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Distributions of Glass Transition Temperatures and Physical Aging and Diffusion Behaviors in Confined Polymer Films and Nanocomposites

JOHN TORKELSON, Northwestern University

Thin polymer films and nanocomosites exhibit strong effects of nanoscale confinement: apparent Tg's can change by 50+ K; glassy-state relaxation can be strongly suppressed; and diffusion coefficients of small molecules in polymer can be altered by an order of magnitude or more. Here, we summarize key results from fluorescence studies that show how interfaces (polymer-air, polymer-substrate, polymer-nanofiller) perturb properties and the length scales, often > 100 nm, over which interfacial perturbations can propagate into the polymer. We also show via multilayer film studies that ultrathin layers of one species can have their glass transition dynamics "slaved" to that of neighboring domains of other polymers.