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Confinement-Induced Stiffening of Thin Elastomer Films: Linear and Nonlinear Mechanics vs Local Dynamics

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ABSTRACT: Constant-pressure molecular-dynamics simulations have been carried out of a bead–rod model polymer confined between two attractive crystalline substrates. Three different substrate–substrate separations (i.e., film thicknesses) were used and two different polymer–substrate interaction strengths. The density profiles show a monomer layering close to the polymer–substrate interface. A higher density was found in this region compared to the middle bulklike layers of the films. The dependence of the film-averaged density on temperature and thickness was measured for all polymer films. Decreasing the film thickness leads to an increase of this density and of the film-averaged glass-transition temperature. Layer-resolved analysis of the segmental dynamics of the thickest films shows a gradient of the mobility upon approach of the polymer–substrate interface, while the middle-layer dynamics exhibits bulklike behavior. With decreasing film thickness, these gradients become overlapping. All polymer films were deformed uniaxially normal to the substrates beyond their linear viscoelastic regime; their elastic moduli but also their secant moduli at larger strain amplitudes were extracted. In the linear regime, the stiffness was found to increase with decreasing film thickness; this correlates well with the layer-resolved segmental dynamical behavior. A strong drop of the stiffness was observed upon increasing the deformation amplitude; this drop was more pronounced for stiffer films. It is shown that the drop in stiffness can be qualitatively explained by the drop of the relaxation times as well as by the increased heterogeneity of the dynamics in different film layers upon deformation. The thickness dependencies of the structural, dynamical, and mechanical properties become more pronounced with stronger adsorption to the substrates.

1. INTRODUCTION

Elastomer-based nanocomposites usually consist of a mixture of a pure elastomer and hard submicron-size filler particles, such as carbon black (CB) or silica.1−7 At high volume fractions, these form a reinforcing network inside the polymer matrix, and the resulting composite proves to be much stiffer. This macroscopic reinforcement of filled elastomers has been widely used in many technological applications.8−10 Nevertheless, and despite extensive work in the field within the past years, the origin of the reinforcement and its sensitive dependence on filler volume fraction,7 dispersion,11 and interfacial energy12,13 has not yet been completely understood. This is of great importance, in view of the nonlinear mechanical behavior, in which a rapid drop of reinforcement is observed already at small deformation amplitudes (the so-called Payne effect14).

Various studies have suggested that the polymer dynamics is modified when approaching the surface of a filler particle.2−5,13,15−20 Molecular dynamics (MD) simulations of a filler particle surrounded by a coarse-grained polymer melt17 have shown that the polymer Tg can rise or decrease compared to the bulk value, when attractive or excluded-volume interactions, respectively, were assumed for the polymer–filler interaction potential. Additionally, the dynamics was found to gradually change in approach of the filler surface. Similar behavior was observed by NMR measurements in silica-filled rubbers, notably the existence of a gradient in the polymer Tg close to the filler surface.2,3 An increased Tg was also found near the filler surface of CB-filled EPDM.16 This modified segmental dynamical behavior close to fillers has been considered to be an important factor for the overall mechanical reinforcement of a filled elastomer.4,5,19,21−25 Indeed, earlier studies suggested an extension of the solid area beyond the filler particles due to the creation of glassy layers around it, so a higher volume fraction of reinforcing solid.4,5 This idea has been supported by molecular dynamics simulations of nanofilled rubber which showed an increase of reinforcement with increase the filler–particle interaction range.26 The importance of the rubber–filler interaction was also suggested recently by Liu et al.27 Moreover, an optimal filler volume fraction for the large-strain rubber reinforcement was found in this study. In a model...
proposed recently, the authors have assumed that the gradients of the glass-transition temperature, as found close to attractive filler surfaces, will overlap at high filler volume fractions, thus creating low-mobility polymer bridges between neighboring fillers. According to this argument, a percolative path of filler particles connected through glassy bridges is created, and consequently, the overall stiffness of the composite is strongly increased. Moreover, the authors assumed a reversible breaking of the low-mobility polymeric bridges and decrease of the glass-transition temperature under mechanical loading. This model provided a realistic scenario of the linear and nonlinear (Payne effect) behavior of nano-filled elastomers. The modification of the segmental dynamics of polymer glasses under deformation has been confirmed by various studies. In simulations of glassy polyethylene an increased rate of the dihedral-angle transitions has been observed under deformation. Acceleration of the translational motion upon deformation has been reported in simulations of atactic polystyrene and bisphenol A polycarbonate. Recently, a strong decrease of relaxation times of a lightly cross-linked PMMA was shown upon deformation below the yield point. Moreover, the increase of mobility was found to be stronger for higher strain rates.

In the case of high filler volume fractions, the polymers are strongly confined between neighboring filler particles. The effect of confinement on the polymer dynamics has been extensively studied in recent years, and the results have been rather contradictory. Most of the experimental studies focus on the \( T_g \) behavior of films supported by substrates of either strong or weak substrate attraction. The glass-transition temperature of PMMA films has been found to drop upon confinement in the case of weakly adsorbing substrates, while it slightly increased when strongly attractive substrates were used. Additionally, the annealing procedure, as well as the method that \( T_g \) is measured with, has proven to be of high importance and to affect the \( T_g \) behavior under confinement in opposite ways. Finally, as shown by molecular dynamics simulations, \( T_g \) reductions have been found for supported polystyrene films, independent of the substrate attraction strength.

In order to explain the dynamics of polymers under nanoscale confinement, Varnik and co-workers suggested that close to \( T_g \) the dynamics should be affected by the emergence of cooperatively rearranging regions (CRRs) of many particles together, as introduced by Adam and Gibbs. According to their argument, at some temperature, the maximum cluster size \( \xi \) of the CRR’s equals the film thickness and the maximum relaxation time is \( \tau_\xi \sim \xi^\nu \). Based on this assumption, it may be concluded that finite-size scaling effects may lead thinner films to exhibit faster dynamics. The idea of Varnik et al. is strongly supported by the results of our previous works on confined polymer films, in particular the acceleration of the film-averaged dynamics which was found for decreasing film thickness. Indeed, by performing NVT ensemble simulations, the overall density was held constant at all temperatures, and the same high value was used for all film thicknesses in these studies. Therefore, average-density deviations from the bulk because of increased polymer–substrate interface effects with decreasing film thickness were not in order, and finite-size scaling in the segmental dynamical behavior could be shown; the gradual decrease of the mobility close to attractive substrates proved not enough for the creation of a low-mobility polymeric bridge in the case of small substrate–substrate separations.

Generally, the majority of studies on the dynamical behavior of polymers under confinement indicate a strong dependence of the dynamics on various parameters, such as the technique with which the dynamics is measured, the substrate–polymer interactions, the extent of confinement, etc. Therefore, a one-to-one relation between the mechanical properties of thin polymer films and the dynamical behavior should not be immediately assumed. Indeed, recent studies of various supported poly(methacrylate) films showed that the modulus decreases upon confinement, but this drop was not found to be correlated with the \( T_g \) decrease in films of the same thickness. Changes in the Young modulus upon confinement have also been reported in other studies. Recently, Dequidt et al. made DPD simulations of the reinforcement of polymer films confined under strongly attractive substrates. They found thickness-dependent peaks in the plots of reinforcement vs temperature at temperatures above the bulk \( T_g \) which were attributed to the increased \( T_g \) of the films due to the presence of the attractive surfaces. Another factor that affects the stiffness of confined polymer films has been found to be the backbone rigidity of the polymer chains.

The aim of this paper is to explore the relation between the polymer dynamical and mechanical behavior of films capped between attractive crystalline substrates. All simulations were performed in an \( NpT \) ensemble, so a constant pressure normal to the substrates was applied to all polymer films. This model is different from the models presented in our previous studies since now the density of the films is expected to change with confinement. Indeed, the crystalline nature and the attraction of the substrates induces monomer layering, resulting in an increase of density in the ordered area. The range of the wall-induced density oscillations (4–5 nm) is pronounced when simulating coarse-grained polymer melts, although the smaller effect (1–2 nm) has been observed in molecular dynamics simulations of atomistically detailed polymer melts. As shown in refs 61–63, this effect may arise from the absence of torsional potentials in coarse-grained models. The volume fraction of the ordered area is increasing with decreasing film thickness. With a proper truncation distance of the pair interaction potential the film-averaged density is also increasing with decreasing film thickness. Therefore, the finite-size scaling effect as found in refs 46 and 47 is in competition with the effect of increasing density upon stronger confinement.

The films were deformed in the perpendicular direction. In the linear regime of deformation, the rigidity of the films has been studied in terms of the elastic modulus \( E_T \). The evolution of the film rigidity at strain amplitudes beyond the linear regime of deformation has also been studied. To do so, we measured the strain dependencies of the secant moduli for the different film thicknesses and substrate attraction strengths. Moreover, an attempt is made to connect the nonlinear mechanical behavior of different films with the changes upon deformation in their layer-resolved segmental orientational mobility. We stress here that the main idea of the present study is not yet to provide mapping of the present model to any realistic filled rubber, but rather to give insights into the influence of confinement on linear and nonlinear mechanical properties.

The paper is organized as follows. In section 2 a short description of the simulated model is presented. In section 3.1, the inhomogeneities are shown in the density profiles due to
the existence of the attractive substrates. Section 3.2 shows the thickness- and substrate-attraction-strength dependence of the film-averaged glass-transition temperature $T_G$. For the case studies, the segmental dynamics is analyzed in different film layers in section 3.3. The possible mechanical reinforcement of the films is examined in section 3.4, where the thickness, temperature, and strain rate dependencies are shown in sections 3.4.1, 3.4.2, and 3.4.3, respectively. All results presented in section 3.4 were obtained after averaging over 10 independent samples. Studies of the mechanical and dynamical properties beyond the nonlinear viscoelastic regime are presented in section 3.5; the deformation-induced softening is shown in section 3.5.1, and the layer-resolved segmental mobility upon deformation is shown in section 3.5.2. Summary and conclusions follow in section 4. The paper ends with an Appendix that explains the method used to obtain the stress response at different strain amplitudes.

2. MODEL AND SIMULATION DETAILS

In this paper we simulated polymer films capped between two attractive crystalline substrates. The coarse-grained polymer is a random copolymer where each chain has 50 beads consisting of 80% of type A particles and 20% of type B particles, all in random positions along the chain. The samples were prepared following the procedure described in our previous work.

The interactions for all nonbonded monomer pairs were described by the Lennard-Jones potential

$$V_{ij}(r) = \begin{cases} 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] & \text{if } r \leq r_c \\ 0 & \text{if } r > r_c \end{cases}$$

with a cutoff distance $r_c = 3.5\sigma$. As shown in our previous work in $NpT$-ensemble simulations of systems with interfaces this large cutoff distance is essential to achieve in the middle of thick films a density corresponding with that of bulk polymer under the same $NpT$ conditions.

All quantities are expressed in reduced Lennard-Jones units, where $\sigma$, $\varepsilon$, $m$, and $\tau = \sigma(m/\varepsilon)^{1/2}$ are the units of length, energy, mass, and time, respectively. The temperature is expressed in units of $\varepsilon/k_B$, the density in units of $m/\sigma^3$, and the pressure in units of $\varepsilon/\sigma^2$. For the type A monomers we chose $m = m_A$, $\sigma = \sigma_A$ and $\varepsilon = \varepsilon_{AA}$ and for the type B monomers $\varepsilon_{BB} = \varepsilon_{AB}$, $\sigma_B = 1.2\sigma_A$, and $m_B = (1.2)^3 m_A$. The size of substrate particles was chosen to be $\sigma_A = 0.8\sigma$, so smaller than the polymer particles in order to reduce the polymer volume fraction which penetrates into the substrates. The interaction energy between the substrate particles was $\varepsilon_{ss} \gg 1$. The high value of $\varepsilon_{ss}$ is essential to ensure the crystallinity of the substrates at the highest simulated temperatures. The bond length was chosen to be $\sigma$. The $\sigma_{AB}$, $\sigma_{sp}$, and $\varepsilon_{sp}$ were calculated according to the Lorentz–Berthelot rules $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ and $\varepsilon_{ij} = \left( \varepsilon_i \varepsilon_j \right)^{1/2}$.

The polymer–substrate interaction strengths were chosen to be either $\varepsilon_{sp} = 1$ or $\varepsilon_{sp} = 10$. All films were subject to the application of a constant pressure $P_{ss} = 1$ normal to the substrates. The equilibration and production procedure took place at the high temperature $T = 5$. Cooling down until $T = 0.15$ followed, with a constant cooling velocity of $0.0003[\varepsilon/(k_B)\tau]$.

The temperature coupling during the equilibration and cooling procedure took place with the help of the velocity-rescale thermostat, and the time constant was chosen to be $\tau_T = 0.3\tau$. The same time constant was used for the production runs, while the thermostat was switched to the Nosé–Hoover.

The pressure coupling was achieved with the help of the Berendsen barostat, where the time constant for the barostat was chosen to be $\tau_P = 1.5\tau$. The P-LINCS algorithm, which is a parallel version of the LINCS algorithm, has been used for constraining the polymer bonds. Periodic boundary conditions were applied in all three directions. The leapfrog variant of the velocity Verlet algorithm has been used to integrate Newton’s equations of motion, with an integration time step $\Delta t = 0.0005-0.005\tau$ (depending on the system and temperature). In all simulations we have used the open-source MD simulation package GROMACS.

The chosen film thicknesses are $D \approx 30\sigma$, $D \approx 10\sigma$, and $D \approx 4\sigma$ (the exact values correspond to film-averaged densities $\rho = 1$). The thickness $D$ was calculated as the distance between the top and bottom substrate. To estimate this distance, we measured the distance between the center of mass of the nearest particles between the two substrates and subtract the quantity $\sigma_{sp}$ (note that the $\sigma_{sp}$ and not the $\sigma_i$ matters for this calculation). The bulk radius of gyration for this polymer model is $R_g \approx 3.8\sigma$; therefore, the film thickness is varied from $D \approx R_g$ (strong confinement) to $D \approx 8R_g$ (weak confinement).
Figure 2. (a) Density profiles at temperature $T = 0.75$ for films of large thickness $D \approx 30$ (black lines) and small thickness $D \approx 10$ (red lines). The substrate–polymer interaction strength is $\varepsilon_{sp} = 1$. The middle of the films exhibits bulk-like density, while close to the substrates ($0 < z < 5$), in the so-called substrate layers (defined up to the vertical dashed-dotted-dotted line), the density is increasing roughly by 5%. (b) Similar to (a), but for the case of strong adsorption to the substrates. In the latter case the density in the substrate layers is increasing by 10%.

Figure 3. (a) $\rho$–$T$ measurements for the bulk as well as for films of different thicknesses confined between energetically neutral substrates (i.e., $\varepsilon_{sp} = 1$). The dashed lines are examples of the extracted film-averaged glass-transition temperatures. (b) Thickness dependence of the glass-transition temperature for both substrate–polymer interaction strengths $\varepsilon_{sp} = 1$ and $\varepsilon_{sp} = 10$. The results have been normalized with the bulk $T_g$.

3. RESULTS AND DISCUSSION

3.1. Density Profiles. The density profiles of the polymer films were measured for different thicknesses and substrate–polymer interaction strengths $\varepsilon_{sp}$. Figure 2 shows a comparison of the density profiles at temperature $T = 0.75$ for films of thicknesses $D \approx 30$ and $D \approx 10$ (the exact values correspond to film-averaged densities $\rho = 1$). The case of $\varepsilon_{sp} = 1$ is presented in Figure 2a and the case of $\varepsilon_{sp} = 10$ in Figure 2b.

Similar behavior was found for both film thicknesses and strengths of adsorption to the substrates. Strong monomer ordering is observed close to the substrates ($0 < z < 5$, where $z$ denotes the distance from the nearest substrate), and sharp density variations are visible, especially in the proximity of the polymer–substrate interface ($0 < z < 2$). The monomer ordering can be seen in Figure 1 as well. For the high film thickness $D \approx 30$ the ordered area (the so-called substrate layer) decays and a smooth density regime follows, where the monomer beads are completely disordered (the so-called middle layer). Similar behavior has been found in earlier studies of polymers close to crystalline surfaces. 59,60 The density of the middle layer was measured (see Figure 2) and found equal to the bulk density; $\rho_{middle} \approx \rho_{bulk} \approx 1.02$, indicating the bulk-like behavior of the middle part of the thickest films. For $\varepsilon_{sp} = 1$ an increase of density roughly by 5% was found in the ordered layers close to the substrates ($0 < z < 5$); in the case of $\varepsilon_{sp} = 10$ the density increased by 10%, but again bulk-like density was observed in the middle of the film.

For thin films, (i.e., $D \approx 10$) the middle layer vanishes, while the density profile close to the substrates is not affected. As a result, the overall density increased with decreasing film thickness under the same NpT conditions. The possible effect of the increased density with decreasing thickness on the segmental dynamics will be evaluated in the following sections.

3.2. Glass-Transition Temperature. As shown in section 3.1, the density close to the attractive substrates is increasing compared to the bulk polymer (Figure 2). In order to estimate the effect of this density change on the glass-transition temperature, the dependencies of density on temperature...
have been calculated for all film thicknesses and substrate attraction strengths and compared to those of the bulk.

Figure 3a depicts the film-averaged densities for film thicknesses $D = 4-30$ for the case of $e_{sp} = 1$ and for a wide range of temperatures, $T = 0.15-0.85$. The bulk density is also presented (green inverse triangles). In each case, the $T_g$ was determined by fitting with straight lines in the low- and high-temperature regimes and then finding the intersection point. By analyzing Figure 3a, we observed that the effect of increased density near the substrates found in the density profiles of Figure 2, applied at all simulated temperatures. In ultrathin films (i.e., $D \approx 4$), the high-density ordered layers (see Figure 2) overlap resulting in a further increase of density, compared to the case of $D \approx 10$.

Similar curves were produced for all simulated film thicknesses and for both $e_{sp} = 1$ and $e_{sp} = 10$. The bulk $T_g$ was measured as $T_g = 0.47$, a value which is in good agreement with the values found in simulated polymer melts.\textsuperscript{69,70} Decreasing film thickness leads to an increase of the film-averaged $T_g$ for both substrate--polymer attraction strengths. Similar behavior has been found for confined films between attractive substrates in earlier studies.\textsuperscript{71} The raise of $T_g$ is more pronounced for high $e_{sp}$ and especially in the case of ultrathin polymer films ($D \approx 4$), where $T_g$ increases by 140% compared to the bulk value.

### 3.3. Layer-Resolved Segmental Dynamics

We analyzed the local dynamical behavior of the confined polymer films by calculating both the film-averaged and a layer-by-layer spatially segmental orientational relaxation. For that purpose the Legendre second-order autocorrelation function (ACF)

$$P_2[\vec{b}(0) \cdot \vec{b}(t)] = \frac{1}{2} \left( \frac{3}{2} (\vec{b}(0) \cdot \vec{b}(t))^2 - \frac{1}{2} \right)$$

was used, where $\vec{b}$ is the bond vector between two neighboring beads as measured at time 0 and time $t$. The brackets denote a time averaging as well as an averaging over all bonds. In case of layer-resolved analysis of the dynamics, $P_2$ was calculated in different layers of width $l \approx 1.3\sigma$, by averaging only the bonds which belong to each layer. Each bond was assigned to a layer according to the position of the center of the bond at the beginning of the production run, so at time $t = 0$. The chosen layer width is large enough in order for the relaxation of the majority of the bonds to take place inside the layer.\textsuperscript{46}

Figure 4a shows the evolution of the film-averaged $P_2$ ACF for the bulk as well as for film thicknesses $D = 30-4$ in the case of substrate-attraction strength $e_{sp} = 1$. The results are at temperature $T = 0.6$, which is well above the bulk glass-transition temperature $T_g = 0.47$. By analyzing Figure 4a, it is seen that $P_2$ decays more slowly with decreasing film thickness, indicating a slowing down of the film-averaged segmental dynamics. Such behavior is in line with the $\rho-T$ behavior of these films and the corresponding film-averaged glass-transition temperature (Figure 3).

Similar curves were produced for all simulated thicknesses and substrate-attraction strengths as well as for different layers of the polymer films. In order to extract characteristic relaxation
times, the final parts of the $P_z$ ACF’s were fitted with the Kohlrausch–Williams–Watts (KWW) stretched-exponential function:

$$P_z(t) = \alpha \exp \left( -\frac{t}{\tau_p} \right)$$

(3)

In eq 3, the prefactor $\alpha$ describes the initial, very fast relaxation due to the ballistic motion of beads and is smaller than unity, $\tau_p$ is the characteristic relaxation time, and $\beta$ shows the nonexponential nature of the relaxation process. When $\beta \rightarrow 0$, strong inhomogeneities in the dynamics exist, while $\beta \rightarrow 1$ shows the homogeneous distribution of the segmental relaxation. Note that the fitting with stretched exponentials is performed to give a qualitative estimate of the corresponding relaxation times. As shown in refs 61–63, the more advanced fitting could be necessary, especially for the polymer chains in the substrate layers.

Figure 4b shows the evolution of the relaxation times with the distance from the substrates for $0 < z \leq D/2$ (where $z$ denotes the distance from the nearest substrate). Focusing on the thickest film ($D \approx 30$), we find a gradient in the mobility at short distances from the substrates ($0 < z < 5$), followed by homogeneous, bulk-like, dynamics. For decreased film thickness (i.e., until $D \approx 10$), the segmental dynamical behavior was still rather similar to that of high film thickness; a small increase of the relaxation times is observed close to the substrates, while the middle bulk-like layer vanishes. In ultrathin films (i.e., $D \approx 4$), the gradients of the mobility overlap, and the resulting relaxation times increased further (Figure 4b). The pronounced slowing down in the middle layer ($1.3 < z < 2.6$) of the ultrathin film of thickness $D \approx 4$ results from the mutual attractive forces of both substrates on this layer.

Increasing substrate attraction from $\varepsilon_{sp} = 1$ to $\varepsilon_{sp} = 10$ resulted in a qualitatively similar layer-resolved dynamical behavior (Figure 4c). However, for all thicknesses, the strong substrate attraction resulted in the creation of a glass-like layer in the vicinity of the polymer–substrate interface ($0 < z < 1.3$), where the relaxation times are tremendously increased in comparison with the bulk values. Note that the higher $T_s$ found in ultrathin films indicates that the values of the relaxation times presented in Figure 4b can be affected by aging effects. Another interesting effect can be observed in the region $2.6 < z < 5.2$ when comparing the relaxation times for the cases of $D \approx 30$ and $D \approx 10$. In the thin films the relaxation times are increased by roughly 1 order of magnitude in this region. This cannot be explained by the increased density in thinner films; the density profiles in Figure 2b show negligible density changes in the substrate layers with decreasing film thickness. A possible explanation of the much slower relaxation can be given by looking at the ratio of the film thickness and the radius of gyration, $D/R_g \approx 3$. The motion of a chain with the center of mass in the middle of this thin film will be mutually affected by chains near either substrate surface. Part of the latter chains is strongly attached to the substrates, due to the high $\varepsilon_{sp}$. In the case of temporary entanglements between the middle-layer chains and the substrate-layer chains, the relaxation of the middle-layer chain should slow down. This effect is also seen in the middle layer of ultrathin films (i.e., $D \approx 4$). In the latter case, also the density is higher, due to the overlapping of the ordered substrate layers (see Figure 2). Consequently, the relaxation times are also additionally increased.

The results of Figure 4 suggest that under moderate pressures the effect of increased density with decreasing film thickness (Figures 2 and 3) correlates well with the segmental dynamical behavior.

The effect of overlapping low-mobility regions with decreasing the film thickness, as was illustrated in Figure 4, is in qualitative agreement with the assumption presented in the literature for the mechanical reinforcement in filled elastomers:21–24 the mobility gradients close to the attractive surfaces become overlapping for small filler–filler distances, and therefore an overall stiffness enhancement can be assumed with decreasing film thickness. In the next section, we argue about the possible modification of the mechanical properties of the polymer films due to this overlap.

### 3.4. Mechanical Properties in the Linear Viscoelastic Regime

#### 3.4.1. Thickness Dependence of Mechanical Reinforcement

The stiffness in the simulated capped polymer films has been studied by forcing the films to a uniaxial elongation normal to the substrates and measuring the stress response to obtain elastic modulus $E_\text{f}$. The strain rate

$$\dot{\gamma} = \frac{v}{D_{(t=0)}}$$

(4)

was chosen equal to $\dot{\gamma} = 10^{-3} \tau^{-1}$. Note that in the above method the lateral dimensions of the films were kept constant,
thus resulting in an increase of volume under deformation. Therefore, the measured elastic modulus should not be connected with the Young modulus $E$. For the latter, a constant pressure normal to the direction of tension should be also applied. Because of the crystalline nature of the substrates, this pressure may result in breaking of crystallinity. The measured modulus $E_Y$ in our simulations is a combination of the Young’s and bulk moduli such as

$$\sigma_{yy} = K \frac{1 + \frac{E}{K}}{1 - \frac{E}{K}} \gamma = E_Y \gamma$$

(5)

For a better comparison, the bulk samples were similarly deformed by keeping the lateral dimensions constant.

Different film thicknesses have been studied; therefore, different deformation velocities were used, varying between $0.0035 \sigma / \tau$ and $2.95 \sigma / \tau$, in order to achieve the same film-averaged strain rate for each film thickness. As shown in Figure 3a, the film thickness is temperature dependent (but also substrate-attraction-strength dependent). Therefore, the abovementioned constant strain rates were achieved by adjusting the deformation velocities at all temperatures, film thicknesses, and substrate-attraction strengths.

In Figure 5a, the stress–strain behavior is depicted for films of different thicknesses in the case of $\epsilon_{sp} = 10$ and temperature $T = 0.6$, which have been deformed uniformly along the z-axis with the same initial strain rate $\dot{\gamma} = 10^{-3} \text{ s}^{-1}$. The chosen temperature mimics room temperature conditions, since it is above $T_g = 0.47$ (or, equivalently, above $T_g \approx 250$ K for typical rubbers). At this temperature our polymer model may mimic well the intermediate (between glassy and rubbery states) behavior, when the relaxation between cross-links is especially sensitive to the temperature. The normal stresses $\sigma_{yy}$ at different strains have been calculated for each film only for the polymer part of the simulation box (see Appendix). This is a computationally expensive procedure; thus, the used strain rates had to be relatively fast compared to simulated rates in the literature. In order to extract the elastic modulus $E_Y$, each plot was fitted with a straight line in the linear-elastic regime. This regime was taken for strain amplitudes $\gamma < 1\%$ (Figure 5a). The results show an increasing slope of the stress–strain plots with decreasing film thickness, thus indicating a thickness-dependent mechanical behavior.

The linear response to the uniaxial deformation was also studied for the case of energetically neutral strengths of adsorption to the substrates (i.e., $\epsilon_{sp} = 1$), and the corresponding elastic moduli were extracted. Additionally, the film-averaged reinforcement $R$ has been calculated, which we define as

$$R = \frac{E_Y(\text{film})}{E_Y(\text{bulk})}$$

(6)

with $E_Y(\text{film})$ and $E_Y(\text{bulk})$ the elastic moduli of bulk polymer and films, respectively. The results are presented in Figure 5b, where the mechanical reinforcement is shown for different film thicknesses $D$ and substrate-attraction strengths $\epsilon_{sp}$. It is seen that decreasing film thickness leads to an increase of the mechanical reinforcement $R$. The effect is rather small for the case of $\epsilon_{sp} = 1$, but pronounced for $\epsilon_{sp} = 10$. This picture is in qualitative agreement with the results presented in Figure 4b for the segmental orientational relaxation. Indeed, the attractive nature of the substrates resulted in a slowing down of the segmental mobility close to the polymer–substrate interface. For thick films ($D \approx 30$), this slowing down enhances local stiffness, but due to bulk-like middle layer (see Figure 4b), the overall stiffness is weakly affected compared to the bulk. In thinner films (i.e., $D < 10$) the low-mobility regions were found to overlap, thus resulting in the raise of reinforcement, as shown in Figure 5b. Nevertheless, the deviation of the reinforcement $R$ from the bulk value even for thin films ($D < 10$) is rather small in the case of $\epsilon_{sp} = 1$. This can be attributed to the only modest decrease of mobility (compared to the bulk) in the middle layers, as found in Figure 4. This weakest link in the polymer bridge which is connecting the two substrates appears to strongly determine the film-averaged mechanical reinforcement.

In the case of strong adsorption to the substrates (i.e., $\epsilon_{sp} = 10$), a clear shift to higher values of reinforcement was found with decreasing film thickness. Following the same argument as above for $\epsilon_{sp} = 1$, the thickness-dependent behavior of the reinforcement can be qualitatively explained from the layer-resolved segmental dynamics shown in Figure 4c. For thickness $D \approx 30$, the contribution of the low-mobility layers to the overall reinforcement is rather small, due to the wide bulk-like middle layer. Because of overlapping low-mobility regions in thinner films (i.e., $D \approx 10$) as well as to the observed slowing down in their middle layer (see Figure 4c), an increase of the reinforcement is observed. In the case of ultrathin films, the glass-like bridge created between the two substrates results in a strong enhancement of the reinforcement. This picture is in qualitative agreement with the proposed glassy bridge reinforced model (GBRM) that was recently introduced in order to explain the mechanical reinforcement in filled elastomers.

3.4.2. Temperature Dependence of the Mechanical Reinforcement. The elastic modulus of polymers strongly depends on temperature, and in between the rubbery plateau and glassy plateau it is rapidly increasing. In Figure 3 the stress–strain dependence of the glass-transition temperature $T_g$ was shown. Consequently, the mechanical reinforcement of the polymer films as found in Figure 5 should be temperature dependent.

The effect of changing temperature on the mechanical reinforcement in films of different thickness was studied for the case of strongly adsorbing substrates (i.e., $\epsilon_{sp} = 10$) with a constant strain rate $\dot{\gamma} = 10^{-3} \text{ s}^{-1}$ at all temperatures. The results are shown in Figure 6. In the case of thick films ($D \approx 30$), the reinforcement is fairly constant at all temperatures. This can be attributed to the large bulk-like middle layer of the films, which determines the mechanical behavior perpendicular to the films. For thinner films (i.e., $D \approx 10$), the middle part exhibits lower mobility compared to the bulk (Figure 4c). Consequently, higher reinforcement was observed at temperatures above the bulk $T_g$. In the case of ultrathin films (i.e., $D \approx 4$), a clear decrease of the reinforcement is observed with decreasing temperature due to the glass-like behavior of the films well above the bulk $T_g$ (Figure 3b). Indeed, the elastic modulus of the ultrathin films lies even at high temperatures on the glassy plateau and weakly depends on temperature. Therefore, the resulting reinforcement strongly decreases due to the increasing modulus of the bulk polymer with decreasing temperature.

3.4.3. Effect of Strain Rate on the Mechanical Reinforcement. The different temperature-dependent mechanical reinforcements in the films, as shown in Figure 6, indicate a consequent strain rate dependency as well, according to the
time—temperature superposition principle. Therefore, the effect of changing strain rate on the elastic properties of the films and the bulk is examined. Figure 7a shows the evolution of the elastic moduli of the bulk with strain rate, when this was varied by 4 orders of magnitude ($\dot{\gamma} = 10^{-6} - 10^{-2}\text{r}^{-1}$). Two different temperatures have been studied: below (red dots) and above (black squares) the bulk $T_g$. At a temperature below $T_g$ that is $T = 0.35$, the effect on elastic modulus $E_{Y(\text{bulk})}$ of decreasing strain rate is minor within the simulated range of strain rates and $E_{Y(\text{bulk})}$ was found to fluctuate around an average value of $E_{Y(\text{bulk})} = 75$. On the other hand, at temperature $T = 0.6$, which is well above $T_g$, slowing down the strain rate from $\dot{\gamma} = 10^{-2}$ to $10^{-6}$ resulted in a decrease of the modulus by 30%. Since the simulated polymer chains are not cross-linked or physically entangled, the elastic modulus at equilibrium should be equal to zero. The results of Figure 7a prove that the measured modulus should only be understood in connection with a given strain rate $\dot{\gamma}$. The films will exhibit a nonzero modulus when the characteristic deformation time (which scales inversely with $\dot{\gamma}$) is smaller than the maximum Rouse time ($\tau_R \sim N g^2 \approx 2500\tau$).

Figure 7b shows the strain-rate dependence of the mechanical reinforcement for films of different thicknesses confined under strongly attractive substrates (i.e., $\epsilon_{sp} = 10$). The temperature is $T = 0.6$, so above bulk $T_g$ and equal to that of the results presented in Figures 4 and 5. The strain rate was varied by 2 orders of magnitude, $\dot{\gamma} = 10^{-2} - 10^{-4}$. Decreasing the strain rate resulted in an increase of the reinforcement at all film thicknesses. The effect is rather small for thick and thin films (i.e., $D \approx 30 - 10$), but it is pronounced in the case of ultrathin films (i.e., $D \approx 4$). Indeed, at temperature $T = 0.6$, the ultrathin films are deep in the glassy state (see Figures 3b and 4c), and their elastic properties are negligibly affected by decreasing $\dot{\gamma}$, although the bulk elastic modulus decreases (see Figure 7a). Similar behavior was found in Figure 6, when increasing temperature in the range of bulk $T_g$ and above.

3.5. Mechanics and Local Dynamics in the Nonlinear Regime. 3.5.1. Deformation-Induced Softening. The stress—strain behavior has been analyzed beyond the linear regime of deformation and up to 12% of deformation; an example can be seen in Figure 5a. It is seen that near this strain value the monomers start to flow. Beyond 1% strain, stress increase with strain deviates from the linear behavior; this deviation is getting stronger at higher deformation amplitudes, indicating a softening of the films.

In what follows, we evaluate the rigidity of the films by measuring the slope of the line which connects each point of the stress—strain plot with the initial point. To define the initial point, we fitted with a straight line to the data between $\gamma \approx 0$ and 1% and then found the intersection point with the $y$-axis. The slope defined in such way corresponds to the secant modulus $E_s$.

The secant modulus was calculated at different strain amplitudes for the bulk polymer and for all film thicknesses, both for weakly ($\epsilon_{sp} = 1$) and strongly ($\epsilon_{sp} = 10$) attracting substrates and at temperature $T = 0.6$. Figure 8a shows the thickness and strain-amplitude dependencies of the secant modulus for $E_s$. At small deformation amplitudes ($\dot{\gamma} < 1\%$), $E_s$ fluctuates around an average value which equals to the elastic modulus $E_Y$. When deforming beyond the linear regime, a drop of the secant moduli $E_s$ is observed. For the bulk this drop is approximately 50%. Similar behavior is observed for thick films (i.e., $D \approx 30$), but a stronger drop of $E_s$ is seen with decreasing film thickness; at strains $\gamma > 10\%$, $E_s(\text{film}) \approx E_s(\text{bulk})$ for all film thicknesses, thus indicating a stronger drop of reinforcement $R_s$ in thinner films.

Increase of substrate attraction (i.e., to $\epsilon_{sp} = 10$) leads to a similar strain dependence of the secant modulus of the films. An increase of stiffness is seen in the linear regime of deformation; as shown earlier, this is associated with the reduced segmental mobility due to the strong substrate attraction. The effect is very pronounced in ultrathin films (i.e., $D \approx 4$). For all film

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**Figure 6.** Temperature dependence of the mechanical reinforcement for films of different thickness, capped under strongly adsorbing substrates (i.e., $\epsilon_{sp} = 10$). At all temperatures, the same initial strain rate $\dot{\gamma} = 10^{-3}\text{r}^{-1}$ was used for the uniaxial elongation. The results are averaged over ten independent samples.

**Figure 7.** (a) Elastic modulus of the bulk at temperatures above and below $T_g$ and for different strain rates, varying from $\dot{\gamma} = 10^{-2}\text{r}^{-1}$ to $10^{-3}\text{r}^{-1}$. (b) Effect of strain rate on the mechanical reinforcement of the films for the case of strong substrate attraction $\epsilon_{sp} = 10$. 4697 dx.doi.org/10.1021/ma3003744|Macromolecules 2014, 47, 4690–4703
thicknesses, the secant modulus rapidly drops after the linear regime. For thick films (i.e., \( D \approx 30 \)), the drop of modulus is about 55%, but for ultrathin films, the corresponding drop of \( E_s \) increases to approximately 80%. Note that, as discussed in the beginning of section 3.4, the simulated method for the deformation of the films results in an increase of the films volume; the drop of modulus after some strain could be a result of possible cavitation. The condition of the fixed lateral dimensions in our simulations is also different from the experimental situation where lateral relaxation of a polymer matrix confined between fillers is allowed. The results of Figure 8 indicate that the strong drop of modulus appears even at very low strains (i.e., \( \gamma < 5\% \)) where similar studies have shown that cavities are absent. The origin of the induced large-strain softening with decreasing film thickness is evaluated in the following section by calculating the layer-resolved segmental orientational dynamics at different deformation levels. To that end, we focus only on film thicknesses \( D \approx 10 \) and \( D \approx 4 \) and compare the results to the bulk polymer. As shown in Figure 8, the thickest simulated films (i.e., \( D \approx 30 \)) exhibit bulk-like mechanical behavior and therefore were not analyzed.

3.5.2. Deformation-Induced Increase of Segmental Mobility. In order to understand the nonlinear mechanical properties of the simulated polymer films, we analyzed the segmental orientational mobility at different strain amplitudes in the range of \( \gamma = 0 \text{--} 10\% \).

For each film, the particle positions were saved at strain amplitudes \( \gamma = 1, 2, 3, 4, 5, \) and 10%. A production run followed in an NVT ensemble at this fixed deformation and the orientational ACF’s were calculated in different film layers. For simplicity, the films were split in the same number of layers at each strain amplitude; this results in a slightly increasing layer width \( l \) with increasing deformation. Figure 9 shows an example of the strain-dependent decay of the ACF’s in two different layers of a film of thickness \( D \approx 10 \), confined under strongly attractive substrate (i.e., \( \epsilon_{sp} \approx 10 \)). It is seen that deformation of the films results in faster decay of the \( P_0 \) both in the middle and in the surface layers (e.g., \( 0 < z < 1.3 \), where \( z \) denotes the distance from the nearest substrate); this behavior is in agreement with the drop of rigidity shown in Figure 8b. For all strain amplitudes \( P_0 \) decays faster in the middle of the film compared to the surface layers. This inhomogeneity in the dynamics was used in section 3.4.1 in order to explain the observed mechanical reinforcement \( R \).

The layer-resolved \( P_2 \) ACF’s were analyzed further for different film layers at different strain amplitudes, and the relaxation times as well as the applied normal stresses \( \sigma_{zz} \) at each strain amplitude were extracted. The results are presented in Figure 10; the relaxation times \( \tau_\mathrm{P} \) for each layer at different stresses are normalized with those in the undeformed state. In polymer glasses, the accelerated mobility under deformation as a function of stress can be described with the Eyring model which predicts that the response of the relaxation time \( \tau_R \) to an applied stress is

\[
\tau_R \propto \sigma / \sinh \left( \frac{\sigma v}{2k_B T} \right)
\]

where \( \sigma \) is the measured stress, \( v \) is the activation volume, and \( T \) is the temperature. Following earlier studies we use the rotational relaxation time \( \tau_{\phi} \) as the \( \tau_R \) in eq 7. According to Eyring’s approach, the applied stress produces linear shifts of the energy barriers surrounding a monomer, thus enhancing monomer diffusion in the direction of stress. According to eq 7, the relaxation times should exhibit an inverse parabolic decrease at low stresses, while exponential decrease will follow at higher stresses, since the external loading significantly lowers the energy barriers for molecular motion in the forward direction and the caged monomers effectively start to flow. The Eyring
The average yield time is \( \tau_{\text{yield}} = 0.1 \). Therefore, to ensure glass-like behavior in this deformation time window, the substrate attraction strength is \( \varepsilon_{\text{sp}} = 1 \). A similar stronger linear decrease (in the semilog plot) of the relaxation times was found when increasing substrate attraction (i.e., \( \varepsilon_{\text{sp}} = 10 \)) for distances \( z > 1.3 \sigma \) (where \( z \) denotes the distance from the nearest substrate) but not in the substrate layers (0 < \( z < 1.3 \)); these were deeply in the glassy state and the small acceleration of its segmental mobility can be well described by eq 7 (Figure 10b).

Figure 10c shows the evolution with stress of the relaxation times for ultrathin films (i.e., \( D = 4 \)) for the case of \( \varepsilon_{\text{sp}} = 1 \). For deformations beyond the linear regime, a similar acceleration of the dynamics is observed in both the surface and the middle layer. In both layers, the relaxation times, higher by 2 orders of magnitude at \( \gamma = 0\% \) compared to the bulk value (Figure 4b), are strongly decreasing with increasing stress. For small values of stress \( \sigma_{\text{sp}} < 1.5 \), the drop of the times can be described by the Eyring picture; a deviation from the Eyring prediction is observed for larger stresses, thus showing the transition from glassy to liquid-like behavior. Therefore, we can assume that the drop of \( E_s \) as shown in Figure 8a, is a result of collective softening of the whole film in case of ultrathin films (i.e., \( D \approx 4 \)) confined under weakly attractive substrates (i.e., \( \varepsilon_{\text{sp}} = 1 \)).

A similar deviation from Eyring’s model was not found for higher attraction strengths (i.e., \( \varepsilon_{\text{sp}} = 10 \)) in ultrathin films. The drop of the relaxation times both for the substrate (i.e., 0 < \( z < 1.3 \)) and the middle layer (1.3 < \( z < 2.6 \)) follow the Eyring prediction, although there is scatter in the data. The acceleration of the dynamics is stronger in the middle layers. In the latter case, the dynamics were also found to be strongly

![Figure 10](image_url)
heterogeneous; the KWW $\beta$ parameter decreases from $\beta \approx 0.45$ to $\beta \approx 0.18$ upon deformation, while in the previously mentioned results of Figure 10 and for all film layers, $\beta$ only dropped down to 0.4 even at the largest studied strain amplitude $\gamma = 10\%$. This heterogeneity (i.e., small value of $\beta$) in the middle layer suggests that a percolative glassy path connecting the two substrates still remains at the simulated strain amplitudes, which would explain the still high rigidity at strain $\gamma = 10\%$ (Figure 8b).

In all the fittings performed in Figure 10, the activation volume was found to decrease for higher values of the relaxation time in the undeformed state. Indeed, an activation volume $v = 2.42$ was found for both layers of Figure 10c, with $\tau_{P_l(undeformed)} \approx 10^5$. For the substrate layer $(0 < z < 1.3)$ of thickness $D = 10$ (Figure 10b) with $\tau_{P_l(undeformed)} \approx 5 \times 10^8$, the activation volume was found equal to $v \approx 1.93$. Still lower values were obtained for the middle $(1.3 < z < 2.6)$ and substrate $(0 < z < 1.3)$ layers of the ultrathin films of Figure 10d, namely $v = 1.2$ and $v = 0.4$, respectively; the correspondingly zero-stress relaxation times were $\tau_{P_l(undeformed)} \approx 5 \times 10^7$ and $\tau_{P_l(undeformed)} \approx 10^9$. So when the polymer is deeper in a glassy state the activation volume is smaller, and the out-of-cage motion becomes more an isolated event. Generally, we conclude that the Eyring picture, where applicable, once more proves the existence of the glassy regions during deformation.

4. SUMMARY AND CONCLUSIONS

In this paper results were presented of molecular dynamics simulations of bead–rod random copolymer chains which were confined between two attractive crystalline substrates. Different substrate–substrate separations (i.e., film thicknesses) as well as substrate–polymer interaction strengths were used. All films were simulated under the application of an external normal pressure $p_{zz} = 1$ (NpT-ensemble simulations). Bulk samples were also created under the same pressure and with the same density as in the middle of the thick films, and their dynamical and mechanical properties were used as a reference point.

The density profiles of the thickest simulated films (i.e., $D \approx 30$) showed a monomer layering close to attractive substrates, while a bulk-like behavior was found in the middle of the films (Figure 2). In the ordered region, the averaged density was found to increase by 5% compared to the middle layers. With decreasing film thickness the middle bulk-like layer vanished, and an overall increase of the film density was found. The effect of increasing density was found to be more pronounced when increasing the substrate attraction strength. The thickness- and substrate-attraction-strength dependencies of the film-averaged density were studied for all simulated film thicknesses and strengths of adsorption (Figure 3a). Moreover, the glass-transition temperatures were extracted. $T_g$ was found to increase with increasing confinement but also with stronger adsorption strength (Figure 3b).

The segmental orientational mobility was calculated with the help of the $P_2$ ACF (eq 2). This was found to decay more slowly for thinner films, thus indicating a slowing down of the dynamics with decreasing film thickness (Figure 4a). This behavior was understood from the layer-resolved analysis of the mobility, which showed a strongly inhomogeneous distribution of the relaxation times across the different film layers. In the thickest films, a slowing down of the relaxation times was found close to the substrates, which was followed by a bulk-like behavior in the middle of the films (Figure 4b). The bulk-like part vanished for thinner films, thus explaining the overall slowing down of the mobility. By increasing the substrate attraction $\varepsilon_{pp}$ (Figure 4c), glassy layers were created in the vicinity of the polymer–substrate interface. These caused an additional slowing down in the dynamics of the middle layers of the films of thickness $D \approx 10$. Moreover, a glass bridge between the substrates was found in the case of ultrathin films (i.e., $D \approx 4$).

In order to study the possible mechanical reinforcement in the linear viscoelastic regime, all films, as well as the bulk, were elongated along the $z$-axis. The stress response at different strain amplitudes was calculated, and the elastic moduli were extracted (Figure 5a). At temperatures above bulk $T_g$ the reinforcements, i.e., the stiffnesses compared to that of the bulk polymer, were found to increase with decreasing thickness as well as with increasing strength of adsorption to the substrates (Figure 5b). Moreover, the thickness dependence of the reinforcement proved in qualitative agreement with that of the layer-resolved segmental dynamics. The overlapping low-mobility regions, as shown in Figure 4c, resulted in a strong increase of the reinforcement.

Depending on film thickness, the effect of changing temperature affected the reinforcement of the films in different ways. The effect was studied for the case of $\varepsilon_{pp} = 10$, where strong changes of the reinforcement were observed with changing temperature (Figure 6). At temperatures just above bulk $T_g$ the reinforcement of films of thicknesses $D \leq 10$ was found to increase with increasing temperature. This effect was explained from their higher glass-transition temperature compared to the bulk and from the corresponding weak temperature dependence of their elastic moduli. On the other hand, when decreasing temperature below bulk $T_g$ the reinforcement decreased for all film thicknesses.

All films were deformed along the $z$-axis with the same initial strain rate. The stiffness of each film was measured by calculating the film-averaged secant modulus $E_s$, at different strain amplitudes. At small deformations (linear regime), the secant modulus was found to fluctuate around an average value which, as expected, equals the elastic modulus. When deforming beyond the linear viscoelastic regime, a different large-strain behavior of the secant modulus was found in different films; stiffer films showed a stronger softening upon large deformation, toward the corresponding bulk stiffness at the same strain amplitude (Figure 8, nonlinear regimes).

The layer-resolved segmental orientational mobility was calculated at different deformed states. Upon deformation, an acceleration of the polymer mobility took place across the films. In case of weak polymer–substrate interactions the relaxation times exponentially decreased with stress, thus showing liquid-like response on the applied stress. A stronger acceleration was observed near the substrates. Different behavior was found for the case of strongly adsorbing substrates. Because of the strong monomer bonding to the substrates, the acceleration effect at different stresses was smaller in the glass-like surface layers compared to that in the middle layers (Figure 10b,d). The existence of glassy-like layers near the substrates during deformation was confirmed from the Eyring model; the evolution of the relaxation times with stress can be qualitatively described by Eyring’s equation (eq 7). For ultrathin films, deformation resulted in a strongly heterogeneous dynamics of the middle layer; low-mobility percolative paths seem to connect the two substrates, up until the largest strain.
amplitudes studied; thus, the secant modulus did not converge to the bulk value.

All studies so far of the mechanical properties were performed with strain rate \( \dot{\gamma} = 10^{-3} \text{s}^{-1} \). The effect of strain rate on the elastic modulus of the bulk was studied for a wide range of strain rates \( (\dot{\gamma} = 10^{-6} - 10^{-2} \text{s}^{-1}) \). At temperatures above \( T_p \) the bulk elastic modulus was found to decrease by roughly 30% for slower strain rates, while minor changes on \( E_T \) were found at temperatures below \( T_p \) (Figure 7a), as expected. The mechanical reinforcement in the case of confined films with strong substrate attraction (\( \epsilon_{sp} = 10 \)) was also studied for different values of \( \dot{\gamma} \), that is, \( \dot{\gamma} = 10^{-6} - 10^{-2} \text{s}^{-1} \) (Figure 7b). For all film thicknesses, the reinforcement was found to increase with decreasing \( \dot{\gamma} \). This was attributed to the different glass-transition temperatures of the confined films and to the corresponding different dependencies of the their elastic moduli on the strain rate.

To conclude, the segmental dynamics of confined polymer films was found to slow down with decreasing film thickness. This is contrary to the results presented in our previous publications\(^{46,47} \) and is explained from the density increase with thickness decrease under \( NpT \) conditions. Additionally, the very high densities used in previous studies lead to finite-size scaling effects; such effects were not found with the moderate pressures (and the resulting densities) used in the present work. The main conclusion from this work is that both the linear and nonlinear mechanical behavior of confined elastomer films can be qualitatively understood in correspondence with the behavior of the layer-resolved segmental mobility in confinement. This is in qualitative agreement with earlier DPD simulations on filled elastomers and the proposed glassy bridge reinforced model (GBRM)\(^{21–24} \) which was recently introduced, in order to explain the Payne effect. As discussed in the Introduction, simulations of atomistically detailed polymers show that the layering effects near the walls are smaller\(^{61–63} \), which, in turn, could lead to the smaller increase of rigidity under confinement.

### APPENDIX

As mentioned in section 2, the Lennard-Jones energies \( \epsilon_{ws} \) between the substrate particles are chosen to be very high in order to ensure the crystalline structure even at high temperatures. At low temperatures the interaction energy \( \epsilon_{ws} \) should be high enough compared to the substrate–polymer interaction \( \epsilon_{sp} \) so that the crystallinity of the substrates will remain under uniaxial deformation.

The high values of \( \epsilon_{ws} \) result in strong pressure fluctuations inside the substrate, since the interacting forces between the substrate particles are high as well. This can be seen in Figure 11, where the pressure profile of the \( p_{zz} \) component of the internal pressure is presented for the case of the thickest simulated film \( (D \approx 30) \) at temperature \( T = 0.6 \) and for substrate–polymer interaction strength \( \epsilon_{sp} = 1 \). The pressure profile was obtained with the local-pressure version 4.5.2 of GROMACS. More information about the calculation of pressure locally can be found in ref 77.

By analyzing Figure 11, it is seen that the pressure in the polymer films \( (0 < z < 30) \) slightly fluctuates around an average value \( p_{zz} = 1 \), which equals the applied external normal pressure. The deviations from the average value are rather reasonable in view of the thermal fluctuations. On the other hand, roughly 2 orders of magnitude stronger fluctuations can be seen inside the substrates. These can be attributed to the high Lennard-Jones energies of the substrate particles but also to the layer width used for the calculation of the pressure profile; this was chosen smaller than the particle diameter \( \sigma \).

The strong pressure fluctuations inside the substrates, as presented in Figure 11, are resulting also in strong pressure fluctuations of the simulation box as a whole, when \( p_{zz} \) is calculated over time during, for example, a uniaxial deformation. Additionally, under deformation the finite deformation rate may give inertial vibrations in the crystalline lattice; these will cause strong fluctuations in the internal pressure of the substrates. Therefore, the corresponding normal stresses at different strain amplitudes can be miscalculated. Figure 12a depicts the stress–strain behavior under uniaxial deformation at \( T = 0.6 \), with constant strain rate \( \dot{\gamma} = 10^{-2} \text{s}^{-1} \) for a film of thickness \( D \approx 30 \), when \( \epsilon_{sp} = 1 \). The black line corresponds to the normal stress of the whole simulation box and the red line to that of the polymer film only, as calculated with the help of the lp-version of GROMACS.\(^{77} \) This calculation was achieved by producing similar pressure profiles (at each strain) as the one shown in Figure 11 and then averaging all values over the polymer film. The results are obtained after subsequently averaging over ten independent samples. Despite the relatively good statistics, the fluctuations of the normal stress, when this is calculated for the whole simulation box, are still strong, while rather small fluctuations are observed when the normal stress is calculated only for the polymer film. Moreover, the whole-box normal stress (black line) appears to fluctuate around the polymer-film normal stress (red line) during the deformation.

In order to test the validity of the results for the pressure profiles as produced from the lp-version of GROMACS, the bulk sample was uniaxially deformed, again at \( T = 0.6 \) and for constant strain rate \( \dot{\gamma} = 10^{-2} \text{s}^{-1} \), and the corresponding normal stresses were calculated at different strains (Figure 12b). The normal stress at each strain was calculated both for the whole simulation box by using version 4.5.5 of GROMACS (Figure 12b, black line) as well as by averaging the different values of the film pressure profiles (Figure 12b, red line). Both results in Figure 12b correspond to an averaging over ten independent bulk samples. Negligible differences can be found when comparing the two curves, thus ensuring the validity of
averaging the normal stress over the pressure profiles obtained using the lp-version of GROMACS.\(^7\)

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**Notes**
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