Network Topology and Blend Properties of Polybutadiene Vitrimers

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Rubbers consist of polymer chains covalently bonded by permanent cross-links. Their elasticity, toughness, and solvent resistance make them essential in the aerospace, agricultural, and automotive industries. Their permanent cross-links, however, hinder recycling and create significant challenges for end-of-life disposal. In contrast, vitrimers are polymer networks featuring dynamic covalent cross-links that engage in an associative exchange — new bonds form before old ones break. This mechanism preserves network connectivity while allowing topological changes, rendering vitrimers insoluble yet processable at high temperatures. Although these paradoxical traits suggest that vitrimers may be a promising rubber replacement, the relationship between their molecular structure and macroscopic properties remains an open question. Here, we combine experiments and theory to elucidate the underlying physical chemistry of vitrimers. Our study focuses on a model system composed of polybutadiene (PB) networks cross-linked by dioxaborolane linkages that exchange via a metathesis mechanism, alongside control PB networks with permanent cross-links. First, we evaluate the static network properties. Cross-link density is quantified using a network disassembly approach. Differential scanning calorimetry, shear modulus, and vapor swelling measurements indicate that PB vitrimers contain fewer network topology defects than their permanent counterparts. Second, we perform linear viscoelastic measurements. PB vitrimers exhibit two distinct relaxation regimes. The fast dynamics correspond to segmental motions of the PB backbone. The slow dynamics, however, exhibit a much stronger temperature sensitivity than predicted by sticky Rouse theory. Third, we prepare blends of PB and polydimethylsiloxane vitrimers to investigate the relationship between morphology and viscoelasticity.