

# A THERMODYNAMIC ANALYSIS OF THE SHAPE MEMORY ASSISTED SELF HEALING POLYMERS

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## ABSTRACT

Self-healing polymers (SHPs) can revert to their original state with full or partial recovery of mechanical strength after damage. In most recently reported SHPs, the self healing is mainly achieved by manual intervention. A completely autonomous self-healing strategy is recently demonstrated by applying a blend system consisting of cross-linked poly network interpolated with linear poly system. The crosslinked network shows shape memory (SM) property while the linear polymer system shows a good viscous flow behavior at high temperature. The SM property of the chemically cross-linked network helped the linear polymer system go back to its initial place after deformation, and the further diffusion and entanglement of the linear polymer network across the interface realize the self healing of the crack. This shape memory assisted self healing polymers (SMSHP) shows a wide potential engineering application. To assist the design and engineering application of the proposed SMSHP, a thermodynamic model is developed to reflect the fundamental mechanism of the shape memory assisted self healing. In the model, a interpolated network model is proposed to simulate the cross-linked network and linear polymer system, respectively. The shape memory property of chemically crosslinked network is captured by a viscoplastic model considering the typical glass and rubbery transformation in the material, while the mechanical property of the linear polymer system is modeled by a viscoelastic model. A micro-mechanism based polymer fracture model is developed by scaling theory, and the monomer diffusion based self healing model is established. After the material parameters identified by experiments, a typical self healing process is simulated as: (1) stretch the polymers to a state with crack surface at room temperature, (2) relax the constrains and the cracked surface is fixed, (3) reheat the polymer to assist the recovery of the deformation, (4) the cracked surface is self healed after a period of time. The simulated results are compared with experiments and a good agreement demonstrates efficiency of the developed model.

**Key words:** self healing, shape memory polymer, thermodynamic analysis

## 1 INTRODUCTION

Self healing polymeric (SHP) materials are the materials system can revert to their virgin state fully or partially mechanical property after damaged[1, 2]. The idea of SHP is developed from the biological systems where an autonomous damage healing takes place. These materials can be categorized into stimuli-induced and autonomic classes. A lot of self-healing researches can be found based on stimuli-induced formation of bonds including reactions induced by heat treatment or

irradiation. Most applied method in designing self healing materials is through healing agents embedded into a polymer matrix. Upon damage, the encapsulated chemical embedded into polymer matrix are dispersed into the cracks in polymer when ruptured by propagating cracks. When meeting the catalyst in the polymer outside the capsules, the chemicals will rouse repair of the cracks in the materials. Another developed self-healing systems these years is based on dynamic covalent chemistry, as an example proposed in the work. However, the SH systems described above all rely solely on a rebonding reaction, but do not provide often needed crack closure before healing. Recently, a shape memory assisted self-healing system is developed, where both shape memory and self healing mechanism exhibit[3]. To get a deep understanding of the materials and provide assistance for material design, a consistent thermodynamic model is needed, which is the topic in this work.

Lot of self healing model in framework of continuum mechanics are proposed[4, 5]. Most of them are phenomenological on macroscale. The physically mechanism based self-healing model is limited. In this work we built a model basing on the work by [1], where a self healing mechanism is discussed by applying scale theory. The model is applied in the self-healing simulation and shows good prediction.

## 2 THEORETICAL MODEL

### 2.1 CONSTITUTIVE RELATIONS

The shape memory assisted self-healing polyer network consists of two network, the linear polymer network and the crosslinked network. The L-PCL linear polymer network is modeled by viscoelastic model while the n-PCL network is captured by viscoplastic model. By applying thermodynamic theory, and after a derivation, the second Piola-Kirchhoff stresses for equilibrium and non-equilibrium part can be defined as[6]

$$\mathbf{S} = \mathbf{S}^V + \mathbf{S}^{eq} + \mathbf{S}_{(1)}^{neq} + \mathbf{S}_{(2)}^{neq}, \mathbf{S}^V = p\mathbf{J}\mathbf{C}^{-1},$$

$$\mathbf{S}_{(1)}^{neq} = \mathbf{F}_{(1)}^{vp^{-1}} \cdot \widehat{\mathbf{S}}_{(1)} \cdot \mathbf{F}_{(1)}^{vp^{-T}}, \mathbf{S}_{(2)}^{neq} = \mathbf{F}_{(2)}^{vp^{-1}} \cdot \widehat{\mathbf{S}}_{(2)} \cdot \mathbf{F}_{(2)}^{vp^{-T}}, s = \frac{\partial \psi}{\partial T}, \quad (1)$$

where,  $\mathbf{S}^{eq}$  is the stress contribution from the equilibrium branch,  $\widehat{\mathbf{S}}_{(1)}$  is the stresses for the nonequilibrium part of crosslinked network, and  $\widehat{\mathbf{S}}_{(2)}$  is the stresses contribution from the linear network, and

$$p = \frac{\partial(\rho_{RT}\psi_V)}{\partial J}, \mathbf{S}^{eq} = J^{-2/3}\tilde{\mathbb{P}}^{eq} : \frac{\partial(\rho\psi^{eq})}{\partial \bar{\mathbf{C}}},$$

$$\widehat{\mathbf{S}}_{(1)} = J^{-2/3}\tilde{\mathbb{P}} : \frac{\partial(\rho_{RT}\psi_{(1)}^{neq})}{\partial \bar{\mathbf{C}}_{(1)}^e}, \widehat{\mathbf{S}}_{(2)} = J^{-2/3}\tilde{\mathbb{P}} : \frac{\partial(\rho_{RT}\psi_{(2)}^{neq})}{\partial \bar{\mathbf{C}}_{(2)}^e}, \quad (2)$$

$$\text{where } \tilde{\mathcal{P}}_{(i)} = \frac{\partial \bar{\mathbf{C}}_{(i)}}{\partial \mathbf{C}}, \bar{\mathbb{P}}_{(1)}^e = \mathbb{I} - (1/3)\bar{\mathbf{C}}_{(1)}^e{}^{-1} \otimes \bar{\mathbf{C}}_{(1)}^e, \bar{\mathbb{P}}_{(2)}^e = \mathbb{I} - (1/3)\bar{\mathbf{C}}_{(2)}^e{}^{-1} \otimes \bar{\mathbf{C}}_{(2)}^e.$$

An internal variable indicating the damage is defined by reflecting the fraction of the debonding chains across interfacial face according to the intact equilibrium case[7],

$$\mathbf{D} = \left( 1 - \frac{\bar{C}_B^{eq}}{C_B^{eq}} \right) \mathbf{I}, \quad (3)$$

where  $C^d, C$  are the concentration of the debonded and intact network chains.

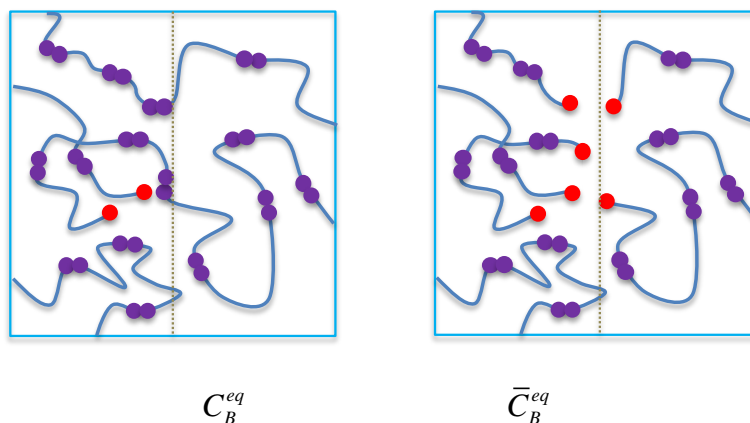


Fig. 1 schematic of damage variables across interface (a) the bonded pairs concentration at equilibrium; (b) the bonded pairs concentration after damage at equilibrium state

## 2.2 FRACTURE MODEL

Basic ingredients of fracture in rubbers at finite strain can be micro-mechanically motivated by a network theory. To break a particular bond within the chain, it is necessary to subject all other bonds, which are lying in the same chain, by the same breaking force. Each unit in the chain must be strained up to rupture before the chain will break. If the surface energy required to rupture a monomer unit is  $g_{monomer}$ , the energy required to rupture a single chain consisting of  $N$  monomers is

$$g_{chain} = N g_{monomer}, \quad (4)$$

Considering the randomly jointed chain distribution with probability density per unit of the radius  $r$  of a sphere. Then when macroscopic crack propagation occurs on the network scale, a number  $n_\Gamma$  of chains that is crossing a unit area has to be broken to create the new surface  $\Delta\Gamma$ , and the micromechanically motivated expression for the macroscopic critical energy release rate is for crack propagation in rubbery polymers networks is

$$g_c = n_\Gamma g_{chain}. \quad (5)$$

## 2.3 BREAKING AND RE-HEALING OF THE NETWORK

### 2.3.1 STICKERS CONCENTRATION

We consider sticky dangling chains attached to a polymer network by effective chains fixed in space at one end and containing associating groups at the other end. When is broken, the 1-PCL network is reversed to its initial state by the n-PCL network, a typical thermally activated shape memory behavior. Each dangling chain is a linear polymer containing  $N$  monomers.

Under the tension, an “ideal cut” is introduced along the  $xy$ -plane through the middle of the simulation model. Then as for a waiting period, after the “ideal cut” updates of sticky bonds are switched on, but during the waiting period no reversible bonds are allowed to form across this fracture plane and the confining potential is kept on. The concentration of the sticky group change for different time as the following[1].

$$(1) \tau_{open}^i < t < \tau_R$$

The initial local concentration of open stickers in the interface zone within distance  $R_0$  of the fresh cut is proportional to the total concentration of stickers, and

$$c_{open}^i \approx c_{Tot} \approx 1/(b^3 N), \quad (6)$$

As for the Rouse time of single chain, with  $\tau_R \approx \tau_0 N^2$ . The decrease of the excess number of open stickers per unit area in the fractured layers follows the anomalous diffusion and can be obtained by

$$\sigma_{open}(t) \approx R_0 c_{open}(t) \approx \frac{1}{R_0^2} \left( \frac{t}{\tau_R} \right)^{-3/4}, \quad (7)$$

$$(2) \tau_R < t < \tau_b$$

Associations between open stickers during waiting time slows down since there are no available partners easily reachable by the remaining open stickers. This state corresponds to one open sticker per chain area  $R_0^2$ , and we have

$$\sigma_{open}(t) \approx R_0 c_{open}^* \approx \frac{1}{R_0^2}, \quad (8)$$

where  $\tau_b$  is the average time two stickers spend in a bonded state before a successful separation on molecular distance, monomer length,  $b$ .

$$(3) \tau_b < t < \tau_{eq}$$

Then, the hopping recombination becomes possible and the number of excess open stickers will further decrease. Then the decrease of the number density of open stickers per unit area during the waiting time is

$$\sigma_{open}(t) \approx \frac{W(t)}{V_{expl}} \approx \frac{1}{R_0^2} \left( \frac{t}{\tau_b} \right)^{-1/2}. \quad (9)$$

### 2.3.2 FORMATION OF THE BONDS

After some waiting time, fractured surface are brought back by n-PCL network, and after shifting, the confining potential is turned off by increasing temperature, and the chains are allowed to interpenetrate and from sticky bonds across the fractured interface.

Then the formed bridge concentration for the time less than  $\tau_{eq}$  can be calculated

as

$$c_B(t) \approx \frac{1}{b^2} \left( \frac{\tau_0}{\tau_w} \right)^{1/2} \frac{t}{\tau_w}, \quad (10)$$

The linear increase of surface density of bridges slows down at healing time of about  $\tau_w$ . This is because at such time scale the concentration of open stickers in the surface layer starts to effectively decrease toward equilibrium value due to the formation of loops.

Actually some bridges are still formed at times between  $\tau_w$  and  $\tau_{eq}$  due to rare open stickers reaching the interface from places further away from the interface without recombining with other open stickers from the same side of the interface. We propose a convenient interpolation formula that covers the whole time range

$$\sigma_b(t) \approx \frac{1}{b^2} \left( \frac{\tau_0}{\tau_w} \right)^{1/2} \frac{t}{\tau_w} \frac{1}{const + \frac{t}{\tau_w} + \left( \frac{t}{\tau_w} \right)^{1/2}}. \quad (11)$$

Using the defined damage variable  $D$  relating the bridge concentration to material constant, then substitution of the bridge concentration across the fracture surface calculated in (Eqs.6-11) in constitutive relations (Eq. 2) yield a damaged model in continuum form. Calculating the model yield fracture and self healing characteristics of the material.

### 3 RESULTS AND DISCUSSION

In this section, the results predicted by the model are presented and compared with experiment results. Fig. 2 shows the force-displacement curve for a notchedl-PCL50:n-PCL50 sample under room temperature. The sample was stretched in its damaged state, and the initial crack opening and then crack transition, and finally the partial crack propagated. The simulated results shows a good agreement with the experiment results, demonstrating validation of the proposed model. Then the damaged sample is self healed when increase temperature. After the self-healing process for 30mins, the healed sample is stretched. Fig. 3 presents the force-displacement curve of the virgin and self-healed samples. A nearly completed healed state is attained comparing with the virgin sample. The theoretical results shows a good prediction.

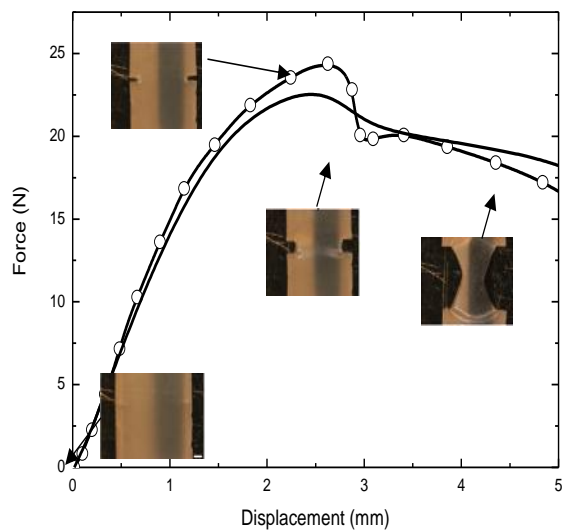


Fig. 2 Comparison of force-displacement relation of SMSHP between experiment and simulation

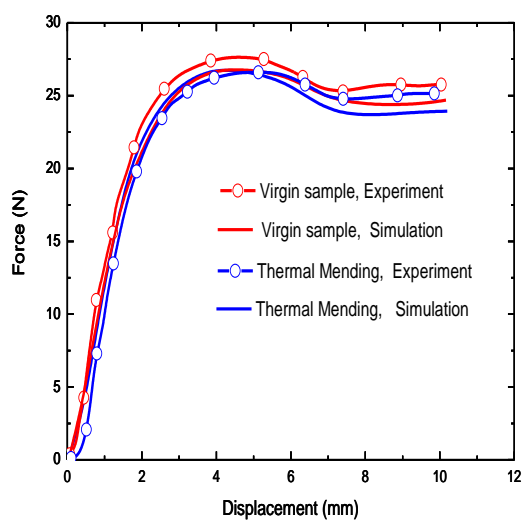


Fig. 3 Force-displacement relation of SMSHP for the virgin sample and the re-healing sample

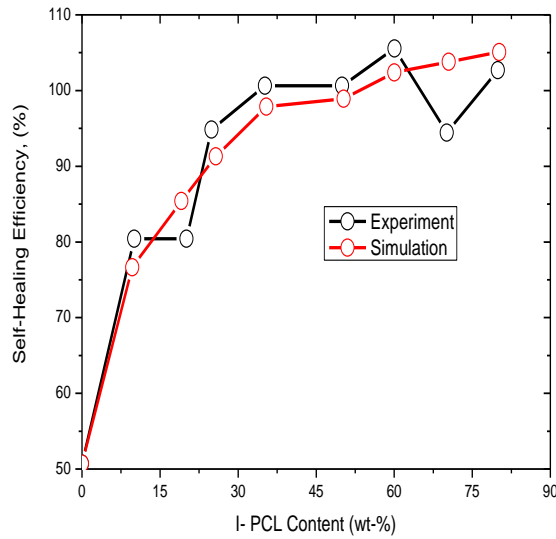


Fig. 4 The self-healing efficiency of the SMSHP

Figure 4 shows the SH efficiency trend for different compositions by experiments and simulation. SH efficiency was calculated as a function of I-PCL wt % for the first thermal mending treatments. It is found that compositions containing 20 wt % I-PCL and below have only modest SH efficiency ranging from ~50-80%. An increase of I-PCL containing leads to a higher SH efficiency after the first thermal mending treatment. When the composition containing over 25 wt% I-PCL, an excellent shape-memory assisted self healing is achieved. It is explained that a higher containing of I-PCL leads to a higher energy dissipation under stretch, and the n-PCL network maintains intact, while there is some fraction of n-PCL network are broken for the case with lower I-PCL containing. It can be concluded the SMASH system has capacity of healing both the region of damage while recover the elastic and plastic region.

#### 4 CONCLUSION

A thermodynamic model is developed for the shape memory assisted self healing polymers (SMSHP). In the interpolated network of SMSHP, the I-PCL network is captured by viscoplastic model while the n-PCL network is modeled by viscoplastic model. A damage variable is brought forward to indicate the break of the chain of the network, and accordingly a continuum damaged viscoplastic model is developed. Under external loading, the I-PCL network and n-PCL network are both stretched, and break of bonds will take place in the I-PCL network to a threshold state. When increase temperature, the n-PCL network would recover, bringing the broken i-PCL chain to its initial state. The self-healing state of two fractured surface is reflected by the bridge formation rate under motion of sticky group applying scale theory. The proposed model show excellent prediction capability by comparing with experiment

results. Results shows that when the composition of l-PCL is 20 wt % and below, only a modest SH efficiency ranging from ~50-80% is attained. When increase l-PCL containing leads to a higher SH efficiency. When the composition containing over 25 wt% l-PCL, an excellent shape-memory assisted self healing is achieved.

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