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Solvent-Sensitive Reversible Stress-Response of Shape Memory Natural Rubber

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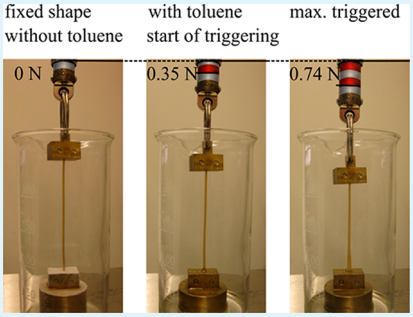
Supporting Information

ABSTRACT: We found that constrained shape memory natural rubber (SMNR) generates mechanical stress when exposed to solvent vapor. When the solvent vapor is removed, the material reprograms itself. This process is reversible and the stress answer is proportional to the solvent vapor concentration. Further, the stress answer is specific to the solvent.



KEYWORDS: *responsive materials, shape memory, natural rubber, polymer network, solvent detection*

INTRODUCTION

Shape memory polymers (SMPs) can memorize a programmed (temporary) shape and recover their original (permanent) shape in the presence of external stimuli. The most typical stimulus is heat.[1−5] Other examples are the exposure to UV light,[6,7] to alternating magnetic fields,[8] or to liquids.[7,9−11] Recently we presented the shape memory effect of lightly cross-linked natural rubber, referred to as Shape Memory Natural Rubber (SMNR).[12] This astounding material distinguishes itself from other SMPs by extremely large storable strains, energy,[13] and cold storage[12] caused by heat uptake during the retraction process, a physically tunable trigger temperature during as well as after programming, and the potential of mechanical[14,15] and solvent triggering.[12]

We recently noticed that the contact of programmed SMNR with solvent vapor e.g. by holding it over an open toluene bottle causes immediate triggering and results in complete shape recovery. This effect was also found for other solvents such as chloroform, n-heptane and tetrahydrofuran (THF). Since all tested solvents caused complete recovery in this unconstrained experiment, any qualitative and quantitative information on the trigger capability of these different solvent vapors is lost (see trigger process in Figure 1a).

To gain this lost information on the solvent vapor trigger capability of SMNR, we applied a rarely used technique where the ends of the programmed samples were fixed while they are exposed to a trigger. So far this technique was only used to gain the maximal stress answer of programmed SMPs upon thermal triggering or immersion in liquids.[5,7,16−18] We hypothesize that the stress answer contains quantitative information on the interactions between SMNR and solvent vapors. As seen in the illustrating experiment in Figure 1b a programmed SMNR mounted between a fixed clamp and a spring scale and exposed to toluene vapor is quickly building up mechanical stress.

To exclusively allow measuring a stress answer without dimension change along the axis of elongation, all samples were stress-free fixed between two clamps, one of them connected to a piezo force transducer. For these experiments we chose a SMNR with a degree of cross-linking (fraction of cross-linked monomeric units) of 0.2%. All samples were identically programmed showing a fixed strain of 900% and a trigger-temperature of 33 ± 0.5 °C. The whole setup was placed in a custom-made tensile creep apparatus[19] that allows measuring and adjusting the solvent vapor pressure, temperature, and stress. Prior to the solvent vapor exposure the chamber was evacuated to a pressure below 10 Pa.

In an initial experiment the toluene vapor pressure was adjusted to about 80% (∼2500 Pa) of its equilibrium vapor pressure p^{LV}. During this experiment the temperature was kept constant at 20 °C. When applying toluene vapor the piezo force transducer immediately measures that the polymer tries to pull the clamps together. This is in contrast to the behavior of any nonprogrammed stress-free clamped polymers where the solvent vapor would cause just swelling and thus pressing the clamps apart. The only explanation for this behavior is that the solvent vapor triggers the SMNR, which then tries to recover its original shape. Obviously the latter effect is much larger than possible swelling effects.

The constrained SMNR sample responded with a force of about 1.7 N within 15 min. This is the first example of a SMP

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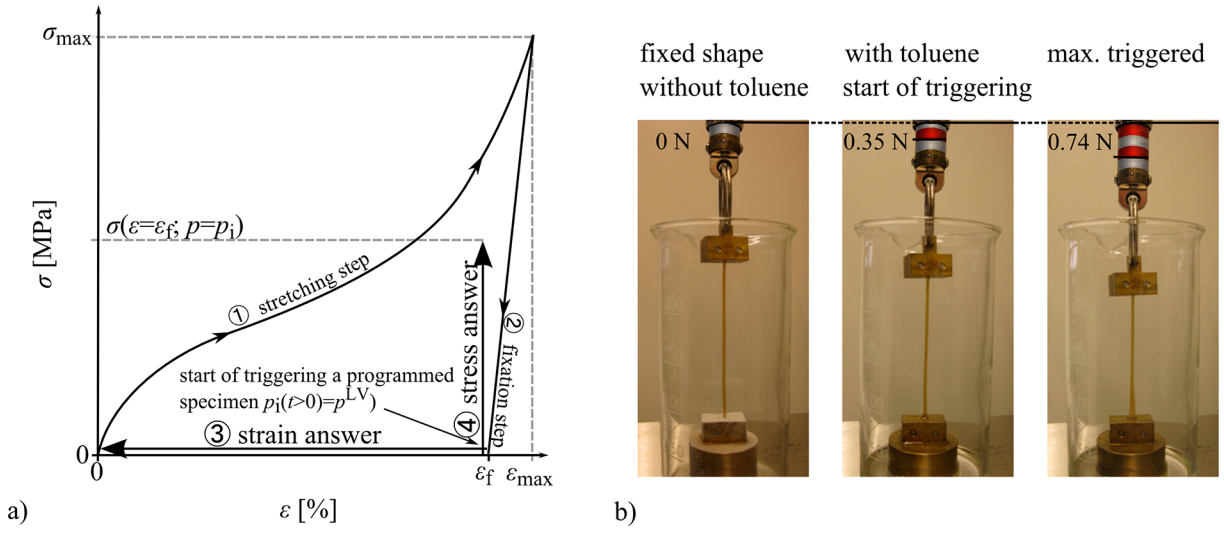

Figure 1. (a) Stress−strain plot of the programming process of SMNR, elucidating the stretching step (1) and the fixation step (2). Triggering a SMNR sample under unconstrained conditions results in a strain answer (3), whereas triggering under constrained conditions results in a stress answer (4).[7] (b) Photographs of an experiment that illustrates the stress built-up by exposure to toluene vapor. Here, the programmed SMNR was mounted between a fixed clamp at the bottom and a spring scale to determine the pulling force.

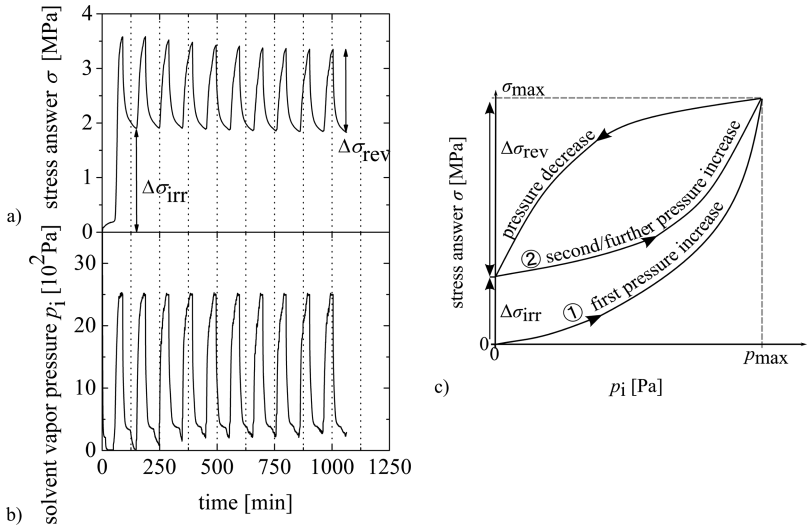

Figure 2. Temporal progress of (a) stress-answer σ of constrained SMNR with (b) changing vapor pressure p_i plotted. (c) Schematic illustration of the irreversible and reversible stress answer caused by the solvent vapor pressure during the first ($\Delta\sigma_{irr}$) and all following cycles ($\Delta\sigma_{rev}$).

triggered by solvent vapor. In order to see if the sample was fully triggered the toluene vapor was evacuated, the apparatus was then brought to atmospheric pressure and the sample was unclamped. Surprisingly, the SMNR did not recover its original shape, but still stabilized 800% strain. Obviously the sample was not fully triggered. To find out whether this phenomenon is due to a partial triggering or to triggering and reprogramming after solvent removal, we performed a cyclic experiment where the toluene vapor pressure is added and removed in constant time intervals while continuously measuring the stress. As seen in Figure 2 when increasing toluene vapor pressure p_i to 2500 Pa in the first cycle, the sample stress increases to 3.6 MPa. After 15 min, the toluene vapor was evacuated below 300 Pa. Unexpectedly, the sample-stress decreases significantly to a value of 1.8 MPa after 15 min. The only explanation of this phenomenon is a reprogramming of the SMNR sample. This would be the first example of a two way stress-response of a SMP. The repeating of the toluene vapor pressure cycle for several times shows full reproducibility of this effect (shown in Figure 2a). Comparison of panels a and b in Figure 2 shows that the stress-answer directly follows the vapor pressure increase. It is worth noting that the stress-answer does not return to its initial value after evacuation. This is even true after 24 h when the stress was still as high as 1.7 MPa (experiment not shown). Thus, the solvent-sensitive stress answer of SMNR on toluene vapor is composed of an irreversible stress-answer $\Delta\sigma_{irr}$ that remains after the first cycle and a reversible stress-answer $\Delta\sigma_{rev}$, as depicted schematically in Figure 2c.

Besides toluene, vapors of further "good" solvents for natural rubber such as chloroform, n-heptane and THF as well as acetone as example for a "poor" solvent were brought in contact with constrained SMNR using the above-described procedure for up to 5 cycles. The solvent vapor dependent stress response found for n-heptane, chloroform and THF was similar to that of toluene (see the Supporting Information). In order to compare the individual trigger potential of these

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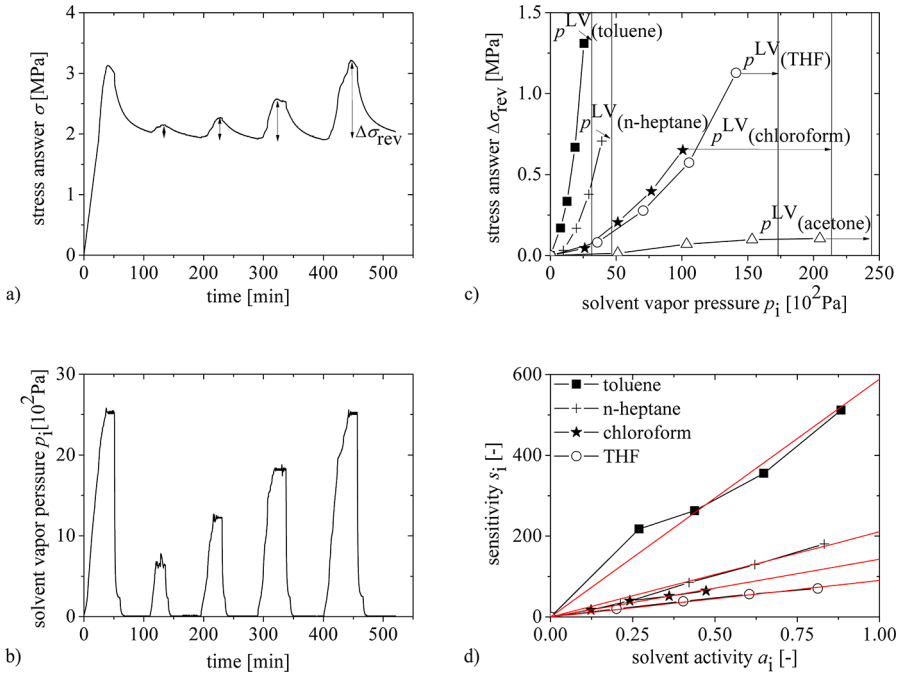

Figure 3. (a) Solvent-sensitive stress answer σ of constrained SMNR to toluene vapor pressure p_i, alternating between (b) 0.5 and 8, 13, 19, 25 × 10^2 Pa, respectively. (c) Plot of reversible stress answers σ_{rev} to absolute solvent vapor pressures p_i of toluene, n-heptane, THF, chloroform, and acetone (arrows indicate equilibrium vapor pressures p^{LV}). (d) Plot of calculated sensitivity $s_i = \Delta\sigma_{rev}/\Delta p_i$ against solvent activity a_i.

solvents, we carried out experiments with varying vapor pressure peaks (exemplarily shown for toluene in Figure 3a, b).

As seen in panels a and b in Figure 3, the reversible stress answer $\Delta\sigma_{rev}$ is highly sensitive to the applied vapor pressure p_i of toluene. The same is true for all other investigated solvents with the exception of acetone (shown in Figures 4–6 in the Supporting Information). To compare the solvent specific sensitivities, we plotted $\Delta\sigma_{rev}$ versus p_i (Figure 3c). As seen in this figure, the reversible stress answer to solvent vapor seems to follow a parabolic-like progression with the exception of acetone. The equilibrium vapor pressure p^{LV} of each solvent, indicated by a vertical line, is the theoretically applicable maximum solvent vapor pressure. The solvent sensitivities of constrained SMNR are defined as $s_i(p_i) = \Delta\sigma_{rev}/\Delta p_i$ with the solvent activity of $a_i = p_i/p^{LV}$. Acetone as a poor solvent was not further considered. As shown in Figure 3d, the sensitivity $s_i(p_i)$ of the probed solvents increases linearly with rising solvent activity a_i. In order to quantify the individual stress generating potential of the solvents, we calculated the maximal sensitivities $s_i(p_i = p^{LV})$ by extrapolation of these linear trends to the respective equilibrium vapor pressures p^{LV} ($a_i = 1$). The maximally theoretically achievable reversible stress-answer $\Delta\sigma_{rev,max}$ to solvent vapor is defined by $\Delta\sigma_{rev,max} = s(a_i = 1)\ p^{LV}$. Although the highest solvent sensitivity was found for toluene, the highest possible stress-answer would be $\Delta\sigma_{rev,\ max} \approx 3$ MPa for chloroform. Unfortunately, application of chloroform vapor above 1 × 10^4 Pa, which is about half of p^{LV}, resulted in rupture of the sample. The highest measured reversible stress-answer was found for toluene vapor.

It is worth noting that the sensitivities are approximately in the same order as the solubility parameters according to Hildebrand and Hansen.[20,21]

CONCLUSION

In closing, constrained SMNR is the first example showing a reversible solvent specific mechanical stress increase. We believe that this concept is generic for SMPs. Because these materials are known in great variety, their responsiveness might be adaptable to many different chemical vapors or liquids. Thus the concept of constrained programmed SMPs might open versatile numerous applications for this class of materials.

EXPERIMENTAL SECTION

Synthesis. Natural Rubber (Standard Malaysian Rubber − SMR10) with an initial molecular weight of about 3 000 000 g/mol was masticated for 10 min using a heatable double-roller operated at 80 °C, subsequently mixed with dicumylperoxide (DCP) for further 5 min and cross-linked in a heating press at 160 °C for 35 min. Using 0.2 parts per hundred rubber DCP resulted in a M_c of 34 000 g/mol (0.2% degree of cross-linking), measured according to the Mooney-Rivlin theory.[22] The stretching of the specimen was done at 60 °C to a strain of 950% with a fixed strain of 900%.

Analysis. The trigger measurements under constrained conditions initiated through solvents were arranged in an air thermostatted chamber and two film-tension clamps which fasten the programmed specimen of SMNR. One clamp is connected to a force transducer with a range of measuring of up to 20 N and a reproducibility of ±0.003 N.[19] During setting different solvent vapor pressures the stress answer is in its stationary state after a soaking time of 15 min.

All used solvents were of analytical grade or purer and were obtained from Sigma Aldrich.

■ ASSOCIATED CONTENT

Supporting Information

Measuring data of stress response of SMNR to n-heptane, chloroform, and THF. 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.

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