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Molecular-dynamics simulations of crosslinking and confinement effects on structure, segmental mobility and mechanics of filled elastomers

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Abstract. The significant drop of the storage modulus under uniaxial deformation (*Payne effect*) restrains the performance of the elastomer-based composites and the development of possible new applications. In this paper molecular-dynamics (MD) computer simulations using LAMMPS MD package have been performed to study the mechanical properties of a coarse-grained model of this family of nanocomposite materials. Our goal is to provide simulational insights into the viscoelastic properties of filled elastomers, and try to connect the macroscopic mechanics with composite microstructure, the strength of the polymer-filler interactions and the polymer mobility at different scales. To this end we simulate random copolymer films capped between two infinite solid (filler aggregate) walls. We systematically vary the strength of the polymer-substrate adhesion interactions, degree of polymer confinement (film thickness), polymer crosslinking density, and study their influence on the equilibrium and non-equilibrium structure, segmental dynamics, and the mechanical properties of the simulated systems. The glass-transition temperature increases once the mesh size became smaller than the chain radius of gyration; otherwise it remained invariant to mesh-size variations. This increase in the glass-transition temperature was accompanied by a monotonic slowing-down of segmental dynamics on all studied length scales. This observation is attributed to the correspondingly decreased width of the bulk density layer that was obtained in films whose thickness was larger than the end-to-end distance of the bulk polymer chains. To test this hypothesis additional simulations were performed in which the crystalline walls were replaced with amorphous or rough walls.

Keywords: molecular-dynamics, Payne effect, polymer segmental relaxation, polymer film, crosslinking.
PACS: 81.05.Qk; 81.05.Lg; 68.35.bm; 62.20.de

INTRODUCTION

Polymer nanocomposites are materials with an abundant of industrial applications, e.g., in the manufacturing of car tires. The mechanical properties of elastomer-based nanocomposites made of inorganic nanoparticles (Carbon black or silica as typical examples) dispersed in the polymer matrix depend drastically on the details of interactions between the polymer matrix and the nanofillers.[1-2] By tuning these interactions the desired increase of mechanical reinforcement can be obtained at low deformations. However, a significant loss of the composite's rigidity appears at larger strains. This loss of rigidity is colloquially called the 'Payne effect'[3] and is believed[4] to have its origin in the interrelation of the material's viscoelastic properties with its microstructure, the polymer's segmental mobility and the polymer-filler interactions[5].

To study the structure, segmental dynamics and mechanics of filled elastomers we performed molecular-dynamics (MD) simulations of a bead-spring model of a polymer film confined between two solid (crystalline and amorphous) walls representing filler surfaces. The simulations of the corresponding bulk polymer have also been performed to provide with necessary comparisons. We discuss the influence of the walls' structure on the density distribution and segmental mobility of the confined polymer. Essentially, it has been confirmed earlier that the glass-transition temperature in films is significantly different than that of the bulk, depending on the strength of the wall-polymer interactions[6]. In addition, molecular-dynamics simulations of a filler particle surrounded by polymer chains showed that for attractive polymer-filler interactions the glass-transition temperature was higher than in the polymer bulk, whereas the opposite was observed when unfavorable adhesion interactions were employed[7].

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Despite the high attention that has been given to the effect of confinement and adhesion interactions on the glass-transition temperature and segmental dynamics in thin polymer films, the combined effect of crosslinking and confinement is much less investigated. This is exactly our purpose of this paper, i.e., to provide with rather general insights on the effects that the surface structure (crystalline vs amorphous), crosslink density ρ_{cl} and film thickness L_{film} may exert on the glass-transition temperature and segmental relaxation of the bead-spring elastomer model, and to make possible connection with material's macroscopic mechanics. In the next section the employed model and our main findings and conclusions are presented.

MODELS AND SIMULATION DETAILS

We performed molecular-dynamics constant temperature – constant pressure (NPT) simulations of non-entangled polymer chains confined between two crystalline or amorphous walls using the LAMMPS MD software package[8]. The polymer model is built of 100 bead-rod random-copolymer chains, each chain consists of 50 monomers, with 80% monomers of type A and 20% monomers of type B, which differ in their sizes (i.e., the Lennard-Jones (LJ) interaction parameters), $\sigma_{\mathrm{B}}= 1.2\sigma_{\mathrm{A}}$. and masses ($m_{\mathrm{B}}= 1.2^3 m_{\mathrm{A}}$). Different beads are randomly placed along each chain. Each of two substrates which represent the surfaces of a filler particle, consists of three layers of LJ spheres in an HCP or in some random arrangement, Fig. 1; the diameter of each sphere is $\sigma_{\mathrm{s}} = 0.85\sigma_{\mathrm{A}}$. The substrate-polymer interaction strength $\varepsilon_{\mathrm{sp}}$ was chosen equal to that of the polymer-polymer interaction strength, that is $\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}} = \varepsilon_{\mathrm{AB}} = 1$. More details about the simulated polymer model and equilibration details can be found in our previous publications[9-10].

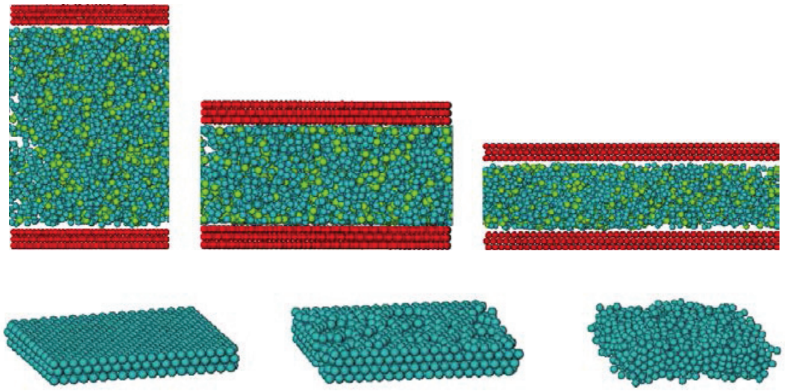


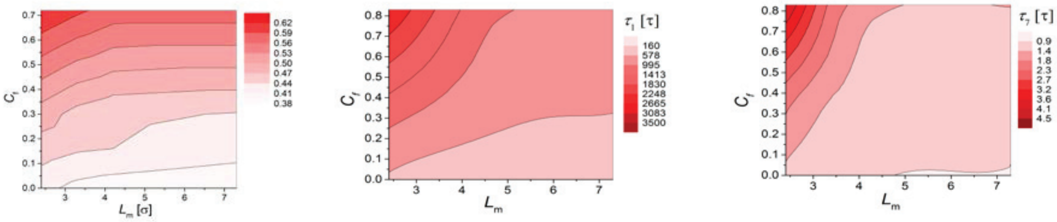
FIGURE 1. (Upper panel): The simulated films of three different thickness (denoted in this paper as thick, thin and ultrathin) confined between two crystalline walls. For thinner films larger lateral dimensions were used so as to maintain a constant density. Distinct colors denote different bead types. Periodic boundary conditions were implemented in all three dimensions. (Lower panel): three types of substrates that were used in this study, from left to right: crystalline, rough, and amorphous.

The chosen film thicknesses (in units of σ_{A}) are varied from ~4 to ~20, Fig. 1. The bulk radius of gyration for a single chain is $R_g = 3.6 \pm 0.1\sigma$, therefore the film thickness is varied from D/R_{g} ~1 (strong confinement) to D/R_{g}~5 (weak confinement). The interactions for all non-bonded monomer pairs were described by the Lennard-Jones potential with a cut-off distance $r_{\mathrm{c}} = 3.5\sigma_{\mathrm{A}}$. Polymer bulk samples have been created as well, and used as a reference point. The temperature coupling was controlled with the help of the velocity-rescale thermostat; the chosen time constant was set to $\tau_{\mathrm{T}} = 0.5$ (in the units of LJ characteristic time). The Berendsen barostat with $\tau_{\mathrm{P}} = 2.5$ has been used. Periodic boundary conditions were applied in all directions. The integration of Newton's equations has been done with the leap-frog variant of the velocity Verlet algorithm. The time step was chosen to be $\Delta t = 0.001$.

Covalently-bonded beads interact through a combination of an attractive Finite-Extensible-Nonlinear-Elastic (FENE) potential and a repulsive and truncated LJ 12-6 potential.[11] We simulated both crosslinked and non crosslinked polymer systems, using a static method of crosslinking to produce the polymer networks. Namely, the last snapshot of the equilibration trajectory of each system was used to create crosslink bonds between randomly chosen pairs of monomer units (regadless of their type) until the desired value of the crosslink (number) density ($\rho_{\mathrm{cl}} = \{1, 2, 3, 4, 8\}$ crosslinks per chain) was achieved with a mesh size of $L_{\mathrm{mesh}} = \{4.7, 3.0, 2.3, 2.2, 1.7\}\sigma$.

RESULTS AND DISCUSSION

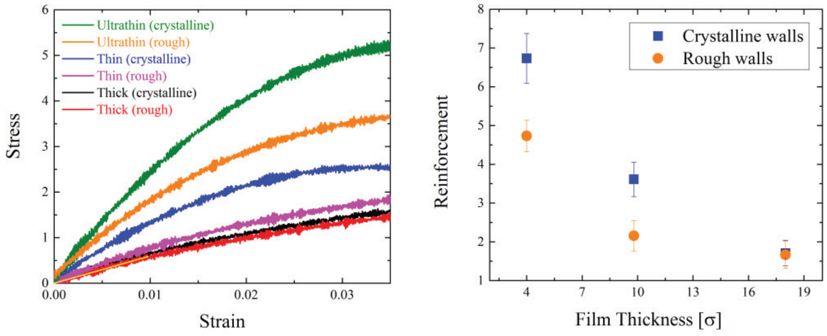
For the calculation of the glass-transition temperature we have performed NPT MD simulations by lowering the temperature of bulk and films with crystalline substrates, with a cooling rate of $2\cdot10^{-5}$ $(\varepsilon/k_{\mathrm{B}})/\tau$, where τ is the corresponding LJ time, in a stepwise fashion from 0.8 to 0.1 $\varepsilon/k_{\mathrm{B}}$. The glass-transition temperature was determined from a change in the slope above and below the transition region. We observe that the difference in the thermal expansivity below and above the T_{g}, is larger in the films than in the bulk. The simulations also showed that the values of the film glass-transition temperature T_{g} were affected by variations in both crosslink density (or equivalently, the mesh size L_{mesh}) and film thickness (or equivalently, the confinement degree C_{f}, defined as the ratio of the chain gyration radius to the film thickness) but to a different extent. The calculated T_{g} in the films was higher than the T_{g} in the bulk under the same constant mesh size value, Fig. 2a: thinner films have higher T_{g}. The size of the crosslinked mesh was found to affect the T_{g} only when it was smaller than the radius of gyration of the non-crosslinked chains.



a) **b)** **c)**

FIGURE 2: a) The film glass-transition temperature as function of the degree of confinement and the average mesh size. b), c) Dependence of the relaxation times on the degree of confinement and the average mesh size. The chain-scale (b) and the segmental-scale (c) relaxation times are presented.

The polymer segmental mobility has been quantified by the calculation of the incoherent scattering function, $S_{\mathrm{inc}}(q,t)$.We have extracted the segmental relaxation times by fitting the simulated $S_{\mathrm{inc}}(q,t)$ with modified stretched exponentials, taking into account the finite plateaus that are present in the cross-linked systems at large times. The relaxation time increases linearly with the cross-linking density and degree of confinement, across all length-scales, Fig. 2b,c. Tremendous slowing down is seen for ultrathin films, when the chain gyration radius is comparable to the film thickness.



a) **b)**

FIGURE 3: a) Stress-strain dependences for films of different thickness and with different structure of confining substrates. b) The reinforcement degree as function of the film thickness.

Finally, the films were uniaxially deformed with a constant strain rate. The elastic modulus was extracted by fitting the stress-strain curves, Fig. 3a, in the linear regime of small strains, $\varepsilon < 1\%$. We define the reinforcement as the ratio of the modulus of the filled polymer (i.e., of the film) to the modulus of the pure polymer melt. The reinforcement increases with decrease of the film thickness (or with increase of the filler volume fraction effectively), Fig. 3b. The reinforcement observed in the ultrathin film was quite large in comparison to the rest of the studied systems, which is a consequence of the tremendous slowing down of the segmental dynamics in films which thickness is comparable to the chain radius of gyration. In the thick film the reinforcement curves for different substrates overlap; in thinner films, with larger influence of the substrate structural details, crystalline walls resulted in a higher reinforcement value.

In conclusion, we see very strong effects of both confinement and crosslinking, on both structural and dynamic composite properties, and somehow weaker effects of the substrate structure (crystalline *vs.* amorphous). These changes in structure and mobility are connected to the differences in the mechanical reinforcement, but this requires additional investigation.

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