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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.4868231

Published: 01/01/2014

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Molecular-dynamics simulations of thin polyisoprene films confined between amorphous silica substrates

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(Received 21 November 2013; accepted 25 February 2014; published online 20 March 2014)

I. INTRODUCTION

When fillers are added to polymer matrices, they lead to the enhancement of resulting composite mechanical properties.1 However, the quantitative relationship between the structure, local polymer-segmental dynamics, final mechanical properties of nanocomposites, and the chemical constitution and interactions of their components, remains unknown. Among all nanocomposites, the elastomer-based materials are widely known for their technological applications in producing tires, high-performance plastics, and structural parts of advanced equipment. Macroscopic properties of these nanocomposites are determined by many factors, such as the chemical constitution of their components, polymer structure and degree of polymer-chains ordering, effective glass-transition temperature, polymer-segmental dynamics, the dispersion, size, surface energy, volume fraction of the filler, and filler–polymer bonding, and can vary significantly through thickness of a polymer matrix.

Nowadays, the market of truck and passenger car tires is filled with carbon-black reinforced materials.2 Carbon black as a filler provides a polymer nanocomposite with enhanced stiffness, high wear resistance, and relatively low material weight, when compared to metals.3,4 At the same time carbon-black reinforced nanocomposites demonstrate the loss of rigidity at high loading and decrease of the dynamic modulus, that is called Payne effect,5 which adversely affects tire applications. In the tyre applications, tyre rolling resistance is defined as the energy consumed by the tyre per unit distance of travel as a tyre rolls under load. This energy dissipation depends on the loss modulus and (in idealized experiments) is measured by the loss factor, i.e., the ratio of dynamic mechanical moduli tan δ = G′′/G′ in the resulting nanofilled rubbers. The lower is the rolling resistance, the lower is the energy consumption and, consequently, the fuel consumption. Experiments6–9 have suggested a novel approach of reinforcing elastomers by small quantities of inorganic silica nanoparticles which are cheap, have thermal stability and wear and chemical resistance. The resulting nanocomposite may have both enhanced stiffness and toughness,1 have light weight and perform better rolling resistance,2 thus reducing fuel consumption and CO2 emission, increasing wet grip, decreasing wear and, last but not least, improving safety.

Though many experimental, computer-simulation and analytical studies have been devoted to the investigation of reinforcement of elastomers and to such a nonlinear behavior of this reinforcement,10–25 it is still difficult to predict quantitatively the elastomer-composites properties, the variation of the dynamic modulus with temperature, and the conditions for a better final reinforcement. Multiscale simulation
approach and theoretical predictions based on these simulations are expected to be suitable tools gaining insight into the best tire reinforcement and for development of environmentally more friendly, "green" tires, elastomeric sealants, and other advanced rubber materials.

The nice review of the existing understanding of polymer nanocomposite properties is summarized in Ref. 26. In order to describe the Payne effect, some studies were focused on the association of filler particles into large agglomerates, which break under loading. Carbon black reinforced nanocomposites were analyzed extensively,10–15 using a vast majority of experimental techniques, such as AFM,12, 13 X-ray and neutron-scattering,14,15,18 and the existence of the above mentioned agglomerates were confirmed. Fractal-aggregate structure was analyzed with AFM, and small-angle scattering allows determining shape and size of the filler. Using small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) methods fractal network was also found in silica-filled nanocomposites.17,18

When explaining Payne effect, the importance of the polymer-filler bonding should be taken into account. Gauthier et al.21,22 investigated how the properties of silica-filled butadiene rubbers are related to the modification of silica particles with different silanes as covering agents. They showed that the amplitude of Payne effect is different in differently coated systems. Based on these results it was assumed that polymer bonds to silica surface lead to the mechanical reinforcement. Under the loading the debonding happens which, in turn, leads to the nonlinear mechanical behavior, and, ultimately, to Payne effect. The thickness of the bonded polymer may vary significantly depending on the silica-surface modifier areal density, its molecular weight and parameters of the noncovalent interactions with a polymer matrix.1,7,28

Much of the attention has been also focused on the changes of polymer segmental dynamics close to the substrates, where the existence of glassy layers was suggested10 and confirmed by many studies.19,25,30 Due to the presence of the glassy layers the effective increase of the filler volume fraction leads to better reinforcement of nanocomposite. Using NMR for composites where silica nanoparticles of about 50 nm size were dispersed in a polymer bulk with average distance of 10–20 nm between nanoparticles, Berriot et al.31 observed recently strong modification of the polymer dynamics in the filler proximity. Zhang and Archer12 determined the segmental-relaxation dynamics of entangled cis-PI confined in a porous glass using broadband dielectric spectroscopy. The pore size was chosen almost equal to the random coil size, so that the dielectric relaxation dynamics was influenced mainly by the adsorption effects. Two relaxation processes were found: (i) slow normal-mode relaxation, which corresponds to the global chain relaxation with broader lower frequencies maxima as compared to bulk, and (ii) additional fast relaxation mode controlled by the adsorption of chain segments at the filler surface. Serghei and Kremer33 applied the same technique to study the relaxation dynamics in (1,4) cis-PI thin layers and found as well the additional confinement-induced relaxation process due to the immobilization of chain segments at the interface. Various recent studies have also shown that the polymer dynamics is modified when approaching the surface of nanocomposite. Papon et al.34 characterized the silica dispersion by SANS in combination with reverse Monte Carlo modeling, and the mobility modification of the polymer by low-field proton NMR spectroscopy in a silica-filled model elastomer. The authors quantified the amount of interparticle connections and correlated it with the magnitude of the Payne effect taken from shear rheology. Using NMR and differential scanning calorimetry, Papon et al.35 observed the slowing-down of the dynamics of a polymer and quantitatively described this with a gradient of glass-transition temperature. Strat et al.36 studied mechanical reinforcement in model elastomer nanocomposites with tuned microstructure and interactions prepared by solvent-casting. Nanocomposite microstructures were analyzed by SAXS and TEM and viscoelastic behavior and the mechanical reinforcement in the rubbery state by dynamical mechanical analysis experiments.

It is rather established now that the effect of confinement, along with polymer-filler interactions, is responsible for the resulting nanocomposite properties. In some previous studies, it was shown that the dynamic and structural properties of filled elastomers and model thin polymer films confined between two filler substrates are similar.37,38 This assumption allows one to consider a thin polymer film as the nanocomposite model. Many studies showed recently that dynamical properties of a polymer melt in a thin film differ from those in bulk.39–42 This difference can be seen, for example, in a shift of the glass-transition temperature \( T_g \) and in the accompanying slowing down or accelerating of polymer-segmental dynamics43–45 in films of several tens of nm thickness. Zhu et al.46 investigated recently the influence of confinement on glass transition and molecular mobility for thiolated polystyrene (PS-SH) on gold nanoparticles. The majority of the groups39–42 revealed that in supported or capped polymer films the shift in \( T_g \) of 10–50 K can be observed when the polymer–substrate interaction strength changes. Some studies showed that the annealing procedure40 and the way of \( T_g \) measurement47 also affects the \( T_g \) value. Recent simulations of supported polystyrene films reveal that weaker polymer–substrate interactions always lead to the decrease of \( T_g \)41 and to the acceleration of the segmental dynamics at some fixed temperature. At the same time, it was found that the dynamics of polymer chains is slowed down in the vicinity of attractive substrates and accelerates closer to the repulsive substrate. In general, the polymer dynamics near \( T_g \) is highly heterogeneous, with distribution of relaxation times spanning more than four decades.48–50

Recently proposed Percolation of Free Volume Distribution (PFVD) theoretical model of Payne effect51–53 is based on these experimental findings. PFVD model is the extension of the well-known free volume model54,55 suggested by Long et al.51,52,56 which takes into account the domains of slow dynamics. According to the PFVD model, the heterogeneities in segmental dynamics correspond to density fluctuations and the macroscopic dynamics is controlled by the dynamically slowest polymer bridge.51 The authors suggested that the stiffness of these bridges depend on the filler volume fraction. When the filler volume fraction is high, i.e., the filler particles are close to each other, the layers with
low mobility surrounding the filler particles, together with the gradients of the glass-transition temperature overlap and create low-mobility polymer bridges. By using dissipative particle dynamics (DPD) simulations the authors were able to observe the break and re-birth of these bridges under deformation, thus providing the quantitative scenario of the Payne effect. Baljon et al. analyzed the heterogeneous segmental mobility in molecular-dynamics (MD) simulations of thin polymer films supported by an absorbing surface using a coarse-grained bead-spring model. They showed that the immobile domains percolate throughout the film in the direction perpendicular to the substrate, at temperatures close to the glass transition. In order to explain Payne effect in carbon black filled elastomers, Maier and Göritz proposed the model which is based on the adsorption mechanism of network chains on the surface of the filler particles. In a recently suggested model, the nonlinear large-strain mechanical behavior of nanofilled elastomers has also been explained using the debonding effect.

Some recent experiments question the existence of the glassy layers, thus reveal the inconsistency with the majority of previous experimental results, and show that the situation is far from being completely understood. Bogoslovov performed modulated differential scanning calorimetry and dielectric relaxation measurements for poly(vinyl acetate) filled with silica nanoparticles. The obtained relaxation times and relaxation dispersion did not indicate immobilization of polymer chains. Robertson et al. did not find the significant dynamics modification in filled rubbers. Glomann et al. performed high resolution neutron spectroscopic investigations of polyethylene glycol matrices interacting attractively with SiO2 nanoparticles, and also found that the adsorbed layer near silica nanoparticles is not glassy but undergoes fast picosecond local dynamics. Ediger and Forrest discuss recent experiments that directly measure mobility of glassy polymers at or near surfaces, and indicate that it can exceed the mobility in bulk by several orders.

Allegra et al. reviewed some recent simulation studies on nanocomposites. The vast majority of simulation efforts have invoked short coarse-grained linear polymer-chain models without attempting to represent specific chemical constitutions. A single nanoparticle, often of icosahedral shape, is usually placed in the simulation box. Ghanbari et al. performed coarse-grained molecular-dynamics simulations of free and grafted polystyrene chains surrounding a spherical silica nanoparticle. The authors found that increasing of grafting density and matrix chain length results in slowing down of polymer segmental dynamics. This effect strongly depends on the grafting density and the matrix-chain molecular weight. More realistic simulations of chemically specific polyethylene matrix and silica substrate have been performed by Brown et al. The analysis of the self-part of the intermediate scattering function has shown that the polymer-chains dynamics between attractive surfaces is slower and more heterogeneous than in a bulk. Employing classical atomistic simulations, the dynamical behavior of confined 1,4-polybutadiene between attracting graphite walls was recently investigated. The polymer mobility in the vicinity of the surface was found to be slower than in the bulk. Slowing down of local polymer dynamics was also observed recently in the molecular-dynamics simulations of short-chain polystyrene films between two parallel gold surfaces. Ndoro et al. used molecular-dynamics simulations to reveal the increase of segmental relaxation times of free and grafted atactic polystyrene chains surrounding silica nanoparticle. The atomistic molecular-dynamic simulations were recently performed by Komarov et al. to study the static properties of the polyimide matrix and surface-modified silica substrate interface. The polymer-matrix properties were found to be strongly influenced by the molecular weight and the surface density of the modifier. Thus, the existence of glassy bridges was confirmed in many computational studies. Bulk cis-PI has been previously extensively investigated in many theoretical, experimental, and simulation studies.

In summary, the molecular simulation has been invoked to address the thermomechanical properties of polymer nanocomposites. Molecular modeling usually focuses on structure and short-time dynamics, employing generic models that do not account for chemical detail. Atomistic simulations, whenever attempted, have been confined to oligomeric, unentangled systems, and have disregarded chemical crosslinking. No atomistically detailed dynamic simulations exist which can shed light on the static and dynamic behavior of filled rubbers and which can check the existence of the glassy bridges in PI films between silica substrates. This is the ultimate goal of the present study. The additional relaxation processes compared to the bulk system have been seen in experiments of Zhang and Archer, Serghi and Kremer, Tsagaropoulos and Eisenberg, and in simulations but not, to the best of our knowledge, in atomistic simulations of PI films confined between amorphous silica surfaces. In general, no theoretical/simulation framework exists for predicting from chemical constitution the strain amplitude-dependent dynamic and storage moduli of rubber (for example, PI) matrix nanocomposites, their spatially heterogeneous segmental dynamics, their hysteretic response to large-strain cyclic deformation, or the intriguing reduction of viscosity exhibited by nanoparticle-filled polymer melts relative to the pure matrix. The insight in the nanoscopic mechanisms that may affect mechanical reinforcement and nonlinear behavior of filled elastomers under stress is based on the understanding of PI local segmental dynamics modification when approaching the filler surface, and the influence of the overlapping glassy bridges between the fillers. That is why in the present study we concentrate mainly on the PI segmental dynamics near the silica surfaces.

In the present study, we set up atomistic NpT molecular-dynamics simulations of polymer films separating the surfaces of nanoparticles, in order to quantify the polymer structure and segmental dynamics in a nanocomposite. Samples of the non-crosslinked, non-entangled (1,4) cis-PI films confined between flat amorphous silica surfaces, and the corresponding bulk polymer sample have been prepared and simulated with the Gromacs engine (Gromacs version 4.5.6). The thermodynamic (pVT measurements), statistical (density and order parameters profiles), and dynamical properties (orientational correlation functions for various bonds, and associated
relaxation times at various temperatures) of the confined films and bulk polymer have been calculated and analyzed.

The rest of the paper is organized as follows. In Sec. II, we describe the simulation models and detailed force-fields for PI and the silica substrate, and the simulation algorithm. Section III reviews the equilibration procedure and other details of simulation. In Sec. IV, the results on both structural and segmental dynamical properties are presented and discussed. The main conclusions are summarized in Sec. V.

II. SIMULATED MODELS AND METHODS

A. Models of the simulated PI-silica composite and force-fields details

1. Polymer model

The PI model used in the present study resembles that from the existing literature. In some more detail, the united-atom representation for (1,4) cis-PI monomer has been used. Fig. 1(a). We have simulated (1,4) cis-PI bulk (Fig. 2(a)) of 200 chains and four PI films of different thickness, Fig. 2(c). Each simulated film contains 12, 25, 50, or 100 PI chains depending on its thickness. Both bulk samples and films are monodisperse, all chains are created of 20 monomers (100 united atoms, with molecular weight of about 1360 g/mol per chain), with equilibrium radius of gyration \( R_g \) in bulk at \( T = 420 \) K (well above the PI bulk \( T_g \)) found to be about 1 nm. The simulated PI films have thickness \( H \) in the range from 0.8 nm to 8.3 nm at temperature \( T = 420 \) K, which correspond to the values of \( H/R_g \) in the range from 1 (thin film, strong confinement) to 8 (thick film, weak confinement), respectively. At ambient conditions of \( T = 420 \) K and normal pressure \( p = 1 \) atm, the equilibrated simulation box for the PI bulk has dimensions of \( 5.7 \times 5.7 \times 16.9 \) nm\(^3\), for PI films the lateral dimensions of the box were also fixed to 5.7 nm, at the same time the film thickness was allowed to change in response to the changes of temperature or/and pressure. The silica substrate height, Fig. 2(b), is about 2 nm and was practically constant at different external conditions. Periodic boundary conditions (PBC) have been applied in all three directions.

The initial topology and conformation of the individual PI chain have been produced by using Materials Studio package from Accelrys Software, Inc. (Accelrys MS Modeling.)

2. Silica substrate

The silica substrate (Fig. 1(b)) was modelled with 603 atoms representing about one monolayer. To denote different types of atoms, three different colors are used, red for oxygen, yellow for silicon, and grey for hydrogen atoms. Periodic boundary conditions have been used in X and Y directions. (c) A typical snapshot of PI film (silica substrate and its image, and PI of 4 nm height in between) at \( T = 420 \) K. All PI chains are made of 20 monomers. Periodic boundary conditions are used in all three directions. Silica substrate has dimensions of \( 5.7 \times 5.7 \times 2 \) nm\(^3\).
3.0). The PI chain was further equilibrated by the energy minimization and by performing a short MD run in Npt ensemble for about 20 ps using GROMACS. In the simulated models, the non-bonded atoms and atoms separated by three bonds were all fixed (see Table I for values) using 12-6 potential using a cut-off distance of 1 nm. PI covalent bond lengths were all fixed (see Table I for values) using LINCS constraint algorithm. The angle bending, torsion interactions, and improper dihedral potentials have been used to describe all the corresponding bonded contributions to the force field. Atom 4, Fig. 1(a), was allowed to interact with atom 10 of the next monomer through LJ 12-6 potential with some difference in surface roughness for the united-atom and dummy-hydrogen-atom representations of the surface. This difference in the surface roughness can have some influence on the polymer-matrix properties. This is one of the reasons behind the need for a detailed description of all the PI force-field parameters.

### Table I. The force-field parameters used for the (1,4) cis-PI model.

<table>
<thead>
<tr>
<th>Bond length (nm)</th>
<th>Bond angle $\theta_0$ (deg)</th>
<th>$k_o$ (kJ mol$^{-1}$ rad$^{-2}$)</th>
<th>$k_i$ (kJ mol$^{-1}$ rad$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{LJ}(r_{ij}) = \left( \frac{A}{r_{ij}^6} - \frac{B}{r_{ij}^12} \right)$</td>
<td>$V_{imp}(\xi) = \frac{1}{2} k_i (\xi - \xi_0)^2$</td>
<td>$V_{rot}(\phi) = \sum_{n=1}^{6} k_n (1 + \cos(n\phi - 180^\circ))$</td>
<td>$V_{t}(\phi) = \sum_{n=1}^{6} k_n (1 + \cos(n\phi - 180^\circ))$</td>
</tr>
<tr>
<td>C=  C=</td>
<td>1.799</td>
<td>0.0835</td>
<td>2.4265</td>
</tr>
<tr>
<td>C=  CH=</td>
<td>1.799</td>
<td>-0.0835</td>
<td>2.4265</td>
</tr>
<tr>
<td>CH=  CH=</td>
<td>-2.071</td>
<td>-1.297</td>
<td>-8.4515</td>
</tr>
</tbody>
</table>

### 2. Silica model

The amorphous, periodic in X and Y directions, fully atomistic silica surface, Fig. 2(b), has been generated using the pcf force field and implementing the computational procedure suggested in Ref. 82. The fully atomistic representation of the silica surface is taken in the present study in view of the further perspectives of the whole project. In the nearest future, we intend to put more chemical details into both PI matrix (by introducing chemical cross links) and silica (by covering the surface with coupling and covering agents). Moreover, our recent studies of polystyrene surfaces show some difference in surface roughness for the united-atom and dummy-hydrogen-atom representations of the surface. This difference in the surface roughness can have some influence on the polymer-matrix properties. This is one of the reasons...
why the fully atomistic representation of the silica surface is implemented in the present study.

Basically, the procedure of the surface construction have been performed using few steps. The coarse-grained monomers of \( \beta \)-cristobalite have been prepared first and put randomly into the periodic simulation box. After the initial relaxation of the \( \beta \)-cristobalite melt, the reactive atoms corresponding to oxygen and silicon atoms in the atomistic model are crosslinked. At the next stage, the optimization of the obtained amorphous topological structure is implemented, in order to reduce the internal stresses, with the help of Monte Carlo energy minimization procedure. After that, the values of all the bond lengths are additionally being checked to be smaller than the interatomic distances of the chosen (pcff) force-field in order to avoid the presence of the non-existing long bonds in the system and Monte Carlo energy minimization has been repeated. The inverse mapping of the produced coarse-grained model back to the fully atomistic level has been performed next. The resulting structure has been cut by two planes in order to get a layer of given thickness, the free valences formed during this procedure were subsequently filled with hydrogen atoms. Finally, the equilibration of the atomistic silica sample by molecular dynamics has been carried out.

In the simulated model of the silica surface, the inter-and intra-molecular interactions between atoms separated by more than three bonds are described with a truncated LJ 12-6 potential with a 1 nm cutoff. Charged atoms interact with a Coulomb potential.

### 3. Polymer–silica interactions

Polymer and silica interact via LJ excluded-volume interactions with a 1 nm cutoff. The cross interactions in the LJ contributions, wherever not available, are described using the Lorentz-Berthelot rules. The major force field parameters are summarized in Table II.

### B. Other simulation details

The leap-frog algorithm for integrating Newton’s equations of motion has been implemented. The integration time step is set to 2 fs for PI bulk and 0.5 fs for PI film. The integration time step was chosen smaller for the PI films in order to prevent instability of the simulations caused by the fast librations of the silica hydrogen atoms. All the simulations have been performed in the isothermo-isobaric \( NpT \) ensemble. Berendsen thermostat with the time constant of 1 ps and Berendsen barostat have been used with the semiisotropic pressure (pressure is (on average) equal in the X and Y direction, but can be different in the normal-to-substrate Z direction) coupling type, compressibility of \( 4.5 \times 10^{-5} \) bar\(^{-1} \) and using the time constant of 0.5 ps in order to keep the temperature and pressure at the desired level. The equilibration of the bulk PI was done in a broad, 260–600 K, temperature range, see Sec. III. The MD production runs for both PI bulk and PI films have been performed in a temperature range from \( T = 280 \) K to \( T = 420 \) K and at normal pressure of \( p = 1 \) atm.

The particle-mesh Ewald summation was used to take electrostatics into account. The Fourier-spacing parameter which determines the maximum spacing for the fast Fourier transform (FFT) grid in the Ewald procedure was set to 0.6 nm; the parameter which controls the interpolation order was set to 4, the relative strength of the electrostatic interactions at the cut-off distance was set to \( 10^{-5} \). All the production runs have been carried out using SKIF “Chebyshev” supercomputer with 60 TFlops of the total peak performance and “Lomonosov” supercomputer with peak performance of 1.7 PFlops at the Lomonosov Moscow State University Research Computational Center.

### III. EQUILIBRATION PROCEDURE

#### A. Equilibration of the bulk PI sample

In order to prepare the well-equilibrated PI bulk sample, the individual PI chains (see Sec. II) were put randomly into the large simulation box of \( 5.7 \times 5.7 \times 100 \) nm\(^3 \). The PI sample was compressed further in a normal direction using \( NpT \) ensemble simulations at high pressure, \( p = 10000 \) atm, and at temperature \( T = 413 \) K, well above the experimental glass-transition temperature \( T_g = 199–204 \) K for PI bulk of molecular weight \( M = 0.62 \times 10^6 \) g/mol. The compression stops when the simulated PI density reaches the value of \( \rho = 0.825 \) g/cm\(^3 \). This value is obtained by extrapolating the PI density from Harmandaris et al. to the desired molecular weight of 1360 Da for the PI chains in the present simulations.

After this initialization, the PI bulk sample, Fig. 2(a), has been instantly heated up to \( T = 600 \) K and equilibrated for 15 ns at pressure \( p = 1 \) atm, then instantly cooled down at the same pressure to \( T = 540 \) K, where additional 50 ns of equilibration has been carried out.

#### B. Equilibration of the silica substrate

For the initial equilibration of the silica substrate, the LAMMPS simulation package (LAMMPS version from 6 December 2012) has been used together with the pcff force field, see Table II for specific parameters. As mentioned in Sec. II, the high-frequency librations of the silica-surface hydrogen atoms are the main limiting factors which define the value of the integration time step. Increasing the torsional-interactions parameters for the surface Si–OH groups by a factor of 10 allows us to use the time step of 0.5 fs. We have checked that the increasing of these torsional parameters does not influence significantly the thermodynamical and dynamical properties of the polymer itself, they only fix the spatial shape of the silica surface and may increase its Young’s modulus and decrease its coefficient of thermal expansion. In this way, we efficiently convert the substrate model to the united-atom representation, as a trade-off using a combination of the united-atom model for polymer matrix and the fully atomistic model for silica substrate.

#### C. Equilibration of the polymer–silica composite

In order to prepare PI–silica films, the individual pre-equilibrated (see Sec. II) PI chains were randomly put into the...
TABLE II. The force field parameters used for the amorphous silica model. The names of the atoms correspond to those used in Fig. 1(b).

Lennard-Jones interactions \( V_{LJ} = \left( \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} \right) \)

<table>
<thead>
<tr>
<th>(ij)</th>
<th>(A) (kJ mol(^{-1}) nm(^{12}))</th>
<th>(B) (kJ mol(^{-1}) nm(^6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSH OSH</td>
<td>1.97195 \times 10^{-6}</td>
<td>0.00229</td>
</tr>
<tr>
<td>OSS OSS</td>
<td>1.93368 \times 10^{-6}</td>
<td>0.00229</td>
</tr>
<tr>
<td>SZ SZ</td>
<td>4.41235 \times 10^{-6}</td>
<td>0.00161</td>
</tr>
<tr>
<td>HOS HOS</td>
<td>1.19753 \times 10^{-8}</td>
<td>1.40713 \times 10^{-4}</td>
</tr>
</tbody>
</table>

Stretching \( V_s(r) = C_2(r - r_0)^2 + C_3(r - r_0)^3 \)

<table>
<thead>
<tr>
<th>Bond length (nm)</th>
<th>(C_2) (kJ mol(^{-1}) nm(^{-2}))</th>
<th>(C_3) (kJ mol(^{-1}) nm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSH SZ</td>
<td>0.16125</td>
<td>0.1757423 \times 10^6</td>
</tr>
<tr>
<td>OSH HOS</td>
<td>0.09457</td>
<td>0.2940891 \times 10^6</td>
</tr>
<tr>
<td>SZ OSS</td>
<td>0.16155</td>
<td>0.1361686 \times 10^6</td>
</tr>
</tbody>
</table>

Bending \( V_b = \sum_{n=0}^{5} C_n(\theta - \theta_0)^n \)

<table>
<thead>
<tr>
<th>Bond angle (\theta_0) (deg)</th>
<th>(C_1) (kJ mol(^{-1}) rad(^{-1}))</th>
<th>(C_2) (kJ mol(^{-1}) rad(^{-2}))</th>
<th>(C_3) (kJ mol(^{-1}) rad(^{-3}))</th>
<th>(C_4) (kJ mol(^{-1}) rad(^{-4}))</th>
<th>(C_5) (kJ mol(^{-1}) rad(^{-5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ OSH HOS</td>
<td>123.4920</td>
<td>0</td>
<td>0</td>
<td>124.37992</td>
<td>-144.47112</td>
</tr>
<tr>
<td>SZ OSS SZ</td>
<td>110.6120</td>
<td>0</td>
<td>0</td>
<td>645.12971</td>
<td>-287.27824</td>
</tr>
<tr>
<td>OSS SZ OSS</td>
<td>110.6700</td>
<td>0</td>
<td>0</td>
<td>491.6569</td>
<td>-208.75356</td>
</tr>
<tr>
<td>OSH SZ OSH</td>
<td>115.0310</td>
<td>0</td>
<td>0</td>
<td>285.93347</td>
<td>206.82594</td>
</tr>
</tbody>
</table>

Torsions \( V_t(\phi) = \sum_{n=1}^{6} k_n(1 + \cos(n\phi - 180^{\circ})) \)

<table>
<thead>
<tr>
<th>(k_1) (kJ mol(^{-1}))</th>
<th>(k_2) (kJ mol(^{-1}))</th>
<th>(k_3) (kJ mol(^{-1}))</th>
<th>(k_4) (kJ mol(^{-1}))</th>
<th>(k_5) (kJ mol(^{-1}))</th>
<th>(k_6) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOS OSH SZ OSH</td>
<td>19.360</td>
<td>4.799</td>
<td>1.632</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HOS OSH SZ OSS</td>
<td>99.485</td>
<td>-0.289</td>
<td>-21.941</td>
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<td>0</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>0.700</td>
<td>0.001</td>
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</table>

Coulomb interactions \( V_c(r_{ij}) = f \frac{q_i q_j}{r_{ij}} \), \( f = \frac{1}{4 \pi \varepsilon_0} = 138.935485(9) \) kJ mol\(^{-1}\) nm e\(^{-2}\),

<table>
<thead>
<tr>
<th>(i)</th>
<th>Charges (q_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=</td>
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</tr>
<tr>
<td>CH=</td>
<td>0</td>
</tr>
<tr>
<td>CH2</td>
<td>0</td>
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<td>CH3</td>
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<td>SZ</td>
<td>0.26–0.66 (^a)</td>
</tr>
<tr>
<td>HOS</td>
<td>0.0641</td>
</tr>
</tbody>
</table>

\(^a\)The exact value depends on the chemical environment of the SZ atom.
large periodic simulation box containing infinite silica substrate at the bottom and its periodic image at the top (the bottom of the adjacent box). The whole system was compressed further to the film-averaged density of $\rho = 0.825$ g/cm$^3$ at $T = 413$ K and then simulated for a few ns at $p = 1$ atm. The resulting density in PI film middle parts at $T = 413$ K and $p = 1$ atm was found to be the same as in PI bulk at the same conditions. The PI films obtained in this way with thickness $H$ of 0.8 nm, 1.9 nm, 4 nm, and 8 nm (see Fig. 2(c)) were equilibrated at $T \sim 600$ K and $p = 1$ atm for at least 50 ns.

To ensure the good quality of equilibration, the averaged chain radius of gyration, the components of the gyration tensor in PI bulk and films have been calculated, Fig. 3. We observe that both for PI bulk and for different films the values of the chain gyration radius or the gyration tensor components do not drift with time, and, at the end of the equilibration, fluctuate around the corresponding average values with deviations about 3%–5%, see Fig. 3.

For the statistical and dynamical analysis, the resulting polymer bulk and film samples were launched in the $NpT$ ensemble at atmospheric pressure and different temperatures in the range from 280 K to 420 K, above the PI bulk glass-transition temperature. In PI bulk simulations, the energy and pressure corrections for the potential truncation have been implemented; the PI films were simulated without these corrections.

The PI bulk and film samples equilibrated at $T = 420$ K were further cooled down at a cooling velocity of 0.1 K/ps and $p = 1$ atm. The glass-transition temperature has been estimated by identifying the changes in slope in the corresponding temperature-density dependences. At each intermediate temperature, the MD production run has been carried out for 25 ns–100 ns depending on the system size, and the trajectories have been saved every 0.5 ps for further analysis.

IV. RESULTS AND DISCUSSION

The PI structural properties (chain size, chain shape, local segmental ordering, and density profiles) and the segmental-dynamical orientational mobility in different film layers, and averaged over the whole film thickness, have been calculated in PI films of different thickness at different temperatures. Below we present and discuss these results, and compare when possible with the corresponding behavior in a PI bulk.

A. Structural properties

The radius of gyration of a group of atoms is defined as

$$R_g = \left( \frac{\sum m_i \bar{r}_i^2}{\sum m_i} \right)^{1/2}$$

where $m_i$ is the mass of atom $i$ and $\bar{r}_i$ is the position of atom $i$ with respect to the center of mass. The components of the gyration tensor which correspond to the radii of gyration of a group of atoms about the $X$, $Y$, or $Z$ axes, are

$$R_{g,j} = \left( \frac{1}{M} \sum_{i=1}^{N} m_i \left( r_{i,j}^2 - \bar{r}_{i,j}^2 \right) \right)^{1/2}, \quad j = x, y, z.$$  \hspace{1cm} (1)

These properties are calculated for equilibrated earlier PI chains, both in bulk and in films of different thickness, Fig. 3(a). No drastic changes can be seen in the gyration tensor components, which is a sign of a good equilibration. The radius of gyration, both in bulk and in films at $T = 400$ K, was found to be about 1 nm. For bulk all components $R_{g,j}$ are very similar to each other (not shown) and the averaged value only is shown in Fig. 3(a). Contrast to that, the clear shape anisotropy is found for PI chains in films. For example, for 1.9 nm-film the $R_{g,z}$ component is much larger as compared to (similar to each other) $R_{g,x}$ and $R_{g,y}$ radii, the PI chain has an oblate shape in the film plane. To characterize quantitatively the chain anisotropy, the shape parameter $s = \frac{R_{g,z}}{\sqrt{(R_{g,x}^2 + R_{g,y}^2)/2}}$ is calculated for different films, Fig. 3(b). Obviously, this parameter is about unity for thick film and a bulk, and is

\hspace{1cm}

FIG. 3. (a) The time dependences of the PI chain radius of gyration in a bulk and of the components of the gyration tensor for PI chain in a 1.9 nm film at $T = 400$ K. (b) The parameter $s$ of the PI chain shape anisotropy at different temperatures in PI films of different thickness. The result for PI bulk is shown by the horizontal dashed line for reference.
drastically increasing with the film thickness decrease. It is only weakly influenced by temperature, Fig. 3(b). Unfortunately, the error bars of these measurements are rather large, and we cannot see any systematic change of the shape parameter with film temperature.

Another statistical characteristic which has been calculated in order to check the quality of the produced sample, is the characteristic ratio $C_N$ defined as

$$C_N = C_\infty \left(1 - \frac{\alpha}{\sqrt{N}}\right),$$

(2)

where $C_\infty$ is the characteristic ratio for infinitely long chains. The fit with Eq. (2) works quite well for intermediate $N$, Fig. 4. It obviously fails for short interparticle separations, at $N \sim 1$. The produced values of $C_\infty$ are from 4.4 to 5.3 for different samples, are close to the values of 4.5–4.8 simulated earlier, and are within experimentally observed range of 4.8–5.5 for PI bulk at $T = 413$ K. No clear dependence of $C_\infty$ on film thickness has been observed.

The local layer-resolved monomer ordering in simulated PI films is calculated using the averaged second-order Legendre polynomial function

$$P_2(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1),$$

(3)

where $\theta$ is the angle between the $Z$ axis (normal to the film surface), and the CH$_2$–CH$_2$ vector along the PI monomer unit. The angular brackets $\langle \ldots \rangle$ denote both time averaging and the averaging over all equivalent vectors in the system. For PI bulk, the so defined order parameter is close to zero, Fig. 5, which reflects the amorphous nature of the produced PI sample. In PI film the situation is different. The presence of the silica substrate induces some ordering in the nearby monomers, with a trend toward in-plane orientation, the corresponding value of the order parameter $P_2$ is negative. This tendency is increasing slightly with the decrease of film thickness, Fig. 5. The observed ordering is only slightly affected by the temperature. The final temperature range. The monomer ordering disappears when approaching the middle region of the film, where the order parameter is again close to zero.

The PI monomer density profiles are shown in Fig. 6. The ordering discussed above leads to some increase of the polymer density close to silica substrates, for all simulated PI films. At the same time the well-resolved plateau is seen for the films middles, with the value equal to the bulk density at the same temperature, Fig. 6(b), meaning that the substrates have only very limited, spanning about 0.5 nm in length, influence on structural properties for thick films. Note that the induced monomer ordering also disappears after about 0.5 nm from the silica surface. Similar behavior was observed earlier in different polymer-filler composites. The middle-film density is obviously decreasing upon the temperature increase due to the film expansion in constant-pressure simulations.

We also checked the distribution of the chain-ends (i.e., the terminal CH$_3$ groups for each PI chain) over the film width, Fig. 7, where the results are shown for $T = 420$ K. At all simulated temperatures, the chain ends are distributed almost uniformly (within rather large error bars), with some deficit in the very proximity of the silica substrates. The lack of the mobile end groups in the proximity of the substrates can probably explain in some extent the slowing down of the segmental relaxation in surface layers, which will be discussed later.

In order to calculate the glass-transition temperature, the film density $\rho$ is measured, first of all, averaged over the whole film width. The film width is defined as the distance between two points in a density profile where $\rho = \frac{1}{2}\rho_{\text{max}}$. The maximum density $\rho_{\text{max}}$ is calculated as the average of the first two peaks in the density profile. On top of this, the density in
FIG. 6. (a) The monomer density profiles for PI films of different thickness at temperature \( T = 420 \) K. The horizontal solid line denotes the corresponding monomer density in the PI bulk at the same temperature. (b) The monomer density profiles for 4 nm film at different temperatures. The horizontal dashed line denotes the corresponding monomer density in the PI bulk.

the film middle parts has been calculated as well. The middle of the film is defined approximately as the part of the film where density value deviates from the bulk by no more than 8%. The correspondent temperature dependences were averaged over three independent samples and are shown in Fig. 8, together with the PI bulk density results. For all simulated samples, the clear change in the thermal expansion coefficient occurs around 300 K. Fitting the low-\( T \) and the high-\( T \) parts of the curves by the straight lines, the intersection is defined as a simulated glass-transition temperature. For PI bulk sample defined in this way, the value of \( T_g \) is equal to 286 ± 25 K (error bars are calculated by averaging over three independent samples). Fig. 8. It is much higher than the conventional experimental glass transition temperature, \( T_g = 199–204 \) K for PI bulk of molecular weight \( M = 0.62 \times 10^6 \) g/mol,85 due to the enormous difference between the simulated and the experimental cooling velocities. At the same time, the thermal expansion coefficient

\[
\alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)
\]

in the melt state, \( (5.7 \times 10^{-4} \) K\(^{-1}\), calculated at \( T = 400 \) K), is rather close to the available experimental data85 \( (6.6 \times 10^{-4} \) K\(^{-1}\) at \( T = 293 \) K). In a glassy state, the simulated value of the thermal expansion coefficient is much lower, \( 2 \times 10^{-4} \) K\(^{-1}\) at \( T = 200 \) K. We also observe a pronounced decrease of the thermal expansion coefficient when decreasing the film thickness, both in the melt and in the glassy state: for very thin 1.9 nm-film, the thermal expansion coefficient is equal to \( 3.5 \times 10^{-4} \) K\(^{-1}\) in the melt state at \( T \sim 400 \) K and to \( 1.3 \times 10^{-4} \) K\(^{-1}\) in the glassy state at \( T \sim 200 \) K.

For the film-averaged value of \( T_g \), no clear thickness dependence was observed, it fluctuates in the range from 270 K to 320 K. Nevertheless, for very thin, below 2 nm, films the averaged glass transition temperature is much larger as compared to that in a bulk (346 K vs. 286 K). This shift of the glass-transition temperature to larger values for very thin films reflects the importance of the ordered “glassy” layers close to the substrates. Their influence is becoming more important with decreasing the film thickness. Fig. 8(b) results show that the glassy behavior in the middle parts of the films is very close to that in a PI bulk, the density-temperature dependences for films’ middle parts and PI bulk are close to each other within error bars.

B. Orientational segmental dynamics

The orientational segmental-relaxation autocorrelation functions

\[
P_2(t) = \frac{1}{2} \left( 3(\mathbf{u}(t_0) \cdot \mathbf{u}(t + t_0))^2 - 1 \right)
\]

for unit vectors \( \mathbf{u} \) directed along the PI monomer have been calculated and averaged over three independent samples of films and bulk. Here, in (5), the angular brackets denote both
FIG. 8. The temperature dependence of the PI bulk and film densities, (a) the film-averaged PI density, PI films have the glass-transition temperatures from ∼270 K to ∼320 K. (b) PI film densities in the middle parts of the films. Straight lines in both panels show the linear fits used to extract the glass-transition temperature. In both panels, the simulated PI bulk glass-transition temperature, $T_g = 286$ K, is indicated by the solid vertical arrow. The dashed vertical arrow in (a) indicates the glass transition temperature of $T_g = 346$ K for the thinnest 0.8 nm-film.

time averaging over $t_0$, and the averaging over all equivalent vectors in the system. As can be seen, Fig. 9(a), the film-averaged segmental relaxation is slowed down in thin films as compared to bulk. Furthermore, the simulations show that segmental relaxation is slowed down with decrease of temperature (not shown).

To quantify the possible changes in polymer dynamics when approaching silica substrate, the polymer films have been split in 30 layers of equal width. It has been considered that a unit vector belongs to a specific layer if the Z coordinate of this vector belongs to this layer at $t = 0$. The substrate layer was defined as the second layer close to the substrate, the middle layer was defined as the 15th film layer. In order to extract the corresponding characteristic orientational relaxation times, the autocorrelation functions (5) were fitted with the Kohlraush-Williams-Watts (KWW) function

$$ P_2(t) = \alpha \exp \left( -\left( \frac{t}{\tau} \right)^\beta \right), $$

where $\alpha < 1$ is the prefactor which takes into account the initial, not-resolved short-time relaxation, $\tau$ is the characteristic relaxation time, $\beta$ is the stretching exponent which reveals the non-exponential character of the relaxation. Fig. 9(b) demonstrates that orientational autocorrelation functions relax slower in substrate layers in comparison with the film middle layers and PI bulk. This is also reflected in Fig. 10 where segmental relaxation times are plotted as functions of normalized distance from the substrate for different films. Clear slowing down is observed in the layers close to substrates, the
FIG. 10. Layer-resolved segmental relaxation times for unit vectors along the PI monomer for PI films of different thickness. Temperature is $T = 420$ K. Horizontal solid line shows the corresponding relaxation time for PI bulk, $\tau = 40$ ps, at the same temperature.

relaxation times are more than 150 times larger as compared to those in the film middles. This slowing down affects few layers in the proximity of silica substrate, and disappears toward the film middle part where the relaxation times are close to the corresponding values of PI bulk. Still, in spite of the fact that there are fast relaxation processes in the film middle, its overall relaxation is slower as compared to that in a bulk sample. Overall, the segmental relaxation in all film layers is shifted to larger times with decreasing the PI film thickness.

The orientational segmental relaxation has been analyzed further using the CONTIN method. The normalized distribution functions of segmental relaxation times

$$P_2(t) = \int_{-\infty}^{+\infty} F(\ln \tau) \exp(-t/\tau)d(\ln \tau)$$

have been calculated for PI bulk and films, averaged over all monomers, Fig. 11(a). For PI bulk, the segmental relaxation distribution function is very symmetric, reveals one single maximum around 40 ps at $T = 420$ K. For PI films of different thickness, the segmental relaxation is changing drastically. For thick films, the distribution function is becoming clearly asymmetric, its maximum shifts to larger relaxation times. With further decrease of the film thickness the distribution function of relaxation times is becoming bimodal, two relaxation processes are clearly visible, Fig. 11. The first peak, at about 100 ps at $T = 420$ K, is similar to that in a PI bulk. Its intensity is decreasing with the decrease of film thickness. The well-separated new, second peak, at about 3 ns, reflects the effect of the silica substrates. This resolved even better when the orientational autocorrelation functions for the middle PI-films layers only are analyzed, Fig. 11(b). For this analysis, the 6 layers in the middle of each PI film are taken. Comparing with the layer-resolved relaxation times shown in Fig. 10, we conclude that this second relaxation process at $\tau \sim 3$ ns is mainly due to the slow motions of PI segments in the first layers (about 10% of the whole film width) near the silica substrates. In these layers, the segmental relaxation takes place at times larger than 3 ns. These “slow” segments indirectly influence the segmental dynamics in the film middles. The CONTIN analysis indicates that the distribution function of the relaxation times for monomers in the substrate layers is again unimodal, but we must mention that it is rather difficult to produce the reliable results with CONTIN due to very slow relaxation of the $P_2$ functions in the substrate layers. The recent molecular-dynamics simulations of free-standing atactic polystyrene thin films also reveal that interfaces affect the segmental-relaxation processes. For example, it was shown that the $\beta$ relaxation is faster in the center of the polymer film as compared to the free surface; for the $\alpha$ relaxation an opposite trend was observed.

As has been pointed out in the literature, PI in bulk is characterized by two modes of relaxation. The normal mode is determined by the motions of only few monomer units,
and segmental mode describes the relaxation of the PI chain end-to-end distance. It is this normal mode which contributes mainly to the $P_2$ relaxation. Normal mode, due to the slow relaxation of the backbone end-to-end vector, does not influence significantly the simulated monomer $P_2$ relaxation. In the presence of confinement, the third, confinement-induced mode, has been observed experimentally due to the physical adsorption of the PI chains to silica substrate. The 3 ns peak in the distribution function of the $P_2(t)$ relaxation times in the film middle part can also be due to this confinement-induced mode. The thin glassy layer of monomers in the vicinity of the silica surface has been created due to the polymer-silica excluded-volume interactions, or due to some trapping of polymer segments in cages existing in the amorphous silica surface. This glassy layer definitely suppresses the segmental relaxation in PI film in comparison to the PI bulk.

V. CONCLUSIONS

The detailed, systematic molecular-dynamics simulation study of a non-crosslinked $(1,4)$ cis-PI melt confined between two amorphous silica surfaces has been presented. The structural and dynamical properties of the PI in films were demonstrated to depend on the distance from the surface. The structure of PI in films was analyzed calculating the chain size, chain shape, local segmental ordering, and density profiles in different film layers, and averaged over the whole film thickness. The PI structure in the middle of the films is similar to that in a PI bulk at the same conditions, whereas the silica substrate induces some ordering in the nearby PI layers. This ordering can be clearly distinguished in the PI density profiles where density increases close to the silica substrates. Calculation of the segmental ordering parameter, averaged radius of gyration, and components of the gyration tensor of PI chains allowed us to check that the preferable orientation of the PI monomers is in the plane of the substrate. We have also shown the shift of the film-averaged value of the glass-transition temperature $T_g$ to larger values for very thin (below 2 nm) films.

The orientational segmental dynamics was investigated through the analysis of the bond-vectors relaxation. It was shown that the averaged film-averaged segmental relaxation is slowed down in thin films as compared to PI bulk, and the segmental relaxation of the film middle parts is close to the corresponding values in PI bulk. The slowing down of the segmental mobility is caused by the substrates, where the relaxation times can be few orders of magnitude larger due to PI-silica non-bonded interactions and due to the trapping of PI monomers in the cages. Thus, the existence of the glassy layers suggested in the previous studies of polymer nanocomposites was confirmed for the present model.

The normalized distribution functions of segmental relaxation times for PI bulk and films, averaged over all monomers, have been calculated. With the decrease of film thickness the additional relaxation process appears which is absent in a PI bulk, and the distribution function becomes bimodal. It can be attributed to the slow motions of PI segments close to the silica substrates. Furthermore, these “slow” segments indirectly influence the segmental dynamics in the middle of the film. These results are in a good agreement with existing literature data which show that in PI films, the third, confinement-induced mode exists. This mode is due to the physical adsorption of the PI chains to silica substrate and is absent in a bulk where only two relaxation modes appear, the normal mode determined by the motions of few PI monomers and the segmental mode from the relaxation of the chain end-to-end vector.

The study of the cross-linked PI samples with realistic coupling and covering agents in PI-silica films is in progress now, in order to quantify their role in segmental dynamics, also under the influence of mechanical deformation. The latter is important to clarify the atomistic nature of the Payne effect.

ACKNOWLEDGMENTS

The fruitful discussions with M. A. J. Michels, D. N. Theodorou, J.-Y. Delannoy, A. V. Chertovich, P. G. Khalatur, A. V. Berezkin, and C. Batistakis are gratefully acknowledged. We would like to thank J. R. Rustad for his help in preparation of under-coordinated silica surfaces. A.V.L. and D.V.G. acknowledge the FP7-NMP-2011-EU-RUSSIA program CompannoComp, Grant Agreement No. 295355. F.V.K. acknowledges the FP7 EU-Russia coordinated project “Multiscale computational approach to the design of polymermatrix nanocomposites,” Contract No. 16.523.12.3001. The simulations have been performed using the computational resources of the Research Computing Center at Lomonosov Moscow State University.