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Time Scales and Mechanisms of Relaxation in the Energy Landscape of Polymer Glass under Deformation: Direct Atomistic Modeling

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Molecular-dynamics simulation is used to explore the influence of thermal and mechanical history of typical glassy polymers on their deformation. Polymer stress-strain and energy-strain developments have been followed for different deformation velocities, also in closed extension-recompression loops. The latter simulate for the first time the experimentally observed mechanical rejuvenation and overaging of polymers, and energy partitioning reveals essential differences between mechanical and thermal rejuvenation. All results can be qualitatively interpreted by considering the ratios of the relevant time scales: for cooling down, for deformation, and for segmental relaxation.

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In the macroscopic deformation of polymer glass formers striking differences occur between polymers of similar topology. For example, tensile-testing experiments [1] reveal that atactic polystyrene (PS) has little plastic deformation before brittle failure, while (bis)phenol-A polycarbonate (PC) withstands significant strains. PS exhibits substantial strain softening as compared to PC, but the amount of strain softening is influenced by the thermal history of the material (quenched or annealed) and/or mechanical predeformation. It was shown recently [2] that after mechanical rejuvenation both PS and PC become very ductile and can be made to deform by shear yielding.

Severe post-yield strain softening for PS is usually connected to the process of structural relaxation (or "physical aging") [3]. After the yield point the stress drops to a value which is independent of aging time, and it was concluded that mechanical extension erases the polymer thermal history [4]. Calorimetry [5] and positron-annihilation lifetime spectroscopy [6] above the yield point show that yielding does not rejuvenate the polymer material, but brings it to a different "equilibrium state." This is seen also for colloidal glasses [7], and is a generic consequence of a rugged energy landscape [8]. In [9] it was shown that mechanical preconditioning strongly reduces the amount of strain softening. In [10,11] simulations of aging and rejuvenation were carried out for the first time for a noncrystallizing binary Lennard-Jones mixture, showing [11] in particular differences between mechanical rejuvenation and reversed aging. Nevertheless, a molecular understanding of aging via structural relaxation and strain softening is still lacking, and even more so for polymers. The sum of the aging and deformation times compared to the internal relaxation time is what finally determines the yield stress of low-molecular-weight glasses, as has been shown recently by molecular-dynamic (MD) simulations [12].

In this Letter we perform direct atomistic MD modeling of the processes of deformation, mechanical rejuvenation, and overaging (acceleration of aging) for the two mentioned typical polymer glass formers, which differ in the time scales of their segmental relaxation, in each case we prepared different thermal histories (annealing and quenching). We will show that the differences observed under deformation can be understood in terms of the ratios of three different characteristic time scales: τ_c, the characteristic time of cooling down from high-temperature melt, τ_β, the relaxation time of segmental motions within the cage formed by the neighboring polymer segments, and, finally, τ_y, the time to reach the yield peak. We will also show that mechanical and thermal rejuvenation involve different segmental processes, and are indeed different, in agreement with recent experimental observations [5].

Models and simulation procedure.—United-atom models for nonentangled polymer melts are used; they have been described in detail by Lyulin *et al.* [13,14]. Briefly, constant temperature-pressure NPT MD simulations are carried out for a system of 4–8 atactic PS chains of $N = 80\text{–}160$ monomers each, and 64 PC chains of $N = 10$ monomers. The size of the PS and PC samples is comparable to or even larger than the samples of the previous computational studies [11] for much simpler models. A Berendsen barostat and a collisional thermostat have been used. Five independent samples are created for each polymer and the final results are averaged. The samples are equilibrated at $T = 540$ K (highly mobile melt) for 10 ns. The quality of the equilibration is checked by standard methods.

After equilibration continuous cooling is implemented, with cooling rates spanning more than three decades in time: from more than 30 K/ps (simulated quenching) to 0.01 K/ps (simulated annealing). These cooling rates are extremely fast from an experimental point of view. However, the glass-transition temperature increases only logarithmically with cooling rate [14], and realistic values

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of T_g can be obtained by extrapolating the simulated data towards experimental cooling rates. The PS and PC samples are cooled down to the corresponding glass-transition temperatures ($T_g = 375$ K for PS and $T_g = 435$ K for PC) [14], and to the room temperature $T = 300$ K. The 4×160 PS system is also cooled down to $T = 260$ K, with two different cooling rates: above 30 K/ps (quenching) and 0.05 K/ps (annealing).

Effect of cooling protocol.—In Fig. 1 the evolution of the difference in the internal energy between the initial ($T = 540$ K) melt and the final ($T = 300$ K) glass is shown. For both polymers the energy difference is largest with slowest cooling, in agreement with an energy-landscape presentation [8] where the polymer is allowed to explore deeper energetic minima when cooled down slower. For both polymers there is only a small difference in final internal energy for glasses produced with cooling rates of 0.01–0.1 K/ps. The energy difference is much more severe for faster cooling, above these rates. This allows us to distinguish typical annealed samples (slow cooling, relaxed in energy) from quenched samples (fast cooling, not relaxed in energy).

For both *nondeformed* polymers the distribution functions of the segmental orientational relaxation times [15] reveal the existence of two different processes: relaxations within the cage, β motions, and α relaxation of the cage itself. This picture is universal for orientational motions of different polymer segments, but there is one important difference between the two polymers. At $T = 260$–300 K the simulated β relaxation for PS monomers is rather fast (time scale τ_β is about 50 ps), and is well separated from the α relaxation (time scale τ_α above 100 ns). The simulated β relaxation for PC monomers is slower, τ_β is about 500 ps; α relaxation for PC occurs approximately at the same times as for PS. As is clear from Fig. 1 it is these β motions that distinguish well-annealed samples from quenched samples. In the energy-landscape picture (energetic profile as a function of some coordinate for β motion) the β relaxation (aging kinetics) during annealing leads to a rugged energy landscape, with well-developed deep minima, separated by rather large barriers. The final minima are deeper for PC: the energy difference between annealed and quenched PC is 0.9 kJ/mol as compared to 0.5 kJ/mol for PS. For both polymers α processes do not contribute much to the development of the energetic landscape as τ_α is an order of magnitude above the slowest cooling time. Other relaxation processes (not accessible by our simulations) will further deepen the energetic minima, and again compete with longer cooling times. For our quenched polymers even β processes cannot relax on our time scale of cooling, $\tau_{c,q}/\tau_\beta \ll 1$, and the corresponding energetic landscape for both polymers is relatively smooth.

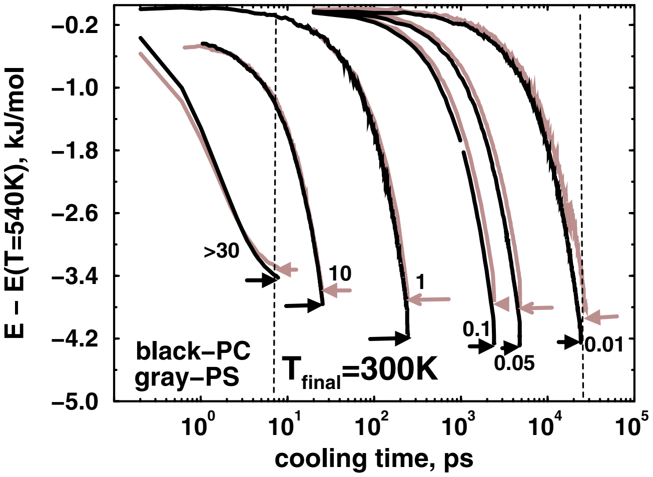

FIG. 1 (color online). The internal energy for PS and PC cooled down with different cooling rates from $T = 540$ K. Numbers indicate cooling velocity in K/ps, arrows indicate final state at the end of the cooling. Cooling times τ_c for annealed (right) and quenched (left) samples are shown by dashed lines.

Uniaxial deformation.—Uniaxial deformation is applied with different deformation velocity (from 0.05 to 0.0005 Å/ps) at $T = 260$–300 K to polymer samples prepared by the cooling procedure explained above. The deformation was simulated in the *NPT* ensemble, with the same barostat and thermostat as earlier, and was applied along one of the Cartesian axes (X, Y, or Z) to each of the five samples for each polymer. The deformation rate (normalized by the characteristic size of the initial sample in the undeformed state, about 50 Å) is very large (10^9–10^7 s^{-1}) compared to experimental values. However, on a macroscopic level both deformation times and relaxation times will scale up, the latter because additional slower sub-T_g polymer relaxational processes, not accessible by the present simulation, will show up, and should be taken into account. Notice nevertheless that the slowest deformation rates implemented here are lower than or comparable to those of previous simulation studies [16]. In Fig. 2 quenched and annealed samples of PS and PC are uniaxially deformed with the deformation rate of 10^8 s^{-1}. The characteristic time τ_y to reach the yield peak, in this case 1 ns, is introduced.

Annealed glasses.—For both polymers the yield stress is well developed and it is higher for PS; moreover, pronounced strain softening is observed for PS. This softening is very weak for annealed PC. These differences are also observed in macroscopic experiments [14]. In the absence of deformation no additional aging on the time scale of simulation has been observed for both annealed polymers, Figs. 2(c) and 2(d). In each case some increase of energy under deformation becomes pronounced just close to the yield peak.

For both polymers the time for annealed cooling, $\tau_{c,a} = 25$ ns, is much larger than either the relaxation time $\tau_\beta = 50$–500 ps of the β processes or the time $\tau_y = 1000$ ps. Using the energy-landscape framework [8], we conclude that the initial local structure is well relaxed due to these β

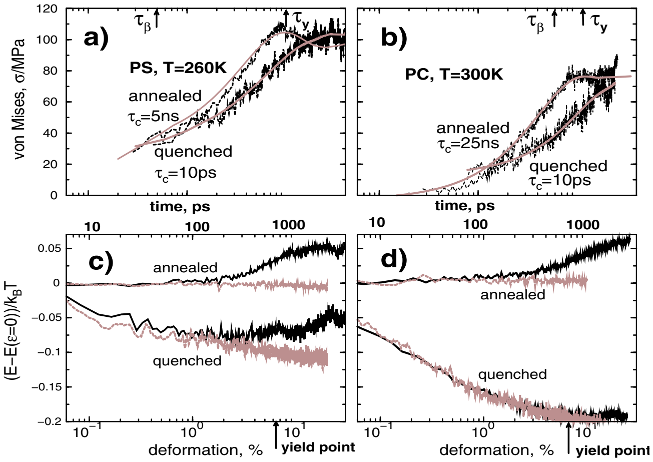

FIG. 2 (color online). von Mises [10] stress-strain [(a),(b), with solid gray lines as guides to the eye] and energy-strain [(c),(d), black lines)] dependencies for PS (4×160 melt) at $T = 260$ K (left) and PC at $T = 300$ K (right), with different thermal histories. Gray (black) cooling (τ_c), deformation (τ_y), and relaxation (τ_β) times are indicated. Deformation velocity is 0.005 Å/ps.

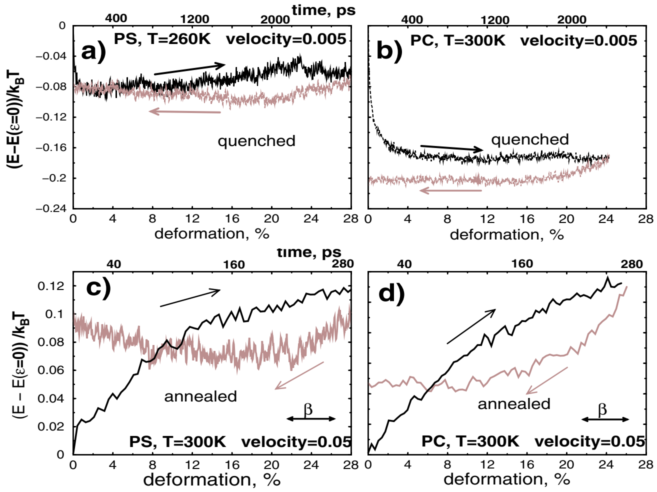

FIG. 3 (color online). Energy evolution during closed deformation-recompression loops, for quenched (a),(b) and for annealed (c),(d) polymers. Temperatures and deformation velocities (in Å/ps) are indicated. Results demonstrate mechanical overaging (a),(b) and rejuvenation (c),(d). Horizontal arrows indicate the time scales of the β processes.

processes, and the resulting minima will add to the barriers for forced cage-to-cage α motion under deformation. The barrier crossing will lead to softening. Experimentally both annealed polymers show this softening, but the effect is more pronounced for PS than PC. This is substantiated by our results, and is likely due to the much faster β relaxation back (which restores the deep energetic minima) for PS during constant-rate deformation: $\tau_\beta/\tau_y = 0.05$ for PS and 0.5 for PC; additionally, deformation may lead to a different conformation and energy partitioning than met in free β relaxation, with associated additional barriers to be crossed (see below).

Quenched glasses.—For both polymers the yield stress is much lower as compared to the case of annealing, and the softening is absent, Fig. 2. Moreover, there is pronounced aging (energy relaxation), with and without deformation. For quenched PC (in contrast to PS) deformation has no effect on aging: up to 2000 ps (or 20% strain, well above the yield strain) aging under deformation coincides with aging in the absence of deformation. Again, these observations can be placed against the time scales involved. The time of quenching, $\tau_{c,q} = 10$ ps, is smaller than either β relaxation time, so the initial energetic landscape is smoother and indeed softening is absent. For both polymers no energy difference (with or without deformation) is visible on times $t < \tau_\beta$, while the energy drops are comparable to those in cooling (with a larger one for PC); the polymer relaxes its energy while adapting to the deformation without buildup of an elastic barrier.

Overaging of quenched samples.—In Figs. 3(a) and 3(b) the time evolution of the internal energy of the quenched polymers ($\tau_c/\tau_\beta = 0.2$ and 0.02 for PS and PC, respectively) under large extension, as shown in Fig. 2, is followed by the evolution under recompression with the same but reversed velocity. The extension-recompression loops lead at these deformation rates ($\tau_y/\tau_c = 100$) to significant reduction of the internal energy, i.e., to overaging. This effect (0.5 kJ/mol for PC compared to 0.2 kJ/mol for PS) is more than twice stronger for PC than PS. PS (small τ_β) shows an initial relaxation on a short time scale, but both in extension and compression new elastic energy barriers seem to appear, which again may be due to nonequilibrium conformations and energy partitioning. Both in tension and compression the energy of quenched PC relaxes on the time scale τ_β, after which the polymer seems to have obtained a configuration for steady flow.

Rate-dependent rejuvenation of annealed samples.—Extension-recompression loops have also been applied to annealed samples of PS and PC at room temperature and with velocities of 0.05 Å/ps, Figs. 3(c) and 3(d), and 0.005 Å/ps (not shown). The energy at maximum strain strongly increases with strain rate, i.e., with τ_y^{-1}; this is logical since in all simulations τ_y (time for forced out-of-cage-motion) is much smaller than the time τ_α (time for cage relaxation), and α processes are unable to relax the corresponding barrier for this out-of-cage motion. The energy after recompression is a combination of energy increase by forced out-of-cage motion, and possible energy recovery under β relaxation. For annealed PS it is significantly higher than the original energy, so the polymer appears "rejuvenated." Upon recompressing PS relaxes its energy on the time scale of the β motion, 50 ps, after which the energy increases again since new barriers will have formed; the "rejuvenating" PS will thus explore a different part of phase space (see below). For annealed and

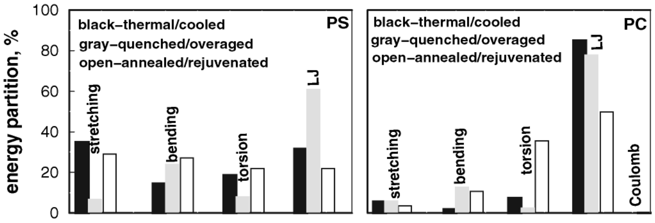

FIG. 4. Partitioning of the final-energy difference for three cases ($T = 300$ K): quenching versus annealing; quenching versus additional mechanical overaging (deformation velocity 0.05 Å/ps); annealing and mechanically rejuvenation (deformation velocity 0.005 Å/ps) versus annealing. Mechanical extension-recompression loops may bring the polymers in different parts of phase space; however, for PC mechanical overaging resembles thermal aging in terms of energy partitioning. LJ stands for the Lennard-Jones energy.

stretched PC under the same deformation velocity the recompression time is shorter than the time of β motion, 500 ps, and no significant new barriers seem to appear. At the lowest deformation velocity the annealed and stretched PC even decreases in energy after recompression (not shown); i.e., it overages, also due to the low energy at maximum strain. Such an overaging is observed in recent experiments on PC under long-term loading [17] and in simulations of a binary Lennard-Jones liquid [11].

Thermally versus mechanically rejuvenated glasses.— Partitioning of the energy between different force-field contributions clearly shows that the energy differences upon cooling (quenched minus annealed), or mechanical rejuvenation (end-of-loop minus annealed), or overaging (quenched minus end-of-loop) may be very different; see Fig. 4. For PC the thermal rejuvenation is for more than 80% due to weaker van der Waals interactions, while the difference after a mechanical rejuvenation is for about 40% due to increased torsion of the chains. The partitioning of the energy for mechanically overaged initially quenched PC is very similar to the partitioning of the energy for thermally rejuvenated polymer, so β relaxations may indeed play the same role in both. For PS the in-monomer (stretching, bending, torsion) and intermonomer (van der Waals) contributions are roughly equally partitioned. In their recently reported MD simulations of a model polymer glass, Capaldi *et al.* [16] also observed pronounced changes in the torsional energy under the deformation. The much more diverse partitioning for PS in the various simulations indeed points at exploration of different parts of phase space.

Summary.—For the first time we have simulated on detailed atomistic level cooling and deformation for two typical glassy polymers with different mechanisms of their in-cage segmental motions. The main message of our study is that differences in stress-strain and energy-strain curves between the polymers could be interpreted in terms of ratios between the relevant time scales: the times for cooling down from the high-temperature melts, the times for deformation up to the yield point (forced out-of-cage motion), and the β-relaxation times. The results give insight into the energy landscapes and relaxation mechanisms of the deforming polymer glasses, in terms of differences between quenched and annealed samples, between deformations at different rates, and between thermal and mechanical rejuvenation. Qualitatively these conclusions can be translated towards upscaled experimental conditions. We believe that the direct modeling of the energetic landscape should be performed next.

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