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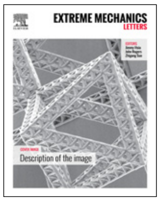

Interfacial stiffening of polymer thin films under nanoconfinement

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ABSTRACT

Changes in the mechanical properties of polymer thin films due to substrate and free surfaces determine the performance of soft nanomaterials. Here we systematically investigate how these interfaces influence the elasticity of supported polymer thin films. Our simulation results demonstrate that the substrate–film interfacial interaction has a strong effect on the elastic response of the films, in which the modulus increases with the strength of interfacial interaction with a nonlinear scaling relationship. The investigation of the local stiffness within the film reveals that there exists an interfacial stiffened region near the substrate and a soft region with reduced stiffness near the free surface. Both regions exhibit similar length scales on the order of nanometers. Our analyses explain the molecular origins of recently observed interfacial stiffening and softening phenomena in polymer thin films, and provide a high-resolution description of the local stiffness gradients in polymer thin films.

1. Introduction

The characteristic dimensions of polymer thin films used in devices and sensors are becoming increasingly miniaturized in applications such as nanoelectronics [1] nanocomposites [2], sensors [3], and bioengineering [4]. The elasticity and fracture behavior of nanoscale polymer thin films diverge from the bulk properties of the material constituents because polymer chain structural and dynamic properties near free surfaces and interfaces are drastically altered due to the interfacial confinement effects. For instance, as the thicknesses of thin films approach tens of nanometers, remarkable changes in glass-transition temperature (T_g) and elastic modulus associated with changes in chain dynamics, orientations, and fragility have been observed [5–9]. Nanostructured polymers have large free surface and substrate interface areas compared to their volume, and the changes near these regions lead to stability and reliability issues in these systems [10]. Therefore, understanding the mechanical responses of polymer thin films, particularly property gradients in these systems, is necessary to predict and advance the performance of polymer nanostructures.

While investigations of T_g and chain dynamics of polymer thin films under confinement effects have been widely conducted over the past two decades, the mechanical behaviors of these systems still remain to be fully explored. Several experimental techniques have been developed to assess mechanical properties of nanoscale polymer thin films, such as atomic force microscopy (AFM)-based

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nanoindentation [11], buckling-based metrology [7,12,13], Brillouin light scattering (BLS) [14,15], beam-bending deformation [16], and bubble AFM imaging technique [17]. In film wrinkling experiments, significant depression in the elastic moduli with respect to bulk has been reported for poly(methyl methacrylate) (PMMA) and polystyrene (PS) thin films with thicknesses less than ∼40 nm, which is attributed to the soft surface layer with reduced modulus and enhanced mobility [7,16]. Using the same technique, Torres et al. [12] have shown that the elastic moduli of sub-100 nm methacrylate films decrease with thickness, but is not correlated with the T_g reduction, which suggests that independent measurements of both T_g and elastic modulus of polymer thin films may be necessary. Similar observations were reproduced from molecular dynamics simulations of polymer nanostructures [18,19]. In addition to surface effects, earlier studies have shown that mechanical properties of polymers can be altered due to interfacial interactions with a substrate or embedded nanoparticles [20–23].

More recent efforts have been engaged in understanding the local elastic properties of polymer thin films near free surfaces and interfaces, which governs the overall mechanical response of these systems. It is therefore critical to determine the length scales of interphase regions where the local modulus changes due to confinement. Using an indentation technique combined with finite element modeling, Watcharotone et al. [24] illustrated that a higher local modulus in a small interphase region near the silicon substrate can enhance the overall modulus of PMMA thin films with thicknesses up to hundreds of nanometers. Previous molecular simulation studies of free-standing films suggest that the length scale of the polymer–air interfacial region is roughly several nanometers based on local dynamical and mechanical measurements [25,26], which is much smaller than the length scale at which the overall film modulus begins to deviate from the bulk. Recently, Cheng et al. [27] proposed a method to directly measure the local modulus based on the AFM technique. In their study, the indentation tests were performed on the lateral face of the PMMA film parallel to the silica substrate instead of the top surface, which allows spatial measurement of the local modulus at different locations. AFM measurements typically report that the length scale beyond which elastic properties converge to bulk values exceeds ∼100 nm. It should be noted that AFM experiments typically involve relatively large tip diameters in the range of ∼10 nm or so, and measurements are dependent on both the substrate stiffness and stress distribution in the film. Thus, reported values are more likely to be average elastic responses over broader regions of the film compared to other techniques and simulations. Another issue pertaining to the experiments on supported thin film modulus measurements is the presence of both a substrate–polymer interface and a free surface in these systems. The respective effects of these two different interfaces on the film modulus are convoluted and it is currently difficult to distinguish them from each other.

In order to facilitate a deeper understanding of the molecular origins of interfacial effects on mechanical properties of polymer thin films, here we employ atomistically informed coarse-grained molecular dynamics (CG-MD) simulations for PMMA films. The CG-MD approach provides a higher resolution description of the nanoscale behavior of confined thin films compared to experiments, and thus has the potential to illustrate local features that are not otherwise observable. Compared to all-atomistic simulations, CG-MD is more computationally efficient, allowing the study of larger length and time scales. In this study, we systematically investigate how the interfacial interactions between substrate and film influence the elastic behavior of the film by carrying out biaxial tension simulations. We present a systematic characterization of the local stiffness and elastic property gradients in polymer thin films.

2. Simulation methods

2.1. Overview of 2-bead coarse-grained model

Here we employ an atomistically informed and experimentally validated CG model for PMMA developed through the thermomechanically consistent coarse-gaining (TCCG) methodology [28,29]. The model involves a two-bead-per-monomer mapping scheme for atactic PMMA, where the backbone bead incorporates the methacrylate group and side-chain bead includes the methyl group. The mass and force center locations of the CG beads are illustrated in Fig. 1(a). Bonded interactions including bond, angle, and dihedral terms are trained to match all-atom bonded probability distributions via the Inverse Boltzmann method (IBM) [30–32]. The non-bonded pairwise interactions are represented by the 12–6 Lennard-Jones (LJ) potentials that are systematically tuned to match the density and glass transition temperature. The model captures the experimental elastic modulus, and predicts self-diffusion coefficients of the liquid monomers to be on the same order of magnitude as all-atom simulations. Further details of the PMMA coarse-grained model can be found in our previous work [28].

2.2. Thin film configuration

CG-MD thin film simulations are carried out using the LAMMPS software package [33]. The thin film systems consist of 52–104 chains with 100 monomers per chain, resulting in film thicknesses ranging from ∼5 to ∼19 nm (along the z axis) based on the maximum and minimum film z coordinates at room temperature. Periodic boundary conditions are applied in the x–y plane and non-periodic boundary conditions are applied in the z direction. The z-dimension of simulation box is ∼20 nm larger than the film thickness in order to create the surfaces. The substrate interacting with the film is simulated by a perfectly smooth implicit wall underneath the film, captured by a 12–6 LJ potential of the form:

$$E_{sub}(z) = 4\varepsilon_{sp}\left[\left(\frac{\sigma_{sub}}{z}\right)^{12} - \left(\frac{\sigma_{sub}}{z}\right)^{6}\right] \quad z < z_{cut} \tag{1}$$

where z is the distance of a CG atom from the wall, σ_{sub} is the distance at which E_{sub} is zero with a value of 4.5 Å, and ε_{sp} is the interfacial interaction strength, which is the depth of the surface potential well. The cutoff distance of the interaction z_{cut} is 1.5 nm. In our simulations, the