MESOSCALE SIMULATION OF STRESS RELAXATION IN THIN POLYMER FILMS AND THE CONNECTION TO NANOCOMPOSITES

Brendan Abberton[1], Wing Kam Liu[2] and Sinan Keten[3]

[1] Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, babberton@u.northwestern.edu
[2] Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, w-liu@northwestern.edu
[3] Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208, s-keten@northwestern.edu

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Polymer nanocomposites have shown great promise for improving the mechanical performance of neat polymers used in structural materials. As the filler size approaches the nano-scale, composite materials tend to exhibit remarkable enhancements of thermomechanical properties, even with the addition of small filler volume fractions. These observations defy standard composite theories and are largely attributed to the high surface area to volume ratio of the particles that lead to strong nanoscale interfacial phenomena that can induce long-range effects on polymer chain dynamics. Consequently, Young's modulus, stress relaxation dynamics, yield stress, ultimate stress and strain, fracture toughness, shock resistance, and glass transition temperature (T_g) can all be drastically altered in these materials. Despite decades of research aimed at elucidating interfacial effects and optimizing composite properties, it is not currently possible to accurately *predict* the changes in these important material properties directly from the filler and matrix characteristics. As such, discovery and design of polymer nanocomposites continue to rely on slow and costly Edisonian approaches.

The key challenge in predicting the performance of a polymer nanocomposite is to quantify the spatially varying changes in interphase constitutive behavior resulting from polymer confinement and controlled by polymer-filler interaction, as a function of filler volume fraction and distribution morphology. Key insight into interphase formation and confinement effects in nanocomposites has come from studies on polymer thin films supported on solid substrates. In these thin films, both the free surface and the solid supporting layer cause complex changes in the behavior of the polymer.

The range and magnitude of these effects have been singled out recently by systematically varying the boundary conditions (free standing film, supported thin film, and polymer layer confined between two surfaces) and surface/polymer chemistry. Most importantly, the Schadler group [1], as well as the Torkelson group [2], have shown a quantitative equivalence between nanocomposites and thin films with regards to *glass-transition temperature* (T_g) via the calculation of an equivalent metric of confinement within the nanocomposite from the distribution of filler surface-to-surface distances. This finding is important because it allows for direct prediction of the T_g of the nanocomposite directly from thin film measurements and microstructural statistics, leveraging current capabilities in accurate computational/experimental characterization of film properties. However, it is currently unknown whether the thin-film analogy can be extended into the constitutive

behavior of polymer nanocomposites, most importantly the stress relaxation behavior of the matrix that governs viscoelastic behavior.

With an ultimate aim to address this issue, we have begun examining the stress-relaxation in doubly supported polymer thin films through coarse grained simulation using the FENE model. The current work elucidates the connection among film thickness, interfacial energy, and stress relaxation dynamics for both entangled and unentangled polymer chains. In order to characterize the dynamic relaxation behavior of the films at constant temperature, we calculate via the Green-Kubo relation the linear shear-relaxation modulus $G(t)$ from equilibrium coarse-grained simulations of the bulk and of films of varying thickness. We then fit the simulated relaxation modulus to the theory for bulk polymer developed by Likhtman and McLeish (LM) [3, 4] (originally based on the based on the tube model [5, 6]), with the additional changes proposed by Hou, Svaneborg, Everaers, and Grest [7].

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