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Why do some diluents alter the magnitude of nanoconfinement effects on the glass transition?[1] JAYACHANDRA HARI MANGALARA, NICHOLAS WEINER, MICHAEL MARVIN, DAVID SIMMONS, University of Akron — Polymers subject to nanoconfinement can exhibit large alterations in their glass transition and associated dynamic and mechanical properties. Several studies have indicated that introduction of small-molecule additives can attenuate the magnitude of nanoconfinement affects, offering a potential method of tuning the properties of nanostructured polymers in applications from microelectronics to structural nanocomposites. However, the relationship between additive molecular properties and their effects on nanoconfined glass formation remains poorly understood. A number of studies have implicated changes in the fragility of glass formation in mediating these effects; however, this remains a matter of considerable debate. Here, we report on two sets of simulations of nanoconfined polymer films: one in which we introduce several oligomeric additives with effects ranging from suppression to enhancement of bulk Tg and fragility; one in which we reduce the polymer's bulk fragility via a simple, additive-free, structural modification. Results provide new insight into the impact of additives on nanoconfined glass formation as well as into the role of fragility in determining nanoconfinement effects.

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