Molecular Modeling of Physical Aging in Epoxy Polymers

Ananyo Bandyopadhyay, Gregory M. Odegard
Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931
Correspondence to: Gregory M. Odegard (E-mail: *gmodegar@mtu.edu*)

ABSTRACT

Epoxy resins are often exposed to prolonged periods of sub-T_g temperatures which cause physical aging to occur. Because physical aging can compromise the performance of epoxies and their composites and because experimental techniques cannot provide all of the necessary physical insight that is needed to fully understand physical aging, efficient computational approaches to predict the effects of physical aging on thermo-mechanical properties are needed. In the current study a new method is developed to efficiently establish molecular models of epoxy resins that represent the corresponding molecular structure at specific aging times. Although this approach does not simulate the physical aging process directly, it is useful in establishing molecular models that resemble physically-aged states of epoxies. Such models are useful for predicting the thermo-mechanical properties of aged epoxy resins to facilitate the design of durable engineering structures. For demonstration purposes, the developed method is applied to an EPON 862/DETDA epoxy system for three different crosslink densities.

INTRODUCTION

Epoxy resins are the prime constituents in many adhesives, paints, coatings, sealants, and aircraft composite structural components. Epoxies are ideal for these applications because of their high specific strength, high specific stiffness, ease of manufacture, and chemical compatibility with reinforcing composite fibers. Because most of these applications demand long-term exposure to various environmental conditions, it is important to understand the influence of these conditions on the structural integrity of epoxy materials.

Physical aging is generally characterized as an increase in mass density (volumetric relaxation) and/or a decrease in molecular conformational energy (enthalpy relaxation) of amorphous or semicrystalline materials when exposed to temperatures below the glass transition (T_g) for extended periods of time. Physical aging usually results in decreases in toughness and viscoelastic response of polymers and other glassy materials. This is clearly a concern for the industries that use epoxy resins for applications that require acceptable levels of structural integrity for extended periods of exposure to sub-T_g temperatures.

During the last several decades, a large number of studies have focused on the experimental characterization of physically-aged epoxies.[1] These studies have described a great number of observed thermo-mechanical behaviors of aged epoxies and speculated on the physical nature of these observations. However, despite the breadth of data and theories on observed physical aging behavior, many questions still exist regarding the exact molecular mechanisms that are

associated with physical aging. It is possible that some of these questions can be answered using computational molecular modeling techniques in which the molecular structure and behavior of epoxy networks can be simulated for a wide range of exposure conditions.

Several studies have focused on the molecular modeling of physical aging in glassy material systems.[2-8] In general, these studies have followed an approach in which molecular structures of simple coarse-grained material systems are simulated until critical relaxation events (volume and enthalpy relaxation) occur in the molecular structure. These simulated events generally occur over ambiguously-defined time frames. The reason for the simulation of relatively simple materials over ambiguous time frames is due to the immense computational expense of detailed molecular simulations. While physical aging events occur over the course of hours, days, or years; molecular simulation of fully atomistic models, using approaches such as Molecular Dynamics (MD), can only simulate molecular behavior on the femtosecond to nanosecond time scales. Although these studies incorporate neither the specific molecular structure of engineering materials nor clearly-defined time scales, they have provided valuable insights into the molecular-level behavior of glass materials when subjected to physical aging. However, to fully understand the physical nature of physical aging of specific material systems, fully atomistic models of engineering materials must be simulated.

The objective of this study was to develop a MD simulation method to predict the molecular structure of an epoxy material when subjected to various levels of physical aging. This approach is important for efficient and accurate prediction of the influence of physical aging on epoxy resin mechanical behavior, which is important in the design of durable engineering components and structures. Because of the computational challenges described above, the developed approach did not directly simulate the physical aging process. Instead, a method was established to efficiently predict the molecular structure that closely resembles that of the epoxy at specific times during the physical aging process. In this paper, a detailed description of physical aging of epoxies is followed by descriptions of the epoxy material (EPON 862/DETDA) and of the simulation procedure. The method is demonstrated by applying it to the epoxy aged at a temperature 40°C below T_g for a range of crosslink densities. From these simulations, the influence of crosslink density on the physical aging process is established. It is important to note that this study does not consider the molecular modeling of chemical aging (changes in chemical bonds) and hydrothermal aging (extended exposure to moisture). The modeling of these aging mechanisms is highly complex and should be addressed in separate studies.

PHYSICAL AGING OF EPOXY RESINS

Epoxy resins are generally formed from the crosslinking reaction of polyepoxides (monomer) and polyamines (hardener) to form a rigid network (upper left of Figure 1). Although an ordered molecular structure could conceptually exist (upper right of Figure 1), the overall molecular structure of a crosslinked epoxy is amorphous because of the size and complexity of the constituent molecules and the conditions under which they are crosslinked under (amorphous state in Figure 1). Because of the rigidity and complexity of the crosslinked network, the structure exists in a glassy state that cannot realistically re-structure itself into a purely ordered state.
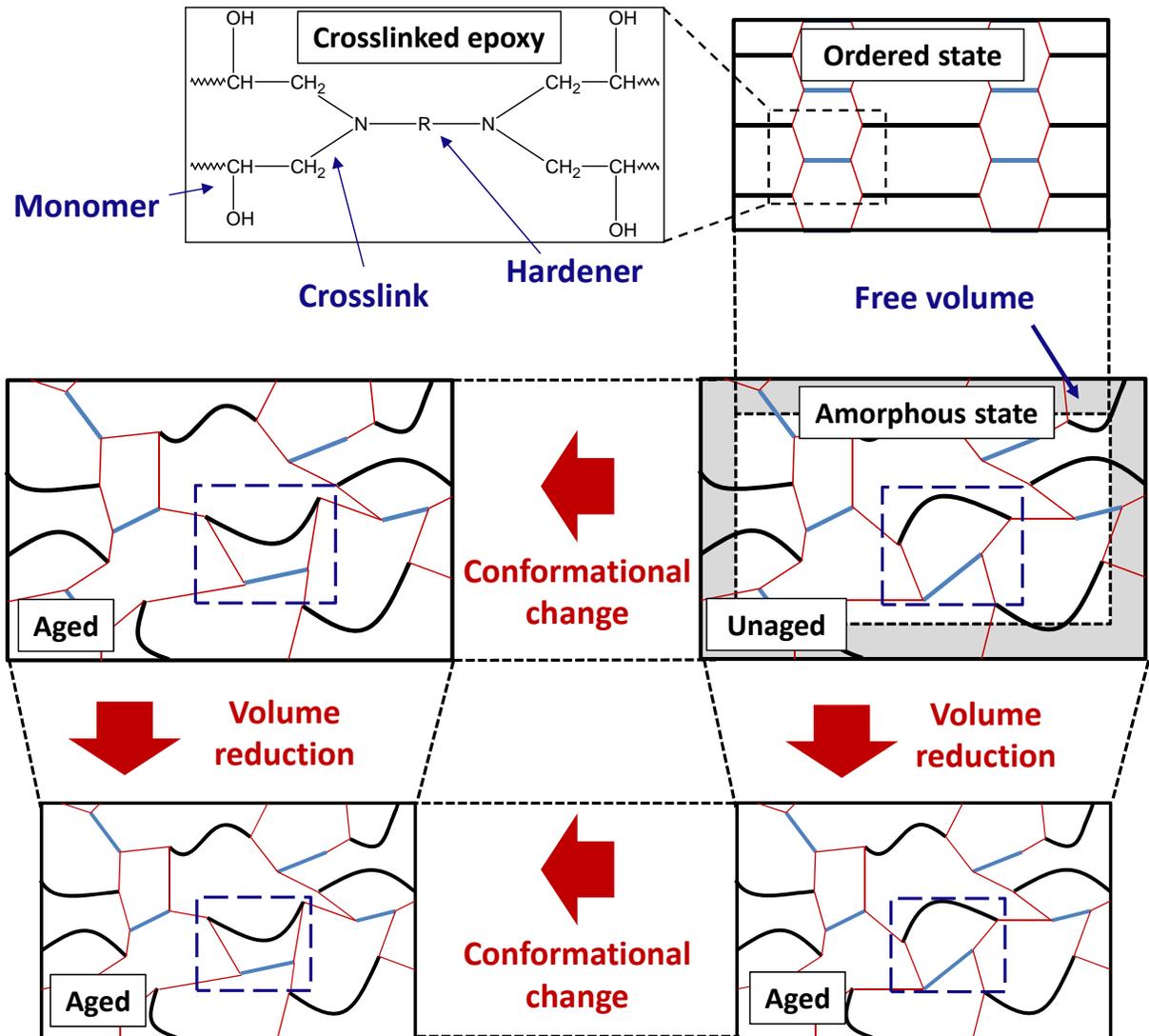
Figure 1 - Schematic showing the definition of free volume, volumetric reduction, and conformational change in a crosslinked epoxy polymer

As a consequence of the locked-in amorphous molecular structure, there exists significant free volume in the molecular structure, that is, specific volume in excess of that found in the ordered state at a given temperature (shaded region in Figure 1). It is important to note that many authors define free volume as the volume that is not occupied by polymer molecules; however, this definition is complicated by the ambiguous definition of the volume of a molecule in an amorphous structure. The free volume decreases as the amorphous structure is aged at sub-T_g temperatures for extended periods of time. This reduction in free volume occurs as the material contracts to achieve a lower-energy molecular state. Figure 1 (lower right) shows how the unaged amorphous state undergoes decreases in free volume such that the overall volume is decreased (mass density increased), yet the orientation of the molecules remains the same.

During the physical aging process, conformational changes on the molecular level can occur in epoxies that do not result in an overall change in the amount of free volume when an epoxy is subjected to sub-T_g annealing. This process is shown in Figure 1 (middle left) where the unaged polymer exhibits a re-arrangement of molecular segments to achieve a lower-energy structure. Following a volume reduction or conformational change event, a further volume reduction or conformational change event can occur, leading to an aged state that consists of both types of events (lower left of Figure 1).

A thermodynamic quantity that serves as a useful metric to characterize the physical aging state of the epoxy shown in Figure 1 is the specific enthalpy, h

$$h = u + pv$$

where u is the specific internal energy, p is the pressure, and v is the specific volume. The enthalpy definition is more useful when considering its change from a reference point by

$$dh = du + pdv + vdp \tag{1}$$

The process of physical aging is usually observed under conditions of constant pressure. If it is assumed that the pressure exerted onto an aging material does not change during the aging process, then Equation (1) becomes

$$dh = du + pdv \tag{2}$$

The first term on the right-hand side of Equation (2) represents the change in the internal energy during the physical aging process. The internal energy represents the change in sum of the potential and kinetic energies associated with the atoms that form the molecular structures. The change in internal energy can be induced by the type of conformational and volumetric changes shown in Figure 1. The second term on the right-hand-side of Equation (2) represents the contribution to the enthalpy change from the change in volume (reduction in free volume). Therefore, the specific enthalpy incorporates the influences of volume change and molecular conformation on the thermodynamic state of the material held at a constant pressure.

Despite the increasing knowledge of the influences of physical aging on thermo-mechanical properties, there is still an unexplained difference in the overall relaxation rates of volume and enthalpy in polymers.[9] Therefore, it is assumed herein that dv is specifically associated with the change in volume (free volume) of the simulation box, not necessarily the change in bulk volume due to volumetric relaxation (a.k.a. volume recovery). Although the focus on the approach can be switched from enthalpy relaxation to overall volume relaxation, this is beyond the scope of the current study. Ultimately, it is desired for this modeling approach to provide the physical insight necessary to explain the observed differences in bulk enthalpy and volume relaxations.

MODELED MATERIAL

The modeled material consists of the EPON 862 (Di-glycidyl ether of Bisphenol-F) monomer and DETDA (Diethylene Toluene Diamine) hardener. The molecular structures of these two

components are shown in Figure 2. EPON 862-DETDA is an epoxy polymer that has a good balance of thermal, mechanical, and electrical properties; and is used extensively in the fabrication of composite structural components used for aerospace applications. Details of the crosslinking reactions that occur for this epoxy system can be found elsewhere.[10]
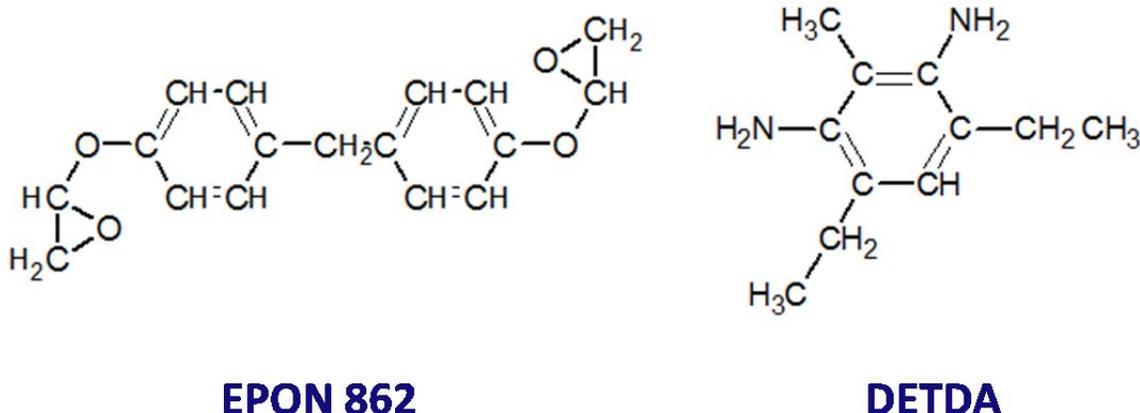

Figure 2 - Molecular structures of EPON 862 monomer and DETDA hardener

MOLECULAR MODELLING PROCEDURE

A series of equilibrated molecular models of the crosslinked EPON 862-DETDA material were established that represented the unaged (baseline) state of the epoxy for various crosslink densities. Details on this procedure are discussed below, as is the general approach for incorporating physical aging into the molecular models. The LAMMPS (Large Scale Atomic/Molecular Massively Parallel Simulator) software package[11] was used for all of the simulations described herein.

Unaged MD models

An initial uncrosslinked molecular structure was established using a procedure similar to that used by Bandyopadhyay et al.[10] A stoichiometric mixture of two molecules of EPON 862 and one molecule of DETDA was modeled first. The initial atomic coordinates were written to a coordinate file in the native LAMMPS format. The OPLS United Atom[12-14] force field was used to define the bond, bond angle, and dihedral parameters of the MD model. In this force field, all CH_3, CH_2, and CH groups were modeled as single united atoms with their corresponding masses. The non-bonded van der Waals interactions were modeled using the 12-6 Lennard-Jones potential.[15] The initial 2:1 structure was formed in a $10 \times 10 \times 10$ Å simulation box with periodic boundary conditions. This structure was subjected to four energy minimizations and three MD simulations in order to minimize internal forces resulting from the construction of bonds, bond angles, and bond dihedrals. After stabilizing at a relatively low energy value, this structure was replicated to form eight more structures within the simulation box so that a 16:8 molecular mixture was established. A slow stress relaxation procedure was performed over a cycle of 20 energy minimizations and 10 MD simulations. All MD simulations were conducted in the NVT (constant volume and temperature) ensemble for 100 ps at 600 K. After every cycle of MD and

5

energy minimization runs, the box size was reduced by a small amount. After all of the runs were complete, a density of 1.21 g/cm^3 was achieved with a final pressure value of 1 atm.
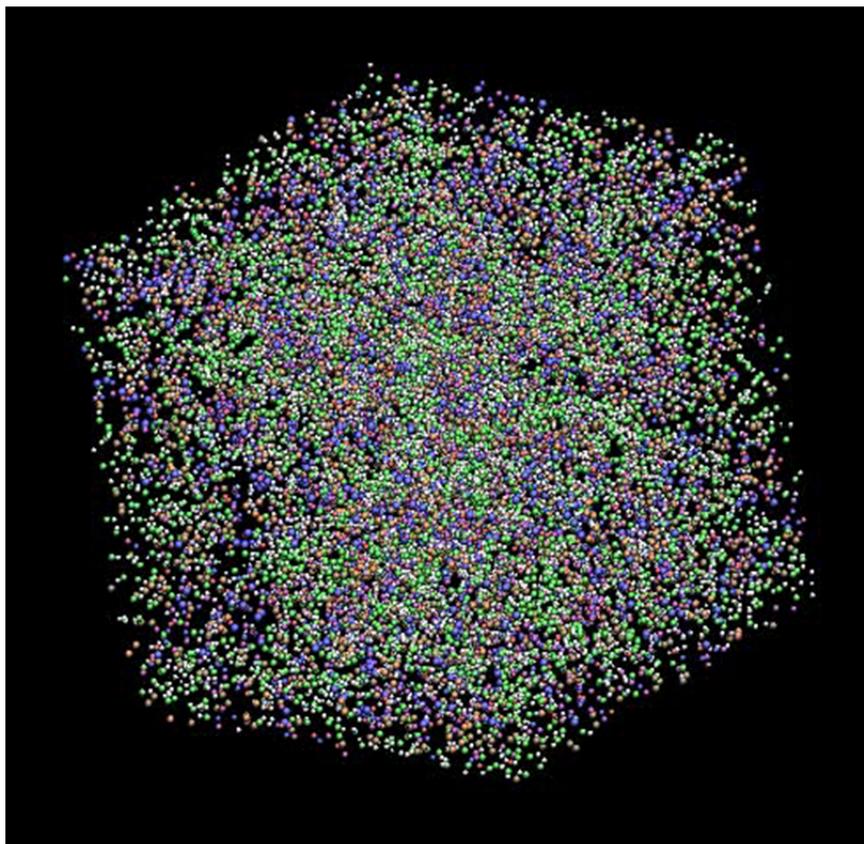

Figure 3 - MD model of the EPON 862-DETDA epoxy system

The equilibrated structure of the 16:8 model was crosslinked based on the root mean square (RMS) distance between the N atoms of DETDA and CH$_2$ groups of the EPON 862 molecules, as described by Bandyopadhyay et al.[10] Simultaneous breaking of CH$_2$-O bonds in the epoxide ends of the EPON 862 molecules and the N-H bonds of the DETDA molecules made the activated CH$_2$ ends capable of forming crosslinks with activated N atoms of the DETDA molecules. A particular activated N could form a crosslink with the activated CH$_2$ of any adjacent EPON 862 molecule within a specified RMS distance. The crosslinked 16:8 models were equilibrated by performing energy minimizations and MD simulations alternatively to remove the residual stresses generated during the formation of the crosslinks. The MD simulations were in the NVT ensemble for 100 ps at 500 K.

The 16:8 models were replicated in a large MD simulation box 26 times for each crosslink density, and each replica was rotated and translated to form a $3 \times 3 \times 3$ array of 16:8 structures for each crosslink density. The large system had 432 molecules of EPON 862 and 216 molecules of DETDA. The resulting MD models contained a total of 17,928 united atoms (representing a total of 25,272 real atoms). Figure 3 shows a representative periodic MD simulation box. These models were further equilibrated using MD and energy minimizations with continuous shrinkage of the simulation box until the models reached densities close to 1.2 g/cm^3. Between 30 and 35

minimizations and 12 NVT simulations (100 ps each) were required for the equilibration of these models.

Once equilibrated, the models were further crosslinked based the RMS cutoff distance approach described above. The additional crosslinking steps were performed so that the 27 sub-units of the molecular model were crosslinked with one another, thus creating a stable solid structure. After this step, a series of crosslink densities were achieved of 63%, 70%, and 76%., where the crosslink density is defined as the ratio of the total number of crosslinks that were formed to the maximum number that could be formed. After this additional process of crosslinking, the structures were further equilibrated at the same volume with two NVT simulations at 500 K and 300 K for 100 ps each with in-between energy minimizations. Multiple samples were established for each crosslink density: 2 samples for 63%, 3 samples for 70%, and 3 samples for 76%.

MD modeling of physical aging

Because physical aging occurs over macro-size time scales (hours to years) and MD simulations occur over nano-size time scales (femtoseconds to nanoseconds), the physical aging process could not be directly simulated for the type of MD models considered here. Instead, an approach was followed to establish a relationship between the aging time t_a of the polymer and the corresponding change in specific volume shrinkage Δv of the MD simulation box in which $\Delta v = (v_0 - v)/v_0$ where v_0 is the specific volume of the unaged state (baseline MD simulation box described above) and v is the specific volume of the MD simulation box for a particular t_a. The t_a-Δv relationship is useful because it allows molecular models of epoxies to be developed for any state of aging, characterized by t_a for a particular aging temperature, by simply reducing the MD simulation box by Δv using an NVT simulation and equilibrating the molecular system. The reduction in the MD simulation box size will reduce the free volume of the system and induce the appropriate level of conformation changes associated with the modeled physically aged state. Thus, the approach used herein provides molecular structures that closely resemble the aged molecular system at snapshots in time without the need to simulate the entire physical aging process. It is important to note that the associated changes in Δv are small enough to avoid the creation of significant residual stresses in the molecular model for realistic physically-aged states.

On the molecular level, the constant dynamic motion of the atoms, as simulated via an NPT simulation, results in brief changes of state that can be characterized by the values of Δh ($\Delta h = h_0 - h$) and Δv. The critical assumption made in this approach is that each pair (Δh, Δv) characterizes a possible state (snapshot in time) of the crosslinked polymer that can represent a physically-aged state for a particular t_a and aging temperature. Because the specific enthalpy of these states can be correlated with specific enthalpies measured experimentally for a particular aging time and temperature, the MD simulation box volume changes (Δv) associated with these states can then be used as an independent parameter that controls the simulated level of physical aging. The resulting MD models can then be used to predict thermo-mechanical properties for a particular polymer at a particular aged state.

The method used in this study consists of three basic steps: (1) Establish a relationship between Δv and Δh via MD simulation for a particular epoxy system, (2) determine the relationship

between Δh and t_a from experimental data for similar epoxy systems, and (3) determine the relationship between Δv and t_a based on the relationships determined in steps 1 and 2. The details of each of these steps for the EPON 862-DETDA epoxy system are described below.
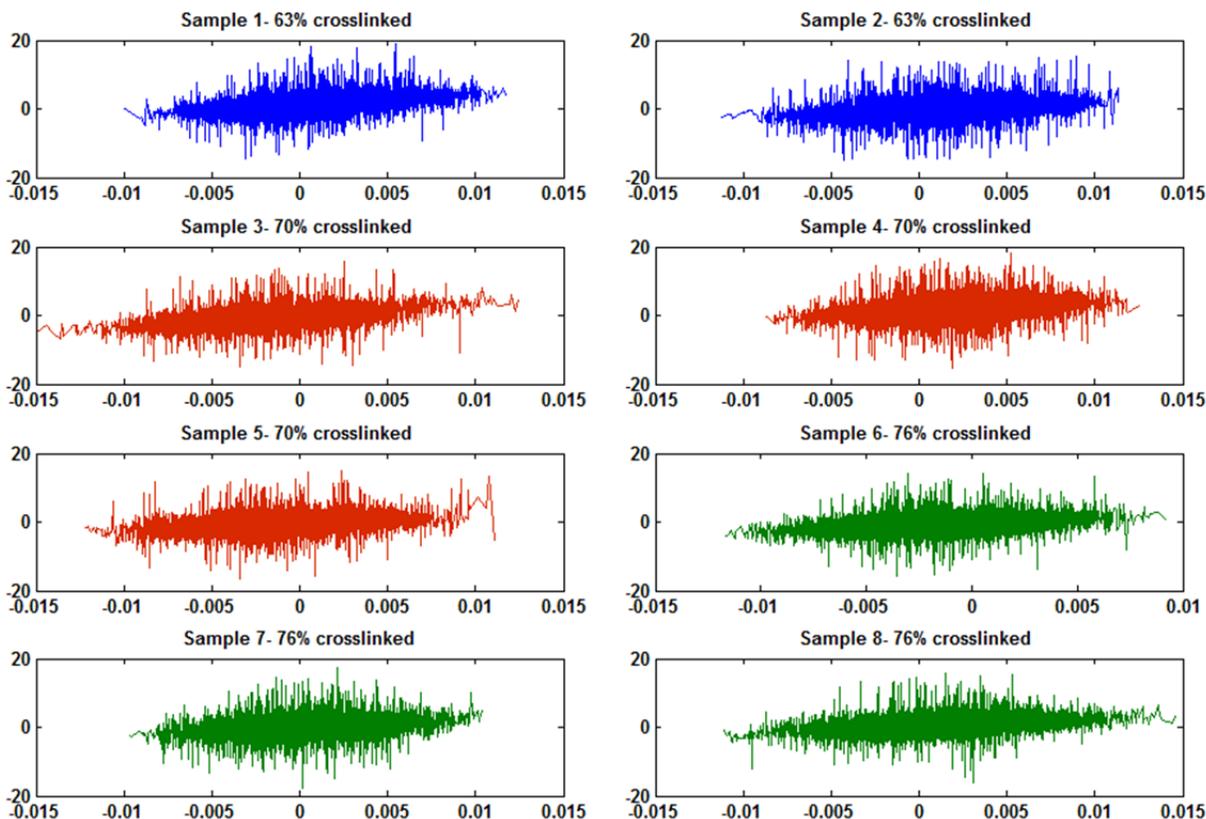

Figure 4 - Reduction in enthalpy (Δh in units of J/g) vs. volume shrinkage (Δv) for eight different samples of crosslinked EPON862-DETDA molecular models

RESULTS AND DISCUSSION

In the first step, the relationship between Δh and Δv was established for each of the samples of each crosslink density. NPT simulations were conducted on the baseline MD models at a pressure of 1 atm for 400 ps at a temperature of T_g- 40°C. The T_g of each of the crosslinked systems was assumed to be 150°C, based on the results of previous studies.[10] At 2 fs intervals during these simulations the values of Δv and Δh were recorded. Each pair ($\Delta v, \Delta h$) represented a state corresponding to a specific fluctuation in free volume and conformational change in the epoxy network. Figure 4 shows the corresponding Δh vs Δv data sets for each of the simulated material systems. A linear regression was fit to each of the data sets, and the corresponding regression slope α represented the Δh vs Δv relationship

$$\Delta h = \alpha \left(\Delta v \right) \tag{3}$$

Although the data shown in Figure 4 shows a large amount of scatter, which is expected for an MD simulation of this size, it was assumed that a linear trend was sufficient to describe the Δh vs Δv relationship, and that *y*-intercept of the regressions were zero-valued. The data in Figure 4 indicate that specific enthalpy relaxation and specific volume shrinkage are positively correlated. That is, both measures increase and decrease simultaneously, as expected.

It is important to note that Equation (3) implies a linear relationship between the enthalpy of the molecular system and the corresponding specific volume of the MD simulation box. It is not assumed that Equation (3) describes a linear relationship between bulk-level enthalpy relaxations and volumetric relaxations. Because bulk-level enthalpy and volumetric relaxations do not have a linear relationship for polymers, as described above, the volumetric term in Equation (3) is intended to only relate to the MD simulation box volume.

Table 1 lists the values of α for each of the samples of each crosslink density. The average values of α shown in Table 1 decrease for increasing levels of crosslinking. This trend is likely because of the decreasing levels of conformational change that can occur as the polymer network is subjected to increasing levels of crosslinking. Because the number of conformational changes decreases, the values of Δh decrease with respect to Δv, thus causing a decrease in the value of α per Equation (3). The standard deviation data in Table 1 also indicates that the predicted values of α was relatively consistent between individual samples. It is expected that increases in the number of atoms in the MD model would result in decreases in the standard deviation of α values, albeit with slower simulation times.

Table 1 - Values of α (J/g) for each sample of each crosslink density

	63%	70%	76%
Sample 1	319.11	302.68	256.35
Sample 2	233.83	238.01	227.71
Sample 3	-	239.59	212.71
Average	276.47	260.09	232.26
Standard deviation	60.302	36.889	22.172

For the second step of the modeling process, experimental data was obtained from the literature[16-19] that relates specific enthalpy relaxation to aging time for T_g-40°C. All four sets of experimental data are for a diglycidyl ether of bisphenol-A (DGEBA - EPON 828) monomer. The hardeners used for the four different systems are all different and result in four different T_g's: 4,4'-diaminodiphenylsulfone ($T_g = 208.1°C$),[16] methyltetrahydrophthalic anhydride ($T_g = 98.3°C$),[17] m-xylylenediamine ($T_g = 104.8°C$),[18] and nadic methyl anhydride ($T_g = 87°C$).[19] All four systems were cured above their respective values of T_g. Figure 5 shows the enthalpy relaxation of the epoxy for various aging times. Although the epoxy systems investigated in these studies[16-19] are not exactly the same as the one considered herein, it is assumed that their enthalpy relaxation response is close to EPON 862-DETDA. The data indicates that all four independent studies show similar enthalpy relaxation behavior for the different epoxy systems. Also shown in Figure 5 is a linear regression line that fits the data to the following form

$$\Delta h = \beta \ln(t_a) + \gamma \tag{4}$$

where β and γ are fitting constants and t_a has units of hours. A least-squares analysis on the combined data sets shown in Figure 5 yielded $\beta = 0.27$ J/g and $\gamma = 0.46$ J/g. Therefore, Equation (4), along with the appropriate values of β and γ, relates the specific enthalpy relaxation to the aging time and acts as a calibration for relating the molecular modeling results to the aging time, as explained below.
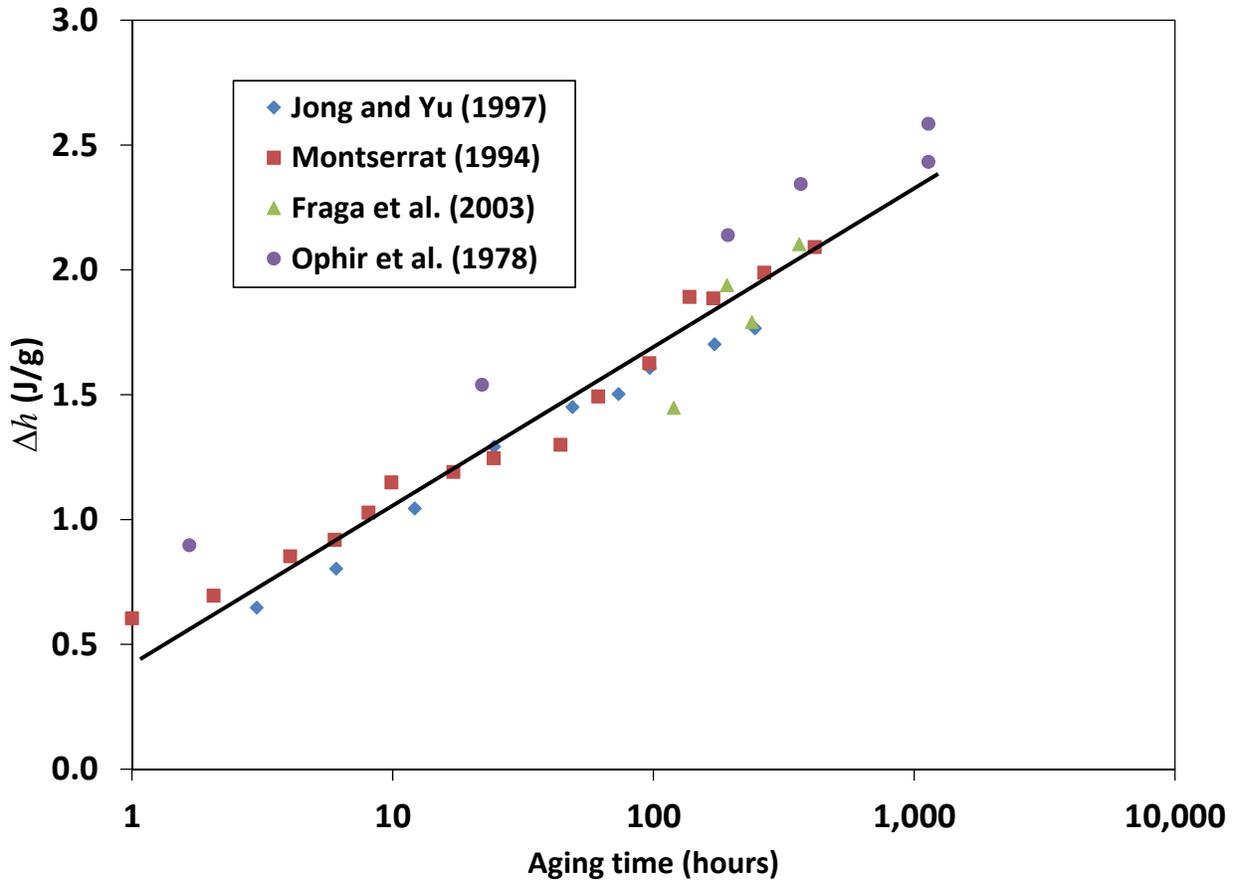

Figure 5 - Experimental data for specific enthalpy relaxation for epoxy. The solid line is a linear regression fit for the four data sets

In the third step of the simulation procedure the specific enthalpy relaxation measure in Equation (3) was directly related to analogous measure in Equation (4). As a result, the specific volume shrinkage of the MD model can be related to the aging time via

$$\Delta v = \frac{\beta}{\alpha} \ln(t_a) + \frac{\gamma}{\alpha} \tag{5}$$

The significance of Equation (5) is that Δv is directly related to the aging time t_a; thus, the desired physical aging time can be input into Equation (5), and the corresponding change in specific volume of the simulation box can be calculated. This change in specific volume can be applied to an equilibrated baseline epoxy molecular model to establish a model that resembles the aged molecular structure. The resulting model will have the corresponding changes in specific volume (free volume) and enthalpy relaxation incorporated directly. The aged molecular models of epoxy can be used further to predict thermo-mechanical properties for particular aging times. It is important to note that Δv only describes the shrinkage of the simulation box specific volume, not the overall relaxation volume of the epoxy. Because volume relaxation and enthalpy relaxation rates are typically different in polymers,[9] and because the method described herein is based on enthalpy relaxation, Equation (5) cannot be used to reliably predict the bulk volume relaxation of epoxy.

CONCLUSIONS

This research has explored the MD modeling of the physical aging of crosslinked epoxy materials. Although the physical aging process cannot be simulated directly due to the large discrepancy between actual and simulated time scales, the method developed can be used to efficiently establish equilibrated MD models of crosslinked epoxies that resemble the corresponding structures that are physically aged for various annealing times. Such models could subsequently be used to predict various thermo-mechanical properties of physically-aged epoxies using standard MD techniques. These predictions are important in the design and selection of materials in engineering structures for three reasons. First, the thermo-mechanical properties can be predicted much faster than they can be measured in long-term aging experiments. Second, the models can provide physical insight into the molecular mechanisms associated with physical aging that cannot be measured by experiment. Finally, the modeling strategy allows for the rapid exploration of material formulations that have not yet been synthesized under laboratory conditions.

The results of this study indicate that MD models of various aged states can be established by simply reducing the volume of MD models and equilibrating the resulting structure. The key to successfully establishing such models is to precisely determine the relationship between reductions in MD simulation box volume and the corresponding physical aging time. It is hypothesized that this relationship can be determined by sampling different states for an extended MD simulation in the NPT ensemble for a fully atomistic system. This relationship has been determined for the EPON 862/DETDA epoxy system for T_g-T_a = 40ºC, and could be determined for other epoxy systems at different aging times in a similar manner.

ACKNOWLEDGMENT

REFERENCES

1. G. M. Odegard and A. Bandyopadhyay, *Journal of Polymer Science Part B-Polymer Physics*, **49**, 1695-1716 (2011).
2. K. Chen and K. S. Schweizer, *Physical Review Letters*, **98**, 4 (2007).
3. B. A. Isner and D. J. Lacks, *Physical Review Letters*, **96**, 025506 (2006).
4. D. J. Lacks and M. J. Osborne, *Physical Review Letters*, **93**, 255501 (2004).
5. J. Rottler and M. O. Robbins, *Physical Review Letters*, **95**, 255504 (2005).
6. M. Utz, P. G. Debenedetti and F. H. Stillinger, *Physical Review Letters*, **84**, 1471-1474 (2000).
7. M. Warren and J. Rottler, *Physical Review E*, **76**, 031802 (2007).
8. M. Warren and J. Rottler, *Physical Review E*, **78**, 041502 (2008).
9. S. L. Simon, D. J. Plazek, J. W. Sobieski and E. T. McGregor, *Journal of Polymer Science Part B-Polymer Physics*, **35**, 929-936 (1997).
10. A. Bandyopadhyay, P. K. Valavala, T. C. Clancy, K. E. Wise and G. M. Odegard, *Polymer*, **52**, 2445-2452 (2011).
11. S. Plimpton, *Journal of Computational Physics*, **117**, 1-19 (1995).
12. W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, *Journal of the American Chemical Society*, **117**, 11225-11236 (1996).
13. E. K. Watkins and W. L. Jorgensen, *Journal of Physical Chemistry A*, **105**, 4118-4125 (2001).
14. S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta and P. Weiner, *Journal of the American Chemical Society*, **106**, 765-784 (1984).
15. J. E. Lennard-Jones, *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences*, **106**, 463-477 (1924).
16. S. R. Jong and T. L. Yu, *Journal of Polymer Science Part B-Polymer Physics*, **35**, 69-83 (1997).
17. S. Montserrat, *Journal of Polymer Science Part B-Polymer Physics*, **32**, 509-522 (1994).
18. F. Fraga, C. Castro-Diaz, E. Rodriguez-Nunez and J. M. Martinez-Ageitos, *Polymer*, **44**, 5779-5784 (2003).
19. Z. H. Ophir, J. A. Emerson and G. L. Wilkes, *Journal of Applied Physics*, **49**, 5032-5038 (1978).