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Size-Dependent Behavior of Macromolecular Solids III: The Role of Entanglements

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Abstract: Chain rotations in macromolecular solids are constrained by entanglements. The effects of constraints on strain deformation and strain gradient deformation were investigated using molecular dynamic (MD) simulation in this paper. The effects on the chains were examined by embedding the chains inside bent beams. For thick beams, the simulated elastic moduli for styrene butyl rubber (SBR), polyimide (PI) and polyethylene (PE) were in good agreement with elastic moduli reported in the literature. The elastic moduli varied linearly with entanglements and inversely with the molecular weight. For thin beams where strain gradients were non-negligible, the results showed that l_2, the higher order rotational length scale material parameter, also varied linearly with entanglements and inversely with the molecular weight. The linear dependence of E_0 and l_2 on entanglements can be correlated within specific chemistry such that the size dependent behavior of solids with the same monomer, but different molecular weight and entanglement can be predicted from the correlations. However, the correlations are chemistry specific, and the size-dependent behavior for a macromolecular solid cannot be casually predicted from the size-dependent behavior of another solid.

1 Single chain size dependence

Deformation of macro-molecular solids is determined by the rotational behavior of the molecular chains [Doi (1996); Treloar (2005)]. In the previous papers of this series [Lam, Keung and Tong (2010); Wei and Lam (2010)], the chain rotational behaviors as a function of deformation were investigated. The relations between rotation gradients and l_2, the higher order rotational material length scale parameter [Mindlin (1968); Ashby (1970); Fleck, Muller, Ashby and Hutchinson (1994)], were examined using single chain molecular simulations. The results showed that the molecular response to the elastic rotation gradients was rooted in the same mechanism as the molecular response to elastic strains. Based on the results, the

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molecular basis for the higher order rotational length scale parameters was established.

In macromolecular solids, chain motions are constrained by neighboring chains and entanglements [Flory and Rehner (1943)]. Constrained movement requires additional energy, and solids with higher constraints would have higher E_0 and l_2. Chain entanglements and interactions between chains were ignored in the previous paper [Wei and Lam (2010)]. The effects of these two constraints on E_0 and l_2 are investigated in this study. The constrained chain behaviors are modeled using a volume-bounded molecular dynamic model for materials with low elastic modulus (SBR) [Boháč and Vretenár (2004)], medium elastic modulus (PE) [Bartczak, Argon, Cohen and Weinberg (1999)] and high elastic modulus (PI) [Lee, Kim and Kwon (2010)]. The effects of the molecular weight and the entanglements have on E_0 and l_2 are investigated using the model.

2 Simulation methodology

In this study, a four-chain model was used to simulate the effects of chain interactions and entanglements (Fig. 2). The model was built using the molecular dynamic module (Forcite with Universal forcefield) in Materials Studio 5.0 from Accelrys [Maranganti and Sharma (2007); Zhu, Xiao, Feng, Ji, Ma and Xiao (2007)]. In the model, chains are anchored at the corners to simulate the constraints experienced by the chains in a solid, while the configurations of the segments between the anchors are allowed to vary dynamically within the box. M_c is the average molecular weight of the chains, and the volume of the cube is calculated from,

$$V = \frac{4M_c}{\rho \cdot N_A}, \tag{1}$$

where is the density of the solid and N_A is the Avogadro number. To examine the deformation of the chains under different deformation, the cubic volume is placed on top of the neutral plane of the beam where the molecular cube is deformed according to the displacement field of the beam under pure bending [Norton (2006)]. After bending, the total deformation energy density of the four chains, u is determined via,

$$u = \frac{\Delta U}{V}, \tag{2}$$

where ΔU is the integral of the deformation energy of the volume from the simulation. From conventional strain-based elasticity [Timoshenko and Goodier (1987)], the energy density of the volume in a bent beam is,

$$u = \frac{1+2\nu^2}{2} E_{eff} \kappa^2 V^{\frac{2}{3}}, \tag{3}$$

where κ is the beam curvature. When the beams are thick and the rotation gradients are negligible, E_{eff} is equal to the conventional elastic modulus E_0. When the beams are thin, additional rotations generated by the rotation gradients increases the E_{eff} beyond E_0 [Fleck and Hutchinson (1997); Fleck and Hutchinson (2001)]. Accounting for contributions from l_2, E_{eff} is given as [Lam, Yang, Chong, Wang and Tong (2003)],

$$E_{eff} = E_o \left[1 + 3(1-\nu)\frac{l_2^2}{h^2} \right] \tag{4}$$

where h is the beam thickness and ν is the Poisson's ratio of the solid. In this investigation, the effects of entanglements on E_0 and l_2 were investigated using bent beams with different beam thicknesses using molecular dynamics.

In molecular dynamic simulation, the energy of a single isolated chain (Fig. 1) is dependent on strain, but is also a function its configuration which varies dynamically with time. The energy variation of a chain over time is shown in Fig. 1, and the cumulative energy distribution is shown in the insert. In this investigation, the energy of the chains in the simulated volume during beam bending was modeled using molecular dynamics. The deformation energy density u was calculated from the peak energies of stable energy distributions.

In the simulation, chains anchored at the corners without entanglement (Fig. 2a) were used as the reference state for comparison and benchmarking with experimental data from the literature. After benchmarking, the number of entanglements (Fig. 2b) in the volume, was increased from 0 to 6 to investigate the effects of entanglements on E_0 and l_2.

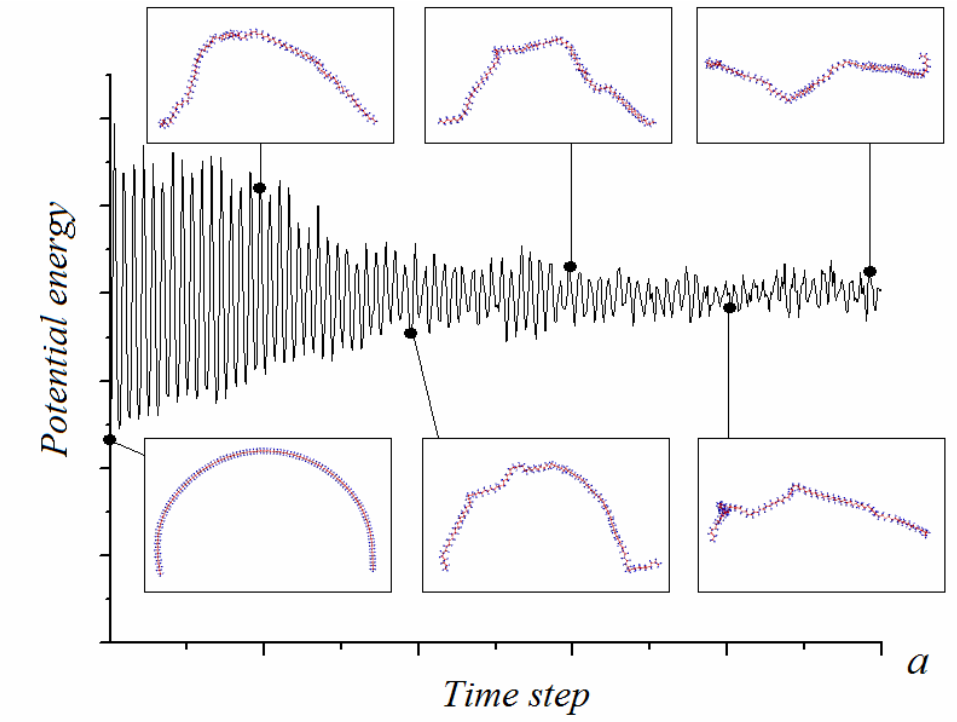
3 Results

3.1 Elastic modulus

The effect of the molecular weight and entanglements on E_0 and l_2 of soft styrene butyl rubber (SBR), medium polyethylene (PE), and stiffen polyimide (PI) were simulated. The simulation setting used is shown in Tab. 1.

Table 1: Parameters used in simulation setting

		PE	SBR	PI
Figure 3	Beam thickness h (μm)	200	100	100
	Simulated M_c (g/mol)	112	428	3220
Figure 7 &	Beam thickness h (μm)	200-100	100-1	100-1
Figure 8	Simulated M_c (g/mol)	1960	1712	3220



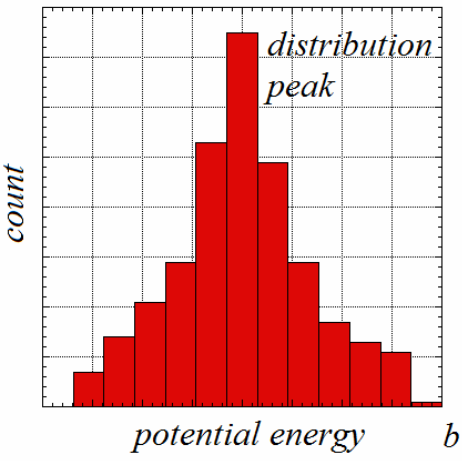


Figure 1: a) A single isolated chain; b) variation of the energy of a single chain as its configuration dynamically varies as a function of time and c) its cumulative distribution.

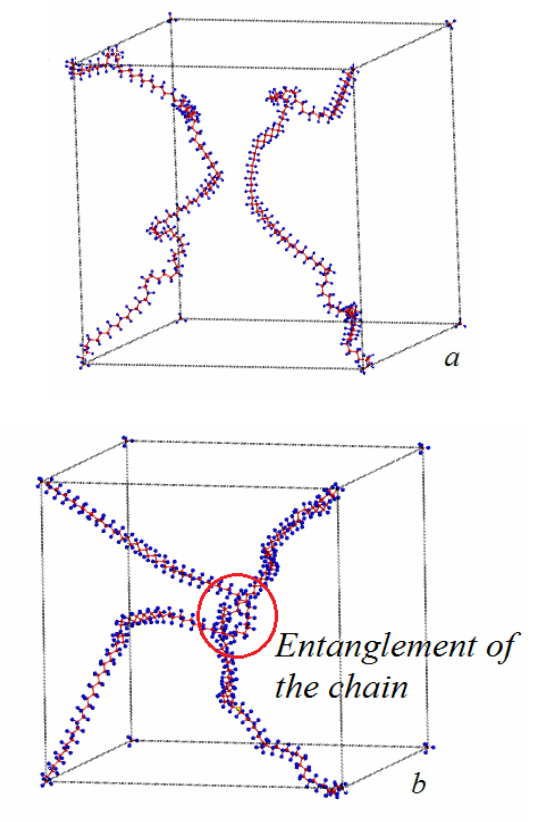


Figure 2: a) Two separate, but interacting chains; and b) two entangled chains.

A comparison of the elastic modulus from the simulation and from the literature is shown in Fig. 3. The comparison showed that the elastic moduli from simulations for all three solids are within 10% of the experimental value (Tab. 2). This indicated that the boundary conditions for the 4-chain model were set properly to account for the external constraints.

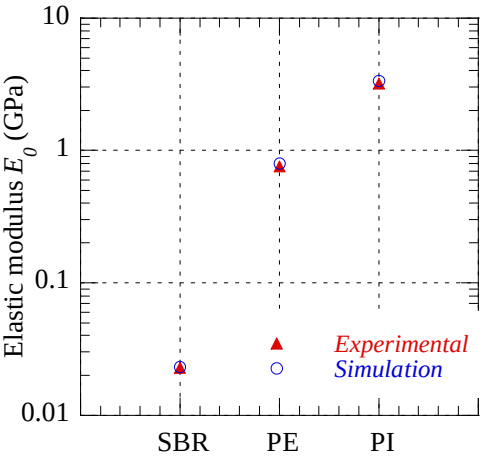


Figure 3: Comparison of the elastic modulus from simulation with experimental elastic modulus for PE, SBR and PI.

Table 2: Comparison of material properties

	SBR	PE	PI
Density ρ (g/cm^3)	1.043	0.9565	1.43
Experimental E_0 (GPa)	0.023	0.756	3.2
Molecular weight M_c[1] (g/mol)	335.92	93.724	3200.0
Entanglement density $v_{e,0}$[2] (mol/m^3)	3.105E-06	1.021E-04	4.469E-04
Simulation E_0 (GPa)	0.0231	0.798	3.35

3.2 Effect of molecular weight

Using the benchmarked procedure, the effective elastic moduli (E_{eff}) of solids with different molecular weights were simulated and plotted in Fig. 4. The For clarity, the size of the chain is described by the number of monomers in the chain as,

$$N = \frac{M_c}{m_0} \tag{5}$$

where M_c is the molecular weight of one chain and m_0 is the molecular weight of one monomer. The results showed that solids with lower molecular weight, i.e., shorter chains, have stronger size effect. From E_{eff}, the materials properties, E_0 and l_2, can be delineated using Eq. (4). The effects of molecular weight on E_0 for PE, SBR and PI are shown in Fig. 5. The figure showed that the E_0 is inversely dependent on the number of monomers, and by definition (Eq. (5)), is also inversely dependent on the molecular weight. The results are in agreement with the classical dependence as predicted by rubber elasticity [Abu-Abdeen (2001); Treloar (2005); Abu-Abdeen and Elamer (2010)] is reproduced successfully by the model. The variation of l_2 with the molecular weight is shown in Fig. 6. For all three families of solids, l_2 also varied linearly with the inverse of molecular weight.

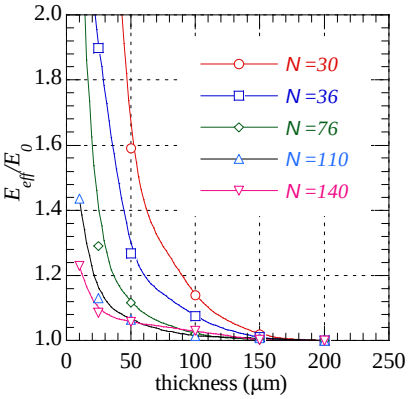


Figure 4: Effective elastic modulus of PE as a function of the beam thickness, where E_0 is the conventional size-independent elastic modulus of PE. The curves are generated by fitting Eq.(4) to the data.

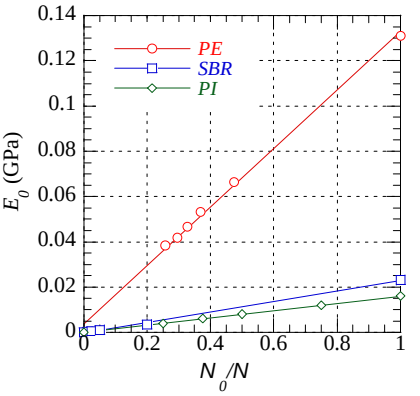


Figure 5: The influence of the number of monomers on E_0. $1/N$ on the X-axis is normalized by its maximum value $1/N_0$, which are 0.028, 1, 0.5 for PE, SBR and PI, respectively.

3.3 Effect of entanglements

In macromolecular solids, the chains are constrained from movement by the entanglements and the neighboring chains. In the simulation, the baseline constraints were simulated by the corner anchors. The resulting elastic moduli were in good agreement with experimental elastic moduli (Fig. 3). The chains within the box were unentangled and their movement was constrained only by the wall and their neighbors in the baseline model. By threading the chains, up to 6 entanglements

can be simulated in our model. The effects of entanglements v_e on E_0 and l_2 are plotted in Fig. 7 and Fig. 8. The results showed that E_0 and l_2 increased linearly with v_e.

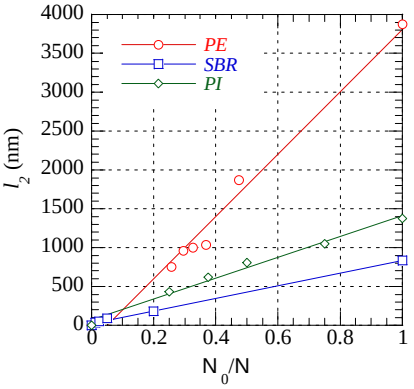


Figure 6: The influence of number of monomers on l_2. $1/N$ on the X-axis is normalized by its maximum value $1/N_0$, which are 0.028, 1, 0.5 for PE, SBR and PI, respectively.

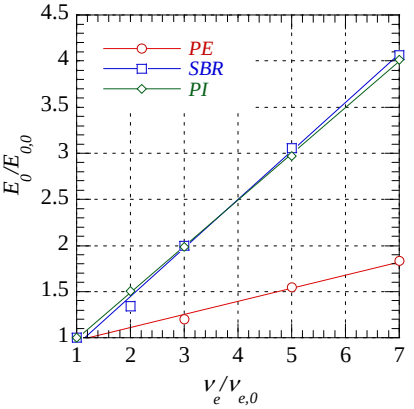


Figure 7: The influence of Nent on E_0 for PE, SBR and PI. The elastic modulus on the y-axis is normalized by E_0 of solids without entanglements, i.e., $E_{0,0}(PE) = 3.85E-2$ GPa, $E_{0,0}(SBR) = 4.51E-3$ GPa and $E_{0,0}(PI) = 3.35$ GPa.

4 Discussion

The simulation results showed that the molecular weight and entanglements have analogous effects on the elastic modulus E_0 and l_2. Lowering the molecular weight reduces the distance between the anchors and increases the constraint on the chains. Since the deformation mechanism underpinning E_0 is chain rotation, stronger constraints would increase E_0. Analogously, l_2 is also inversely dependent on the molecular weight since both $l_2$and E_0 are material properties underpinned by chain rotation of the same molecules.

Similar to the inverse dependence on the molecular weight, adding entanglements into the solid volume increases the constraint on chain movement and increases $l_2$and E_0. In fact, E_0 and l_2 for solids with the same chemistry system can be correlated linearly. E_0 and l_2 can be predicted for solids with different entanglements and molecular weight can be predicted from the correlations, i.e., from known molecu-

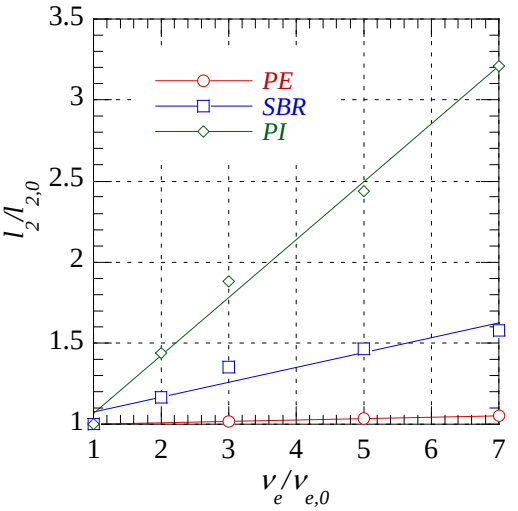


Figure 8: The influence of Nent of l_2 from PE, SBR and PI simulation. The l_2 on the y-axis is normalized by l_2 of solids without entanglements, i.e., $l_{2,0}(PE) = 747.75$ nm, $l_{2,0}(SBR) = 194.88$ nm and $l_{2,0}(PI) = 429.14$ nm.

lar weight and entanglement series of E_0 and l_2. However, the correlations are not generalizable across different chemistries; and further work is needed to investigate the effect of chemistry has on E_0 and l_2.

5 Conclusions

Simulations were conducted to examine the effects of molecular weight and entanglement on the size dependence of macromolecular solids. The simulations were benchmarked using solids that are soft (SBR), medium (PE) and stiff (PI). The comparisons showed that the inverse dependence of simulated elastic modulus E_0 on the molecular weight is in good agreement with literature. The simulation also showed that l_2 varied linearly with entanglements and inversely with the molecular weight. Both dependences can be correlated with E_0's dependence on entanglement and molecular weight, but the correlations are limited to solids that share the same macromolecular chemistry, and are not generalizable to other solids with different chemistry.

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