**Linear viscoelasticity of vitrimer melts**

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Vitrimers are covalently cross-linked polymer networks that are insoluble in good solvent but still processable at elevated temperatures. These paradoxical traits are enabled by their cross-links, which engage in dynamic associative exchange reactions. Altering the chemical structure of the vitrimer cross-linker, backbone, or both modifies flow and mechanical properties. Here, we employ a generalized inhomogeneous Rouse model (IHR) to illuminate structure-viscoelasticity relationships for unentangled vitrimer melts with cross-link densities well above the gel point. The model accounts for interactions between relaxation modes of regular backbone monomers and those that are “sticky” (*i.e.*, the associative cross-links). We use the IHR to evaluate the effect of temperature and chemical structure on the zero-shear viscosity and characteristic relaxation time. Polydimethylsiloxane and polybutadiene vitrimers (which have flexible backbones) follow an Arrhenius temperature dependence for the zero shear viscosity, while polystyrene and poly(methyl methacrylate) vitrimers (which have rigid backbones) are only Arrhenius at high temperatures. During stress relaxation, the short time dynamics describe monomer friction, while the long time dynamics portray 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 effective rheological activation energy is estimated *a priori* from the cross-link exchange activation energy and the backbone Williams-Landel-Ferry parameters. Predictions of the IHR model are compared with experimental measurements on polydimethylsiloxane and polybutadiene vitrimers.

**Ralm G. Ricarte Biography**

Ralm G. Ricarte is an Assistant Professor in the Department of Chemical and Biomedical Engineering at the Florida A&M University-Florida State University College of Engineering (FAMU-FSU CoE). In 2011, he earned a BS in Chemical Engineering from The University of Texas at Austin. In 2016, he earned a PhD in Chemical Engineering from the University of Minnesota, where he was advised by Marc A. Hillmyer and Timothy P. Lodge. From 2017 – 2019, he served as a Marie Curie and PRESTIGE Postdoctoral Fellow at ESPCI Paris, where he was advised by Ludwik Leibler.



At the FAMU-FSU CoE, the Ricarte Lab investigates how molecular structure affects the fundamental physical properties of dynamic polymer networks. In particular, the lab has active projects in the areas of vitrimers and polymerization induced self-assembly. The potential applications of their work include energy storage, separations, medicine, consumer products, and advanced performance materials. They use scalable polymer synthesis techniques to create materials with intricate functionality. To study these complex systems, they routinely use cryogenic and analytical electron microscopy, scattering, rheology, and theoretical modeling.

Dr. Ricarte has earned several honors throughout his career, including the NSF CAREER Award and the Oak Ridge Associated Universities Ralph E. Powe Junior Faculty Enhancement Award.