# Facile Fabrication of a Shape Memory Polymer by Swelling Cross-Linked Natural Rubber with Stearic Acid

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S *Supporting Information*

ABSTRACT: A facile method was developed for fabrication of a robust shape memory polymer by swelling cross-linked natural rubber with stearic acid. Commercial rubber bands were swollen in molten stearic acid at 75 °C (35 wt % stearic acid loading). When cooled the crystallization of the stearic acid formed a percolated network of crystalline platelets. The microscopic crystals and the cross-linked rubber produce a temporary network and a permanent network, respectively. These two networks allow thermal shape memory cycling with deformation and recovery above the melting point of stearic acid and fixation below that point. Under manual, strain-controlled, tensile deformation the shape memory rubber bands exhibited fixity and recovery of 100% ± 10%.
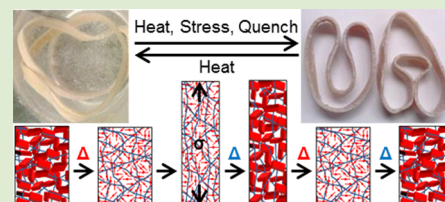
Shape memory polymers (SMPs) are functional materials that are programmed to change their shape in response to an external stimulus, such as temperature, light, or magnetism, with temperature being the most common.[1] Typically a polymer is used that is an elastomer at high temperature, where the entropic forces generated during deformation drive shape recovery.[2] As SMPs are fabricated from a wide array of polymeric materials, they have attracted interest for applications in a diverse range of areas including medicine, aerospace, and textiles.[3]

Commodity polydiene elastomers (i.e., natural rubber (NR), synthetic *cis*-polyisoprene (PI), *cis*-polybutadiene (PB), styrene–butadiene rubber (SBR)) are attractive materials for SMPs. They are inexpensive, have high elasticity, have good mechanical properties, and are readily cross-linked using robust chemistries. This combination of traits has led to their wide use in tires where NR, PB, and SBR are the top three elastomers in terms of consumption.[4,5] However, polydienes have seen minimal use in SMPs compared to other classes of polymers, such as thermoplastic polyurethanes.[6] PI, PB, and SBR are amorphous polymers with a glass transition temperature (T_g) well below room temperature. They are able to act as SMPs near T_g where the deformed elastomer can be fixed by vitrification,[7] but the subambient conditions are not useful for most applications. Tiller and co-workers[8−12] demonstrated that lightly cross-linked natural rubber acts as an SMP where strain-induced crystals act as a temporary network to fix the deformed shape. Depending on the cross-link density, deformation temperature, and the stressed state of the deformed sample, the trigger temperature for shape recovery can be tuned from 0 to 45 °C. Shape memory polydienes can also be generated from specialty polymers, such as *trans*-polyisoprene, *trans*-polybutadiene, or polycyclooctene, that are semicrystalline at room temperature or chemically modified polydienes, such as epoxidized natural rubber.[13−16] Unlike condensation polymers, whose synthesis can be varied through choice of polyol, specialty modifications and synthesis of polydienes are antithetical to the benefit of using commodity elastomers for SMPs.

An alternative to chemical modification and synthesis is blending in a second component that forms a temporary network to fix the deformed elastomer. This has been accomplished by blending an elastomer with a low molecular mass organic compound, namely, a wax or fatty salt, which forms percolating, crystalline, load-bearing networks. In 1971, IBM disclosed a method for preparing heat shrinkable elastomers by swelling rubber tubing with carnauba wax, but no detailed experimental results were provided.[17] Weiss and co-workers showed that the addition of fatty acids or fatty acid salts to ionomers such as sulfonated ethylene propylene diene monomer[18−20] and sulfonated poly(ether ether ketone)[21] made robust SMPs with high fixity and recovery. The fatty acid (salts) formed a crystalline phase that the authors proposed was intimately bonded to the ionomer through ionic or dipolar interactions. The switching temperature of the compound was tuned by varying the crystalline melting point by judicious choice of the fatty acid (salt). A similar approach to produce a SMP was used by Feng and co-workers[22,23] who added paraffin wax to poly(styrene-*b*-(ethylene-*ran*-butene)-*b*-styrene) (SEBS). In that system, the triblock copolymer microstructure served as the permanent network, and the paraffin formed a reversible network within the poly(ethylene-*ran*-butene) mid-block microphase. In that work the materials were solvent cast, which has the drawback of handling organic solvent waste. In the case of the ionomer a polymer modification step was required. A patent application by Xu[24] (PolyOne Corp.) based on thermoplastic elastomers, including SEBS, filled with

paraffin is currently pending. Similarly, Ding and co-workers[25−27] reported making shape memory elastomers from compounds of silicone rubber filled with paraffin that exhibited two-way, dual, and triple shape memory for compressive deformations. However, those compounds exhibited relatively poor shape fixity (<90%), except for high loadings of wax (40 vol %), and low compressive strains (<10%). The origin for this may have been the poor solubility of the paraffin in the silicone. It was reported that an unstable dispersion formed on the cessation of stirring and produced large micrometer-sized aggregates in the silicone as evident by scanning electron microscopy (SEM).

This letter demonstrates the fabrication of a SMP using a generic, sulfur cross-linked, filled rubber band by swelling it in molten stearic acid to generate a shape-fixing, temporary network. Stearic acid is commonly used in combination with zinc oxide at low concentration (1−3 phr) as an activator for sulfur-based curing of polydiene rubbers and is known to crystallize at these concentrations.[28] However, the use of stearic acid to generate SMPs has not been reported. In addition to using NR, the main difference of this work, from previous compounded SMP elastomers, is that the fabrication steps are reversed. Here the NR is already compounded and cross-linked before the stearic acid is added. While the focus in this letter is on a commercial rubber band, as they lend themselves to uniaxial shape memory testing, the scope of the fabrication process is quite broad. This process is applicable to any cured elastomer provided a small crystalline molecule is selected that would swell the elastomer to the extent of forming a percolating network. This fabrication could prove advantageous as it allows the conversion of readily available commercial elastomers, such as sheeting or tubing, into shape memory polymers. In terms of elastomer processing it negates any effects the small molecule additive would have on the shaping and curing of the elastomer and would not require any reformulation of the base polymer compound in the SMP.

Generic rubber bands were purchased at an office supply store for use in fabricating a SMP. The extent of swelling of a rubber by a solvent is ultimately thermodynamically controlled through a balance between the osmotic force and the elastic force. Rubber bands were swollen in stearic acid at 75 °C, which is above its melting point (69 °C). An average swelling of 34 wt % $\pm$ 4% stearic acid was observed (40 vol % and 125 phr equivalent). The effective cross-link density for a filled rubber can be determined using the Flory−Rehner equation[29] (eq 1)

$$-[\ln(1 - v_r) + v_r + \chi v_r^2] = V_s n(v_r^{1/3} - v_r/2) \tag{1}$$

where v_r is the volume fraction of the rubber band in the swollen sample; χ is the Flory−Huggins interaction parameter; V_s is the molar volume of the solvent; and n is the effective cross-link density of the filled rubber.[30] A χ of 0.0003 at 75 °C was calculated based on the Hansen solubility parameters[31] of stearic acid (δ_1 = 17.52 MPa$^{1/2}$) and NR (δ_2 = 17.55 MPa$^{1/2}$) where $\chi = V_s/RT(\delta_1 - \delta_2)^2$. The molar volume of stearic acid was based on it forming a dimer (652 cm^3/mol), which is known to occur for carboxylic acids in nonpolar solvents.[32] Using the swelling data, v_r was calculated as 0.60 $\pm$ 0.03, which leads to an effective cross-link density of 0.91 mmol/cm^3 $\pm$ 0.14. The same experiments, repeated with toluene, gave an average cross-link density of 0.97 mmol/cm^3 $\pm$ 0.10. The similarity between the measurements indicates that the swelling conditions were able to reach equilibrium concentrations of stearic acid in the rubber band.

The composition of the stearic acid swollen rubber band was determined by thermal gravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). FTIR analysis (Figure S1, Supporting Information) identified NR and silica based filler. TGA heating traces from 25 to 900 °C were obtained on the initial rubber band, stearic acid, NR tubing, and the stearic acid swollen rubber band. The rubber band data in Figure 1
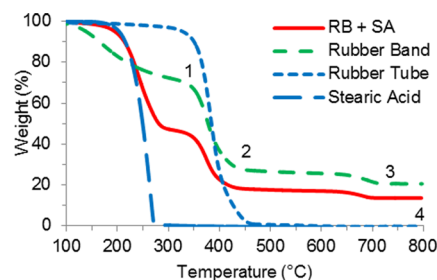

Figure 1. TGA analysis used to calculate the stearic acid loading of the rubber band. The weight loss for the rubber band is (1) 29%, (2) 44%, (3) 7%, and (4) 20% residual. The weight loss for the stearic acid swollen rubber band is (1) 54%, (2) 28%, (3) 4%, and (4) 14% residual.

show three main mass losses, a broad one from 25 to 325 °C, sharper ones from 325 to 475 °C and from 650 to 750 °C, and a residual ash content of 20 wt %. The highest temperature degradation and the ash content are attributed to the silica filler in the rubber band. Comparison with the natural rubber tubing shows that that intermediate mass loss can be assigned to NR. The initial mass loss is attributed to additional organic material in the rubber band. The composition of the original rubber band was determined to be 44 wt % NR, 27 wt % silica, and 29 wt % additional organic material. The stearic acid TGA shows that the material decomposed below 300 °C. Therefore, the initial mass loss in the stearic acid filled rubber band is a combination of both the stearic acid decomposition and the additional organic material in the rubber band. Assuming that the stearic acid does not affect the higher temperature (>300 °C) decomposition of the natural rubber and inorganic filler, the composition of the swollen rubber band was estimated to be 28 wt % NR, 18 wt % inorganic filler, 19 wt % additional organic material, and 35 wt % stearic acid. This loading level of stearic acid is consistent with the gravimetric swelling experiments.

The shape memory properties of the stearic acid swollen rubber band were characterized under uniaxial tension using a modified crescent wrench, shown schematically in Figure 2. This experimental setup allowed for rapid heating and cooling of the sample by immersion into different temperature water baths and consistent strain control. For the shape memory testing the clamped rubber band was immersed in a 75 °C water bath, stretched, and then immersed in a 10 °C water bath. Shape recovery was initiated by immersing the unclamped rubber band in the 75 °C water bath.

The shape memory behavior was assessed by calculating the shape fixity (F) and shape recovery (R) efficiencies using eqs 2 and 3

$$F = \varepsilon_f/\varepsilon_s \times 100\% \tag{2}$$

$$R = (\varepsilon_f - \varepsilon_r)/(\varepsilon_f - \varepsilon_i) \times 100\% \tag{3}$$

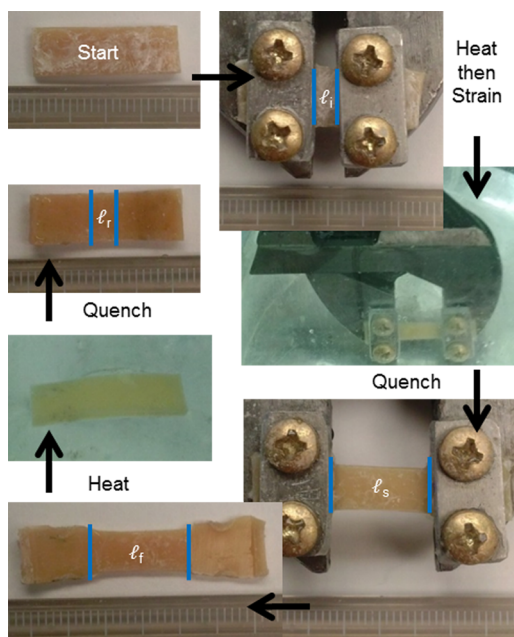**Figure 2.** Shape memory cycle rapidly tested with modified wrench.

Figure 3. DMA shape memory cycle with preconditioning from 0 to 25 min. Fixity is 99% and recovery is 88%.

where $\varepsilon_k = (l_k - l_i)/l_i$ and l_i, l_s, l_f, and l_r correspond to gauge lengths of the initial sample, stretched sample, fixed sample, and recovered sample, respectively.[1] The rubber band exhibited excellent shape memory properties during this test. The fixity was 100% for the eight samples tested. The recovery was 99% ± 7%. However, the measurement resolution was 0.5 mm which results in an error propagation of ±10%. Multiple shape memory cycles were also performed and showed excellent reproducibility of 100% fixity and 95% recovery over five consecutive cycles.

The shape memory properties were also measured in tension with stress-controlled conditions using dynamic mechanical analysis (DMA) over one shape memory cycle. An initial heating/cooling cycle was conducted before the main shape memory cycle to minimize the underlying creep of the elastomer during testing, at elevated temperature. We attribute this creep primarily to a constant force applied by the lower clamp in the DMA. We have found that it is difficult to perfectly calibrate the clamp weight to zero the load on an unstrained sample. This produces a non-negligible downward force on a low modulus sample resulting in creep even at "zero" preload force and no applied stress. As shown in Figure S2 (Supporting Information), a creep of 24% occurs when holding the sample at 75 °C for 17 min. Therefore, preheating the sample allows this creep to reach a plateau region giving a more accurate measure of shape memory properties. The shape memory cycle consisted of heating to 75 °C and applying a stress of 0.1 MPa, resulting in a strain of 66%, cooling to 20 °C to fix the shape and remove the applied load, and reheating the sample to 75 °C to monitor the shape recovery. On the basis of the DMA data, shown in Figure 3, a shape fixity of 99% and a shape recovery of 88% were obtained. While the fixity was similar to that in the strain-controlled test, the recovery is lower. This is attributed to the constant tensile force applied by the failure to zero the clamp weight, which results in additional creep of the sample during shape recovery and also resists the recovery that is driven by the entropic restoring force of the cross-linked NR network.
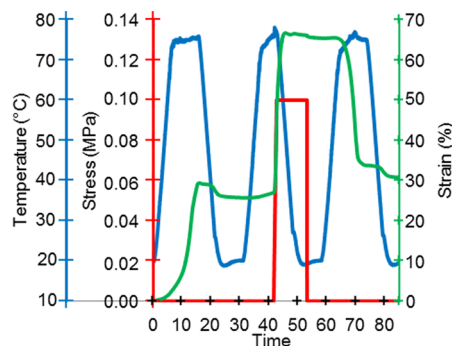
Stearic acid is known to form bilayers which grow as crystal platelets. Fatty acids are known to gel vegetable oils,[33] and analogous platelet crystals formed by alkanes and paraffin waxes are known to gel organic fluids through the formation of a three-dimensional load-bearing network (i.e., "house of card" type structure).[34,35] To verify this morphology, a film of synthetic polyisoprene, cross-linked with dicumyl peroxide, was cast on a glass slide and swollen with stearic acid. Figure 4
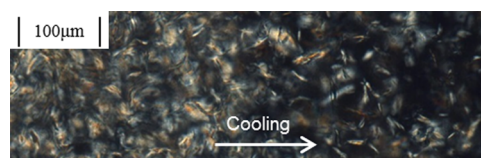

Figure 4. Birefringent crystals of stearic acid form interconnected platelet structures in polyisoprene.

shows an optical micrograph through cross-polarizers of a film with 50 wt % stearic acid near the crystallization front during cooling. Birefringent stearic acid crystals are observed to form a continuous network, and the platelet formation can be seen on the crystallization front.

The main drivers of the shape memory are the melting/crystallization of the stearic acid network and the entropic recovery force of the cross-linked NR. Other components in the rubber band, such as silica based filler, that influence the mechanical properties, were not believed to be integral to the shape memory behavior. That conclusion was supported by the shape memory behavior of NR surgical tubing swollen with stearic acid. While NR surgical tubing is compounded with a cross-linker, activator, and accelerator, it is typically purified and unfilled to meet biomedical regulations. Evidence of that can be observed in Figure 1, where the TGA trace of the NR tubing shows a single decay due to the natural rubber degradation. The tubing was too thick to be mounted in the DMA, but strain-controlled shape memory testing with the modified wrench showed 100% fixity and 95% recovery. The good fixity and recovery of the sample demonstrate that NR and stearic acid are the prime components driving the shape memory behavior.

■ EXPERIMENTAL SECTION

Materials obtained were rubber bands (Office Max Economy 3 1/2″ × 1/4″), stearic acid (Acros 97%), rubber tubing (Fisher Scientific 14−178A), synthetic PI (Goodyear Natsyn 2200), and dicumyl peroxide (Acros 99%).

The swelling of the rubber band was tested by immersing ten 1.0 cm × 0.6 cm × 0.1 cm strips in a beaker of molten stearic acid at 75 °C

for 1 h followed by quenching in a beaker of ca. 10 °C water. The raw data are presented in Tables S1−S3 (Supporting Information).

TGA was conducted using a TA Instruments Q50. Samples were heated at 10 °C/min to 900 °C under N_2. The average sample size was 0.01 cm^3. Fourier transform infrared spectroscopy was conducted using a Nicolet 4700 TGS Detector, with 4 cm^{-1} scan resolution. ATR Fixture: SensIR Technologies, DuraScope, diamond crystal, single bounce. Reference FTIR spectra were obtained from the HR Industrial Coating Library.

A 10 in. Dewalt crescent wrench was tapped with adjustable clamps for securing a 3 cm × 0.8 cm × 0.2 cm strip of the swollen rubber band. For the shape memory testing the clamped rubber band was immersed in a 75 °C water bath for 15 s, stretched to 100% strain, and then immersed in an ca. 10 °C water bath for 15 s. Shape recovery was initiated by immersing the unclamped rubber band in the 75 °C water bath for 15 s. This combination of temperatures and immersion times allowed for complete melting or crystallization of the stearic acid for the chosen sample size. Gauge length was marked on the sample with a pen and measured with calipers.

DMA was conducted using a TA Instruments Q800. The samples were 0.8 cm × 0.2 cm with a gauge length of 0.5 cm. All temperature ramps were 10 °C/min. The preheat cycle was: ramp to 75 °C, isothermal for 10 min, ramp to 20 °C, and isothermal for 10 min. The shape fixing was: ramp to 75 °C, isothermal for 5 min, ramp stress at 0.10 MPa/min to 0.10 MPa, ramp to 20 °C, isothermal for 5 min, step stress to 0.00 MPa, and isothermal for 5 min. The shape recovery was: ramp to 75 °C, isothermal for 10 min, ramp to 20 °C, and isothermal for 10 min.

PI and dicumyl peroxide were dissolved in chloroform to target 0.3 mmol/cm^3 cross-link density. The mixture was evaporated in a glass crystallization dish and heated under vacuum to 150 °C for 6 h to cross-link the film. A piece of the film was transferred to a glass slide, and molten stearic acid was pipetted on top by weight to 50 wt % and allowed to diffuse in. The crystallization pattern of the stearic acid in the film was observed under dark field, through crossed polarizers, with an Olympus BX51 optical microscope, with 10× + 10× magnification. An INSTEC HCS302 hot stage was used to heat (75 °C) and cool (10 °C) the sample.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Data for cross-link density measurements and strain-controlled shape memory tests. FTIR spectra. DMA thermal equilibrium. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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