

SHAPE MEMORY POLYMER BLENDS EXHIBITING SELF-HEALING

Erika D. Rodriguez^{1,3}, Xiaofan Luo^{2,3} and Patrick T. Mather^{2,3}

¹Mechanical and Aerospace Engineering, Syracuse University, Syracuse, NY 13244
Email: edrodr02@syr.edu

²Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244
Email: xluo@flowpolymers.com, ptmather@syr.edu

³Syracuse Biomaterials Institute, Syracuse University, Syracuse, NY 13244
Email: xluo@flowpolymers.com, edrodr02@syr.edu, ptmather@syr.edu

Keywords: Shape memory (SM), Self-healing (SH), Rebonding, Crack healing

ABSTRACT

We report a new strategy that utilizes shape memory (SM) to yield novel SH polymers that are capable of simultaneously closing and re-bonding cracks with a simple thermal stimulus [1]. This strategy, termed “shape memory assisted self-healing (SMASH)” is demonstrated in a blend system consisting of crosslinked poly(ϵ -caprolactone) network (n-PCL) with linear poly(ϵ -caprolactone) (l-PCL) thermoplastic SH agent, and interpenetrates the network, and exhibits a combination of SM response from the network component and SH capacity from the SH agent.

The SMASH system exhibits reversible plasticity, a form of shape memory (SM) where plastic deformation is fully recovered due to the entropy elasticity of the network that is triggered by heating the network above melting temperature ($T_m \sim 55$ °C). One single heating event can tackify crack surfaces while bringing them into molecular contact, resulting in SMASH to recover its mechanical strength. This is accomplished by the linear thermoplastic component, l-PCL, molecularly interpenetrating the SM n-PCL component and molecularly diffusing to the damaged site to re-bond cracks formed during damage. SM was accomplished at RT to achieve a desired strain percentage before reversible recovery was attained. SH studies show that after damage, the initial crack made prior to stretching and the propagated crack created while stretching have healed when l-PCL is greater than 25 wt-%. Complete healing is observed where necking at the initial crack regions is evident when the healed samples are re-stretched.

Thiol-Ene PCL network chemistry (Figure 1) was used to prepare the PCL networks from PCL telechelic diacrylates and a tetrathiol crosslinker, yielding excellent shape memory. The healing component, l-PCL used had a high M_w ($M_w \sim 65k$ g/mol) to enable re-entanglement after diffusion across the damaged interface for healing.

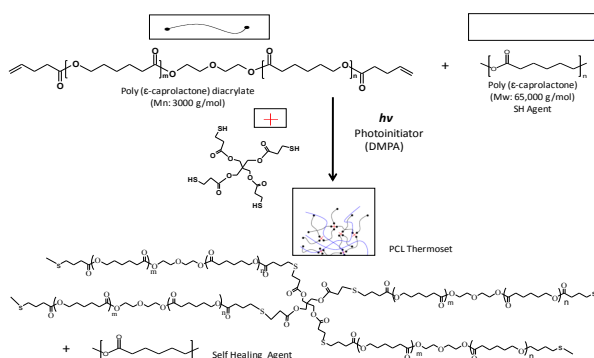


Figure 1: UV-initiated thiol-ene polymerization chemistry using n-PCL and l-PCL polymers to form SMASH systems.

SH experiments were conducted on dogbone samples (ASTM D638-03 Type 1, scaled down by a factor of 3) using a dogbone cutting die. The Linkam TST350 Tensile Testing System was used to uniaxially stretch the samples. The virgin samples were stretched first to obtain a force vs. displacement baseline curve and then recovered. A custom made double edge notch punch was used to create a double-edge notched tensile (DENT) damage on the sample [2]. The sample was then stretched for crack growth, healed and then cooled to RT and re-stretched to compare the SH efficiency among the peak loads of the virgin and healed states of the sample (Figure 2a).

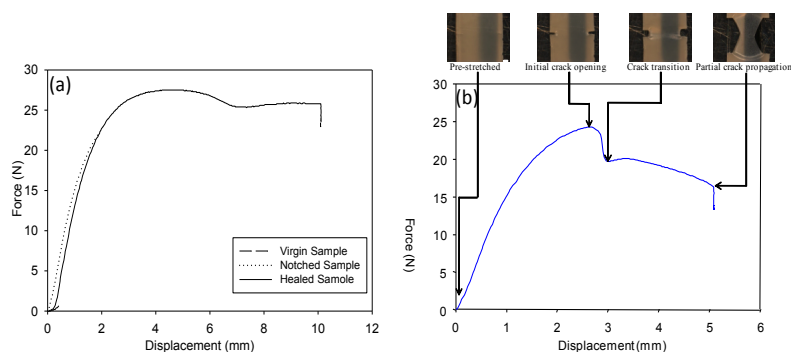


Figure 2: (a) Force vs. displacement curves of the virgin, damaged and healed state of a l-PCL₅₀:n-PCL₅₀ sample. (b) Notched l-PCL₅₀:n-PCL₅₀ sample showing stereo micrographs of deformation and crack growth (scale bar: 500 μ m).

The sequence of five stages of SH within the SMASH material is indicated in Figure 3a. After SM allows for crack-face contact, the l-PCL chain entanglements across the site of fracture proceeds in steps: (1) polymer rearrangement, (2) surface approach, (3) surface wetting, (4) chain diffusion, and (5) equilibrium and randomization (Figure 3a). Figure 3b shows stereo micrographs of SMASH as a function of temperature.

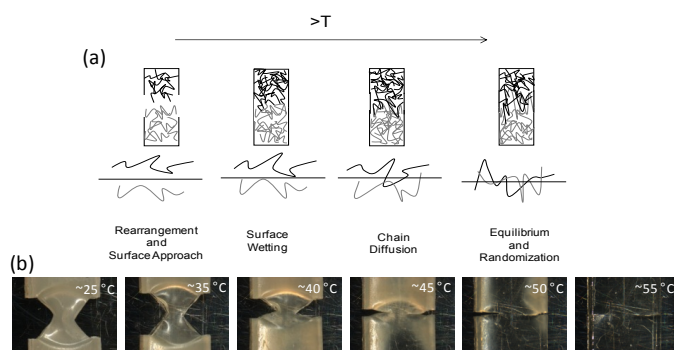


Figure 3: (a) Polymer chain entanglement schematic of five stages of healing (b) Micrographs of crack closure and crack rebonding when sample heated from RT to above its T_m (stereo micrographs scale bar: 500 μ m).

Ongoing studies include water submersion SMASH to understand whether shape recovery and healing can occur with full and continuous submersion in a liquid water environment. Further studies also include variation in the Mw of the l-PCL healing agent to investigate its impact on healing kinetics. Applications for SMASH systems include self-healing bladders, inflated structure membranes, and architectural building envelopes.

REFERENCES

- [1] Erika D. Rodriguez, X. Luo, and P.T. Mather, Linear and Crosslinked Poly (ϵ -Caprolactone) Polymers for Shape Memory Assisted Self-Healing (SMASH), *ACS Applied Materials and Interfaces* **3** 152-161 (2011).
- [2] Fayolle, B.; Tcharkhtchi, A.; Verdu, J., Temperature and molecular weight dependence of fracture behaviour of polypropylene films, *Polymer Testing* **23**, 2004, pp. 939-947.