inherent in conventional aromatic-based (meth)acrylate thermosets. Traditional thermosets predominantly rely on petroleum-derived bisphenols, such as bisphenol A (BPA) and bisphenol F (BPF), which raise significant environmental and health concerns due to their endocrine-disrupting potential. In contrast, lignin, an abundant aromatic biopolymer sourced from plant biomass, offers renewable, non-food-competing, and structurally versatile phenolic precursors with comparable or superior performance. Lignin-derivable (bis)phenolic monomers exhibit reduced estrogenic activity, enhancing the safety profile of resultant materials. Moreover, lignin's intrinsic methoxy substituents promote intermolecular interactions, which can be leveraged to tailor network architectures and mechanical properties. To this end, this work systematically explores lignin-derivable building blocks for developing renewable, high-performance (meth)acrylate networks *via* tailored molecular designs and property engineering.

First, bio-derivable acrylate thermosets were synthesized from lignin-derivable diacrylates (vanillyl alcohol diacrylate [VDA] and bisguaiacol F diacrylate [BGFDA]) and a bio-derivable reactive diluent, *n*-butyl acrylate (BA). Variations in aromatic content and diacrylate composition allowed tuning of thermomechanical properties and network architectures. Increased diacrylate content enhanced storage moduli, while higher aromatic content yielded structurally complex networks exhibiting broadened thermal relaxation behavior, highlighting their suitability as sustainable alternatives to petroleum-based resins. Expanding upon the sustainability, lignin-derivable aromatics were incorporated into reprocessable thiol-acrylate vitrimers employing transesterification as the dynamic covalent exchange mechanism. Lignin-derivable vitrimers

exhibited superior mechanical robustness, including higher Young's modulus, toughness, and elongation-at-break relative to petroleum-derived analogues. This enhanced mechanical performance was attributed to intermolecular interactions facilitated by methoxy substituents in lignin-derived structures. Additionally, lignin-based vitrimers demonstrated comparable bond exchange dynamics and exceptional thermal healing capabilities, underscoring their utility for reprocessable polymeric materials. Finally, lignin-derivable semi-interpenetrating polymer networks (SIPNs) incorporating a flexible, thermoplastic lignin-derivable non-isocyanate polyurethane (BGF-NIPU) were designed to address brittleness in highly crosslinked, aromatic acrylate networks. The resultant SIPN demonstrated significantly enhanced toughness—a 30-fold increase relative to the single network. Morphological and fractographic analyses revealed that this substantial toughness enhancement originated from the effective energy dissipation through methoxy-promoted interphase interactions, illustrating lignin-derivable building blocks' unique potential to optimize mechanical performance through tailored intermolecular interactions.

Overall, lignin-derivable building blocks represent versatile molecular platforms for designing sustainable, high-performance polymer networks, with their structural adaptability, reduced toxicity, and renewability positioning them as critical components for next-generation polymeric materials.