ATOMISTIC PREDICTION OF PLANE STRESS BEHAVIOR OF GLASSY THERMOSETS

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ABSTRACT

When any covalent bond energy reached a threshold indicative of incipient bond scission, the simulation was stopped. This method was used to examine the responses of three highly-crosslinked epoxy systems. Systems were large enough to include 110 to 480 crosslink sites. Both elastic and yield properties show good agreement with the experiments of others. Continuum yield theories commonly applied to polymers are compared with the data. A Drucker-Prager pressure-dependent yield function applied best in the second and third quadrants of the $\sigma_1 \sigma_2$ domain. In the first quadrant, however, data more closely match a normal-stress-yielding criterion. In biaxial tension and simple tension, plastic behavior and large growth in nanoporosity were observed. Ductility was lowest in simple tension and biaxial compression. In simple tension, the bonds at crosslink sites and in ether linkages were the most highly strained whereas carbon-carbon backbone bonds between phenyl groups were highly strained in other cases. When system energy at imminent bond rupture was divided on a per-atom basis, consistency with Peterlin's theory for molecular rupture was found.

Introduction

Characterization of plane stress behavior of a given material is of great utility. For example, knowledge of yield strength and plastic flow behavior in plane stress can be used to estimate the plastic zone size and shape ahead of a crack tip and therefore support the estimation of material toughness. When plane stress properties can be expressed in terms of a small number of parameters, the results can be readily embedded in numerical simulations and therefore enable prediction of stress and deformation in objects having more complicated shapes. When

plane stress behavior is derived from atomistic interactions, fundamental insight is provided into the ways atomic and molecular structural quantities affect bulk response.

Numerous yield theories have been put forth to provide a generalized yield threshold or lower bound. These are aimed at capturing the general continuum behavior in terms of underlying key independent variables (e.g., strain energy) or a small number of measured properties (e.g., uniaxial tensile yield strength). The classic theories provide, in particular, yield thresholds in terms of invariants (e.g., [1, 2, 3, 4, 5]), shear stress (e.g., [6]), or combined shear and normal stress thresholds (e.g., [7]).

While these theories are often appropriately applied to describe polycrystalline equiaxed metals and basic structural materials (e.g., concrete), they are not as robust for characterizing polymers. While some experiments match some of the afore-mentioned criteria well [8, 9], others indicated distinctly different mechanisms at yield according to load case [10, 11, 12]. In the latter experiments, the materials showed distinctly lower strength in load cases which included positive dilatation. This weakness was inconsistent with the strength in load cases where distortion or negative dilatation were predominant in that the loci of data points among these case types followed differing functional dependencies. Where thermoplastics were investigated, it was generally found that the weakness was associated with crazing whereas shear bands occurred in other load cases. When thermosets were investigated, there were instances where the material would rapidly proceed to fracture whereas it would display measureable ductility in others [8, 12]. In some instances, the onset of these differing responses could be matched with threshold values of stress or strain invariants [11]. Some attempts have been made to explain the origins of these using continuum-mechanics-based arguments [13]. Additional yield criteria based on observations from experiments have been developed [14, 15, 16, 17, 18].

Fundamental insight is provided when stress responses are derived from smaller-scale (e.g., molecular) behaviors. Direct connections among chemical structure and bulk behaviors can be sought to substantiate physical bases for the dependencies that are observed in experiments or included in theories. Some theories for the onset of polymer plastic flow derive from fundamental considerations of molecular mechanical and stochastic behavior. Yannas and Lunn [19] explored and compared the effects of inter- and intra-molecular forces on the energy barriers to backbone dihedral rotation and anticipated that inter-molecular effects would be significant below T_g . Robertson [20] considered the application of shear stress and the resulting probability for backbone conformation changes. He concluded that the system volume would increase and a liquid-like state would exist. Bowden and Raha [21] envisioned strain fields similar to dislocation loops in crystalline metals associated with the rearrangement of molecular chains as shear stress is applied and fit their model to data from experiments. Joseph [22] aimed to provide a model which would display both yield and relaxation transition behaviors based on linearly elastic elements and a potential with multiple barriers. Only systems undergoing pure shear were considered. Argon [23] associated strain with the production of backbone kink pairs and derived the energy barrier due to intermolecular interactions. The theory was tested by checking the fit to compressive and tensile yield measurements for numerous polymers over wide ranges of temperature and strain rate [23, 24]. While it was

asserted that a pressure-modified von Mises yield criterion would apply to generalized plane stress based on selected data [24], the explanation of experimental results associated with void nucleation - and decidedly differing from von-Mises-like functions – was not directly related to the kink pair mechanism.

Experiments have been performed to ascertain the molecular behavior associated with mechanical loading. Some monitored material dilatation by measuring variation of free volume size and distribution due to loading [25, 26, 27, 28, 29, 30, 31]. Others examined distortion by inferring chain reorientation and changes in side group concentration from infrared spectra [32, 33, 34]. At the point of incipient rupture, still others used a combination of techniques to identify correlations among bond scissions, radical concentration, and crack nucleation [35, 36, 37, 38]. The latter results indicate molecular scission generally leads to a cascade of mechano-chemical reactions and the occurrence of micro-scale voids.

We know of no broader thorough exploration of polymer mechanical behavior derived from atomistic simulation. Atomistic simulations of mechanical deformation of glassy polymers thus far have principally involved uniaxial or pure shear loading [39, 40, 41, 42, 43, 44, 45, 46, 47, 48] [49, 50, 51, 52, 53, 54, 55, 56]. Such an investigation is important for the sake of demonstrating the relevance of molecular dynamics results for properties prediction at larger length scales as well as for providing additional insight into the molecular bases for yield, flow, and rupture. While atomistic simulation has been used to predict the yield surface of metallic glass [57], the interatomic potentials appropriate for polymers are more varied and complex. In one instance, a yield locus was asserted based on atomistic simulations of polymers in pure tension and pure compression [58]. As will be shown, however, a thorough investigation in each quadrant of the $\sigma_1 - \sigma_2$ domain shows the effect of hydrostatic stress on yield. A method for applying generalized plane stress to an atomistic system is presented as well as an interpretation of the results for a set of thermoset formulations. The principal independent variable among the formulations is crosslink density. Once the methods and algorithm are described, results are presented and compared with physical experiments of other researchers. System behaviors are expressed in terms of stress and strain invariants. Further, underlying molecular behaviors associated with yield and rupture are elicited.

Methods

Plane stress application

Algorithm

An algorithm was designed to apply a succession of stress states in a sequence of molecular dynamics simulations such that a set proportion of in-plane stresses as well as a target equivalent strain rate were maintained. The stress state is given by

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (1)$$

In what follows, an angle θ will be associated with the stress state. This is depicted in Figure 1. Depending on their relative magnitudes, σ_{xx} and σ_{yy} correspond with principal stresses σ_1 and σ_2

Figure 1. Definition of the angle associated with each applied stress state. As deformation proceeds, the proportion of principal stresses is maintained.

A definition of the stress tensor in terms of quantities germane to molecular dynamics is given by

$$\boldsymbol{\sigma} = - \frac{1}{V} \left\langle \sum_{i=1}^N m_i \mathbf{v}_i \otimes \mathbf{v}_i + \mathbf{W}(\mathbf{r}^N) \right\rangle \quad (2)$$

where $\langle \rangle$ denotes an ensemble average, V is the volume enclosing the system, N is the number of particles, m is particle mass, $\mathbf{v}$ is particle velocity, $\mathbf{r}$ is particle location, and $\mathbf{W}$ is the virial tensor. Thompson, et al. [59] derived descriptions of the virial tensor appropriate for periodic conditions. The atom-cell form of $\mathbf{W}$ is given by

$$\mathbf{W}(\mathbf{r}^N) = \sum_{i=1}^N \mathbf{r}_i \otimes \mathbf{F}_i + \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{H} \mathbf{n} \otimes \sum_{i=1}^N \mathbf{F}'_{i\mathbf{n}} \quad (3)$$

where $\mathbf{H}$ is a matrix of the periodic cell vectors, $\mathbf{n}$ is an integer vector for the offset to the respective periodic image, and $\mathbf{F}$ is the force acting on the particle. $\mathbf{F}'$ is the partial force on the particle due to groups associated with the local cell. $\mathbf{F}$ can originate from both pairwise and manybody interactions.

Plane stress is attained by setting the respective target values for stress tensor terms of an isobaric-isothermal ensemble. In order to maintain a steady strain rate, plane stress states are applied in a succession of brief periods. At the end of each, equivalent strain (based on cell dimensions) is compared against the target value for the corresponding total elapsed time. Equivalent strain is given by

$$\varepsilon_{equ} = \left[\frac{1}{\sqrt{2}} \sqrt{(\varepsilon_x - \varepsilon_y)^2 + (\varepsilon_y - \varepsilon_z)^2 + (\varepsilon_z - \varepsilon_x)^2 + 6(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2)} \right] \quad (4)$$

The applied in-plane stress values for the subsequent period are incremented from the previous interval in proportion to any error in equivalent strain as well as the rate-of-change in strain error. For tension or compression in the x direction, this is given by

$$\Delta \sigma_{xx} = C_1 (\hat{\varepsilon}_{equ} - \varepsilon_{equ}) + C_2 \frac{\Delta (\hat{\varepsilon}_{equ} - \varepsilon_{equ})}{\Delta t}, \Delta \sigma_{yy} = 0 \quad (5)$$

and

$$\Delta \sigma_{xx} = C \Delta \sigma_{yy} = C_1 (\hat{\varepsilon}_{equ} - \varepsilon_{equ}) + C_2 \frac{\Delta (\hat{\varepsilon}_{equ} - \varepsilon_{equ})}{\Delta t} \quad (6)$$

otherwise. $\hat{\varepsilon}_{equ}$ is the target equivalent strain.

Stresses therefore increase, decrease, or remain constant according to whether the material is hardening, softening, or perfectly plastic over the given time period. The algorithm flow is provided in Figure 2.

In addition to calculating strain error, covalent bond lengths are logged after each dynamics interval. If any are found to have reached a length deemed indicative of incipient rupture, the simulation is terminated. Simulation was not continued beyond the first indication of bond rupture because the experimental results of Zhurkhov, et al. [36] provide evidence that bond rupture leads to a cascade of mechano-chemical reactions and a corresponding appearance of large voids. A critical energy level is therefore associated with each covalent bond type. For example, if a harmonic bond stretching potential is given by

$$E = K (r - r_o)^2, \quad (7)$$

a critical bond length associated with a critical energy level is then

$$r_{crit} = \sqrt{\frac{E_{crit}}{K}} + r_o. \quad (8)$$

Values for E_{crit} came from the Morse bond potentials of the corresponding covalent atom pair.

This potential is given by

$$E = D \left[1 - e^{-\alpha(r - r_o)} \right]^2 \quad (9)$$

where D is the energy difference between $r = r_o$ and $r = \infty$. This is treated as E_{crit} .

Figure 2. The flow chart for application of plane stress at a constant equivalent strain rate.

Molecular systems

The molecular systems investigated began as stoichiometric mixtures of monodisperse diglycidyl ether of bisphenol A (DGEBA) resin and methylene diamine (MDA) prepolymers. The principal difference among the systems studied was DGEBA chain length (and therefore cured cross-link density). The molecular structures are shown in Figure 3. These formulations have been carefully studied experimentally to determine their toughness and associated crack tip deformation in plane stress [60]. The systems are summarized in Table 1.

We are exploring whether, at length scales approaching an order of magnitude larger than the mean distance between crosslink sites, the system mechanical behavior takes on a character consistent with observed macro-scale observations.

The systems created represent essentially uniformly crosslinked continuous matrices. While there have been observations of nano-scale inhomogeneity [61] evolving during curing, there are also combinations of reactants and curing conditions that result in a homogeneous network. As discussed by Pascault, et al. [62], if a stoichiometric two-part system with simple functionality (such as those examined here) is thoroughly blended prior to crosslinking and reactions proceed in step-wise (rather than chain-wise) sense, the cured system is highly homogeneous.

Research has shown that mechanical properties are functions of M_c , the mean molecular weight of a strand between crosslinks or entanglements [63, 60, 64, 65, 66]. A closely-related quantity is the cross-link density. The crosslink densities here are similar to those reported for

the same systems [60] in which the values ranged from $135 \times 10^{25} \text{ m}^{-3}$ (for $n=0$) to $33.5 \times 10^{25} \text{ m}^{-3}$ (for $n=5$). The system responses are largely governed by the collective responses of the molecular strands between crosslink sites. The number of strands scales approximately with the number of original molecules (which range from 171 to 738 here). Each strand, then, is a fraction of a percent to the entire system.

Figure 3. Molecular structures of MDA (a) and DGEBA (b). The epoxide group of DGEBA is shown replaced with methyl and hydroxyl groups. During crosslinking simulation, methyl carbon and amine nitrogen atoms become covalently bonded. For the systems investigated, $n = 0, 3$, and 5 .

Systems were cross-linked during molecular dynamics simulation by the method of Rigby, et al. [67]. A proximity-based criterion is used to alter covalent bonds among open epoxide and amine groups to represent amine addition reactions to form secondary and tertiary amines. During dynamics, the proximities among potentially-reactive groups are measured. When any fall within a set range, one hydrogen atom is removed from each group and a new C-N covalent bond is created. Energy local to the new bond is minimized before proceeding with subsequent dynamics. The crosslinking algorithm forms new bonds between crosslink sites based on a succession of searches of increasing radius with dynamics to allow relaxation and diffusion. If a new bond is formed which spears a phenyl ring, the system energy increase would be dramatically larger than that for the formation of a proper cross-link. The algorithm includes an energy increase threshold value. If system energy from one crosslink cycle to the next rises by more than this value, the newly-formed bond is rejected. The molecular system database reverts to that prior to the crosslinking attempt and additional dynamics is performed prior to attempting to form another bond. Curing was performed at 473 K. Pressure was held at 0.5 GPa until the cross-linked extent reached 55%. Pressure then incrementally decreased as additional crosslinking occurred. Crosslink extent is defined as the portion of the original amine N-H

bonds which had reacted. Crosslinked systems were then equilibrated to one atmosphere and 298 K. The criterion used to deem the system as being in equilibrium was that mean system volume (as averaged over 2.5 ps) changed by 0.25% or less over a span of 25 ps. Once crosslinked, the systems were once again equilibrated at elevated temperature and then cooled to the temperature for mechanical testing (298 K) and re-equilibrated.

Because it is well-known that thermoset glassy properties are a function of the difference between the test and glass transition temperatures [62], results are provided to confirm the systems were in a glassy state. Plots of specific volume versus temperature during cooling indicated glass transition temperatures of ca. 455 to 465 K (see Figure 4). While the simulated cooling rate is far greater than created in experiments, as discussed by Pascault, et al. [62] the activation energy associated with the characteristic time to reach equilibrium is very large for thermosets. As a result, the effect of cooling rate on the recorded glass transition temperature is weak. Lemay, et al, [63] found $T_g=432$ K for a short-chain ($n=0.14$) DGEBA/MDA system. Levita, et al. [68] found T_g ranging from 378 to 433 K in DGEBA/DDS systems having the same range of crosslink density examined here.

Atom interactions were specified by the CVFF [69] force field. Harmonic bond potentials were used. Ewald summations were used for long-range interactions. Cutoffs for Lennard-Jones and Coulomb pair interactions were 12 and 16 Å, respectively.

Table 1. Summary of the molecular systems investigated.

System	n	MDA molecules	DGEBA molecules	Total atoms	Equilibrated volume (Å ³)	Crosslink extent	Tertiary/secondary/primary amines	Cross-link density (10 ²⁵ m ⁻³)
n0	0	246	492	33210	343300	0.94	446/37/9	123
n3	3	82	164	31242	333700	0.92	144/15/5	40
n5	5	57	114	31065	334000	0.92	100/10/4	27

Figure 4. Plot of specific volume as a function of temperature for cooling from 698 to 98 K at a rate of 1.43×10^{11} K/s.

Testing

The constants relating strain errors to the magnitude of the applied stress increment as well as the barostat damping time constant were adjusted until reliably steady equivalent strain rate and actual stress proportion values over the duration of each simulation were obtained. Example histories are shown in Figure 5.

Table 2 provides the critical bond lengths and energies for the backbone bond types which, when attained, would trigger the simulation end. The results of experiments have indicated activations energies at a similar level [70]. LAMMPS [71] was used as the dynamics environment and a Berendsen barostat applied. Equivalent strain rate was 10^{10} s^{-1} . Sixty different proportions and signs of in-plane stresses were applied and ranging from biaxial tension to biaxial compression.

a)

b)

Figure 5. Equivalent strain (a) and in-plane stress ratio (b) as a function of time for biaxial compression for system n0. Results and target values are solid and dashed, respectively.

Table 2. Backbone CVFF atom pairs, harmonic potential parameters, Morse potential dissociation energy, and corresponding critical bond length.

Atom type	Atom type	K (kcal / mol Å ²)	r _o (Å)	D (kcal/mol)	r _{crit} (Å)
c	c	322.7158	1.526	88.0	2.048
c	n	377.5752	1.460	72.0	1.897
c	o	273.2000	1.425	68.3	1.925

Results and Discussion

General Behavior

A broad initial comparison among the responses shows the predominant differences according to load case. Five cases (biaxial tension, tension, pure shear, compression, and biaxial compression) for system n0 were compared in terms of relations among stress and strain invariant-based quantities. These are mean stress (eqn. 13), equivalent stress (eqn. 14), the first strain tensor invariant – or volumetric dilatation - (eqn. 16), and equivalent strain (eqn. 17).

$$\sigma_m = \frac{I_1}{3} = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3) \quad (10)$$

$$\sigma_{equiv} = \frac{1}{\sqrt{2}} \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2} = \sqrt{I_1^2 - 3I_2} \quad (11)$$

where

$$I_2 = \sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1 \quad (12)$$

$$J_1 = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (13)$$

$$\varepsilon_{equiv} = \frac{1}{\sqrt{2}} \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_3 - \varepsilon_1)^2} = \sqrt{J_1^2 - 3J_2} \quad (14)$$

where

$$J_2 = \varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3 + \varepsilon_3\varepsilon_1 \quad (15)$$

and where I_1 and I_2 are the first and second stress tensor invariants, J_1 and J_2 are the first and second strain tensor invariants, and stress and strain subscripts denote principal values.

Replicability of the behavior was examined by crosslinking and testing multiple systems. Each system was differently randomized when populating the cell with reacting molecules as well as when dynamics were performed to crosslink and equilibrate. The systems were the same in all other regards. Each was deformed in uniaxial tension. The results are shown in Figure 6. The systems agree to within the stochastic scatter of the data until upper yield. Lower yield values agree to approximately 20 MPa. Differences are most distinct when strain hardening begins. The systems with a higher hardening rate showed higher strength and lower ductility.

Figure 6. Equivalent stress-strain curves for four crosslinked systems. The systems have the same composition as system n0 and are cross-linked to 80 %.

When equivalent stress and strain scalar (quantities often associated with shear-associated deformation) are plotted with respect to each other, there are several distinguishing features. As shown in Figure 7, whereas tension and biaxial tension show an upper yield followed by an extended range of almost perfectly plastic flow, only hardening occurred in the other cases. The system was also distinctly stronger in compression cases than tension cases. Gerlach et al. also observed no strain softening in uniaxial compression tests of a thermoset resin over five decades of strain rate [72]. In experiments carefully controlled to create uniform stress and deformation of amine-cured DGEBA samples, Liang and Liechti [73] measured the large-strain mechanical response of in a variety of load cases. While post-yield softening and shear banding were found in tension, they also found perfectly plastic flow followed by hardening in pure compression and no evidence of shear banding.

Figure 7. Equivalent stress as a function of equivalent strain for five load cases for system n0. Each data point is the average over one hundred 0.05 fs time steps.

The hydrostatic pressure and volumetric dilatation variations in these same five load cases indicate their role in affecting yield and flow behavior. Mean stress is plotted versus J_1 in Figure 8. In tension and biaxial tension, there is initially a proportional increase in mean stress with J_1 . Upon yield, there is a dramatic rise in J_1 with a slight decline in mean stress. The system subsequently stiffens up to the point of bond rupture. In pure shear, there is essentially no dilatation (i.e., no increase in J_1) until yield. There is then a gradual increase in mean stress with J_1 followed by a regime in which the system essentially resists all further dilatation. In both compression cases, J_1 monotonically decreased at a rate which was similar among the two cases.

The dependencies of energy associated with molecular distortion and non-bond interactions are shown in Figure 9. Bonds generally become the most strained in tension cases. In compression cases, bonds initially become generally less loaded as equivalent strain increases from zero and up to yield. Subsequently, bonds take on additional load at approximately the same rate as the other cases. After yield, van der Waals energy is larger in tension cases than shear and compression. Because the structure has dilated in the tension cases, this rise is due to increase in non-bond attraction. To further explore the interplay among bond and pairwise terms during deformation, the contributions of these to the normal stress terms of the stress tensor were

compared among the biaxial tension and biaxial compression cases. The results are shown in Figure 10. It was found that bond and pairwise interactions made the largest contribution to the stress tensor. As a result of crosslinking, there are initially positive contributions from bond terms and negative contributions from pairwise terms. When the system is in biaxial extension, the rate of change in the contributions in all directions have similar magnitudes. When the system is placed in compression, however, there is comparatively little change in the contributions in the xy plane while the changes in the z direction are large and nonlinear. As this occurs, the material is extruded in the z direction.

In tension cases, torsional energy increases gradually and becomes an order of magnitude smaller than the compression cases. It therefore appears positive mean stress has the effect of dilating the structure to a threshold level at which some barriers to chain reformation are removed and plastic flow proceeds. Once initiated, it appears there are then numerous conformations available to the chains at similar or lower energy levels. Conversely, negative mean stress (and the nearly proportional contraction) appears to allow rearrangements with the addition of increasing amounts of work for each strain increment. These effects of mean stress are consistent with experiments. Sternstein and Ongchin inferred that positive mean stress enhances conformational mobility [11]. Knauss and Emri [74] show that the effect of increasing hydrostatic pressure on glassy polymers is to delay yield and suppress post-yield softening.

Figure 8. Mean stress as a function of the first invariant of the strain tensor for system n0.

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a)

b)

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c)

d)

365 Figure 9. The dependencies of van der Waals (a), angle (b), bond (c), and torsional (d)
 366 system energies on equivalent strain for five load cases for system n0. Columbic interaction
 367 energies are not shown because the magnitude of the variations was distinctly smaller.

a)

b)

c)

d)

Figure 10. Net contributions of bond terms (subfigures a and c) and pair-wise terms (subfigures b and d). Subfigures a and b are for biaxial tension. Subfigures c and d are for biaxial compression.

Elastic Properties

In system n0, the bulk moduli in the limit of zero strain were 5.6 and 5.8 GPa and for biaxial tension and biaxial compression, respectively. These compare well with a measured value of 5.4 GPa measured for a DGEBA-TETA system [18]. These predictions also show distinctly better agreement compared to our previous predictions [48] for the same systems using the COMPASS force field. Effective modulus was treated as the initial slope of the equivalent stress-equivalent strain curve. The results show modulus was generally lowest in biaxial tension and generally increased with the largest value in biaxial compression (as shown in a

polar plot for each system in Figure 11). Modulus also increased nonlinearly with crosslink density. While there is a three-fold difference in crosslink density among systems n0 and n3, moduli differed by a far smaller proportion. Further, crosslink density in system n5 was 68 % that of system n3 whereas its modulus was a half to a third that of system n3. This strong nonlinear dependence upon cross-link density is consistent with experiments of Charlesby and Hancock [75] who found (consistent with the theory for amorphous cross-linked polymers) that modulus varied inversely with molecular weight between crosslinks.

Figure 11. Polar plot of effective elastic modulus for systems n0, n3, and n5. The angular position of each point corresponds to the angle θ in Figure 1 associated with the ratio of the in-plane stresses for the respective case.

Elastic modulus and Poisson's ratio were also inferred from the results. Assuming the material to be linearly elastic at small strain, stress and strain in plane stress (in the xy plane) are related by

$$\epsilon_x = \frac{1}{E} [\sigma_x - \nu \sigma_y] \quad (16)$$

$$\epsilon_y = \frac{1}{E} [\sigma_y - \nu \sigma_x] \quad (17)$$

which can be rearranged as

$$E = \frac{\sigma_x^2 - \sigma_y^2}{\sigma_x \epsilon_x - \sigma_y \epsilon_y} \quad (18)$$

$$\nu = \frac{\frac{\epsilon_x}{\sigma_x} - \frac{\epsilon_y}{\sigma_y}}{\frac{\epsilon_x}{\sigma_x} + \frac{\epsilon_y}{\sigma_y} - 1} \quad (19)$$

Most of the inferred elastic moduli ranged from 1.5 to 3.0 GPa with the largest in the range between pure shear and compression (as shown in Figure 12). Littell, et al. [76] tested an EPON 862/Epikure W system (i.e., DGEBA resin 165-173 e.w. and non-MDA aromatic curing agent 43-46 a.h.e.w.) and found moduli in compression and tension of 2.96 and 2.89 GPa, respectively. While Littell's results showed weak dependence of modulus on load type, Kaelble [77] found such dependence varied with the crosslinking molecule used in the formulation. His measured values ranged from 1.31 to 3.50 GPa. He found DGEBA (200 e.w.) crosslinked with the comparatively flexible DETA resulted in a system which was stiffer in tension than compression while the formulation crosslinked with the shorter metaphenylene diamine led to the opposite behavior. The behavior found here is consistent with Kaelble's findings in that the crosslinking molecule used is also comparatively short and stiff (being composed of two phenyl groups bonded by one carbon atom).

The inferred Poisson's ratio ranged primarily from 0.25 to 0.50 (as depicted in Figure 13). Sottos, et al. [78] found values ranging from 0.40 to 0.49 for an EPON 828 (DGEBA 185-192 e.w.) system fully-reacted with an aliphatic curing agent. Littell, et al. [76] found values ranging from 0.35 to 0.43 at room temperature for EPON 862 (DGEBA 165-173 e.w.) cured with a modified polyamidoamine agent. Smith, et al. [18] also found the values ranged from 0.25 to 0.50 for an amine-cured DGEBA and that the value was highest in compression and decreases with the addition of shearing.

Figure 12. Small-strain elastic modulus over the range of load cases for system n0. Biaxial tension and biaxial compression are on the extreme left and right, respectively.

Figure 13. Inferred Poisson's ratio over the range of load cases for system n0. Biaxial tension and biaxial compression are on the extreme left and right, respectively.

Yield

Yield points were identified from fits to the respective stress-strain curves. For responses which included strain softening, yield was defined as the first point of zero slope at which the second derivative was positive (i.e., lower yield). When responses did not include strain softening, the first inflection point was treated as the yield. These features could be easily identified in all simulation results. Lower yield was deemed more appropriate than upper because the results of Girard-Reydet, et al. [79] indicate that strain is not recovered in the former while it is in the latter.

Consistent with the experiments of others, dependence of yield on pressure was found. When compressive, the general effect of hydrostatic stress is to contract the system and therefore reduce the available space for chain segment mobility. When yield strength is plotted as a function of I_1 (as in Figure 14), a linear relation is found for a wide range where strength decreases with increasing hydrostatic stress. Pressure-dependent yield has been found for PC and PVC [14], PMMA [11], and cured DGEBA [9, 8, 12]. The sensitivity of yield strength to I_1 was 0.53 MPa/MPa. This level is greater than experimentally-measured values (ca. 0.1 for PMMA [11], 0.164 for DGEBA/EDA/MEDA/DMEDA [8], 0.175 for DGEBA/diisocyanate [9], and 0.46 for DGEBA/DETA [12]).

The predicted yield values are larger than found from the compression tests of DGEBA cured with various agents by Cook and Mayr [80]. However, these experiments were performed at lower strain rate and they also found distinct hardening with strain rate. Also, the yield values

predicted here show distinctly better agreement than our previous predictions using the COMPASS force field [48].

Another frequently-observed phenomenon, a different dependence on invariants in the first quadrant of the σ_1 versus σ_2 plot compared with the second and third quadrants, is also present. In Figure 14, yield values from the first quadrant are shown as filled symbols. They tend to cluster within a narrower range of I_1 than those from the other quadrants and not display a discernible linear dependence.

Figure 14. Equivalent stress at yield as a function of the first stress invariant. Filled symbols with dark borders represent first quadrant results.

To further illustrate, results were compared with several commonly-used yield criteria to more completely investigate invariant dependence. The von Mises criterion is given by

$$\sqrt{\frac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]} = \sqrt{\frac{2}{3}(I_1^2 - 3I_2)} = \frac{1}{2}s_{ij}s_{ij} = K^2 \quad (20)$$

where s_{ij} is the stress deviator tensor. It is common to set the threshold for the criterion based on the yield strength in uniaxial tension S_{yt} by

$$K = \frac{S_{yt}}{\sqrt{3}} \quad . \quad (21)$$

The Drucker-Prager criterion [1] includes a pressure dependent yield surface and is given by

$$\sqrt{\frac{1}{6}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]} = \sqrt{\frac{1}{3}(I_1^2 - 3I_2)} = A + B I_1 \quad (22)$$

where

$$A = \frac{2}{\sqrt{3}} \left(\frac{S_{Yc} S_{Yt}}{S_{Yc} + S_{Yt}} \right), \quad B = \frac{1}{\sqrt{3}} \left(\frac{S_{Yt} - S_{Yc}}{S_{Yc} + S_{Yt}} \right) \quad (23)$$

and the subscript *c* denotes compression.

The modified Tresca criterion includes pressure-dependent threshold for the maximum shear stress. That is

$$|\sigma_{MAX} - \sigma_{MIN}| = 2 \left(\frac{S_{Yc} S_{Yt}}{S_{Yc} + S_{Yt}} - \frac{1}{2} \frac{S_{Yc} - S_{Yt}}{S_{Yc} + S_{Yt}} I_1 \right) \quad (24)$$

A normal-stress-yielding criterion for plane stress was derived by Sternstein and Onchin [11] to match some of their results

$$|\sigma_1 - \sigma_2| = A + \frac{B}{I_1} \quad (25)$$

This criterion was based on assertions that I_1 was a factor determining molecular mobility and $|\sigma_1 - \sigma_2|$ drives normal yielding. This criterion appeared to hold under conditions in which this threshold would lie within the von Mises envelope.

Based on some of the first-quadrant results of Asp, et al. [12], another test criterion is setting the first invariant equal to the tensile yield strength.

$$I_1 = S_{Yt} \quad (26)$$

Fits to the data according to these criteria for system n0 are shown in Figure 15. The Drucker-Prager criterion overpredicts strength in the first quadrant and provides a very good fit in the second and third. In the third quadrant, both Drucker-Prager and modified Tresca criteria bear resemblance to the trend in the data. There is enough variability in the results that it is unclear which criterion is a better fit; especially in conditions approaching biaxial compression. The modified Tresca and Sternstein-Onghin criteria provide the best fits in the first quadrant. While both provide for weakening with increasing I_1 , they also overestimate strength for conditions approaching biaxial tension. Data in this vicinity tend to form a line parallel to the constant- I_1 line. As shown in Figure 16, the other systems showed a similar general behavior. Also, strength increased with increasing crosslink density.

While some polymers have displayed an I_1 -dependent dichotomy in their responses to biaxial stress, others do not. For thermosets, it appears the type of first-quadrant response depends on the cross-linking molecule flexibility. Asp, et al. [12] tested DGEBA cured with diethylene

triamine (DETA) as well as DGEBA with poly(oxy propylene-amine) (APTA, Jeffamine T-403). While both are aliphatic triamines, the latter has a longer backbone contour length (i.e., DETA has six backbone bonds and APTA has approximately 24). The results showed DGEBA/DETA yield strength could be fit to a constant I_1 criterion in the first quadrant whereas the DGEBA/APTA formulation could be better fit to von Mises or Drucker-Prager criteria. In the results obtained here, strength was consistently between Drucker-Prager and constant- I_1 fits in the first quadrant. Similar to the DGEBA/DETA formulation, the crosslinking molecule used here, MDA, is also comparatively short.

Figure 15. Comparison among several yield models fit to the system n0 results.

Figure 16. Plot of principal stresses at yield for systems n0, n3, and n5.

It has been previously found that when this dichotomy in the yield dependence is present, it is associated with differing macroscopic features (e.g., voids or shear bands) [10, 11]. While the cell length scales here are too small to directly depict these, the results here display features which may be precursors. Because mean stress is one of the factors which affects system dilatation, J_1 at yield is plotted as a function of I_1 in Figure 17. Dilatation generally increases with mean stress. System n0 (with largest crosslink density) has the largest J_1 value for all conditions. The weaker dependence of J_1 on I_1 in compression is associated with the increased barriers to torsional rearrangement (as indicated in Figure 9). Further, the more open structure at low crosslink density (system n5) appears to enable better packing as the system is deformed. For system n5, contraction also occurred in some instances where I_1 was positive. It therefore appears that this contraction was at least partly enabled by the presence of shearing. In all instances of first-quadrant yield, dilatation was positive. To highlight this, first-quadrant points are shown as closed symbols in Figure 17. There is a dramatic increase in the amount of dilatation between uniaxial tension (the lowest solid symbols) and biaxial tension (the highest). Reminiscent of the results of Asp, et al. [12], there is a narrow range of I_1 at which yield occurred.

While the dilatation at yield in the first quadrant appears to be generally uniform across each system, there is evidence that post-yield flow would readily lead to void growth. The free volume in system n0 was investigated. Free volume was defined here as the portion of the cell not

enclosed by the van der Waals diameter of any atom. The diameter of the largest sphere which could be placed entirely within the free volume was monitored as deformation proceeded. The result for several cases is shown in Figure 18. Most notable is the distinct rise in sphere radius in first-quadrant cases. While these occurred at equivalent strain much greater than the value at yield, it should also be recalled that this system was essentially perfectly plastic in tension and biaxial tension. These results indicate that, if the stress on the system were to be held at the yield value in these two cases, plastic flow would rapidly progress and distinct nano-scale porosity would form (whereas it would not form in the other cases). Such voids may be precursors to a larger-scale rupture event. Indeed, actual thermoset systems have been shown to be less stable (i.e., have a stronger propensity to fracture) in first-quadrant loading. Kody and Lesser [8] found brittle behavior in biaxial tension and simple tension and ductile behavior in uniaxial compression.

Figure 17. The relation among first invariants of the strain and stress tensors at yield. Points on the extreme left and top correspond to biaxial compression and tension, respectively. Filled symbols with dark borders are first quadrant results.

Figure 18. Radius of the largest sphere of free volume found in system n0 as a function of equivalent strain.

Rupture

Rupture was here defined as the system state at the first instance of a backbone bond energy reaching or first exceeding its corresponding critical threshold value. These were collected for all systems and numerous load cases. The envelopes differed distinctly from those for yield. As shown in Figure 19, equivalent stress at rupture rises dramatically between biaxial tension and pure tension, rises more gradually between tension and pure compression, and continues to increase with the largest value apparently in biaxial compression. Because each outcome was dependent on the loading of a small fraction of atoms, dependence on crosslink density is difficult to discern.

Ductility was lowest in pure tension and biaxial compression. As inferred from Figure 20, equivalent strain at rupture varied little in the first and second quadrants with the exception of pure tension. It appears the superposition of a small stress level orthogonal to the tensile direction led to sufficient shear stress additional uncoiling and interchain slip. In the third quadrant, ductility generally decreased from compression to biaxial compression. Ductility generally increased with decreasing cross-link density. Between systems n0 and n3, crosslink density decreased by nearly three-fold from 1.4×10^{-3} to $0.48 \times 10^{-3} \text{ Å}^{-3}$. When comparing these two systems, ductility distinctly increased for all load cases. The crosslink density among systems n3 and n5 differed by too small an amount ($0.33 \times 10^{-3} \text{ Å}^{-3}$) to infer a trend. There have been experiments in which large ductility has been observed in epoxy. For example, Glad and Kramer [60] recorded stretch values in tension as high as 1.6 for the same systems as

576 those tested here. Cook and Mayr [80] observed strain to rupture in compression was an order
577 of magnitude greater than the yield strain.

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579 Figure 19. σ_1 σ_2 plot of stress at rupture. Values are MPa.

Figure 20. Equivalent strain at rupture in the form of a polar plot. Polar angle corresponds to principal stress ratio.

Several workers [8, 10, 11] observed distinct differences in the nature of yield and rupture between first quadrant loading and other loading cases. As shown in Figure 21, the level of the first strain invariant at rupture here showed a similar dichotomy among the quadrants. The experiments of [10] on several thermosets inferred first-quadrant J_1 values at rupture ranging from ca. -0.005 to 0.015. Increasing cross-link density tended to decrease the amount of dilation in the first quadrant.

Figure 21. Value of strain tensor first invariant as a function of in-plane principal stress ratio.

The bond type which was first to reach its rupture threshold provides insight into the nature of molecular loading in each load case as well as the possible fracture nucleation sites. Figure 22 shows ruptured bond type according to case for all systems. The most common bond type was between phenyl carbon and aliphatic carbon atoms. In cases for which there was a comparatively large tensile stress in one direction, however, either the carbon-nitrogen bond at the crosslink site or, for system n5, the backbone ether bond was the rupture site. When taken together with the result shown in Figure 20, it appears the lower ductility in cases approximating pure tension is related to the bond type which ruptures. Where there have been numerous experiments to determine the radicals formed from bond scission during tensile deformation of thermoplastics [81], there are no known results from experiments on thermosets against which to compare the results here.

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Figure 22. Bond break type results. Shown are the color-coding of bond types (a) and polar plots showing rupture bond type for systems n0 (b), n3 (c), and n5 (d). Arbitrary units.

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Because inter-atomic interactions are directly represented here, the results can be compared with fracture theories for polymers which include explicit treatment of atomic and molecular phenomena. Two of the most well-known are those of Zhurkhov [82] and Peterlin [83]. In Zhurkhov's model, the bond scission rate K_b becomes biased by the presence of tensile stress. That is

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$$K_b = K_f \exp[-(\Delta E - C\sigma)/kT] \quad (27)$$

where K_f is the molecular oscillation frequency and ΔE represents the size of the energy barrier to break a bond in an unstressed system. $C\sigma$ represents the bias to activation due to the presence of tensile stress. It is also indicative of the energy associated with stress concentration local to the bond. While experiments have identified mechano-radicals formed in thermoplastics under deformation [81], information about the mechanical energetic state local to radicals as they formed wasn't inferred from the measurements.

While the simulations presented here don't include scission kinetics and the associated energy barrier landscape, the state local to selected atoms for a given applied bulk stress can be examined in detail. The energy associated with potential interactions of a given atom with its neighbors as well as its thermal energy can be estimated. Because the former is associated with forces, associated directions can also be determined. The per-atom contribution tensor can be estimated by [59]

$$\begin{aligned} \hat{E}_{ij} = & - \left[m v_i v_j + \frac{1}{2} \sum_{n=1}^{N_p} (r_{1i} F_{1j} + r_{2i} F_{2j}) + \frac{1}{2} \sum_{n=1}^{N_b} (r_{1i} F_{1j} + r_{2i} F_{2j}) \right. \\ & + \frac{1}{3} \sum_{n=1}^{N_a} (r_{1i} F_{1j} + r_{2i} F_{2j} + r_{3i} F_{3j}) + \frac{1}{4} \sum_{n=1}^{N_d} (r_{1i} F_{1j} + r_{2i} F_{2j} + r_{3i} F_{3j} + r_{4i} F_{4j}) \\ & \left. + \frac{1}{4} \sum_{n=1}^{N_f} (r_{1i} F_{1j} + r_{2i} F_{2j} + r_{3i} F_{3j} + r_{4i} F_{4j}) + Kspace(r_{ki}, F_{kj}) + \sum_{n=1}^{N_f} (r_{ki} F_{kj}) \right] \end{aligned} \quad (28)$$

where i and j denote directional indices (i.e., x, y, z), r is particle location, and F is force. The successive terms correspond with kinetic energy, pair, bond, angle, dihedral, improper, kspace, and fix interactions, respectively. Each summation is performed over the number of interactions of the given type in which the atom participates. For terms associated with multi-atom interactions, the associated energy is apportioned according to the number of interacting atoms. Summing the terms in $\hat{E}_{ij}$ for all atoms over the cell volume would result in the stress tensor of the ensemble. Because bond energies are tracked on-the-fly, the state of each atom in the system can be captured when a bond rupture is imminent.

$\hat{E}_{ij}$ results were examined by expressing them as two scalars which contribute to the computation of invariants of the bulk stress tensor. These are

$$\hat{E}_1 = (\hat{E}_{xx} + \hat{E}_{yy} + \hat{E}_{zz}) \quad (29)$$

and

$$\hat{E}_{effective} = \sqrt{\frac{(\hat{E}_{xx} - \hat{E}_{yy})^2 + (\hat{E}_{yy} - \hat{E}_{zz})^2 + (\hat{E}_{zz} - \hat{E}_{xx})^2 + 6(\hat{E}_{xy}^2 + \hat{E}_{yz}^2 + \hat{E}_{zx}^2)}{2}} \quad (30)$$

Analogous to the earlier discussion, $\hat{E}_1$, is associated with dilatational energy present in the vicinity of the atom. $\hat{E}_{effective}$ is associated with local shear energy.

Investigation focused on the energy for atom types which were found most frequently in highly-strained bonds. Further, there were two atom types within these bonds which were not found elsewhere in the molecular structure. These are nitrogen at crosslinks and aliphatic carbon in the backbone (shown circled in Figure 23. The aliphatic interphenyl backbone carbon and crosslink nitrogen atoms investigated.). $\hat{E}$ data was generated for system n0 for five load cases, biaxial tension, tension, shear, compression, and biaxial compression. In all simulations, stress was applied in the x-y plane. The correspondence among load cases and the signs of the respective stresses applied is given in Table 3.

Figure 23. The aliphatic interphenyl backbone carbon and crosslink nitrogen atoms investigated.

Table 3. Signs of the stresses applied for various load cases.

Load case	x	y
Biaxial tension	+	+
Tension	0	+
Shear	-	+
Compression	-	0
Biaxial compression	-	-

Peterlin's theory [83] anticipated that, in tension or shear, various molecular strands would carry differing portions of the applied load with strands having a shorter contour length generally carrying a larger proportion. In order to investigate the geometric ordering of loaded atoms according to strands or other geometric entities, atoms were color coded according to $\hat{E}_1$ and $\hat{E}_{effective}$ levels and displayed by location. $\hat{E}_1$ results are shown in Figure 25 through Figure 29. $\hat{E}_{effective}$ results are shown in

Figure 30 through Figure 34. All figures depict the cell just prior to first bond rupture.

There are two general features associated with the formation of free volume pockets (i.e., nano-scale voids). First, approximately spherical voids formed in both tension cases in numerous locations. In shear, there were fewer voids which tended to be elongated in the direction of positive stress. Consistent with the negative J_1 values presented earlier, compression cases did not show voids. These results are also consistent with those of other researchers who found porosity generated in first-quadrant loading.

Second, atoms at void surfaces did not tend to be at elevated levels of $\hat{E}_1$ or $\hat{E}_{effective}$. This indicates that (unlike the macroscale continuum analog) the presence of concavity in the assembly of atoms did not correlate with a concentration of deformational energy. Rather, it appears these form when adjacent backbone strands move away from each other and that loading redistribution is accommodated by segmental motions.

Consistent with Peterlin, in tensile cases, both atom types along a single strand reached high positive $\hat{E}_1$ and $\hat{E}_{effective}$ levels. The most highly-strained bond occurred along these strands. In shear, it appears there are multiple highly-strained strands. In compression, there is no apparent spatial order to the high- $\hat{E}$ atoms and they are dispersed across the cell. The associated strength in the tension cases is therefore sensitive to the bond interactions among a small portion of the population. This apparent sensitivity is also consistent with results of experiments in which fracture occurs in tension cases whereas ductile flow occurs in compression.

There are several features of the $\hat{E}_{effective}$ results. Crosslinked nitrogen atoms are generally at higher $\hat{E}_{effective}$ than the aliphatic backbone carbon. Unlike the carbons, these nitrogens are located where load is transmitted across junctures among molecular strands. In compression cases, there is more variegation in $\hat{E}_{effective}$ among the carbon atoms than there is among the nitrogens. This lack of good distribution of strain energy among the carbons may be associated with the higher likelihood of carbon-carbon bond reaching critical values (as shown in Figure 22). Rather than generally decreasing $\hat{E}_1$ levels, compression led to higher levels of $\hat{E}_{effective}$. Because plane stress is being applied, the shearing energy indicated by elevated $\hat{E}_{effective}$ may be associated with the bulk shearing strain due to differences among out-of-plane and in-plane strains.

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705 Figure 25. Atom locations at incipient rupture in biaxial tension. Atoms are colored according to $\hat{E}_1$. Colors
706 range from -191 (dark blue) to 572 kcal/mol (red). The large red sphere is the midpoint location of the most

707 highly-strained bond. Shown are cross-linked nitrogen (a), inter-phenyl backbone carbon (b), and all atoms
708 (c). Stresses are applied in the x and y directions (denoted by the red and green marks, respectively).
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Figure 25. Atom locations at incipient rupture in uniaxial tension. Atoms are colored according to $\hat{E}_1$. The color scaling, atoms depicted, and strained-bond mark are the same as Figure 25. Stress is applied in the y direction (denoted by the green mark).

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Figure 26. Atom locations at incipient rupture in shear. Atoms are colored according to $\hat{E}_1$. The color scaling, atoms depicted, and strained-bond mark are the same as Figure 25. Stresses are applied in the x and y directions (denoted by the red and green marks, respectively).

Figure 27. Atom locations at incipient rupture in compression. Atoms are colored according to $\hat{E}_1$. The color scaling, atoms depicted, and strained-bond mark are the same as Figure 25. Stress is applied in the x direction (denoted by the red mark).

Figure 29. Atom locations at incipient rupture in biaxial compression. Atoms are colored according to $\hat{E}_1$. The color scaling, atoms depicted, and strained-bond mark are the same as Figure 25. Stresses are applied in the x and y directions (denoted by the red and green marks, respectively).

Figure 30. Atom locations at incipient rupture in biaxial tension. Atoms are colored according to $\hat{E}_{effective}$. The color scale ranges from 0.0 (dark blue) to 396 kcal/mol (red). Shown are cross-linked nitrogen (a), inter-phenyl backbone carbon (b), and all atoms (c). x and y directions are denoted by red and green marks, respectively.

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Figure 30. Atom locations at incipient rupture in uniaxial tension. Atoms are colored according to $\hat{E}_{effective}$. The color scaling, atoms depicted, axes, and strained-bond mark are the same as Figure 30.

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Figure 31. Atom locations at incipient rupture in shear. Atoms are colored according to $\hat{E}_{effective}$. The color scaling, atoms depicted, axes, and strained-bond mark are the same as **Figure 30**.

Figure 32. Atom locations at incipient rupture in uniaxial compression. Atoms are colored according to $\hat{E}_{effective}$. The color scaling, atoms depicted, axes, and strained-bond mark are the same as Figure 30.

Figure 34. Atom locations at incipient rupture in biaxial compression. Atoms are colored according to $\hat{E}_{effective}$. The color scaling, atoms depicted, axes, and strained-bond mark are the same as Figure 30.

Conclusions

An algorithm and results for atomistic simulation of generalized plane stress in glassy thermosets is presented. This simulation approach is realistic in that stresses are modulated to attain a target strain rate.

Cured epoxy systems scaled to include at least 100 crosslink sites have been investigated. The predicted elastic and strength properties show good agreement with measured values. The system response in plane stress shows agreement with continuum yield theories commonly applied to polymers. The evidence also supports the findings from experiments that strength has a different functional dependency in first-quadrant loading compared with the second and third. The results here show that plastic behavior, the development of nano-scale porosity, large increases in van der Waals energy after yield, and small changes in molecular torsional energy are differentiating features of the first-quadrant loading.

The rupture results provide information that complements the information provided by experiments of others and allows for testing of theories. Differing weak points in the crosslinked molecular structure according to load case are identified. The environment local to covalent bonds can be described. The geometric arrangements of atoms at high energy are consistent with molecular theories of molecular structural rupture in tension and provide insight into the geometric arrangements which may occur in other loading cases.

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807

808