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FAST RETURN AND FULL ELASTIC RECOVERY IN SELF-HEALING ELASTOMERS FOR SOFT ROBOTIC ACTUATION

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Abstract. Soft robotics is an emergent branch of robotics, which involves incorporation of elastomeric elements. Addition of soft materials into robotic devices allows better flexibility and adaptability to the environment than when robots are made of hard and rigid components. However, the soft materials are more prone to damage than their rigid counterparts. Incorporation of self-healing materials into soft robots may permit to fix damages. Equipped with a sensor, the robot could also be able to detect the damage to initiate the repairing process autonomously.
In this work, fibre strain sensors were integrated into self-healing elastomers. It is shown that the stiffness of the soft matrix and the sensor fibre should be close enough to avoid a premature rupture of the fibre due to shear stress at the matrix-fibre interface. Elastomeric matrices based on epoxidized natural rubber (ENR) capable of healing after damage were produced. For damage and deformation detection, the elastomer was filled with conductive carbon black to produce piezo-resistive strain sensors. Laser-cut sensor fibres were implemented into a compression sensor. The resulting actuator exhibited fast elastic return and recovery of mechanical and electrical properties after cut and self-healing.

Key words: Self-Healing Elastomers, Epoxidized Natural Rubber, Fibre Strain Sensor, Stiffness Mismatch, Soft Robotics

1 INTRODUCTION

Soft robotics involves incorporation of elastomeric elements into robotic devices. To protect the soft materials from irreversible damage, incorporation of self-healing (SH) materials is desirable. In addition, the robot should be able to detect the damage to repairing itself autonomously [1].
In this work, fibre strain sensors were integrated into self-healing elastomers. It is shown that the stiffness of the soft matrix and the sensor fibre should be close enough to avoid a premature rupture of the fibre due to shear stress at the matrix-fibre interface. Moreover, mechanical actuation should be fast enough to permit large development of automatic processes. A drawback of common self-healing rubbery materials is the slowness of the material answer at room temperature, when healing is strongly associated to dissipation processes around the glass

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transition temperature of the elastomer. Natural rubber materials are promising candidates to overcome this problem, as their glass transition temperature lays far below room temperature. Elastomeric matrices based on epoxidized natural rubber (ENR) capable of healing after damage were produced here, and filled with conductive carbon black to produce piezo-resistive strain sensors for damage and deformation detection. Laser-cut sensor fibres were implemented into compression sensor exhibiting fast elastic return.

2 METHODS, RESULTS AND DISCUSSION

2.1 Stiffness matching in epoxy-vitrimers containing strain sensor fibre

Strain sensors consisting of an elastomeric material containing conductive fillers were introduced between autonomously self-healing H-bonding epoxy-acid matrices by sandwich welding at moderate temperature (Figure 1).

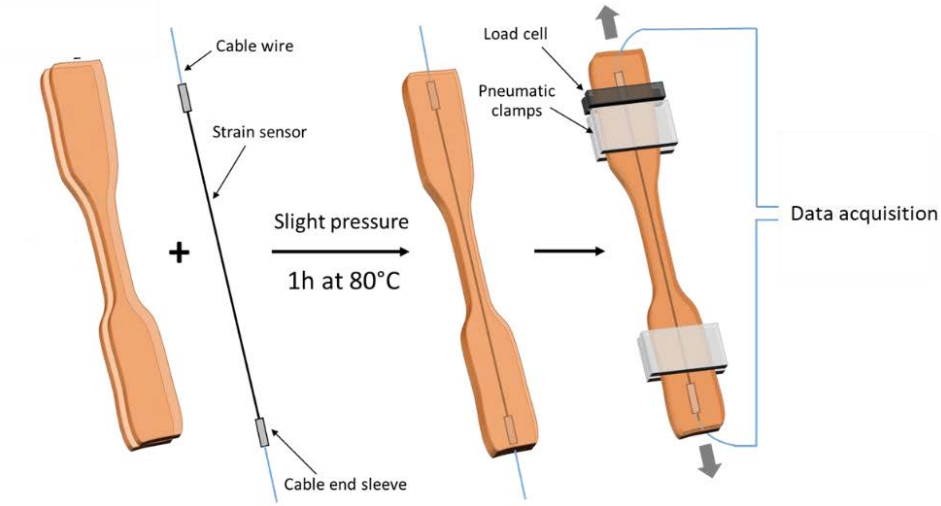

Figure 1: Fibre strain sensors were integrated into self-healing elastomers to measure sample deformation (after [2]).

The sensorized matrices were tested under cyclic tensile experiments (0–20% strain), measuring simultaneously the tensile stress and the electrical resistance of the sensor fibre. The experiments were conducted at 50°C, far enough from the T_g around 12–16°C, as the speed of elastic return is highly influenced by the distance from T_g. Stiffer samples containing 10 mol% epoxy excess (called C_10epoxy) were also synthesized for comparison with the stoichiometric sample called C_0epoxy. Figure 2 displays 20 cycles of tensile stress and relative resistance, which is the ratio of the change in resistance (R-R_0) divided by the resistance at rest (R_0):

$$\textit{Relative Resistance} = \frac{R - R_0}{R_0}$$

At room temperature (not shown), all samples show buckling during cyclic tensile loading due to the vicinity of glass transition, but the sensor fibres withstand the deformation without break.

Around room temperature, stiffness of matrix and fibre are very close. At 50°C, the matrix gets softer whereas the stiffness of the strain sensor remains constant. During cyclic testing at 50°C, the sensor fibre breaks in the matrix after three tensile cycles, as shown by the dashed line of the relative resistance increasing abruptly in Figure 2A. Conversely, the sensor fibre in the stiffer sample C_10epoxy (Figure 2B) shows a linear response with only a small drift along all 20 tensile cycles, with no rupture of the sensor fibre inside the matrix.

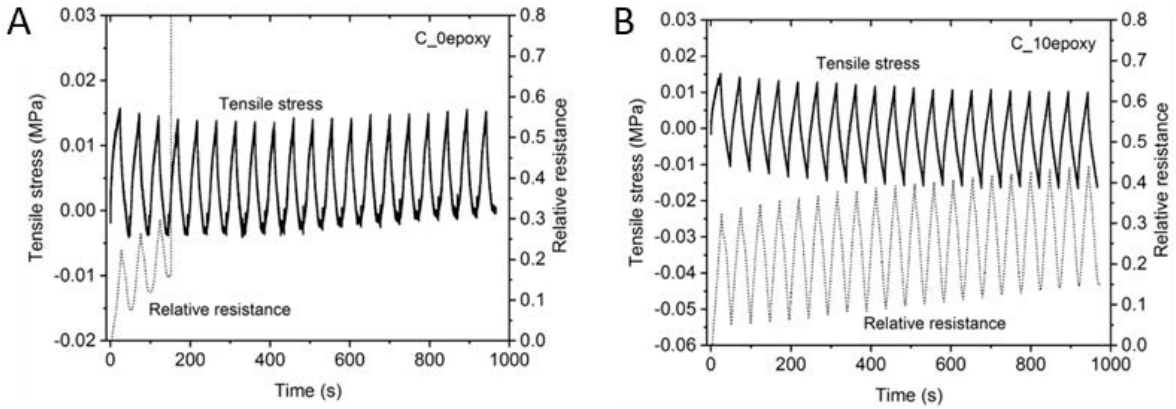

Figure 2: Cyclic tests at 50°C (20 cycles at 0-20% strain) at a deformation rate of 50%.min^{-1}. Solid lines: stress values; dashed lines: relative resistance for A) stoichiometric sample C_0epoxy; B) stiffer sample C_10epoxy.

The conductive filler reinforces strongly the strain sensor which is relatively stiff for an elastomer, which results in a stiffness mismatch between the elastic matrix and the integrated sensor fibre. The mismatch induces shear stresses at the fibre-matrix interface which may lead to the rupture of the sensor fibre inside the matrix. The sensor rupture appears in the shoulder region of the dog-bone samples, as shown by image taken in unpolarized light (Figure 3A,3B). Observations under polarized light show areas of strong shear stress especially in varying cross-section regions, leading to fibre rupture (Figure 3C,3D). Model strength calculations within areas of strong changing cross-section show that small stiffness changes can significantly decrease the shear stress to prevent a fibre rupture [2].

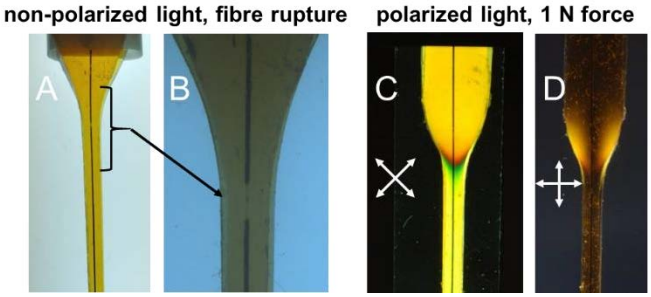

Figure 3: A) Image of stretched sample showing spots of fracture of the sensor fibre; B) Zoom-in on the point of rupture in shoulder region observed with a binocular magnifier; C, D) A sample bearing with 1 N weight observed in polarized light between crossed polarizers oriented at 45° or parallel to the stretching direction, showing areas of high stress concentration due to extensive deformation.

2.2 Fast return and self-healing in crosslinked ENR

A better match between fibre and matrix, and then an enhanced adhesion, should be obtained using same materials for both components. Besides, fast elastic response is expected from elastomer having low T_g, as typically natural rubber derivatives.
Indeed, in the vicinity of glass transition, viscous dissipations are important and samples recover their dimensions quite slowly [3]. Such dissipation effects are apparent in the shape of the tan δ curve (DMA). Figure 4 compares broad tan δ curves of various H-bonding epoxy-acid matrices exhibiting self-healing behaviour at room temperature [2] and curves of rubbery matrices based on epoxidized natural rubber, showing low T_g and strong elastomeric properties at room temperature.

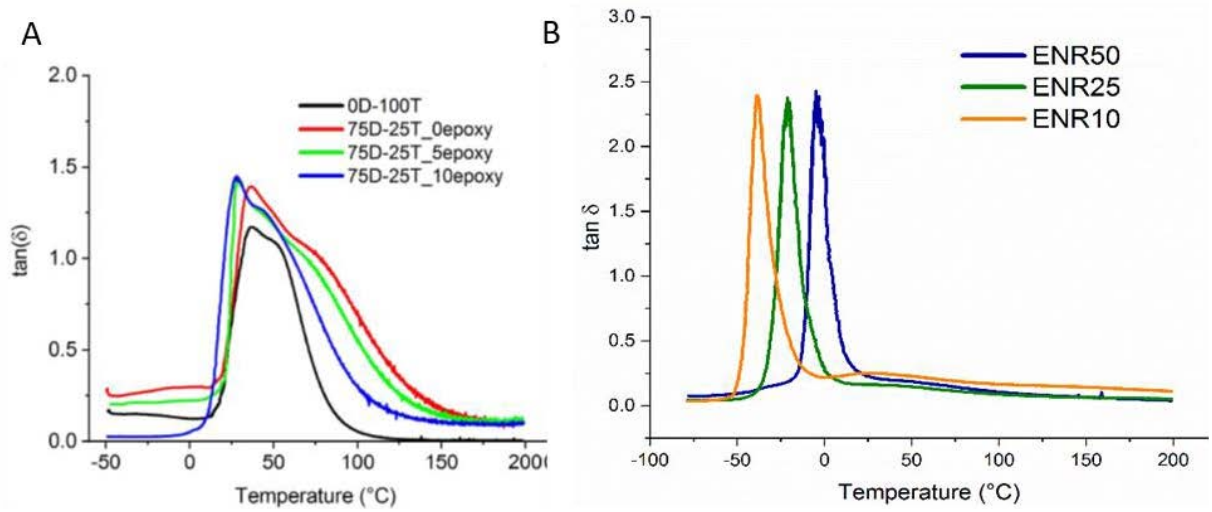

Figure 4: Dissipation factor tan δ measured in film-tension geometry (DMA) for A) various H-bonding epoxy-acid matrices [2]; B) ENR matrices containing 50, 25, 10% epoxy content.

We previously showed that epoxidized natural rubber (ENR) could be efficiently cross linked using dicarboxylic acids DA, reacting with the epoxy functions of ENR (Figure 5)[4]. By varying the nature of the main chain of DA, reprocessable materials were obtained, for instance using dithiodibutyric acid (DTDB) as a crosslinker (Figure 6A)[5]. In this work, we demonstrate that a self-healing ENR10 crosslinked with H-bonding DA derivatives exhibits fast elastic response, using dynamic tensile tests done in a Bose machine at a frequency of 5 Hz with a strain amplitude of 6-30% (Figure 6B). The drift of the signal might be related to the presence of defects (dangling chains, sol molecules), introduced together with the H-bonding moieties which promote SH [2].

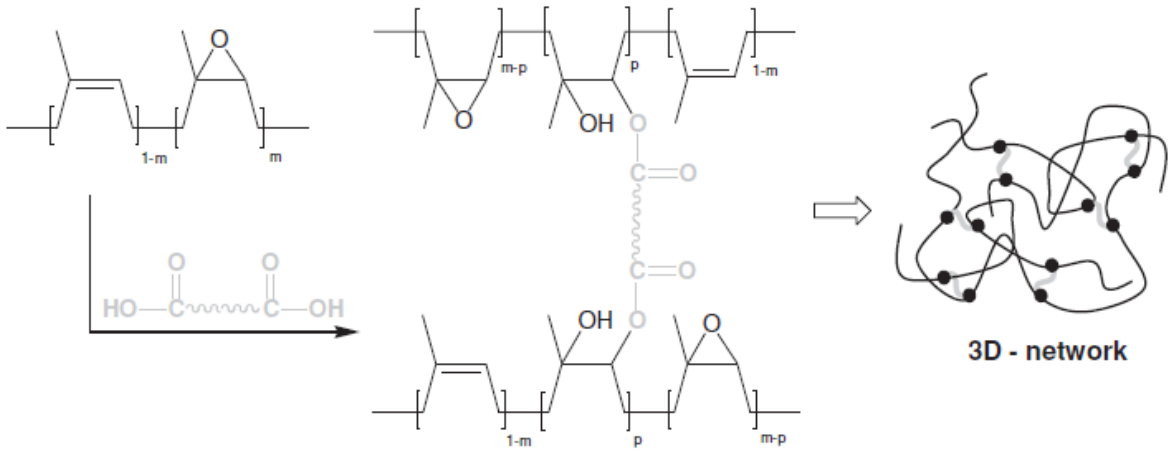

Figure 5: Crosslinking of ENR using dicarboxylic acids DA (after [4]). Main chain of DA may vary (ex: DTDB contains reversible disulphide bonds).

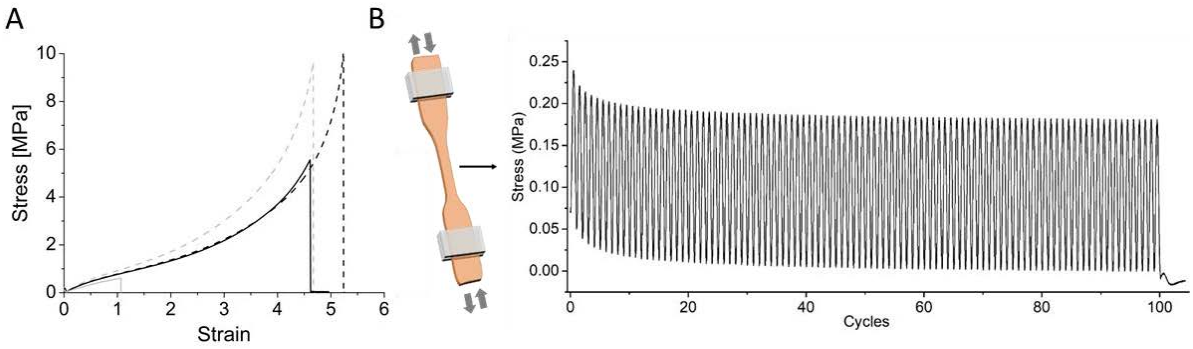

Figure 6: A) Recycling experiments with SH ENR: Tensile test before and after the recycling experiment (black: ENR25-DTDB; grey: ENR25-DA; dashed: before curing; line: after curing) (after [5]); B) Fast return within SH ENR10: 100 tensile cycles at 5 Hz frequency after 1 min of self-healing at room temperature.

2.3 Implementation in smart devices

Experiments were conducted to prospect an application of cross linked ENR10 containing conductive particles as a pressure sensor. Multi-lined shape was laser cut from a cross linked sheet and connected to wires. The sensor, put on the top of a human hand, reveals fast answer under cyclic pressure of a finger (Figure 7).

As for applications in robotic devices, assemblies of sensorized self-healing pneumatic finger are currently under investigation to perform fast cyclic movements. The actuator is composed of a self-healing material based on ENR. Strain sensor fibres integrating carbon black particles for conductivity are glued to an ENR finger-like sample to build a piezo-resistive sensor fibre

actuator. As fibre and finger consist of the same self-healing ENR material, both adhesion and fast elastic response are insured.

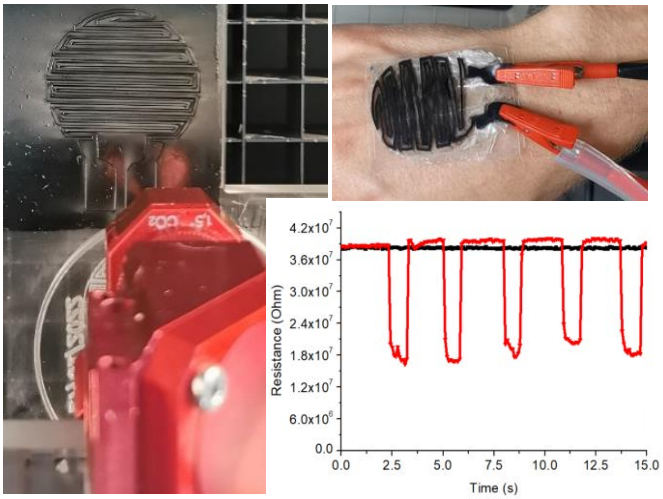

Figure 7: Multi-lined compression strain sensor laser-cut from ENR sheet embedding carbon black particles used as a pressure sensor.

3 CONCLUSIONS AND OUTLOOK

When integrating fibre strain sensors into soft elastomers, stiffness of sensor fibre and matrix should be close enough to avoid a rupture of the fibre due to shear stress at the matrix-fibre interface. Moreover, when based on epoxidized natural rubber, fiber and matrix capable of healing after damage were produced, exhibiting fast elastic return and recovery of mechanical and electrical properties after cut and self-healing. Assemblies of sensorized self-healing pneumatic finger are currently under implementation for applications in soft robotic devices.

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