

Notes

Viscoelastic Properties of Polybutadiene in the Glassy Regime from Molecular Dynamic Simulations

Oleksiy Bytner and Grant D. Smith*

Department of Chemical and Fuels Engineering and
Department of Materials Science and Engineering,
122 S. Central Campus Drive Rm. 304, University of Utah,
Salt Lake City, Utah 84112

Received April 2, 2001

Revised Manuscript Received July 30, 2001

Introduction

A thorough understanding of the dynamic–mechanical properties of polymer melts and glasses is key to many, if not most, applications of polymers as well as to the processing of polymers. It is well-known that amorphous and semicrystalline polymers exhibit viscoelastic response to an applied stress or strain. For a small constant shear strain γ the shear stress is proportional to the strain and is given by the stress relaxation equation¹

$$\sigma(\gamma, t) = G(t)\gamma \quad (1)$$

The constant of proportionality, $G(t)$, is by definition the time-dependent shear stress relaxation modulus. Alternatively, we may be interested in the response of the material to an oscillatory shear strain $\gamma^*(\omega t) = \gamma_0 \exp(-i\omega t)$ ¹

$$\sigma^*(\omega t) = G^*(\omega) \gamma^*(\omega t) \quad (2)$$

The complex shear modulus is related to the shear stress relaxation modulus through the transform¹

$$G^*(\omega) = G'(\omega) + iG''(\omega) = i\omega \int_0^\infty e^{-i\omega t} G(t) dt \quad (3)$$

The relaxation of melts of linear polymer chains shows distinctive regions,¹ illustrated in Figure 1 for polybutadiene (PBD), that can be identified as (i) the flow regime at low frequencies (denoted as the “terminal zone”), (ii) the entanglement regime at intermediate frequencies (“plateau zone”), (iii) transition regime toward the glass, and (iv) the glassy regime. Currently, atomistic MD simulations can cover a time domain of 10^{-3} – 10^5 ps, which for PBD at room temperature corresponds to the glassy regime and part of the transition zone, and this only for unentangled melts. However, we recently² described how reptation models^{3–5} utilizing properties obtained from MD simulations can be used to predict the linear viscoelastic behavior of entangled polymers. By performing atomistic simulations on an ensemble of PBD chains below the entanglement molecular weight using a well-validated quantum chemistry force fields, we were able to predict with chemical accuracy the dynamical–mechanical proper-

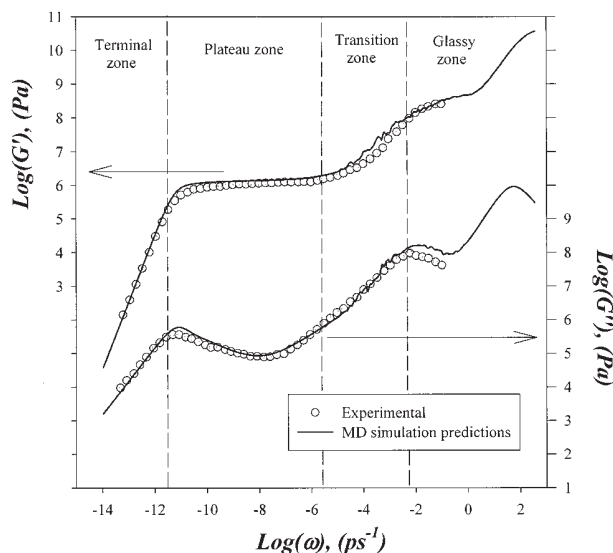


Figure 1. Dynamic regimes of the frequency-dependent complex shear modulus of polybutadiene ($M_w = 1.3 \times 10^5$ Da). The storage modulus G' and loss modulus G'' of polybutadiene at 298 K from experiment and simulation/theory are shown.

ties of an entangled PBD melt (1.3×10^5 Da) inaccessible to direct MD simulations.² We also find good agreement with experiment for the viscosity of PBD melts at zero shear rate over a wide range of molecular weights and at different temperatures, again based on properties of the unentangled melt obtained from simulation.⁶ In these studies the rheological properties of the entangled PBD melts were determined using properties (monomer friction, density, and persistence length) obtained from simulations of unentangled melts. This allows prediction of the dynamic shear modulus utilizing reptation theory with the exception of the glassy behavior, which is based upon an empirical correlation due to Davidson and Cole.⁷ In this paper we demonstrate how the high-frequency (glassy) behavior of the polymer can be determined directly from equilibrium MD simulations.

Methodology

The zero shear rate shear viscosity η can be evaluated by means of standard equilibrium MD simulations using the Green–Kubo expression,⁸ which involves the time autocorrelation function (ACF) of the off-diagonal elements of the stress tensor σ . For a material occupying a volume V at temperature T , one has

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle dt \quad (4)$$

where $\langle \dots \rangle$ denotes an equilibrium average over phase space including circular permutations. η is also given

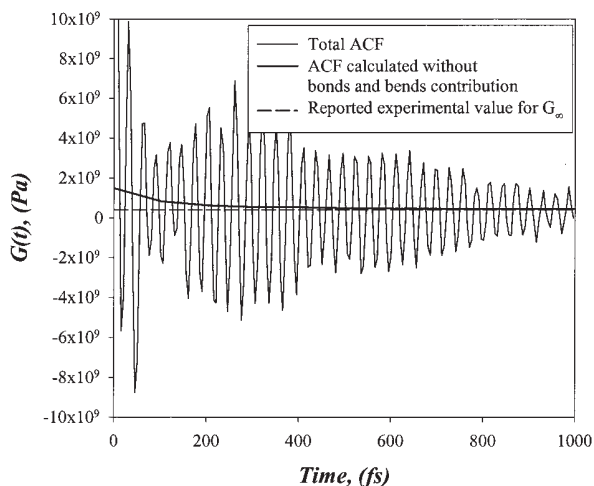


Figure 2. Stress tensor autocorrelation function for unentangled polybutadiene at 298 K from simulation. The solid thin line includes contributions from all modes. The solid thick line shows the ACF computed from the same trajectory excluding contributions from stretching and bending modes. The horizontal dashed line is the experimental glassy modulus of polybutadiene at 298 K.

as the time integral of the shear stress relaxation modulus³

$$\eta = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} = \int_0^{\infty} G(t) dt \quad (5)$$

Hence, the shear stress relaxation modulus is given by

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle \quad (6)$$

We performed MD simulations of a PBD melt using the quantum chemistry based potential described elsewhere.^{9,10} An ensemble of 40 random copolymer chains each comprised of 30 units with a microstructure of 40%/50%/10% 1,4-cis/1,4-trans/1,2-vinyl monomers was generated. Each chain consisted of 114 backbone carbons (BD₁₁₄), which is slightly below the entanglement molecular weight for this polymer.¹¹ All the simulations considered here were performed in the NVT ensemble at 298 K at a density yielding an average pressure of 1 atm. A detailed description of the MD methodology as applied to PBD can be found in our previous work.^{9,10,12} A time step of 0.3 fs was utilized, and stress tensor output was made every 1.0 fs in order to accommodate high-frequency bond vibrations.

Simulation Results and Comparison with Experiment

The stress tensor ACF calculated from a 200 ps simulation of PBD is shown in Figure 2. The ACF exhibits high-frequency oscillations with an amplitude at least 1 order of magnitude greater than the reported value of the PBD glassy modulus G_{∞} at this temperature,¹³ also shown in Figure 2. These high-frequency oscillations correspond to the harmonic stretching and bending deformations of the polymer molecules. This is illustrated by comparing the stress tensor ACF with that obtained when the bond and bend contributions to the virial are excluded, as shown in Figure 2. Capturing the high-frequency contributions of the bond stretching deformations to the dynamic-mechanical behavior is

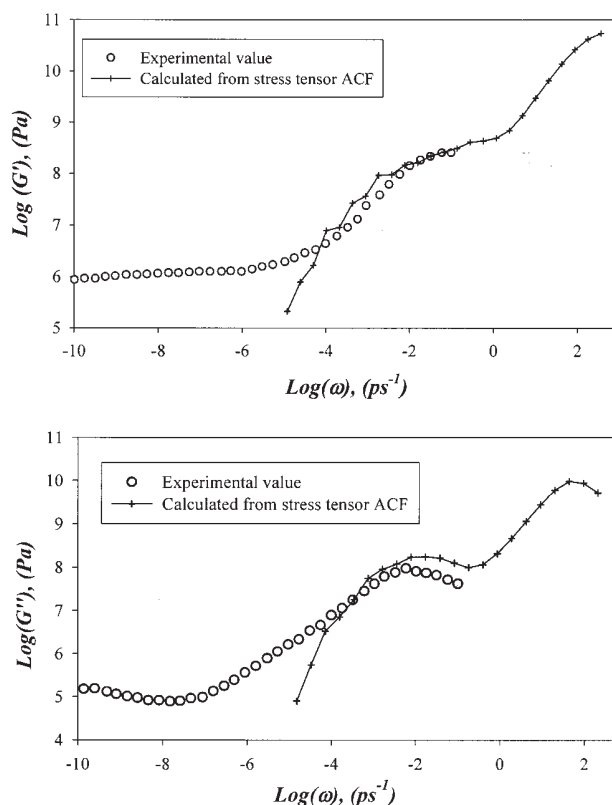


Figure 3. Components of the complex shear modulus of polybutadiene at 298 K from simulations of the unentangled melt. Shown for comparison are the storage and loss modulus from experiment for a $M_w = 1.3 \times 10^5$ Da polybutadiene at the same temperature.

computationally expensive because of the small time integration step and high frequency of data output required. Since the dynamic-mechanical response of the material in this frequency regime (> 20 ps⁻¹) is typically inaccessible experimentally and bond stretching does not significantly influence the dynamic-mechanical properties of the polymer at lower frequencies, we performed more extensive simulations with constrained bonds using the SHAKE algorithm,¹⁴ while other internal degrees of freedom (valence angle bends and torsions) remained flexible. This allowed us increase the simulation time step to 1.0 fs and decrease stress tensor output to every 50 fs. In addition, the amplitude of bond stretching motions in organic polymers is typically poorly represented in classical simulations due to the dominance of zero-point vibrational effects in the real (quantum) system.¹⁵ Consequently, MD simulations will not accurately reproduce contributions of these motions to the modulus of the polymer.

In Figure 3 the components of the complex shear stress modulus $G'(\omega)$ and $G''(\omega)$ obtained from applying eqs 3 and 6 for a 10 ns simulation are compared to the experimental values measured for PBD of high molecular weight (1.3×10^5 Da).¹⁶ Very good agreement with experiment can be seen in the glassy regime, including the glassy modulus and the frequency of maximum loss. At the lower frequencies accessible from MD simulations (transition zone) deviation from experiment resulting from the low molecular weight of simulated polymer, which does not exhibit a reptation or plateau zone, can be seen. Combining the glassy regime behavior obtained directly from simulation of the unentangled chains with

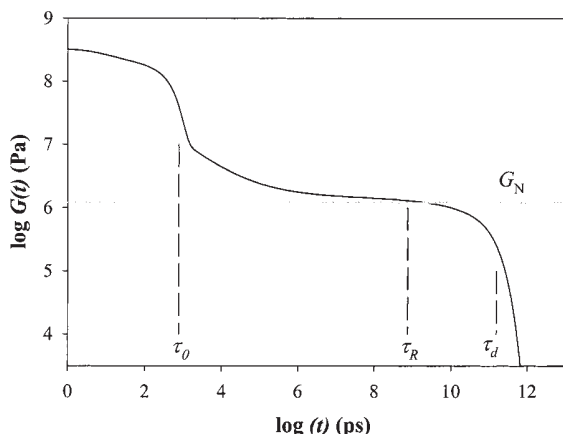


Figure 4. Shear relaxation modulus for a $M_w = 1.3 \times 10^5$ Da polybutadiene at 298 K from simulation/theory. Three characteristic time are shown: (i) $\tau_0 = 1/\omega_{\max}$ glass relaxation corresponding to the high-frequency maximum of the loss modulus, (ii) τ_R = Rouse time, and (iii) τ_d = longest relaxation time for the entangled polymer. Also is shown the experimental value of the plateau modulus G_N .¹⁷

the predictions of the Milner–McLeish⁵ model calculated previously using properties obtained from simulation,² we obtain quite good agreement with experiment for the storage and loss modulus over a wide range of frequency, as illustrated in Figure 1. A reverse transform of the complex modulus yields the stress relaxation modulus shown in Figure 4, again obtained entirely from properties gleaned from simulations of an unentangled melt.

Conclusions

We have shown that the viscoelastic behavior of PBD in the glassy regime can be accurately obtained directly from an equilibrium molecular dynamics simulation of an ensemble of unentangled chains. Combined with the predictions of reptation theory using parameters obtained entirely from MD simulation, we can predict,

using only properties obtained from equilibrium simulations of the unentangled melt, the linear viscoelastic response of a highly entangled polybutadiene over the entire range of experimentally accessible times and frequencies.

Acknowledgment. This research is funded in part by the University of Utah Center for the Simulation of Accidental Fires and Explosions (C-SAFE), by the Department of Energy, Lawrence Livermore National Laboratory, under Subcontract B341493, and by the American Chemical Society, Petroleum Research Fund, through Grant G7-301.

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MA0105690