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Self-Healing, Shape-Memory Polyanhydrides**PI:****Devon A. Shipp**Clarkson University
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The overall goal of the proposed research is to develop and study fully-degradable shape memory elastomeric polymers and composites (SMECs) that allows for reconfiguration of the permanent shape and self-healing. These systems are comprised of polyanhydrides, which we have discovered to have thermally-triggered dynamic covalent exchange, and may also include fibers that consist of polyesters/polyurethanes (for SMEC systems). The work consists of three tasks. (1) The development of degradable soft elastomeric polymers and SMECs, examining thermomechanical properties and degradation behavior. (2) Study of the dynamic covalent exchange chemistry of re-configuration in the polyanhydride-based shape memory polymers. (3) Exploration of degradable SMECs. This report provides some preliminary findings of our work for the period 9/1/2018 – 8/31/2019, which represents year one of the two-year project. The project has involved one full-time graduate student, a portion of a postdoctoral researcher, and one summer undergraduate student.

1. Polyanhydride Shape Memory Materials

We determined that semi-crystalline polyanhydrides can be made using mixtures of 1,6-hexanedithiol (HDT), pentenoic anhydride (PNA), and PETMP (Figure 1). These materials have the two requirements for a shape memory material: a rubbery crosslink component that provides “memory” of the original shape and a semicrystalline phase (primarily due to the HDT) that acts to “fix” the temporary shape. Example of this process is shown in Figure 1. However, as we recently reported, these polyanhydrides undergo dynamic covalent exchange (DCE), which reduces the ‘memory’ of the rubbery phase (*ACS Macro Lett.* **2016**, *5*, 203-207). Hence work is also examining the DCE process in detail so that compositions and conditions may be devised such that exchange can be minimized and therefore allow shape memory behavior to proceed satisfactorily.

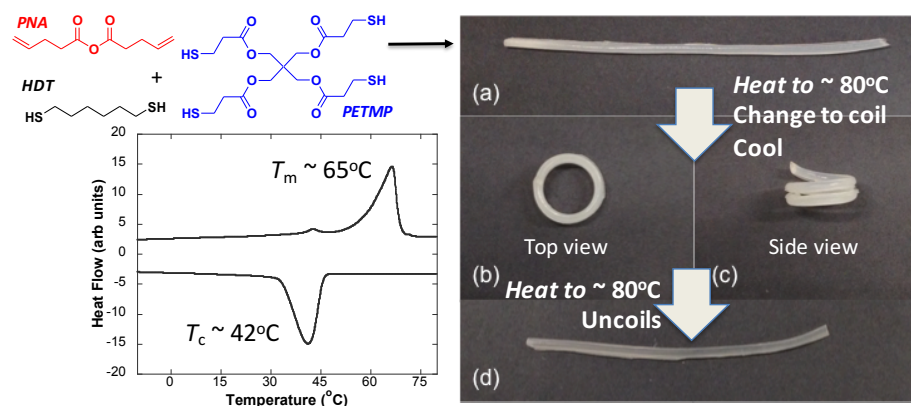


Figure 1. Outline of the synthesis of semicrystalline polyanhydrides, and qualitative demonstration of their shape memory properties (photos (a) – (d)), and DSC curve of polyanhydride made from a monomer mixture of PNA:HDT:PETMP = 100:80:20 (functional group mole ratios).

2. Network Relaxation Studies

Dynamic covalent exchange between the anhydride groups in the polyanhydride network can be monitored by stress-relaxation measurements (creep) using dynamic mechanical analysis. Figure 2 shows an example of such relaxation measurements for various polyanhydride networks made from various monomer ratios (PNA:HDT:PETMP). In these data we can clearly see that relaxation occurs faster at higher temperatures and at lower crosslinker (PETMP) content, as expected.

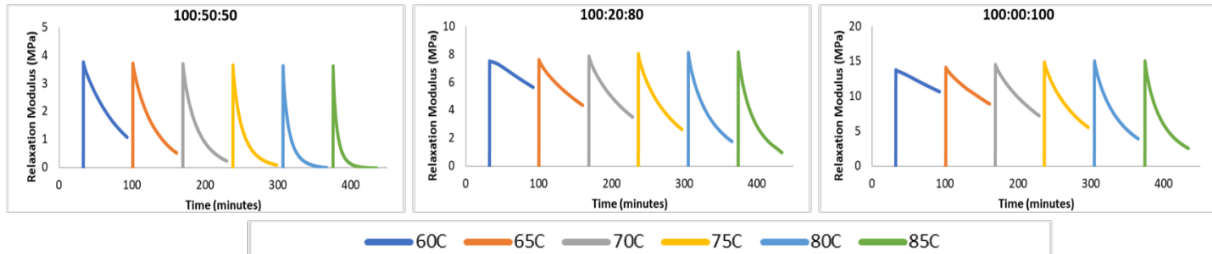


Figure 2. Stress-relaxation curves for polyanhydrides at different temperatures and monomer mixture of PNA:HDT:PETMP (functional group mole ratios).

3. Degradable SMECs

Research on degradable shape memory elastomeric composites (SMECs) focused on the process development and thermomechanical characterization of nanocomposites prepared with Pellethane nanofibrous webs infiltrated with a polyanhydride (PAH) matrix that was photocured. Our processing methodology was refined with the adjustment of electrospinning parameters (for the Pellethane web) and photocuring conditions. Once reproducible and mechanically robust SMEC samples were achievable, our attention turned to thermomechanical characterization that included traditional dynamic mechanical analysis (DMA) and shape memory analysis. The former revealed overlapping glass transition temperatures for the matrix ($T_g = -40\text{ }^\circ\text{C}$) and fiber ($T_g = -10\text{ }^\circ\text{C}$). Shape memory analysis proved to be complex and interesting, ultimately leading to discovery of a new thermomechanical phenomenon. One on hand, we observed that shape fixing was possible – as expected – through PAH reconfiguration under strain at elevated temperature, followed by cooling. On the other, we found that recovery was only possible as long as a finite internal stress was applied by the Pellethane phase on the PAH phase. This forced the development of a new testing protocol that involved a sequence of “stress growth” steps approximately 20 min in duration. A figure shown below shows example results of this new phenomenon.

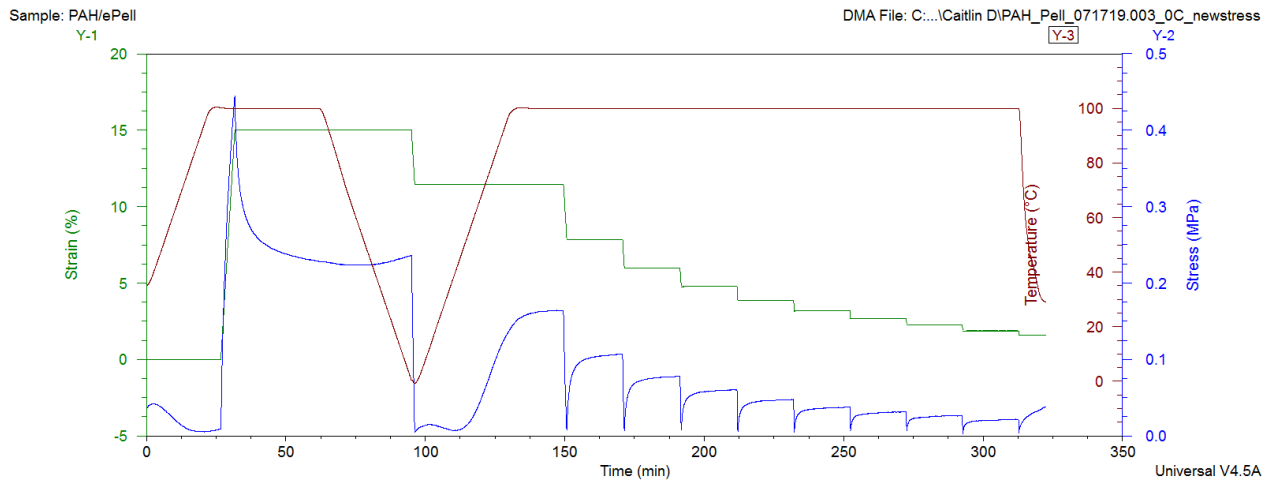


Figure 3. New shape memory showing relatively good shape fixing (small drop in strain as applied stress is removed at 100 min) and good recovery achieved following ten (10) successive steps of stress removal and natural regrowth that occurs during PAH reconfiguration.