Vitrimers: Understanding the Impact of Backbone and Cross-link Interactions

Ralm G. Ricarte
Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310

Vitrimers are covalently cross-linked polymer networks that are insoluble in good solvent, but still flow at elevated temperatures. Their cross-links engage in dynamic associative exchange reactions that preserve network connectivity but allow topology fluctuations. Because of these paradoxical traits – a combination not found in any other type of polymer – vitrimers are essentially a marriage between classical thermosets and thermoplastics, and offer a versatile pathway for converting commodity feedstocks into sustainable high-performance materials. Here, I will detail my efforts to understand the fundamental physical chemistry of vitrimer materials. The talk is split into two portions that focus on vitrimers with (I) homogeneous and (II) heterogeneous morphologies. For Part I, which details a recent collaboration with Prof. Sachin Shanbhag, a generalized inhomogeneous Rouse model (IHR) is used to illuminate structure-viscoelasticity relationships for unentangled vitrimer melts. Using the IHR model to simulate stress relaxation measurements, we find that the short time dynamics characterize monomer friction, while the long time dynamics represent a combination of network strand relaxation and cross-link exchange. The dissimilar temperature dependences of the two processes cause failure of time-temperature superposition. The IHR model also provides a method for estimating *a priori* the effective rheological activation energy of a vitrimer melt. For Part II, which centers on my postdoctoral work at ESPCI Paris, vitrimers featuring polyethylene (PE) as the backbone and dioxaborolane cross-links are experimentally explored. Using a combination of optical and X-ray scattering techniques, we discovered that strong interactions between the backbone and cross-links cause PE vitrimers to self-assemble into complex meso- and nanostructures. Rheological measurements showed that the presence of macroscopic phase separation facilitates the flow and processability of PE vitrimers.