10:00 AM - 10:25 AM

Solvent and Confinement Effects on the Thermomechanical Behavior of Amorphous Polymers

Wenjie Xia, Shawn Mishra, Sinan Keten
Northwestern University, Evanston, Illinois, USA

Abstract

The effect of low molecular weight solvents on polymer microstructure and mechanical behavior is a central problem with broad implications to nanofabrication, biomechanics and multifunctional polymers. Ever present water molecules in the form of humidity, as well as retained solvents after materials processing alter the anticipated behavior of materials significantly by shifting thecharacteristic relaxation times and glass transition temperature. Additionally, surfaces and interfaces in polymer nanostructures and nanocomposites show strong changes in mechanical behavior due to free surface and substrate effects, which compound the complexity of predicting thermomechanical behavior in these emerging applications. The fundamental understanding of these effects call for new bottom-up predictive modeling approaches that can capture molecular structure and dynamics to accelerate advancements in nanofabricated devices and polymer nano fibers. In this study, we present atomistic and coarse-grained molecular simulations that explain how solvent and confinement effects govern the relaxation and glass-transition temperature (T_g) of amorphous polymers, specifically poly(methyl methacrylate) (PMMA). First, we present an approach for quantifying solvent induced T_g suppression using atomistic simulation derived parameters in conjunction with free-volume theory (*Mishra, Keten, APL, 2013*). We build on this approach to establish an analysis of the spatial variation of glass-transition temperature in thin films, illustrating competing effects of attractive substrates and free surfaces using experimentally validated coarse-grained models. Functional usage of heterogeneities to control solvent diffusion and material properties will be discussed. Our results can be directly combined with theoretical models to directly quantify variation in thermomechanical properties without empirical inputs, and corroborate recent experimental findings. Our investigations provide basis for a positive outlook on the potential of applying multi-scale, predictive, simulation-based design approaches to the discovery process of new specialty polymers.