Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information

A hybrid Brownian dynamics/constitutive model for yielding, aging, and rejuvenation in deforming polymeric glasses

Weizhong Zou[#], and Ronald G. Larson[#*]

 # Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109
****Correspondence: email: rlarson@umich.edu, phone: (734) 936-0772***

Equations of bead-spring chain. In this supplementary material, the dimensionless governing equation of bead motion, i.e., Eq. (4a) in the main text, are derived in details as below:

The movement of beads j and $j-1$ of a bead-spring chain shown in Fig. S1 are given by Eq. (3a):

$$\begin{cases} \zeta_b \dot{r}_j = \zeta_b (\nabla v)^T \cdot r_j + F_j^{sp,t} + F_j^R \\ \zeta_b \dot{r}_{j-1} = \zeta_b (\nabla v)^T \cdot r_{j-1} + F_{j-1}^{sp,t} + F_{j-1}^R \end{cases} \qquad (S1)$$

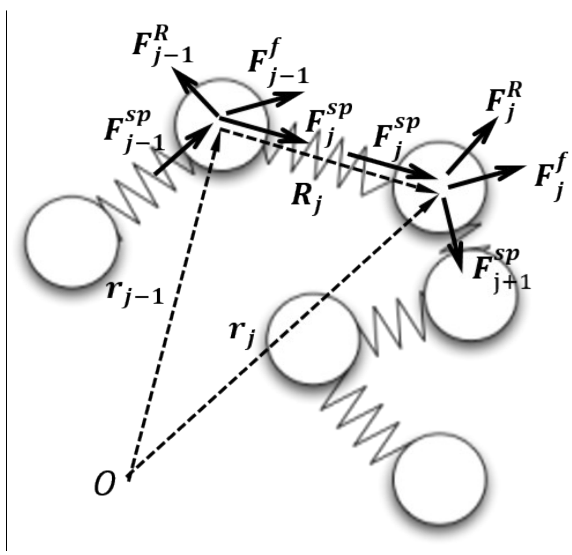

Fig. S1 Illustration of bead-spring chain and the forces exerted on beads j and $j-1$. Note that F_j^f is the friction force defined as $F_j^f = \zeta_b (\nabla v)^T \cdot r_j$

From Fig. S1, we have $R_j = r_j - r_{j-1}$ and $F_j^{sp,t} = F_{j+1}^{sp} - F_j^{sp}$; thus

$$\begin{aligned} \zeta_b(\dot{r}_j - \dot{r}_{j-1}) = \zeta_b (\nabla v)^T \cdot (r_j - r_{j-1}) + \left(F_j^{sp,t} - F_{j-1}^{sp,t}\right) + \left(F_j^R - F_{j-1}^R\right) \\ \zeta_b \dot{R}_j = \zeta_b (\nabla v)^T \cdot R_j + \left(F_{j+1}^{sp} + F_{j-1}^{sp} - 2F_j^{sp}\right) + \left(F_j^R - F_{j-1}^R\right) \end{aligned} \qquad (S2)$$

According to Eqs. (2) and (3b):

$$F_j^{sp} = \frac{3k_BT}{N_{K,sp}b_K^2}\frac{R_j}{1-\left(|R_j|/R_0\right)^2},\ \ R_0 = N_{K,sp}b_K,\ \ N_{K,sp} = \frac{N_K}{N_{sp}},\ \ F_j^R = \sqrt{\frac{6k_BT\zeta_b}{\Delta t}}n_j$$

We substitute the above expressions into Eq. (S2), yielding:

$$\zeta_b\frac{\Delta R_j}{\Delta t} = \zeta_b(\nabla v)^T\cdot R_j + \frac{3k_BT}{N_{K,sp}b_K^2}\left[\frac{R_{j+1}}{f(R_{j+1})} + \frac{R_{j-1}}{f(R_{j-1})} - \frac{2R_j}{f(R_j)}\right] + \sqrt{\frac{6k_BT\zeta_b}{\Delta t}}(n_j - n_{j-1})\ \ (S3)$$

where $f(R_j) = 1-\left(|R_j|/R_0\right)^2$.

And for the polymeric stress,

$$\Sigma^p = \nu\left\langle\Sigma_j^{N_{sp}}R_jF_j^s\right\rangle = \frac{3\nu k_BT}{N_{K,sp}b_K^2}\left\langle\Sigma_j^{N_{sp}}R_jR_j/f(R_j)\right\rangle \qquad (S4)$$

Replacing R_j with the corresponding dimensionless variable $\tilde{R}_j = R_i/\sqrt{N_{K,sp}}b_K$, Eqs. (S3) and (S4) can be rewritten as:

$$\begin{cases}\Delta\tilde{R}_j = (\nabla v)^T\cdot\tilde{R}_j\Delta t + \frac{3\Delta t}{\tau_{sp}}\left[\frac{\tilde{R}_{j+1}}{f(\tilde{R}_{j+1})} + \frac{\tilde{R}_{j-1}}{f(\tilde{R}_{j-1})} - \frac{2\tilde{R}_j}{f(\tilde{R}_j)}\right] + \sqrt{\frac{6\Delta t}{\tau_{sp}}}(n_j - n_{j-1}) \\ \Sigma^p = 3\nu k_BT\left\langle\Sigma_j^{N_{sp}}\tilde{R}_j\tilde{R}_j/f(\tilde{R}_j)\right\rangle\end{cases} \qquad (S5)$$

where $f(\tilde{R}_j) = 1-\left(|\tilde{R}_j|/\tilde{R}_0\right)^2,\ \tilde{R}_0 = \sqrt{N_{K,sp}},\ and\ \tau_{sp} = \zeta_bN_{K,sp}b_K^2/k_BT$.

Since for chains in equilibrium, $\Sigma^p = 0$, and otherwise $\Sigma^p = G^p(\sigma^p - I)$, we have

$$\Sigma^p = G^p\left\{\frac{\left\langle\Sigma_j^{N_s}\left[\tilde{R}_j\tilde{R}_j/f(\tilde{R}_j)\right]\right\rangle}{\left\langle\Sigma_j^{N_s}\left[\tilde{R}_j\tilde{R}_j/f(\tilde{R}_j)\right]\right\rangle_{eq}} - I\right\},\ \ G^p = 3\nu k_BT \qquad (S6)$$

Simulation algorithm. Here we describe our procedure for combining our bead-spring Brownian dynamics simulation results into specific types of deformation, i.e., uniaxial extension and simple shear, in either steady deformation or creep.

Under homogeneous deformation, $\nabla\cdot\sigma = 0$, the original upper-convective Maxwell equation for segmental dynamics (Eq. (5)) can be simplified as:

$$\begin{cases} \dot{\sigma}^s = \sigma^s \cdot \nabla v + (\nabla v)^T \cdot \sigma^s - (\sigma^s - I)/\tau^s \\ \dot{\tau}^s = 1 - \lambda(\tau^s - \tau_0^s), \ \ \lambda = \mu\sqrt{2tr(D \cdot D)} \\ \Sigma^s = G^s(\sigma^s - I), \ \ \tau^s|_{t=0} = t_W \end{cases} \qquad (S7)$$

If we assume the external stress is applied along the z direction, then the detailed form of deformation rate tensor D is given as:[1]

For uniaxial extension:

$$D = \nabla v = \begin{bmatrix} \dot{\varepsilon}_x & 0 & 0 \\ 0 & \dot{\varepsilon}_y & 0 \\ 0 & 0 & \dot{\varepsilon}_z \end{bmatrix} \qquad (S8.1)$$

For simple shear:

$$\nabla v = \begin{bmatrix} 0 & 0 & \dot{\gamma}_{xz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \ \ D = \begin{bmatrix} 0 & 0 & \dot{\gamma}_{xz}/2 \\ 0 & 0 & 0 \\ \dot{\gamma}_{xz}/2 & 0 & 0 \end{bmatrix} \qquad (S8.2)$$

where $\dot{\varepsilon}_x$, $\dot{\varepsilon}_y$, and $\dot{\varepsilon}_z$ are the extension rates in x, y, z directions, and $\dot{\gamma}_{xz}$ is the simple shear rate in xz plane.

The condition of incompressibility, i.e., $tr(\nabla v) = 0$, implies

For uniaxial extension:

$$\dot{\varepsilon}_x = \dot{\varepsilon}_y = - \dot{\varepsilon}_z/2 = \dot{\varepsilon} \qquad (S9.1)$$

For simple shear:

$$\dot{\gamma}_{xz} = \dot{\gamma} \qquad (S9.2)$$

Therefore, application of our simulation model to the above two types of deformations is accomplished by substituting the above expressions into Eqs. (4a) and (S7). Since for both cases, the deformation in the y direction is the same as in the x direction, Eq. (S7) can be rewritten in a scalar form with only x and z components, i.e.,

For uniaxial extension:

$$\begin{cases} \dot{\sigma}_{zz}^s = 2\dot{\varepsilon}\sigma_{zz}^s - (\sigma_{zz}^s - 1)/\tau^s \\ \dot{\sigma}_{xx}^s = - \dot{\varepsilon}\sigma_{xx}^s - (\sigma_{xx}^s - 1)/\tau^s \\ \dot{\tau}^s = 1 - \mu(\tau^s - \tau_0^s)\sqrt{3}|\dot{\varepsilon}| \end{cases} \qquad (S10.1)$$

For simple shear:

$$\begin{cases} \dot{\sigma}_{xz}^s = \dot{\gamma}\sigma_{xx}^s - \sigma_{xz}^s/\tau^s \\ \dot{\sigma}_{xx}^s = -(\sigma_{xx}^s - 1)/\tau^s \\ \dot{\tau}^s = 1 - \mu(\tau^s - \tau_0^s)|\dot{\gamma}| \end{cases} \qquad (S10.2)$$

Equations (S10) are now ready for numerical analysis if a constant deformation rate is imposed. For the imposition of a constant stress, a general force balance can be established as:

$$\nabla \cdot (\Sigma + 2\eta D) = 0 \qquad (S11.1)$$

For uniaxial extension:

$$\Sigma_z^{ext} \equiv A/A_0(\Sigma_{zz} - \Sigma_{xx} + 3\eta\dot{\varepsilon})$$
$$\Sigma_z^{ext} \equiv e^{-\varepsilon}(\Sigma_{zz} - \Sigma_{xx} + 3\eta\dot{\varepsilon}) \qquad (S11.2)$$

For simple shear:

$$\nabla_{xz} \cdot (\Sigma + 2\eta D) = 0$$
$$\Sigma_{xz}^{ext} \equiv \Sigma_{xz} + \eta\dot{\gamma} \qquad (S11.3)$$

where η is a small artificial viscosity ($= 0.33\% G^p \tau_0^s$), which is added to ease numerical simulation, and results are insensitive to this small value as shown by Fig. S2. Σ is the overall stress with contributions from both polymeric (Eq. (S6)) and segmental parts.

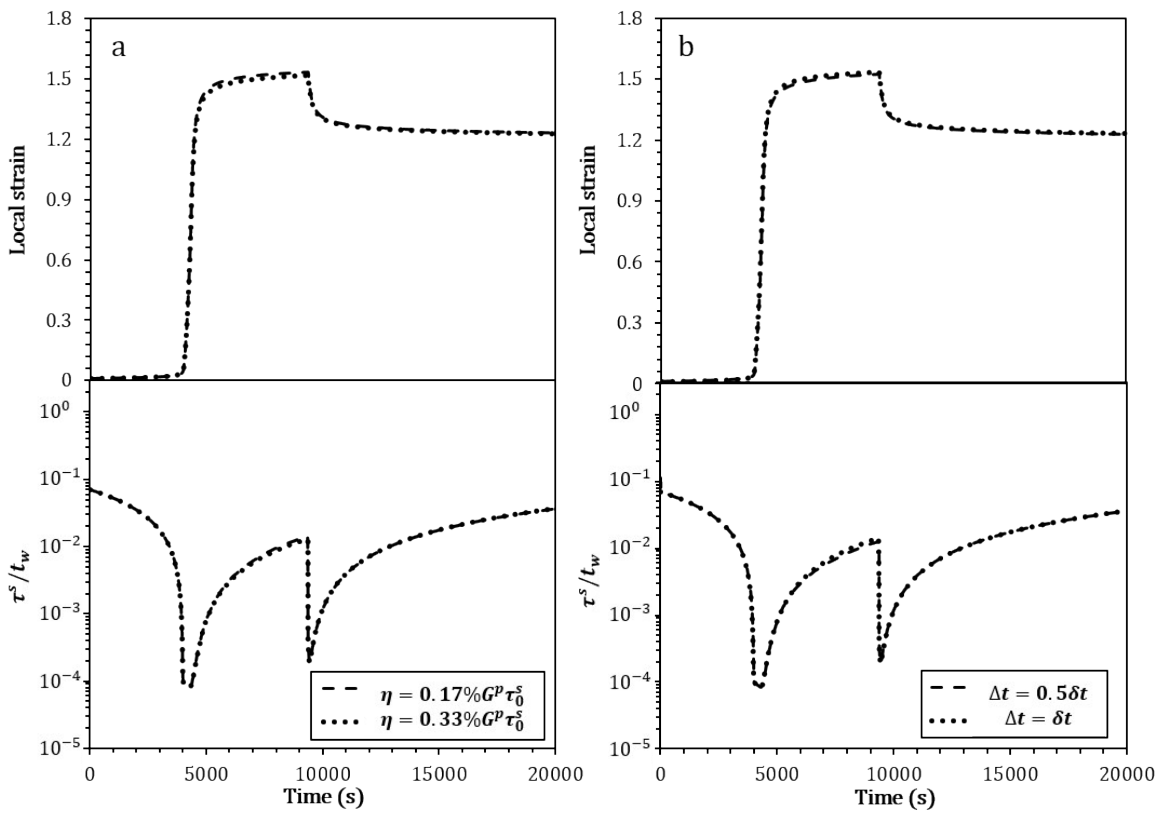

Fig. S2 Illustration of the insensitivity of simulation results to the value of η and simulation time step Δt. The parameters are the standard values listed in Table I.

References

1 R. G. Larson. Constitutive Equations for Polymer Melts and Solutions. Butterworth Publishers, Stoneham, 1988.