

Contents lists available at ScienceDirect

Polymer



journal homepage: http://www.elsevier.com/locate/polymer

Quantifying the contributions of energy storage in a thermoset shape memory polymer with high stress recovery: A molecular dynamics study

properties of TSMPs.

Collin D. Wick^{a,*}, Andrew J. Peters^a, Guoqiang Li^b

^a College of Engineering & Science, Louisiana Tech University, Ruston, LA, 71270, USA

^b Mechanical & Industrial Engineering Dept., Louisiana State University, Baton Rouge, LA, 70803, USA

ARTICLE INFO	A B S T R A C T	
A R T I C L E I N F O Keywords: Shape memory polymers Molecular dynamics simulations Stress recovery	Molecular dynamics simulations were carried out to understand the mechanical and energy storage properties of bisphenyl-A diglycidyl ether cured with isophorone diamine — a thermoset shape memory polymer (TSMP) with both excellent shape memory and stress memory properties. Different cross-linked systems were created to determine which cross-linking percentage gave best agreement with experimental properties. It was found that for a 50% compression programming strain, higher cross-linking percentages stored more bond energy, but at the expense of a lower shape recovery. While bond energy was stored in the change in bond stretches, angles, and dihedrals, the bond angular and dihedral energies stored were significantly higher than bond stretches. Alkyl cyclic rings were able to store the most angular energy, but little to no stretching or dihedral energies. Aromatic rings stored dihedral energy, but little angular energy. The results show that the type of functional group has a	

1. Introduction

Thermoset shape memory polymers (TSMPs) have been a topic of intensive research for years, primarily due to the high mechanical performance, good thermal stability, resistance to creep, long fatigue life, good chemical resistance, and excellent shape recovery [1]. Within the TSMP family, epoxy based polymers are an important member, because of their versatility in chemical reaction and rich supplies in raw materials [2]. While epoxy based TSMPs have excellent shape memory properties, their recovery stress in the rubbery state is low because they exhibit low stiffness above the glass transition temperature. High recovery stress is needed in some applications, such as in self-healing of polymer composites to bring fracture surfaces in contact through the constrained shape recovery [3], in the oil and gas industry to serve as proppants to keep formation cracks open and to prepare expansive cement in order to reduce loss circulation during drilling [4,5], in pavement to serve as sealant to maintain contact with the joint or crack reservoir [6], in deployable structures [7], and in 4D printed actuators [8]. Usually, the requirements for shape recovery and stress recovery are in opposition, namely shape recovery needs lower stiffness in the rubbery state, while stress memory needs higher stiffness in the rubbery state. The primary reason this tradeoff is required is that these epoxy based TSMPs, as amorphous polymers, use entropy as the driving force for shape or stress recovery [9].

significant impact on how bond energy is stored, and could potentially be used to finely tune the shape recovery

Recently, Fan and Li [10] synthesized a new epoxy based TSMP, specifically Bisphenyl-A Diglycidyl Ether (DGEBA) cured by Isophorone Diamine (IPD). This polymer exhibited a very large recovery stress of 17 MPa in rubbery state and in bulk form, instead of the \sim 1–2 MPa in traditional entropy driven epoxy based TSMPs. They concluded the reason for the high recovery stress is that the shape/stress recovery is primarily driven by stored enthalpy through bond length changes. Another recyclable and 3D printable TSMP — composed of Bisphenol A glycerolate dimethacrylate and 2-hydroxy-2-methylpropiophenone — that utilizes this new driving force has also been recently synthesized [11]. Both materials exhibited very high recovery stress in rubbery state and in bulk form [10,11]. Accurately modeling this class of TSMPs will allow a deeper investigation into the fundamental causes of this behavior and allow further optimization.

Previously, Wu and Xu [12] developed a method that can be used with molecular dynamics (MD) simulations to cross-link epoxy polymers. However, the simulation did not focus on the shape memory effect and driving force. Shape memory properties of different polymers have

https://doi.org/10.1016/j.polymer.2020.123319

Received 14 September 2020; Received in revised form 29 October 2020; Accepted 10 December 2020 Available online 15 December 2020 0032-3861/© 2020 Elsevier Ltd. All rights reserved.

^{*} Corresponding author. *E-mail address:* cwick@latech.edu (C.D. Wick).

been studied with atomistic MD simulations, including polyisoprene, polystyrene, and poly(L-lactide) [13–15], along with coarse-grained simulations of generic cross-linked polymers [16]. In another recent study, Yan and Li [17] developed a thermodynamically consistent 4-chain analytical model to obtain theoretical stress-strain curves, which compared favorably with experimental results. This model considered both bond length and angle changes as a means to store enthalpy. However, this non-affine model is still an ideal simplification; it cannot predict the molecular level interactions during deformation. Therefore, an in-depth atomic level analysis of the shape and stress recovery properties of thermoset epoxy polymers is desirable.

The objective of this study was to conduct a comprehensive atomistic study for this new thermoset shape memory polymer DGEBA-IPD. Networks with multiple crosslink densities were generated, and the glass transition temperature, glassy state modulus, and rubbery state modulus were calculated and are compared with experimental results. The effect of bond length, angular, and dihedral energy change on energy storage and release is discussed, along with an estimate of shape and stress recovery properties. Finally, some conclusions are drawn based on the modeling results.

2. Simulation details

2.1. Initial equilibration

The optimized potential for liquid simulations (OPLS) force field was used for all calculations [18-20]. The initial DGEBA and IPD structures were created using the ligpargen software affiliated with the OPLS force field [21]. Once the structures were created, two DGEBA and a single IPD structure were placed in proximity to one another, which was replicated 216 times to create a system with 28,512 atoms. All calculations of the full system were carried out with the LAMMPS simulation software package [22,23]. Hydrogen atomic positions were kept rigid with the SHAKE and RATTLE algorithms [24]. This initial large system was created in a very low density configuration to assure that overlaps were not present, and an equilibration scheme was carried out as follows. The system was minimized (atomic positions and cell sizes), keeping the box length isotropic. A series of NpT MD simulations with the Nose Hoover thermostat and barostat [25] at a set pressure were carried out at a temperature of 398 K. The first MD simulation had a timestep of 0.25 fs, and 300,000 MD steps were carried out at a pressure of 5 atm. This initial simulation was used to compress the system, which was greatly dispersed initially. Then, 200,000 MD steps at a pressure of 1 atm were carried out with the same timestep. Next, 1,000,000 MD steps were run at the same pressure (1 atm), but with a larger timestep of 0.5 fs. The reason for the smaller timestep during the initial equilibration was to preserve system stability during the initial equilibration period. The system configuration was saved after this equilibration, and four additional configurations were saved with 200,000 MD steps carried out in between each for an additional 1,000,000 MD steps overall. The average box length of these systems was approximately 68.4 Å.

2.2. Cross-linking procedure

A cross-linking algorithm similar to what has been used previously was carried out [26,27]. First, 10,000 MD steps (5 ps) at a temperature of 398 K and a pressure of 1 atm were run. Situations in which the terminal glycidyl carbon on DGEBA was within 5 Å of an IPD amine nitrogen with at least one hydrogen bonded to it were identified. For the pair with the shortest distance, a bond between the carbon and nitrogen was formed. A bond between the glycidyl oxygen and the nearest amine hydrogen bonded to this nitrogen was also formed. This is illustrated in Fig. 1 where the dashed lines show bonds to be formed during the crosslinking procedure. Then, the energy was minimized in the entire system in which a smaller force constant of 5.0 kcal mol⁻¹ Å⁻² for the new bonds was enforced. The reason for the much lower force constant



Fig. 1. Schematic of the reaction procedure.

than the traditional OPLS model (which are both over 350 kcal mol⁻¹ Å⁻²) was to allow the transition to the new structure to be gradual. After the initial energy minimization, the regular OPLS force constants were used, and a second energy minimization was carried out. This entire procedure was then repeated until a desired cross-linking percentage was achieved. It should be noted that if there were no terminal DGEBA carbon – IPD amine distances less than 5 Å, then the procedure was repeated without forming any new bonds. The described cross-linking procedure was carried out for each of the five independent configurations, and any uncertainties shown are from the error of the mean of those five configurations.

2.3. Determination of glass transition temperature

To determine the glass transition temperature (T_g) , the systems were heated to 598 K and equilibrated there for 500 ps. After that, a slow cooling over 2.5 ns was carried out from 598 K to 198 K, keeping track of the density as a function of set temperature. The T_g values were estimated by the following procedure. For each of the five independent systems, multiple temperatures were trialed, from 250 K to 550 K in increments of 0.8 K. For each temperature trial, the best fit of a straight line for density versus temperature for all temperatures 40 K above the trial temperature was carried out, along with another best fit straight line for all temperatures 40 K below it. Where these straight lines intersected is reported to be the T_g . The trial that minimized the error between the two straight lines and the density/temperature curve for each of the independent systems, was used to determine its T_g . An example of this is shown in Fig. 2 for the 70% cross-linked system showing density versus temperature, and the two straight line fits for the



Fig. 2. Density as a function of temperature (solid line) for the 70% crosslinked system, along with the straight line fits (dashed lines) of the glassy and the rubbery density versus temperature. The T_g from this was found to be 429 K.

glassy and rubbery states.

2.4. Determination of Young's moduli

Once the T_q was identified for the 60%, 70%, 80%, and 90% crosslinked systems, the Young's modulus for the glassy and rubbery states was calculated for them. Room temperature (298 K) was chosen to calculate the modulus for the glassy state. This was done by the following procedure. Both compression and stretching calculations were carried out independently for each system and in each direction, x, y, and z. For a particular calculation, a linear deformation of 0.25% was carried out over a period of 25 ps, followed by 50 ps of equilibration at the fixed deformation. Succeeding the equilibration, an additional 100 ps run was used to calculate the average stress at that specific deformation. This procedure was repeated four times (increasing the deformation 0.25% of the original length each time) until a deformation of -1.25% for compression or +1.25% for stretching was completed. While having such a small deformation may increase the noise of the simulations, they will help mitigate the challenges faced with slow polymeric relaxation of MD simulations, and are consistent with previous work in the literature [28,29]. For each system and direction, the stress versus strain for the compression and stretching were combined. A linear fit to this data was used to calculate the Young's modulus for each independent system and direction. This gave a total of 15 independent results (5 systems with three directions each), which were used to calculate an average Young's modulus, with the uncertainty being the standard error of the mean. For these simulations, the pressure perpendicular to the deformation was set to 1 atm.

For the rubbery state, the temperature chosen was 30 K greater than the T_{σ} for each system. A procedure to better estimate the rubbery modulus at a slower rate of strain was performed, but still likely provides an estimate of the upper bound of the Young's modulus. To accelerate the relaxation of the system during strain, the previously described procedure was modified as follows. The deformation was carried out at an elevated temperature, 100 K higher than the set temperature in strain increments of -2% or +2% over 50 ps for compression/stretching, respectively. This was followed by a further relaxation at the elevated temperature for 500 ps. The system was then cooled to the set rubbery temperature (30 K greater than the T_g) for 100 ps, followed by another 100 ps run to calculate the stress at that deformation. This procedure was repeated four times for a total of -8% or +8% total change for compression/stretching, respectively. The calculation of the Young's modulus itself is the same as described for the glassy state. For both the glassy and rubbery moduli calculations many different simulation time lengths were investigated, with the arrived at values deemed a good balance between computational expense and accuracy.

2.5. Simulation details for polymer response to programming

To better understand the impact of the prestrain on the dynamic polymer configuration during programming, the 70% and 80% crosslinked systems each had a 50% compression applied over 4 ns in their rubbery state with the pressure perpendicular to the deformation set to 1 atm. Shape memory polymers need to be programmed in order for the polymer to exhibit shape memory effects. While hot (in its rubbery state), warm (in its glass transition zone), and cold (in its glassy state), temperatures can be used for programming [3], Fan and Li [10] used hot programming, which includes deformation in the rubbery state, holding stress or strain constant while cooling down to glassy state, and then load removal [3,30]. The 70% crosslink density system was chosen due to its reasonable agreement with experiment in its Young's modulus of the rubbery state (as described in section 3.1), and the 80% system was chosen to determine the impact of cross-linking percentage. A total of 15 simulations were carried out, three for each of the five independent systems and one for each of the x, y, and z directions.

3. Results

3.1. Glass transition and Young's moduli

The T_g and Young's modulus for the 60%, 70%, 80% and 90% crosslinked systems are shown in Table 1. The T_g has good agreement with experiment for the 60% and 70% cross-linked systems, becoming higher than experiment at higher cross-linking. The higher T_g is consistent with the fact that at a higher cross-linking density, polymer mobility is reduced [31]. The Young's moduli for the glassy systems are somewhat overestimated in comparison with experiment over the entire cross-linking range if we take the static compression test results as comparison. However, if we compare with the moduli by DMA test, the Young's moduli for the glassy systems are somewhat underestimated in comparison with experiment over the entire cross-linking range. Considering the short time scale in the MD model and the small strain used, DMA test results should be more representative of the bulk polymer. For the rubbery state, the Young's modulus is reasonably close to experiment for the 70% systems, while significantly overestimated for the higher cross-liking. This suggests that the actual cross-linked percentage is likely closer to 70% than 90%. Unsurprisingly, cross-linking percentages have little impact on the Young's modulus for the glassy state, while a major impact on the rubbery state.

3.2. Programming

A plot of the average stress versus strain for the glassy and rubbery systems during programming and compression to 50% are given in Fig. 3 for the 70% cross-linked system. The reason the 70% cross-linked system is studied in this context is due to its reasonable agreement with the experimental elastic constants and T_g , as given in Table 1, and that it shows sufficient shape recovery (see section 3.4). To make the simulations tractable, a very high programming strain rate in comparison to experiment had to be used. This makes matching experiment in the rubbery state, where relaxations of long polymer sections are important, difficult. The curve for the glassy state shows an increase in strain at a relatively consistent degree until it reaches 175 MPa, around 10% strain. After that, there is some vielding and strain softening until 30% strain is reached, followed by strain hardening. Comparing with the experimental curve (Figure S14 in the supplementary data in Ref. [10]), these features are all present, but there are some quantitative differences between the curves. The experimental curve has a maximum of 320 MPa around a 57% strain level, while the simulation result hits 325 MPa at a 50% strain.

The rubbery stress curve appears to have similar regions as the glassy curve, but they are not as pronounced. At 50% strain, the stress is around 175–200 MPa. This is significantly higher than what is found experimentally (Figure S8 in the supplementary data from Ref. [10]), which showed 55–60 MPa stress at 50% strain. The much higher strain rate in the simulations in comparison with experiment is likely why simulation overpredicts the stress for the rubbery state, which requires more time for the polymers to rearrange than in the glassy state where shorter deformations are possible. This is why the relaxation procedure at

Table 1

A comparison of the calculated T_g and Young's moduli (E) for the rubbery and glassy states of the systems studied with experiment.

System	<i>T_g</i> (K)	E_{glassy} (GPa)	E_{rubbery} (GPa)
60%	418 ± 6	1.35 ± 0.05	0.025 ± 0.004
70%	429 ± 3	1.72 ± 0.08	0.05 ± 0.02
80%	456 ± 11	1.76 ± 0.05	0.14 ± 0.01
90%	461 ± 22	1.85 ± 0.1	0.42 ± 0.02
Exp(static) ^a	420 ± 10	1.05	0.02
Exp (DMA) ^b	420 ± 10	~ 2.10	~0.06

^a Static compression test from reference [10].

^b Dynamic mechanical analysis (DMA) from reference [10].



Fig. 3. Stress versus strain for the 70% cross-linked system in rubbery and glassy states.

elevated temperatures is used to get a quantitative value for the rubbery modulus. To study the impact of further relaxation for the rubbery state, an additional 4 ns of relaxation was carried out at a fixed strain of 50%. The stress decreased by over 100 MPa to a value of 59 MPa after this additional relaxation for the 70% cross-linked system, approaching the experimental number. It should be noted that experimentally (Figure S8 in the supplementary data in Refs. [10]), a relaxation of around 15 MPa was observed over a long period of time. It may be possible to approach this with simulation, but the computational time for it to occur is prohibitively long.

3.3. Stress recovery

Further simulations were carried out after the 4 ns relaxation described to study stress recovery. The relaxed systems were cooled to 298 K over a 4 ns period at a fixed 50% strain. After that, they were allowed to fully relax for 4 ns at 298 K, in which a small elastic springback strain occurred. The amount the polymer shape changes during this elastic spring-back is a way to determine the ability of the polymer to fix its mechanical deformation. It is described as the shape fixity ratio, and can be calculated after the relaxation at 298 K [9],

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \tag{1}$$

where ε_u is the strain after the relaxation at 298 K and ε_m is the maximum strain applied during the initial programming (50%). For the 60% cross-linked system, the fixity ratio is 1.0, and it is 0.99 for 70%, 0.97 for 80%, and 0.91 for the 90% system, showing that higher cross-linked systems have more elastic spring-back and lower fixity.

After cooling, the systems were heated to their rubbery states at a fixed strain, ε_{u} , over a period of 4 ns, followed by another 4 ns of relaxation at the same fixed strain. The recovery stress achieved with this procedure was 52 MPa for the 70% cross-linked system. This compares with the experimental value near 18 MPa for a system programmed to a 45% strain [10]. Clearly, the simulations significantly overestimate the recovery stress due to the short simulation times achievable with current computational power, which does not allow sufficient time for stress relaxation. While not quantitatively able to match experiment, both the recovery stress and the stress after programming (before the additional relaxation) were approximately three times higher than experiment, indicating that qualitative comparisons should be viable for the rubbery state.

The impact of cross-linking density was also studied for recovery stress, following the same simulation protocols as descried for the 70% cross-linked system. The 90% cross-linked system had a recovery stress of 110 MPa, 76 MPa for 80%, and 24 MPa for the 60% system. This is consistent with the moduli for the different cross-linked ratios, as higher moduli lead to higher stress during programming, which should also increase the recovery stress.

3.4. Shape recovery

After the stress recovery simulations, 2 ns of NPT simulations were carried out at the rubbery state temperature (30 K higher than T_g) at a pressure of 1 atm. The shape recovery ratio can be calculated from the change in strain with respect to the maximum strain, ε_m , after programming [9],

$$R_r(t) = \frac{\varepsilon_m - \varepsilon_p(t)}{\varepsilon}$$

where ε_p is the strain during the shape recovery process as a function of time. Fig. 4 (left) shows the shape recovery ratio as a function of time for the 60%, 70%, 80% and the 90% cross-linked systems. At 30 K above the T_g , the cross-link density is strongly correlated to how fast the system recovers. However, comparing these systems is difficult as higher cross-linked systems have higher T_g values, and thus are being run at a higher temperature. Also, it is clear that the rate of shape recovery is very slow at these temperatures, and higher temperatures should improve the rate to have a chance to approach full shape recovery.

To overcome the kinetic challenges by running the simulations at 30 K higher than their T_g , NPT simulations at 1 atm were carried out at 550 K for both systems for a longer simulation time of 8 ns immediately following the stress recovery simulations. The results of these shape recovery simulations are also given in Fig. 4 (left). The 90% cross-linked system demonstrates the fastest initial shape recovery, but after 1-2 ns, the lower cross-linked systems have the greater amount. For the 60% cross-linked system specifically, its shape recovery stabilizes around 0.55 and doesn't change significantly after that. The higher cross-linked systems show steady increases of shape recovery throughout the entire simulation time with the average increase at 8ns being greatest for the 70% cross-linked system and lowest for the 90% system. To observe full shape recovery would likely take much longer than can be simulated in a reasonable amount of time, but the trends are consistent for 70% crosslinking and above. This result shows that a certain amount of crosslinking is needed for full shape recovery, and there is likely a balance between enthalpy and entropy.

Fig. 4 (right) also gives the energy during the initial shape recovery simulations (those carried out at 30 K higher than T_g). The energy rapidly increases until it reaches a maximum for the 80% and 90% cross-linked systems, and a plateau for the 70% cross-linked system. For the 60% cross-linked system, the energy change is pretty close to zero throughout the entire simulation. The abrupt increase in energy for the higher cross-linked systems can be linked to their higher stress recovery, which is a consequence of the greater enthalpic driving force for shape recovery for the higher cross-linked systems [10]. These energetic contributions will be discussed in detail in the next section. This is the likely reason why the shape recovery rate is faster in the earlier stages of shape recovery for the more cross-linked system.

3.5. Energetic contributions

The energetic contributions were broken down into bonded and nonbonded energies. The results for this are shown in Fig. 5, including the energy during programming, after the 4 ns relaxation at the programming temperature, and after 0.25 ns of shape recovery simulations, where the total potential energy is at a maximum (as shown in Fig. 4 (right)). The energies shown are with respect to their equilibrium values



Fig. 4. Shape recovery ratio as a function of simulation time (left) at the programming temperatures (30 K higher than T_g) being the shorter dashed lines and at 550 K being the longer solid lines. Energy as a function of time at the programming temperatures with units in kJ/mol of hardener (right).



Fig. 5. Energy as a function of programming strain (open circles), after relaxation (open squares), and during shape recovery (solid diamonds). Units are in kJ/mol of hardener.

at their respective programming temperatures in units of kJ/mol of hardener. They were averaged for each 5% strain increment (i.e. 0-5%, 5-10%, up to 45-50%). Furthermore, bonded energies are defined as the

combined bond stretching, bending, and dihedral energies, while the non-bonded energies include Lennard-Jones and electrostatic energies, all as defined from the OPLS force field [18–20]. During programming, the non-bonded energies immediately become positive, but change very little after that. The bonded energies, meanwhile, increase in a fairly linear fashion throughout programming. After relaxation, the bonded energies decrease to approximately half of their values after programming. The non-bonded energies not only decrease, but become negative for both systems. It should be noted that the overall energy (bonded plus non-bonded energies) is still positive after relaxation at 1.48 kcal mol⁻¹ for 70% and 1.62 kcal mol⁻¹ for 80% cross-linking. During shape recovery, bonded energies decrease further, while the non-bonded energies for the systems over their relaxed values, due to the non-bonded energy increase.

Fig. 6 breaks down the bonded energies into bond stretching, angular, and dihedral contributions with respect to their equilibrium values as a function of strain for the 70% and 80% cross-linked systems in units of kJ/mol of hardener. It should be noted that the dihedral energies included both regular dihedral and 'improper torsions' as defined in the OPLS force field [21], and the change in energy from improper torsions was smaller than the uncertainties in the values (less than 0.1 kJ/mol of hardener). The bond angle and dihedral energies increased to a greater degree than the bond stretching energy for both systems, with the 80% cross-linked system showing the greater increases for all energies by around a factor of two in comparison to the 70% system. While not shown, the average bond lengths and angles are



Fig. 6. Bond stretching, bending, and dihedral energies with respect to equilibrium values as a function of strain for the 70% cross-linked system (left) and 80% cross-linked system (right) with open circles representing programming. Open square and filled diamond symbols represent values after additional relaxation, and during shape recovery (see text), respectively. Units are in kJ/mol of hardener.

greater than their equilibrium values before any deformation due to ring strain. Upon compression, they both increase with increased strain. After the programming, the systems were allowed to relax for an addition 4 ns at 50% strain (squares in the figure), which resulted in a significant decrease in bond stretching, angular, and dihedral energies. Moreover, after 0.25 ns of shape recovery, the bond stretching, angular, and dihedral energies were calculated. The bond angular and dihedral energies for both systems reduced further during the initial stages of shape recovery, but were still more positive than the stretching energies. The bond stretching energies changed little, and for the 70% cross-linked system are the same as the equilibrium value within the uncertainty. Previous experimental results made the observation that bond lengths increased with compression for DGEBA-IPD [10], which is in agreement with this observation. However, this previous experimental work did not investigate the role of bond angles, dihedrals, or their energy changes, which is found to be significantly greater than the change in bond stretching in our simulations.

Fig. 7 gives a breakdown of the bond stretching, bending, and dihedral energies into functional group contributions as a function of strain for the 70% cross-linked system, along with values after stress recovery. These were calculated by identifying atoms in each bond stretch (two atoms), angle (three atoms), and dihedral (four atoms). The bond classifications were as follows. For a bond stretch to be considered to be a part of the backbone, both atoms in it needed to be classified as such. Hydrogens, methyl carbons, and alcohol oxygens were all classified as non-backbone. Aromatic bonds and alkyl cyclic bonds were only classified as such if both atoms were part of an aromatic ring or a cyclic ring, respectively. For angles, first a check was done to make sure that all atoms were part of the backbone. If any one of the three of them were not, the angle was classified as non-backbone. If two of them were aromatic or alkyl cyclic atoms, then they were classified as such, and in all other cases, they were classified as non-ring backbone atoms. For dihedrals, if any of the four atoms were not backbone atoms, the dihedral was classified as non-backbone. If two of the dihedral atoms were aromatic or alkyl cyclic, the dihedral was classified as such. As with the angles, all other cases were classified as non-cyclic backbone atoms. Aromatic carbons are a part of DGEBA, while alkyl cyclic carbons are included in IPD. These energies were scaled by the number of them that were present in the system (i.e. number of bond stretches or angles for that particular group type) to give the energy per bond stretch or angle instead of the total energy. The energies were also calculated after 0.25 ns of shape recovery, and all values were scaled with respect to the highest energy after 0.25 ns of shape recovery, which was set to 1.0.

The bond stretching energies increase the most for non-ring backbone atoms, and to a moderate degree for aromatic carbons. The nonbackbone atoms have very little change, while the alkyl cyclic atoms show a decrease in energy throughout programming and after recovery. One should note that after 0.25 ns of shape recovery, the bond stretching energy is essentially zero for 70% cross-linking (see Fig. 5), so it likely has very little impact on overall energy during recovery. The angular energies increase the most for alkyl cyclic carbons, and for a lesser, but substantial degree for the non-ring backbone atoms. During shape recovery, both of these energies are very similar. The aromatic and nonbackbone atoms have only small changes in angular energy. Dihedral energies increase the most with programming for aromatic ring and nonring backbone atoms, while are essentially zero or slightly negative for alkyl cyclic atoms. During shape recovery, all of these values decrease to a significant degree with the aromatic ring energies being the highest at the completion of the simulation. These results show that all atoms in the polymer backbone play a role in the storage of bonded energy, but the type of bonded energy depends on the type. Non-ring and aromatic atoms store the most bond stretching energy, alkyl cyclic and non-ring atoms store the most angular energy, while aromatic atoms store the most dihedral energy. The type of energy stored may have a significant impact on shape memory properties, which is part of ongoing research.

3.6. Coarse structure

To understand the mid and longer ranged structure of the polymer network, the IPD amine nitrogen atoms were tracked throughout the compression simulations. The radial distribution function, RDF, between amine nitrogen atoms on the same IPD molecule (intramolecular N), between IPD amine nitrogens bonded to the same DGEBA molecule (bonded N), and those that are neither in the same IPD molecule or bonded by a DGEBA molecule (non-bonded N) were all calculated. The RDFs were evaluated per atom, and normalized by the volume only. Because of this, as the density of the system changes, there is no change in the RDF normalization, unlike in the traditional way of calculating RDFs [32]. This analysis was done for the 70% cross-linked systems, which were chosen due to the fact that their calculated properties more closely resembled experimental results. All results compare the equilibrated structures to those with moderate strain (15%) and those approaching the maximum tested strain (45%) with respect to the equilibrium structure.

The RDFs between the intramolecular nitrogens are given in Fig. 8. There are two configurations of the IPD structure based on the rotation of the secondary amine group. The one with the smaller r distance (close structure) is shown in Fig. 8a, while the one with the greater distance (far structure) is shown in Fig. 8b. These are snapshots taken from an equilibrated system. With increased strain, there is a shift from close structures to more far structures with the biggest shift occurring at moderate strain rates. The change from moderate to large overall strain mostly resulted in broadening of both the near and far RDF peaks. This is consistent with the overall bond stretching energy (and thus distance) increases with higher strain that was observed.

Fig. 9 gives the RDFs between bonded IPD amine nitrogens (i.e. those connected by a DGEBA molecule) under compressive stress. The distribution in their distances range from around 5 Å to just over 20 Å. The



Fig. 7. Scaled bond stretching energies (left), bond bending energies (middle), and bond dihedral energies (right) as a function of strain between atoms of different functional groups for the 70% cross-linked system. The square symbols represent values during shape recovery (see text).



Fig. 8. Radial distribution function between intramolecular IPD amine nitrogen atoms (top), and snapshots of IPD structure for the close (a) and far (b) structures as defined in the text.



Fig. 9. Radial distribution function between bonded IPD amine nitrogen atoms (see text for definitions).

equilibrium structure has a peak around 17 Å between IPD nitrogen atoms. There is a major difference between the equilibrium RDF and 15% strained system, while little difference between the 15% and 45% strained system can be observed. In both cases, the peak shifts to larger distances. This is despite the fact that the system is under greater compressive force with higher strain rates, but the regions perpendicular to the applied stress expand to cause the volume to shrink by only 2.7%.

To understand the influence of strain direction, the RDF for bonded nitrogens was split into contributions based on the angle, θ , between the vector among these nitrogen atoms and the strain direction. If $\cos \theta > 0.5$, then the nitrogen atoms were considered aligned with the strain direction, while if $\cos \theta < 0.5$, they were considered to be aligned perpendicular to the strain direction. The nitrogens aligned with the

strain direction (cos $\theta > 0.5$) do not show as much of the shift to larger distances than those that are aligned perpendicular to the strain direction (cos $\theta < 0.5$). This is likely a consequence of the Poisson effect. Overall, the bonded IPD amine nitrogens show behavior consistent with the intramolecular IPD nitrogens in that they shift to larger distances with greater strain.

For non-bonded IPD amine nitrogens (those not directly connected by a DGEBA molecule), Fig. 10 gives their RDFs for the equilibrium structure and those under strain. The equilibrium structure has an initial peak around 7 Å, followed by a gradual increase as a function of distance. The reason for this gradual increase is due to shorter distances being occupied by intramolecular atoms and bonded nitrogens. When both the bonded and non-bonded RDFs are combined, the RDF peaks at around 16 Å and fluctuates after that. Upon large compression, the RDF starts to fall off around 18.0 Å due to the box length in the compression direction becoming smaller than 36 Å. The RDFs increase to a significant degree at shorter distances when under strain. Since these values are scaled by volume and not density, the compression of the simulation box is expected to shift the RDFs to shorter values. The RDF between nitrogens aligned with the strain direction are similar to the overall RDF, while those perpendicular to the strain direction show a larger increase in RDF at short to moderate distances. This shows that under compression, the intermolecular nitrogens pack more tightly perpendicular to the strain, while Fig. 9 demonstrates bonded nitrogens pack closer in line with the compression. In other words, compression causes the bonded structures to pack more tightly in line with compression, while bonded structures perpendicular to compression get pushed away due to the Poisson effect. At the same time, non-bonded structures, get pushed into the space between the bonded structures.

4. Discussion

Programming is used to input free energy in the rubbery state via $\Delta G = \Delta H - T\Delta S$, which is then stored in the glassy state. There is a challenge in modeling these systems due to the long timescales required to observe different phenomena experimentally. However, semi-quantitative comparisons can be made. Most of the enthalpic contributions are stored in the bonds, which can be directly calculated by the simulations as described in section 3.4. Throughout all of the deformations in our calculations, the stress increases, and as a consequence, ΔG is positive. While our results are consistent with previous experimental analysis [10], we show that the most significant energy change is due to increase in bond angles and dihedrals, not bond lengths.

Overall, the bond energy increase is much higher at 80% crosslinking than 70%. This indicates that higher cross-linking percentages



Fig. 10. Radial distribution function between non-bonded IPD amine nitrogen atoms (see text for definition).

contribute to greater energy storage during programming, which may increase stress recovery, and is what we find in our simulations with a 50 MPa stress recovery for 70% cross-linking and 77 MPa for 80%. However, the 80% rubbery modulus is much higher than the 70% modulus, reducing the difference between the glassy and rubbery moduli, which may reduce shape memory. This aspect is further shown in our comparisons of the shape recovery, in which after being much faster early on for the 80% cross-linked system, the 70% cross-linked system has more shape recovery after 2 ns of simulation time. The change in rubbery modulus shown in Table 1 indicates a relatively small difference between the moduli of the 60% and 70% cross-linked systems, but a very large difference between 70% and 80%. There appears to be a specific cross-linked percentage that would have a good balance between shape and stress memory for each TSMP, and could be a potential focus for fine tuning the shape memory properties of polymers.

The breakdown of different bonded energy contributions given in Fig. 6 shows that most of the bond stretching energy stored is along the backbone atoms. However, during the initial stages of shape recovery, the amount of bond stretching energy is not significantly different than the equilibrated system. Angular energy increases the most for alkyl cyclic and non-ring backbone atoms, and dihedral energy increases the most for aromatic and non-ring backbone atoms. How bond energy is stored (bond stretching versus bond bending versus bond dihedral) may impact on the balance between shape and stress memory, and is worth considering for future design of TSMPs. For instance, if a polymer with a higher proportion of alkyl cyclic groups was present, more of its energy would likely be stored as bond angular energy. The impact of this is something that will be investigated in future work, and requires comparing among multiple polymer types. It would be expected that bond stretching would be the least impactful property due to its much lower energy increase during programming, and angular and dihedral energies would play a greater role. For dihedral energies, in particular, shifting from gauche to trans configurations during programming may create significant changes in structure. However, the ratio of trans configurations of the entire polymer was calculated during programming and only increased by 0.02%, from 38.295% to 38.315%, for the 70% cross-linked system. As such, most of the dihedral energy increase is due to the shifting to higher energy regions versus major changes in structure. For some polymers, possibly with lower dihedral barriers in certain parts, there may be more potential for major changes in dihedral energies. Overall, future work comparing polymers with different hardeners, including aromatic, alkyl cyclic, and non-ring, should shed additional light on design aspects that will increase energy storage during programming.

5. Conclusions

Using molecular dynamics simulations, a thermoset shape memory polymer, DGEBA-IPD, was investigated for its mechanical and energy storage properties. Reasonable agreement between simulation and experiment was found for tested thermomechanical properties. The higher the cross-linking ratio, the more the bond energy stored, and the higher the recovery stress observed, but at the expense of a lower shape recovery. Overall, more energy was stored in bond angles and dihedrals than stretches, but it depended on the type of atoms involved. For alkyl cyclic atoms, nearly all of the bond energy was stored as angular energy. However, non-ring polymer backbone atoms energy could be stored in bond stretches, angles, and dihedrals, while aromatic atoms stored most of its bond energy in its dihedrals. Non-backbone atoms did not store significant energy. Overall, the results show that all backbone atoms store bond energies, and the balance between bond stretching, angular, and dihedral energies depended on the specific moieties in the backbone. The pair distribution functions for bonded and non-bonded IPD nitrogens were also analyzed. It was found that compression causes the bonded structures to pack more tightly in line with compression, while bonded structures perpendicular to compression get pushed away due to the Poisson effect. At the same time, non-bonded structures, get pushed into the space between the bonded structures. The counterbalancing nature that greater recovery stress has on shape memory creates challenges in designing materials that can increase both of them. Overcoming this challenge likely requires the study of significantly more systems with the need for high level analysis tools such as machine learning. These will be part of the research strategy moving forward.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is supported by the the US National Science Foundation under grant number OIA-1946231 and the Louisiana Board of Regents for the Louisiana Materials Design Alliance (LAMDA). The high performance computing resources provided by the Louisiana Optical Network Infrastructure (https://loni.org) were used for this work.

References

- C. Liu, H. Qin, P.T. Mather, Review of progress in shape-memory polymers, J. Mater. Chem. 17 (2007) 1543–1558, https://doi.org/10.1039/b615954k.
- [2] K.S. Santhosh Kumar, R. Biju, C.P. Reghunadhan Nair, Progress in shape memory epoxy resins, React. Funct. Polym. 73 (2013) 421–430, https://doi.org/10.1016/j. reactfunctpolym.2012.06.009.
- [3] G. Li, Self-healing Composites: Shape Memory Polymer-Based Structures, John Wiley & Sons, Inc., West Sussex, UK, 2014.
- [4] A. Mansour, A. Dahi Taleghani, S. Salehi, G. Li, C. Ezeakacha, Smart lost circulation materials for productive zones, J. Pet. Explor. Prod. Technol. 9 (2019) 281–296, https://doi.org/10.1007/s13202-018-0458-z.
- [5] L. Santo, A. Dahi Taleghani, G. Li, Expandable proppants to moderate production drop in hydraulically fractured wells, J. Nat. Gas Sci. Eng. 55 (2018) 182–190, https://doi.org/10.1016/j.jngse.2018.04.026.
- [6] G. Li, T. Xu, Thermomechanical characterization of shape memory polymer–based self-healing syntactic foam sealant for expansion joints, J. Transport. Eng. 137 (2011) 805–814, https://doi.org/10.1061/(ASCE)TE.1943-5436.0000279.
- [7] Y. Liu, H. Du, L. Liu, J. Leng, Shape memory polymers and their composites in aerospace applications: a review, Smart Mater. Struct. 23 (2014) 23001, https:// doi.org/10.1088/0964-1726/23/2/023001.
- [8] A. Li, A. Challapalli, G. Li, 4D printing of recyclable lightweight Architectures using high recovery stress shape memory polymer, Sci. Rep. 9 (2019) 1–13, https://doi. org/10.1038/s41598-019-44110-9.
- [9] A. Lendlein, S. Kelch, Shape-memory polymers, Angew. Chem. Int. Ed. 41 (2002) 2034–2057, https://doi.org/10.1002/1521-3773(20020617)41:12<2034::AID-ANIE2034>3.0.CO;2-M.
- [10] J. Fan, G. Li, High enthalpy storage thermoset network with giant stress and energy output in rubbery state, Nat. Commun. 9 (2018) 642, https://doi.org/10.1038/ s41467-018-03094-2.
- [11] A. Li, J. Fan, G. Li, Recyclable thermoset shape memory polymers with high stress and energy output: via facile UV-curing, J. Mater. Chem. A. 6 (2018) 11479–11487, https://doi.org/10.1039/c8ta02644k.
- [12] C. Wu, W. Xu, Atomistic molecular modelling of crosslinked epoxy resin, Polymer 47 (2006) 6004–6009, https://doi.org/10.1016/j.polymer.2006.06.025.
- [13] J. Diani, K. Gall, Molecular dynamics simulations of the shape-memory behaviour of polyisoprene, Smart Mater. Struct. 16 (2007) 1575, https://doi.org/10.1088/ 0964-1726/16/5/011.
- [14] J. Moon, J. Choi, M. Cho, Programmed shape-dependence of shape memory effect of oriented polystyrene: a molecular dynamics study, Polymer 102 (2016) 1–9, https://doi.org/10.1016/j.polymer.2016.08.096.
- [15] X.-J. Zhang, Q.-S. Yang, X. Liu, J.-J. Shang, J.-S. Leng, Atomistic investigation of the shape-memory effect of amorphous poly(L-lactide) with different molecular weights, Smart Mater. Struct. 29 (2020) 15040, https://doi.org/10.1088/1361-665X/AB471C.
- [16] J.D. Davidson, N.C. Goulbourne, Microscopic mechanisms of the shape memory effect in crosslinked polymers, Smart Mater. Struct. 24 (2015), https://doi.org/ 10.1088/0964-1726/24/5/055014.
- [17] C. Yan, G. Li, A mechanism-based four-chain constitutive model for enthalpydriven thermoset shape memory polymers with finite deformation, J. Appl. Mech. 87 (2020), 061007, https://doi.org/10.1115/1.4046583.
- [18] W.L. Jorgensen, J. Tirado-Rives, The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin, J. Am. Chem. Soc. 110 (1988) 1657–1666, https:// doi.org/10.1021/ja00214a001.

C.D. Wick et al.

- [19] W.L. Jorgensen, J.D. Madura, C.J. Swenson, Optimized intermolecular potential functions for liquid hydrocarbons, J. Am. Chem. Soc. 106 (1984) 6638–6646, https://doi.org/10.1021/ja00334a030.
- [20] W.L. Jorgensen, D.S. Maxwell, J. Tirado-rives, N. Haven, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids, J. Am. Chem. Soc. 118 (1996) 11225–11236, https://doi.org/ 10.1021/ja9621760.
- [21] L.S. Dodda, I.C. De Vaca, J. Tirado-Rives, W.L. Jorgensen, LigParGen web server: an automatic OPLS-AA parameter generator for organic ligands, Nucleic Acids Res. 45 (2017) W331–W336, https://doi.org/10.1093/nar/gkx312.
- [22] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, J. Comput. Phys. 117 (1995) 1–19, https://doi.org/10.1006/jcph.1995.1039.
- [23] LAMMPS Molecular Dynamics Simulator. http://lammps.sandia.gov (n.d.).
- [24] H.C. Andersen, Rattle: a "velocity" version of the shake algorithm for molecular dynamics calculations, J. Comput. Phys. 52 (1983) 24–34.
- [25] S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, J. Chem. Phys. 81 (1984) 511–519, https://doi.org/10.1063/1.447334.
- [26] C. Li, A. Strachan, Molecular scale simulations on thermoset polymers: a review, J. Polym. Sci., Part B: Polym. Phys. 53 (2015) 103–122, https://doi.org/10.1002/ polb.23489.

- [27] Y. Fu, J.G. Michopoulos, J.H. Song, On investigating the thermomechanical properties of cross-linked epoxy via molecular dynamics analysis, Nanoscale Microscale Thermophys. Eng. 21 (2017) 8–25, https://doi.org/10.1080/ 15567265.2016.1263696.
- [28] A.J. Peters, T.P. Lodge, Comparison of gel relaxation times and end-block pullout times in ABA triblock copolymer networks, Macromolecules 49 (2016) 7340–7349, https://doi.org/10.1021/acs.macromol.6b01921.
- [29] S. Morozova, M.L. Coughlin, J.T. Early, S.P. Ertem, T.M. Reineke, F.S. Bates, T. P. Lodge, Properties of chemically cross-linked methylcellulose gels, Macromolecules 52 (20) (2019) 7740–7748, https://doi.org/10.1021/acs. macromol.9b01401.
- [30] P. Miaudet, A. Derré, M. Maugey, C. Zakri, P.M. Piccione, R. Inoubli, P. Poulin, Shape and temperature memory of nanocomposites with broadened glass transition, Science 318 (80-) (2007), https://doi.org/10.1126/science.1145593, 1294 LP-1296.
- [31] H. Stutz, K. H Illers, J. Mertes, A generalized theory for the glass transition temperature of crosslinked and uncrosslinked polymers, J. Polym. Sci., Part B: Polym. Phys. 28 (1990) 1483–1498, https://doi.org/10.1002/ polb.1990.090280906.
- [32] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1987.