

July 6th – 12th, 2025

Viscoelasticity and extensional rheology of polystyrene based vitrimers

<u>Teresiana Guarino</u>^{1,2*}, Arcangela Russo^{1,2}, Matteo Conti³, Nathan Van Zee³, Renaud Nicolay³, Salvatore Coppola⁴, Dimitris Vlassopoulos^{1,2}

 ¹ FORTH, Institute of Electronic Structure and Laser, Heraklion, Crete 71110, Greece
² University of Crete, Department of Materials Science and Technology, Heraklion 71003, Greece
³ Chimie Moléculaire, Macromoléculaire, Matériaux, ESPCI Paris, CNRS, Université PSL, 10 rue Vauquelin, 75005 Paris, France
⁴Ravenna/Ferrara research center, Versalis S.p.A. (ENI), Ravenna, Italy

*teresianag@iesl.forth.gr

A formidable challenge in soft matter is to develop crosslinked materials that combine the reprocessing capabilities typical of thermoplastics with the shape stability and mechanical strength of conventional thermosets. Most approaches aim to create a crosslinked network using dynamic covalent bonds, which can reversibly form and break in response to changes in thermodynamic conditions. Materials containing these dynamic covalent bonds are referred to as Covalent Adaptable Networks (CANs). A specific subset of CANs, known as vitrimers, was introduced by Leibler and colleagues in 2011. Vitrimers exhibit two key characteristics: they maintain stable network connectivity across a range of temperatures and can relieve mechanical stresses through bond exchange reactions. In this work, we present preliminary results on the extensional rheology of polystyrene based vitrimer systems, where dynamic exchange reactions are facilitated by dioxaborolane metathesis. We show how crosslink density and dynamic bond exchange influence the flow and deformation behavior under both linear and nonlinear deformations, which are particularly relevant for processing operations. In particular, a systematic investigation of the uniaxial extensional response of vitrimer systems is presented, detailing how the presence of dynamic crosslinkers affects strain hardening behavior. These insights contribute to a deeper understanding of the fundamental rheological behavior of polystyrene-based vitrimers and their potential for use in advanced material design.

References:

[1] N. J. Van Zee, R. Nicolay, 2020, Progress in Polymer Science, 104, 101233 [2] M. L. Sentmanat, 2004, Rheol Acta, 43, 657-669