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Effects of Interfaces and Interactions on Stiffness-Confinement Behavior in Polymer Films: Characterization via Fluorescence and Nanoindentation SHADID ASKAR, MIN ZHANG, L BRINSON, JOHN TORKELSON, Northwestern Univ — Although stiffness-confinement effects in polymers have been well studied, disagreement exists regarding even the qualitative nature of such effects. With the exception of one experimental and several simulation studies that characterize stiffness gradients, all others report average stiffness-confinement behavior in polymers. These issues demonstrate the need for comparative studies that characterize stiffness gradients in polymers from interfaces. Here, we use a fluorescence technique that utilizes the sensitivity of pyrene dye fluorescence to local caging and nanoindentation to characterize stiffness gradients in the polymer model nanocomposites. Both techniques are in qualitative agreement that stiffness gradients extend a distance exceeding 100 nm from a substrate, and that stiffness-confinement effects are tunable via surface modification of the substrate. It is observed that PMMA supported on methylated cover glass exhibits less stiffening near the substrate compared to PMMA supported on cover glass with enhanced hydroxyl groups that can hydrogen bond with PMMA. PMMA supported on PDMS shows decreasing stiffness near the interface. These findings help address some of the inconsistencies observed in literature regarding stiffness-confinement effects.

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