SAND2015-XXXXR
LDRD PROJECT NUMBER: 169249
LDRD PROJECT TITLE: Modeling the Coupled Chemo-Thermo-Mechanical Behavior of Amorphous Polymer Networks

PROJECT TEAM MEMBERS: Thao D. (Vicky) Nguyen, Rui Xiao, Jonathan A. Zimmerman [Sandia POC]

ABSTRACT:

Amorphous polymers exhibit a rich landscape of time-dependent behavior including viscoelasticity, structural relaxation, and viscoplasticity. These time-dependent mechanisms can be exploited to achieve shape-memory behavior, which allows the material to store a programmed deformed shape indefinitely and to recover entirely the undeformed shape in response to specific environmental stimulus. The shape-memory performance of amorphous polymers depends on the coordination of multiple physical mechanisms, and considerable opportunities exist to tailor the polymer structure and shape-memory programming procedure to achieve the desired performance.

The goal of this project was to use a combination of theoretical, numerical and experimental methods to investigate the effect of shape memory programming, thermo-mechanical properties, and physical and environmental aging on the shape memory performance. Physical and environmental aging occurs during storage and through exposure to solvents, such as water, and can significantly alter the viscoelastic behavior and shape memory behavior of amorphous polymers. This project – executed primarily by Professor Thao Nguyen and Graduate Student Rui Xiao at Johns Hopkins University in support of a DOE/NNSA Presidential Early Career Award in Science and Engineering (PECASE) – developed a theoretical framework for chemo-thermo-mechanical behavior of amorphous polymers to model the effects of physical aging and solvent-induced environmental factors on their thermoviscoelastic behavior.

INTRODUCTION:

Amorphous polymers exhibit a wide range of complex temperature-dependent and time-dependent behaviors, from elastic and rubbery to viscoplastic and glassy. At high temperatures, polymer structure has high mobility and is in an equilibrium rubbery state. The mobility decreases with temperature, and cooling drives the initially rubbery material out of equilibrium and induces the glass transition. The glass transition mechanism can be exploited to achieve the shape memory behaviors. The programmed shape of these materials can be stored by the tremendous decrease in chain mobility and recovered to an original shape in response to an environmental trigger, such as heat and solvent, which increases the chain mobility. Modeling the shape memory effect of amorphous polymers requires modeling the temperature-dependent and time-dependent behaviors of the glass transition. Simultaneously, the investigation on shape memory behaviors of amorphous polymers can also enrich the understanding the glass transition.

Shape memory polymers (SMPs) are smart materials that can memorize one or multiple temporary shapes and recover to their permanent shape in response to an environmental stimulus,

such as heat, light, electricity, pH or solvent. Among various types of SMPs, thermally-activated SMPs are the most widely investigated due to their ease of synthesis and characterization, tunable mechanical properties, and broad potential applications. Several different thermally activated mechanisms can be employed to achieve the shape memory effect (SME), but the most common mechanism is glass transition of amorphous polymers. Amorphous SMPs are typically programmed at the temperature above the glass transition temperature (T_g), and cooled down below transition temperature to fix a temporary shape. The programmed SMPs are then heated above the T_g to achieve shape recovery. The tremendous change in thermo-mechanical properties during the glass transition is the underlying physical mechanism behind the shape memory effect. Compared with the emerging field of SMPs, the glass transition behaviors of amorphous polymers have been extensively studied for more than half a century. The characterization techniques for the glass transition can be applied to investigate amorphous SMPs, and the theories can be employed to model the shape memory behaviors. Thus, exploiting our knowledge of the glass transition can improve our understanding of the complex thermo-mechanical properties and shape recovery responses of SMPs under various conditions. Simultaneously, the research on amorphous SMPs can also enrich our understanding of glass transition behaviors.

Glass Transition of Amorphous Polymers

The glass transition describes the reversible change of amorphous materials from a hard glassy state to a soft rubbery or molten state. A variety of properties show tremendous change during the glass transition. Among them, the most commonly measured properties to describe the glass transition are the modulus, enthalpy and volume. The dependence of modulus on temperature of amorphous polymers can be measured by commercially available rheometers and dynamic mechanical analyzers. Fig. 1 shows the storage modulus of an acrylate-based amorphous network as a function of temperature measured under a dynamic load with a constant frequency of 1Hz. As shown, at low temperatures, the polymer structure is frozen and exhibits a high glassy modulus. When the material is heated across the transition region, the polymer structure obtains more and more mobility resulting in a dramatic decrease in modulus. The polymer then reaches the rubbery plateau. The Tan(δ), or loss tangent, shown in Fig. 1 describes the viscoelastic dissipation characteristic of the polymers. To distinguish it from T_g, defined as the onset of the glass transition region, the peak of the Tan(δ) is defined as T^{mid}. The measured glass transition region is dependent on the applied frequency, which corresponds to the time-temperature superposition.

Differential scanning calorimetry (DSC) techniques are widely employed to measure the enthalpy change of amorphous polymers with temperature. Fig. 2 plots the DSC scans of annealed and quenched polystyrene specimens upon heating. Structural relaxation plays an important role in the performance of amorphous polymers. Briefly, the structure of amorphous polymers is unable to rearrange towards an equilibrium state instantaneously to a temperature change near T_g. Thus a longer annealing time results in a more sluggish structure (closer to the equilibrium state), which is represented by an increase in density and viscosity, and a decrease in enthalpy and mobility.
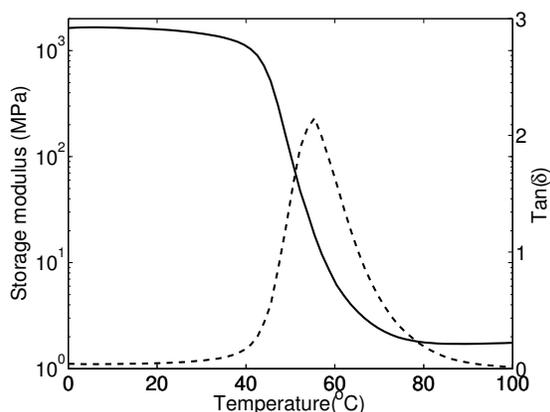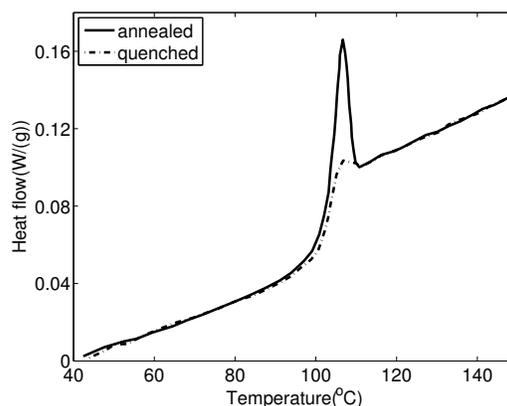
Figure 1. Storage modulus of acrylate-based polymer

Figure 2. DSC scans of an annealed and quenched polystyrene using a heat rate of 10°C/min. (Data extracted from Hasan and Boyce, 1993)

Measuring the thermal expansion using a dilatometer and thermomechanical analyzer is another general method to characterize the glass transition. The volume as a function of temperature is often recorded during a constant cooling test. The coefficient of thermal expansion (CTE) shows a rapid change from a high rubbery CTE α_r to a low glassy CTE α_g around T_g. There are also other experiments that measure the volume change after a sudden temperature drop. In general, experimental observations show that the glass transition process is a kinetic process and that the experimental temperature rate has an important influence on the determination of the glass transition region and thermomechanical properties.

Many theories have been developed to describe the glass transition of amorphous materials. Among them, free volume theory and configurational entropy theory are the most widely accepted. The free volume V_f is defined as the space not occupied by the polymer molecules, which allows the polymer segments to undergo rotation and translation. As the polymer is cooled down from their rubbery state, the free volume continuously decreases and eventually reaches a critical value where segmental motion is forbidden due to insufficient free space, resulting in a transition from the rubbery state to the glassy state.

Another widely accepted approach to model the glass transition uses the configurational entropy concept. The pioneering work of configurational entropy by Gibbs and DiMarzio proposed that the glass transition is in fact an experimental manifestation of the equilibrium second order phase transition. Many experiments imply that measured T_g decreases if the cooling rate is decreased. The underlying theory is derived based on a quasi-lattice theory and the main calculation involves calculating the number of configurations that chains can occupy the lattice.

Although both theories explain the glass transition phenomena with considerable success, there are still limitations. For example, the free volume theory fails to predict the influence of chain length or side chain on the glass transition. The configurational entropy concept fails to explain the glass transition of inorganic networks. The emerging of the new experimental and simulation

techniques may be able to improve the understanding and help develop a universal description of the glass transition.

Objectives of this Work

In this work, we started with exploiting the glass transition to model the thermally activated shape memory behavior. The model adopted multiple discrete relaxation processes to describe the distribution of relaxation times for stress relaxation, structural relaxation, and stress-activated viscous flow. Experimental methods were also developed to obtain the stress and structural relaxation spectra, and viscoplastic parameters. The model was applied to study the deformation temperature and physical aging influence on both partially constrained recovery and fixed-strain recovery responses. The model was able to capture the main features of the shape memory recovery response observed in experiments.

We further extended this model to describe the influence of solvent on the thermomechanical properties and shape memory behavior of amorphous polymers. The solvent increases the chain mobility, decreases the relaxation time and the glass transition temperature. The time-dependent diffusion process was also incorporated into the model. The model showed the ability to predict quantitatively the dramatic softening of the stress response of saturated specimen and the time-dependent solvent-driven shape recovery. In the last part of this work, we developed a thermomechanical theory that couples the structural evolution and inelastic deformation to describe the non-equilibrium behavior of amorphous polymers. We showed that this theory was able to reproduce the temperature-dependent and rate-dependent stress response spanning the glass transition and the effects of physical aging and mechanical rejuvenation on the stress response and enthalpy change observed in experiments.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

Thermally Activated Shape Memory Behavior

Tert-butyl acrylate (*t*BA) poly(ethylene glycol) dimethacrylate (PEGDMA), with typical molecular weight $M_n = 550$, di(ethylene glycol) dimethacrylate (DEGDMA) , and photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were ordered from Sigma Aldrich and used in their as-received condition. A crosslinker solution (XLS) was synthesized by mixing 30 wt% DEGDMA with 70 wt% PEGDMA. Co-monomer solutions were prepared by mixing 10, 20, and 40 wt% XLS with the tBA monomer solution to create three networks of equal T_g and varying crosslinking density once polymerized. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, was added to the co-monomer solution at a concentration of 0.1 wt% of the total co-monomer weight and mixed manually until fully dissolved. The polymer solution was injected between two glass slides separated by a 1 mm spacer to create film specimens for tensile tests or into cylindrical polyethylene molds for compression tests. Polymerization was achieved by exposing the mixture to UV light (Blak Ray B100 A/R) for 15 minutes. For the cylindrically molded specimens, the solution was submerged in ice water to slow the rate of polymerization and avoid cracking in the molds. Following UV curing, all polymer specimens were thermally cured in an oven at 90°C for one hour to ensure complete polymerization. The films specimens were cut to dimensions 1.0 mm x 5.0 mm x 25.0 mm using a laser cutter. The cylindrical specimens were machined to 10 mm in diameter. These were cut to 15 mm in length and sanded

to provide smooth surfaces for uniaxial compression tests.

The thermomechanical properties of unprogrammed tBA-co-XLS materials were characterized using four sets of experiments. Constant cooling rate tests were performed to determine the volumetric coefficients of thermal expansion (CTE) and the T_g at a reference cooling rate. The frequency-dependence of the storage modulus was measured using dynamic frequency sweep at multiple temperatures, and the results were shifted in the frequency domain using the time-temperature superposition principle to construct the master curve of the stress relaxation function and determine the temperature dependence of characteristic relaxation time. To characterize the structural relaxation response, we developed an isothermal recovery test that measured the time-dependent volumetric thermal contraction response to a series of rapid temperature decreases and applied the method of reduced variables to construct a master curve for structural relaxation function. The temperature-dependent and rate-dependent yield strength was measured using isothermal uniaxial compression experiments.

A constitutive model was derived for amorphous polymers near the glass transition. This model integrates the time-dependent mechanisms of viscoelasticity, structural relaxation, and stress-activated yield and post-yield flow. The theoretical foundation and development of the thermoviscoelastic model are explained in detail in the References listed at the end of this report.

The constitutive relations for the stress and thermal deformation response were developed based on considerations of energy and entropy. A thermodynamic theory is needed to determine the thermodynamic requirements of the constitutive relations and to develop a coupled thermomechanical theory for thermally activated shape recovery with heat conduction. We extended the thermodynamic theory of Nieuwenhuizen to include the effects of viscoelasticity and multiple stress and structural relaxation processes. The structural relaxation processes are assumed to be weakly coupled and are entirely separate from the viscoelastic relaxation processes. Each is characterized by different relaxation times and is assumed to be in quasi-equilibrium at a different fictive temperatures. Specialized experiments were designed to fit parameters for this combined mechano-thermodynamic model.

Solvent Induced Shape Memory Behavior
Methyl acrylate (MA), methyl methacrylate (MMA), poly(ethylene glycol) dimethacrylate(PEGDMA),with typical molecular weight M_n =550, and photoinitiator2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma Aldrich and used in their as- received condition. The MA-MMA-PEGDMA solution was mixed in a 5:4:1 mass ratio, and DMPA was added to the co-monomer solution at a concentration of 0.5 wt% of the total co-monomer weight. The polymer solution was either injected between two glass slides to make tensile test specimens or a thin-walled tube mold to make hollow cylindrical specimens. The specimens were placed in a UV oven (Model CL-1000L Ultraviolet Crosslinker) for 15 minutes to polymerize. The specimens were then annealed in an incubator at 80°C for 1 hour to achieve full polymerization.

Time-temperature superposition tests to measure the temperature-dependent viscoelastic properties, isothermal volume recovery tests to measure the structural relaxation properties, and isothermal uniaxial compression tests to measure the temperature-dependent and rate-dependent

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

yield and post-yield behavior. The methods for these tests are described in the previous sub-section. In addition, experiments developed to measure the effect of water absorption on the mechanical properties and shape recovery behavior of the polymer network.

Rectangular specimens with dimension $20.0 \times 20.0 \times 0.95$ mm^3 were used to measure the diffusion coefficient of water into the polymer network. Each specimen was weighed before testing. The specimens were then immersed in de-ionized water and placed in an incubator at either 25°C or 30°C. The specimens were removed periodically and weighed using a high-resolution digital balance with 10^{-4} gram resolution. The specimens were returned immediately to the water bath and placed into the incubator after measurement. The measurements were performed on 4 specimens for each temperature.

Frequency sweep tests were performed on dry and saturated tension film specimens using a TA Q800 Dynamic Mechanical Analyzer (DMA) in multifrequency mode. Dry polymer film specimens were heated from 20°C to 80°C in 5°C increments. The specimens were annealed at each test temperature for 5 minutes to allow for complete heat conduction through the sample, then subjected to a 0.2% dynamic strain at 0.3 Hz, 1.0 Hz, 3.0 Hz, 10.0 Hz, and 30.0 Hz to measure the storage modulus and tan delta. The same frequency sweep was also performed on saturated samples at room temperature to measure the effect of solvent absorption on the storage modulus and tan delta. Saturated specimens were prepared by immersing the dry tension film specimens in de-ionized water and placed in an incubator at 25°C for 48 hours. The saturated specimens were not subjected to measurements at higher temperatures to prevent significant evaporation.

Isothermal uniaxial tension tests were performed on dry and saturated specimens using a custom-built micro-tensile setup designed by Joshi et al. to measure the effect of water absorption on the tensile properties. The experiments used dog-bone shape specimens with a $6.0 \times 2.0 \times 1.0$ mm^3 gage section cut from the film specimen using a digital control mill. Digital image correlation (DIC) was used to measure the local strain in the gage section. The specimens were pulled to 40% engineering strain at a strain rate of 0.002/s.

Isothermal shape recovery experiments were performed to compare the response of dry specimens in air and specimens immersed in water. The experiments used two different specimen geometries: thin film specimens $20.0 \times 5.0 \times 0.75$ mm^3 in size, and tube specimens with length 15.0 mm, outer radius 10.0 mm, and thickness 0.8 mm. The film specimens were equilibrated at 60°C and then stretched to 25 % engineering strain in 100 seconds using the TA Q800 DMA. The deformed specimens were cooled down to 20°C at 5°C/min and annealed for five minutes before unloading to nominally zero force (0.001 N). For recovery in air, the film specimens were heated in the DMA, set to zero force mode, to the test temperature at 10°C/min then held constant for 1 hour. The displacements of the grips were measured under nominally zero force (0.001 N) and used to calculate the shape fixity ratio. The shape recovery experiments in air were performed at four test temperatures: 41°C, 44°C, 47°C and 50°C. For recovery in water, the specimens were immersed in de-ionized water and placed in an incubator at the test temperature. The two test temperatures were 25°C and 30°C. The momentary shape was recorded using a digital camera and the length was measured using the GNU Image Manipulation Program.

We extended our constitutive model to incorporate the effect of solvent absorption on the thermomechanical behavior of amorphous polymers spanning the glass transition. The article by Xiao and Nguyen (*Soft Matter*, 2013) presents details on the formulation of this model.

RESULTS:

Thermally Activated Shape Memory Behavior

Figure 3 shows the dynamic frequency sweep test results at different temperatures. The measurements at each temperature were shifted along the frequency axis to construct the master curve for the storage modulus at $T_0 = 75^oC$. The parameters of the fractional damping model, were fit to the master curve and applied to determine the parameters of the discrete relaxation spectrum to reproduce the frequency response at the reference temperature. The model accurately reproduced the experimental measurements until high frequencies, which corresponded with the onset of the glassy plateau. At higher frequencies, the model provided a larger storage modulus than found experimentally. This may be caused by the inability of the time-temperature superposition principal to describe the approach to the glassy state.
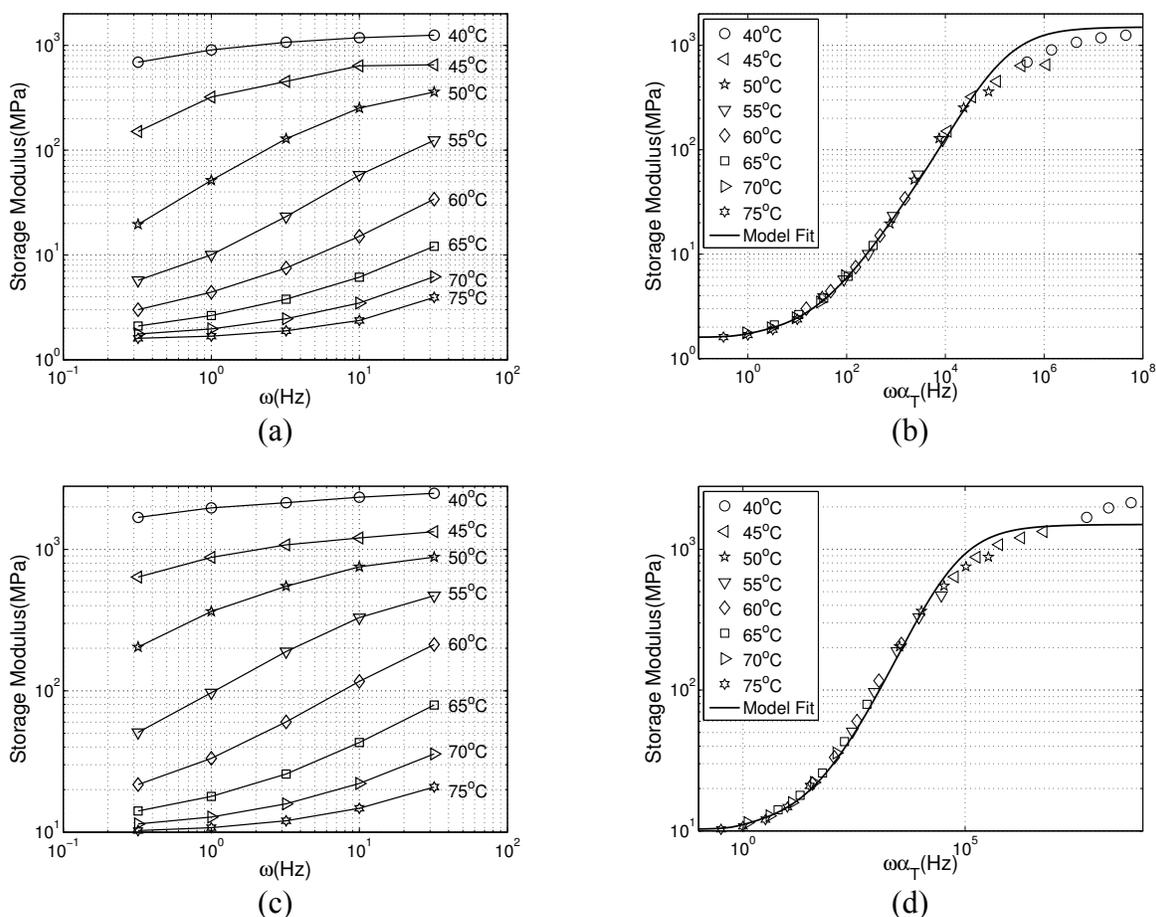

Figure 3. TTS tests for different cross-linker densities:
(a) 10 wt% (b) 10wt% master curve (c) 40wt% (d) 40wt% master curve.

Figure 4(a) plots the structural relaxation function measured in isothermal recovery tests at four different temperatures as a function of time from the beginning of the temperature drop. The recovery rate varied noticeably with temperature. At the highest temperature, the specimens nearly reached equilibrium within the 60 min hold time, while little relaxation was observed at the lowest temperature. The master curve of structural relaxation was obtained by plotting the response function against reduced time, as shown in Fig. 4(b).
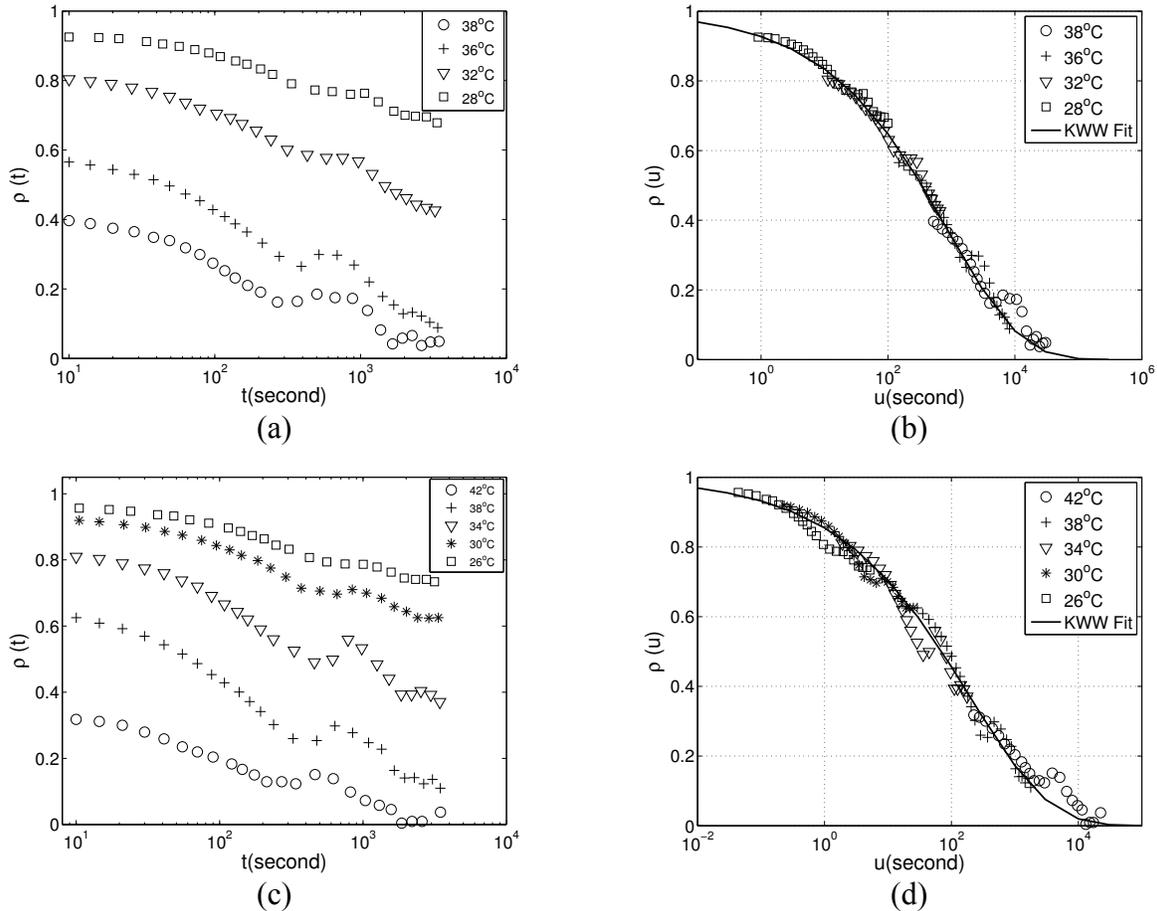

Figure 4. Isothermal recovery tests:
(a) 10 wt% (b) 10wt% master curve (c) 40wt% (d) 40wt% master curve.

Figure 5 shows the stress-strain response for isothermal uniaxial compression performed at various different strain rates and temperatures for 20 wt% and 40 wt% materials. The results showed that the model was able to reproduce the transition from a viscoplastic response, with a distinct yield point and post-yield softening, to a viscoelastic response with increasing temperatures through the glass transition region. The model also captured the strain rate and temperature dependence of the yield strength across the glass transition region. Compared to the single-process model of Nguyen et al., which calculated a stiffer elastic response and smaller yield strains in the glass transition region, the multiple relaxation model more accurately described the temperature-dependence of the yield behavior.
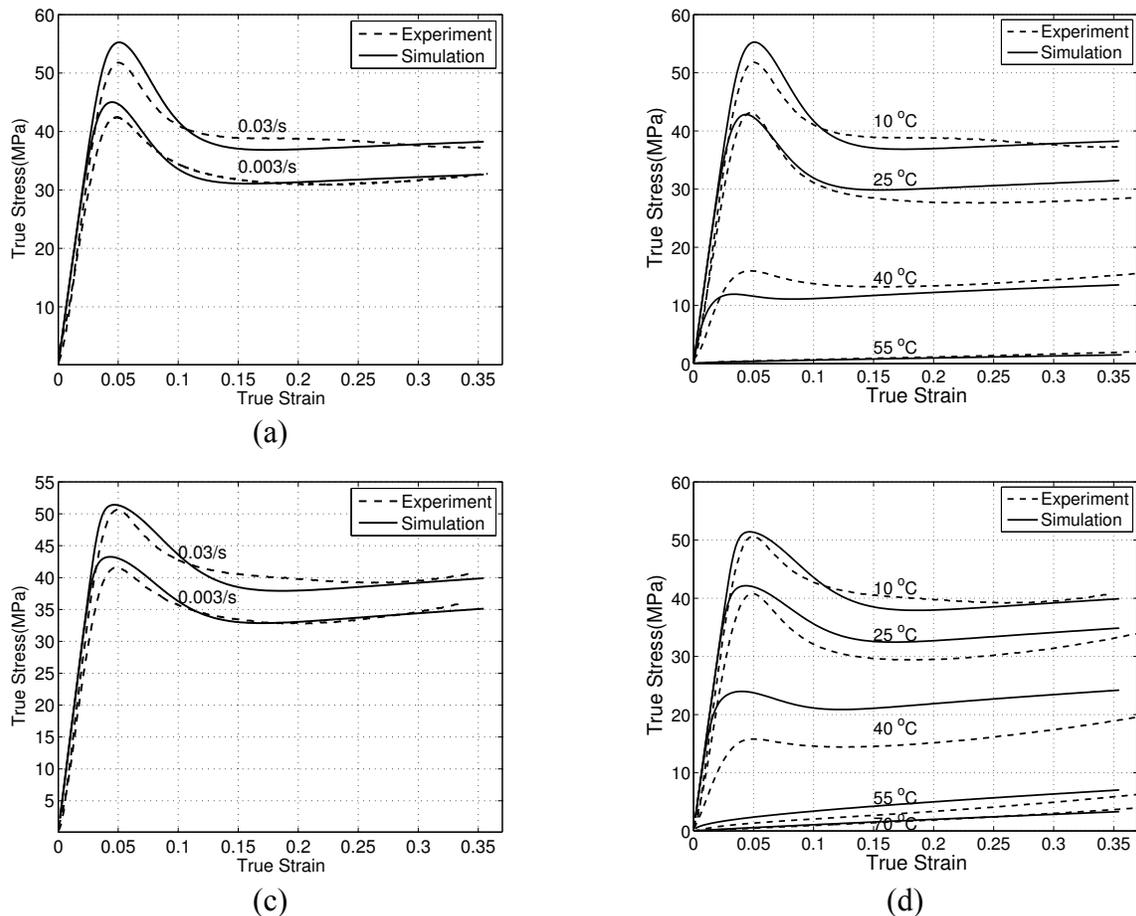
Figure 5: Uniaxial compression tests (a) 20 wt% experimental and simulation results for 10°C (b) 20 wt% experimental and simulation results for strain rate 0.03/s (c) 40 wt% experimental and simulation results for 10°C and (d) 40wt% experimental and simulation results for strain rate 0.03/s.

Figure 6 shows that the activation of strain recovery occurred at lower temperatures (20°C) below T_g and more gradually with a slower recovery rate. Though the simulations also predicted a lower activation temperature, the values were 10°C higher than measured in experiments. The simulations also did not predict a slower initial recovery rate. These discrepancies suggest that the large compressive stresses generated by the initial cold compression had a non-negligible effect on the structural relaxation. Pressure in general increases the structural relaxation time, and a larger structural relaxation time causes a more gradual activation of strain recovery. After activation, the strain recovered non-monotonically with temperature, first increasing to a maximum value then decreasing to the equilibrium value determined by the constraining stress and rubbery modulus. Both the experiments and simulations showed that the strain overshoot increased with increasing constraining stress; though the model generally predicted a lager strain overshoot than measured in experiments.
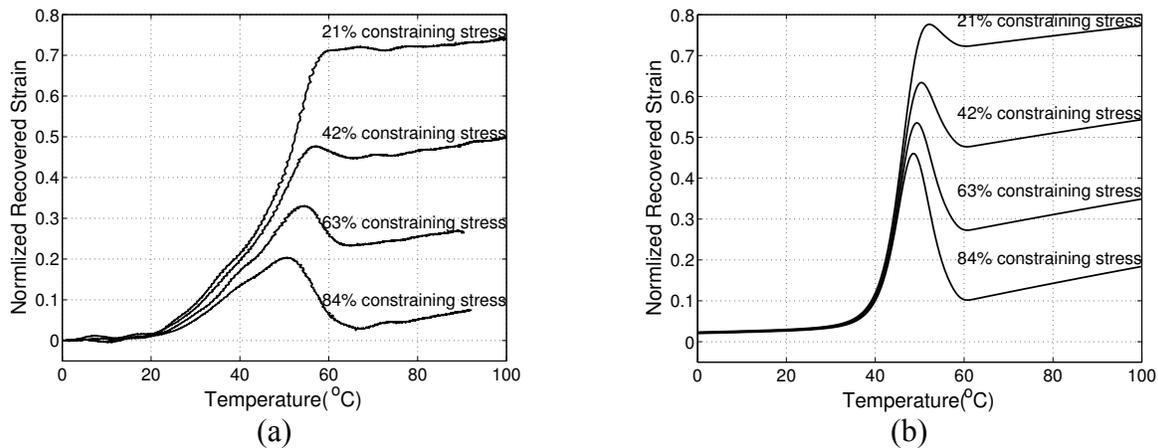
Figure 6: The normalized recovered strain at different constraining stress for 40 wt% materials programmed at 20°C comparing (a) experiment and (b) simulations.

To simulate the fixed-strain recovery response, the sample was either started at 70°C for hot-deformation, or cooled to 20°C at 5°C/min for cold deformation, and held for 10 minutes. For both cases, a 30% compressive engineering strain was applied at 10^{-2}/s and held for 5 minutes to allow for stress relaxation before cooling to 0°C at 5°C/min and annealed 10 minutes. The strain was allowed to vary to allow the stress to fully unload. The temperature was increased to 100°C at 2°C/min while holding the strain constant. Figure 7(a) shows that the maximum stress increased significantly with the applied strain, while Figure 7(b) shows that higher yield strength can generate a higher activation stress.
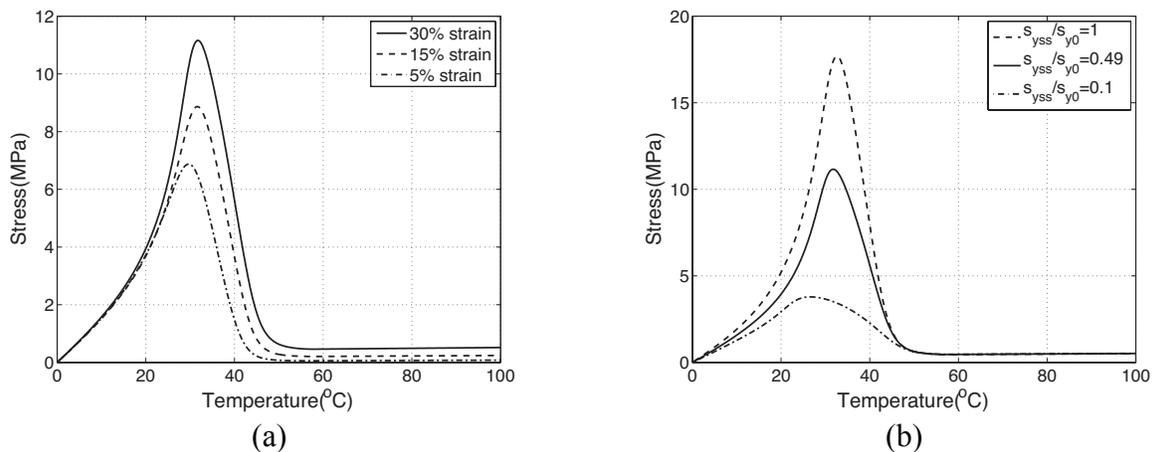

Figure 7: Simulation results for fully constrained recovery for 10 wt %SMPs programmed at 20°C (a) different compression strain influence (b) steady state yield strength influence.

Solvent Induced Shape Memory Behavior

Figure 8 compares the experimental data and simulation results for the isothermal, uniaxial tension stress-strain response of dry and saturated specimens at room temperature. The results showed the dry specimen exhibited a typical hard glassy response with a yield point, post-yield softening, and viscoplastic flow. As expected, the saturated sample showed a compliant rubbery response without a definite yield point. The diffusion of solvent molecules into the polymer

matrix reduced the glass transition temperature from above to below the room temperature resulting in the dramatic softening of the stress response. The simulation results agreed well with the experimental data; though the model slightly underestimated the stress response of the saturated specimen. This may be caused by the loss of hydration during the experiment.
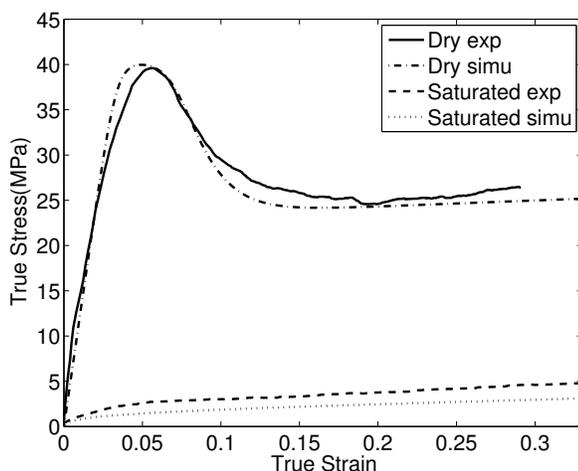

Figure 8: The stress-strain response for dry and saturated specimens at room temperature.

Figure 9 plots the experimental data and model prediction for the shape memory cycle, including the programming and isothermal recovery stage, of dry uniaxial tension specimens. Shape recovery was measured as a decrease in the shape fixity ratio. The results showed the recovery rate increased with increased recovery temperatures. At 41°C less than 30% deformation was recovered after one hour, while at 50°C full recovery was achieved after 15 minutes. For the dry MA-MMA-PEGDMA material, shape-memory programmed specimens showed negligible recovery after months of storage at room temperature. However, the programmed specimens experienced a significant loss of shape fixity after it was immersed in water for several hours.
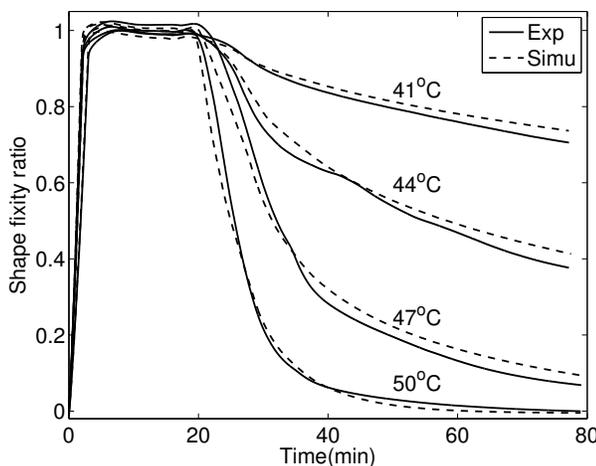

Figure 9: The experimental and simulation results for recovery of tension specimens in air.

DISCUSSION:

We have developed constitutive models for thermally activated and solvent induced shape memory effects. Our thermally activated SME model employs multiple discrete relaxation

processes for stress relaxation, structural relaxation and stress-activated viscous flow. Model parameters were obtained through the dynamic frequency sweep tests, isothermal volumetric recovery tests and uniaxial compression tests. The model was applied to study the influence of deformation temperature on the partial constraint recovery and fixed-strain recovery tests. Simulation results accurately predict the recovery region and recovery ratio of the partially constraint recovery tests as shown in experiments.

A constitutive model was also developed to investigate the influence of low solvent concentration on the mechanical properties and shape memory performance. The Adam-Gibbs model was extended to describe the decrease in the relaxation time due to the increase in configurational entropy through mixing. The diffusion process was incorporated into the model, which was implemented for finite element analysis. A staggered iterative scheme was applied to solve the mechanical and diffusion problems. To verify the model, an acrylate-based copolymer was synthesized. The diffusion tests and frequency tests of dry and saturated specimens were employed to obtain the model parameters. The model with the obtained parameter is able to predict the transition from the viscoplastic stress response of dry specimens to the viscoelastic response of saturated specimens in the uniaxial tension tests. The simulation results on the shape recovery of film specimens and tube specimens in water also show good agreement with the experimental observations. From this it was concluded that the solvent-driven shape memory recovery is caused by the plasticization effect of solvents.

This work – summarized briefly above and described in full detail in the articles listed in the References section – includes the following contributions to the fundamental understanding of the polymer physics:

1. **A detailed experimental method was developed for obtaining the structural relaxation spectrum.** The broad distribution nature of the structural relaxation processes makes it difficult to obtain the spectrum in one single test. Thus the consecutively isothermal volumetric recovery tests were designed to obtain the structural relaxation spectrum. The relaxation tests at high temperatures provide the information for relaxation processes with large relaxation time, while the relaxation tests at low temperatures provide the information for relaxation processes with small relaxation time. This method can also be applied to obtain the structural relaxation spectrum corresponding to changes in pressure.

2. **The stress and structural relaxation time can be described by the same temperature and structure dependence shift factor for the acrylate random copolymer system.** It was demonstrated the individual volumetric relaxation test could be shifted to form a master curve through adopting the same shift factor from the viscoelastic relaxation tests. The shift factor for the stress relaxation can be obtained through the standard time-temperature superposition of small strain viscoelastic tests. In contrast, the shift factor of structural relaxation is difficult to obtain from standard tests. This finding shows that the shift factor for both relaxation processes can be obtained through one single test.

3. **Solvent-driven shape memory effect originates from the plasticization effect**. In this work, the configurational entropy theory was adopted to describe the depression of the

glass transition temperature by solvent introduced plasticization effect. The model parameters were obtained through superposition of the storage modulus of saturated specimens to the master curve of the storage modulus of the dry specimens. This approach can be extended for other theories (free volume, for example) to simulate the shape memory recovery in solvents.

4. **Physical aging and mechanical rejuvenation can be described by one single set of parameters for the acrylate random copolymer system**. This work provides a unified framework to model the influence of thermal history and mechanical deformation on the stress-strain and enthalpy response, which is important for the applications of amorphous polymers as structural materials. The work also shows that the origin of strain softening is structural rejuvenation.

Though these models have achieved considerable success in describing the shape memory performance of amorphous polymers and the general thermomechanical behaviors of amorphous polymers, some limitations of these models should be acknowledged.

First, the current models are limited to moderate strains (less than 30%). In the rubbery state, the Arruda-Boyce eight-chain model is able to describe the stress strain response over a wide strain region. However, the Arruda-Boyce model is inadequate to capture the temperature and strain rate dependent strain hardening behaviors below T_g, which shows strain-hardening modulus increases with decreasing temperature and increasing strain rate.

The model developed adopted the modified Adam-Gibbs model to incorporate the solvent effect into the model by assuming the solvent does not influence the configurational entropy of the dry polymer systems. This assumption may only be valid for the polymer-solvent systems with limited swelling ability. Thus the model cannot be applied to investigate the shape memory recovery of polymers in organic solvent, which involves large solvent concentration.

The diffusion of the solvent in the polymer systems is modeled by the Fick's law, which may also fail to explain the diffusion behaviors of organic solvent in amorphous polymers. For the model developed, it is assumed that a constant fraction of viscous dissipation flows into the configurational subsystems. This assumption needs to be verified over a wide range of strain rate and temperature.

ANTICIPATED IMPACT:

Future directions include further improvement on the current models and the application of the models to describe new experimental observations. The main future directions are listed as follows:

- The current work can be extended for thermoplastic amorphous polymers. The work mainly focuses on the amorphous thermoset with chemically cross-linked networks. Compared with the structures of thermosets, which are formed through strong chemical bonds, the polymer chains of thermoplastic associate through the intermolecular forces. Thus at high temperatures the thermoplastic can be reshaped. When thermoplastic is

adopted as shape memory polymers, the recovery performance is accompanied by some unrecoverable strain. Our model can be modified to exhibit the shape memory behaviors of the thermoplastic amorphous polymers, including the influence of deformation temperature, holding time, and cyclic tests on the shape memory performance.

- The plasticization model developed can be improved to describe high solvent concentration. The dependence of the relaxation time on large solvent con- centration needs to be defined through general polymer solution theories and verified through the experimentally measured dynamic response of polymers with various degrees of solvent concentration. A fully coupled chemo-mechanical model can also be developed. The energy change from mixing polymer and solvent needs to be incorporated into the total free energy, and the diffusion equation for the solvent species needs to be derived from thermodynamics. The model can be further extended to describe the mechanical behaviors of the gels. Most of current gel models assume the dry gels are in their rubbery state. But various gels are in the stiff glassy state at room temperature. As gels swell, the solvent decreases their viscosity. Thus the viscoelastic and viscoplastic effect needs to be included to fully describe the complex swelling and deformation behaviors of gels.

- The structural relaxation spectrum in this study is obtained through isothermal volumetric relaxation tests. The enthalpy structural relaxation spectrum is assumed to have the same shape as the volumetric relaxation spectrum. New experimental procedures need to be designed to obtain the enthalpy structural relaxation spectrum from DSC data. The constitutive model developed, together with new obtained structural relaxation spectrum, can be applied to study enthalpy measurements of amorphous polymers with different thermal histories (cooling rate, aging time) and mechanical deformations (strain).

- The model developed can be applied to simulate the thermomechanical coupling of glassy amorphous polymers. The model needs to be implemented into finite element program by writing a user-defined element subroutine, and can then be applied to study the influence of strain rate and thermal history on heat generation. The *in situ* surface temperature measurement tests need to be performed by an infrared camera to verify the model. The model can also be employed to study the strain localization behaviors of amorphous polymers due to inhomogeneous in geometry and thermal history.

- Strain hardening can be incorporated into the thermomechanical models. The non-equilibrium thermodynamic framework developed can be extended to incorporate the strain hardening effect. Internal parameters will be defined to describe the chain orientation. The evolution equations will be derived based on thermodynamics. The model can be applied to study the influence of temperature, strain rate and pre-deformation on the strain hardening behaviors. The model can also be employed to investigate the shape memory behaviors of samples programmed with large strain below the glass transition temperature.

This work supports the mission of the Department of Energy through scientific discovery and innovation in physical science, engineering and emerging scientific disciplines by developing

advanced models for the physical response of polymers and polymer composites. When coupled with models for piezoelectric materials, this effort presents unique possibilities for the design and development of non-powered, self-aware sensors suitable for DOE, DOD and DHS applications.

During the course of this project, the academic partner (T.D. Nguyen) was awarded an NSF Grant Opportunity for Academic Liaison with Industry (GOALI) 4-year project on Mechanical Activation of Amorphous Shape Memory Polymers; awarded amount ~ $303K.

CONCLUSION:

This work has developed constitutive models to describe the thermomechanics and shape memory performance of amorphous polymers spanning the glass transition. The models incorporate stress relaxation, structural relaxation, mechanical rejuvenation, and plasticization effect. The models capture all the main characteristics of amorphous polymers over a wide temperature region, including the entropy-driven hyperelasticity above the glass transition region, the time and temperature dependent viscoelastic behaviors in the glass transition region, and the viscoplastic performance with yielding and strain softening below the glass transition region. These models have shown the ability to describe the thermally activated and solvent driven shape memory behaviors. To characterize the polymers, both thermomechanical experiments and shape memory recovery experiments were performed. Experiments were also developed to obtain the model parameters.

In order to describe strain-softening behaviors, the models developed adopted a phenomenological evolution equation of the yield strength to a steady-state value with plastic strain rate. This results in a steady-state flow stress that depends on the thermal history, which contradicts experimental observations. These models cannot be directly employed to explain the mechanical rejuvenation phenomena. Also developed was a thermomechanical model that couples structural evolution and inelastic deformation was developed to describe both physical aging and mechanical rejuvenation. The polymers are assumed to be composed of the fast relaxation kinetic subsystem, which is always in equilibrium, and slow relaxation configurational subsystems, which fall out to the equilibrium at low temperatures. Physical aging is caused by the structural evolution of configurational subsystems towards a less mobile state, while the mechanical rejuvenation is caused by the internal plastic work that drives the configurational subsystems towards a more mobile state.

The model was validated by the measured stress-strain response of samples at different temperatures, strain rate, aging time and pre-deformation. The model can also describe the enthalpy change of specimens with different thermal history and mechanical deformation. The simulation shows that the physical aging can result in an endothermic overshoot and that large elastic work can erase the appearance of the endothermic overshoot and create another exothermic undershoot, which are all observed in experiments. This model shows the possibility of providing a unified theory with a minimum set of parameters for a wide range of non-equilibrium behaviors that are typically treated as separate phenomena in current modeling approaches.

REFERENCES:

T.D. Nguyen, C.M. Yakacki, P.D. Brahmbhatt and M.L. Chambers, "Modeling the Relaxation Mechanisms of Amorphous Shape Memory Polymers", *Advanced Materials*, **22**, pp. 3411-3423 (2010)

X. Chen and T.D. Nguyen, "Influence of thermoviscoelastic properties and loading conditions on the recovery performance of shape memory polymers," *Mechanics of Materials*, **43** (3), pp. 127–138 (2011)

N. Lakhera, C.M. Yakacki, T. Nguyen, and C.P. Frick, "Partially-constrained recovery of (meth)acrylate shape-memory polymer networks," *J. App. Poly. Phys.*, **126** (1), pp. 72–82 (2012)

C.M. Yakacki, A.M. Ortega, C.P. Frick, N. Lakhera, R. Xiao and T. D. Nguyen, "Unique recovery behavior in amorphous shape-memory polymer networks," *Macromolecular Materials and Engineering*, **297** (12), pp. 1160-1166 (2012)

R. Xiao and T.D. Nguyen, "Modeling the solvent-induced shape-memory behavior of glassy polymers", *Soft Matter*, **9**, p. 9455 (2013)

R. Xiao, J. Choi, N. Lakhera, C.M. Yakacki, C.P. Frick and T.D. Nguyen, "Modeling the glass transition of amorphous networks for shape-memory behavior", *Journal of the Mechanics and Physics of Solids*, **61**, pp. 1612-1635 (2013)

R. Xiao, J. Guo, and T.D. Nguyen, "Modeling the multiple shape memory effect and temperature memory effect in amorphous polymers," *RSC Advances*, **5**, pp. 416-423 (2015)

R. Xiao, "Thermomechanics of Amorphous Polymers and Its Applications to Shape Memory Behaviors", Ph.D. Thesis, The Johns Hopkins University, Baltimore, MD (2015)

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY