Electronic Supplementary Information:

Chemically crosslinked yet reprocessable epoxidized natural rubber via thermo-activated disulfide rearrangements

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1- Reprocessing experiment

A piece of crosslinked rubber was reduced to a fine powder using a Fritsch Pulverisette 14. Liquid nitrogen was used to process below the T_g of the sample and facilitate the grinding. The obtained powder was then heated at 180 °C for 40 minutes in a Carver press. The same experiment was conducted on DTDB- and DA-cured ENR. The comparison of the two resulting materials is shown on Figure S1a. On this photo, it is clear that the samples behave very differently. The integrity of the sample is fully recovered in the case of the disulfide containing network (on the left) whereas for the test material (DA-cured ENR), the powder is only partially agglomerated. In the case of DA-cured material, the agglomeration can be due to the effect of compression and to a limited inter-diffusion of the crosslinked polymer chains but no chemical exchange reaction is happening. In the case of DTDB-cured ENR, the powder is completely transformed back to one piece of material. This effect is thought to be due to disulfide rearrangements happening at high temperatures.

Three specimens could still be cut from the DA-cured reprocessed material to test the tensile properties. Photos of the samples before and after reprocessing are given on Figure S1b and c.

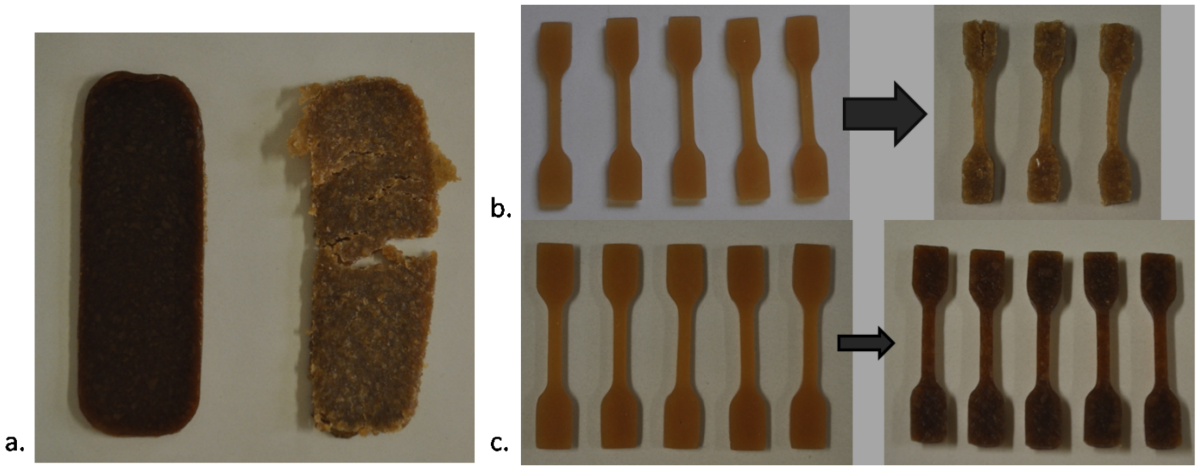

Figure S1. Reprocessing of a grinded sample: **a.** Materials obtained after the reprocessing procedure (left: DTDB-cured ENR, right: DA-cured ENR) **b.** DA-cured rubber before and after reprocessing, **c.** DTDB-cured rubber before and after reprocessing

2- Tensile test: reproducibility

Strain−stress behavior was studied using an Instron machine with a crosshead speed of 500 mm.min^{-1}, until break. Dumbbells of 10 mm effective length and 2 mm width were cut in a 1.6 mm-thick cured rubber sheet (about 2 mm for reprocessed samples) (Figure S1b and c). At least five samples were tested for each material (except for the DA-cured reprocessed ENR from which only three samples could be punched but they show a very good reproducibility). Strain was followed using a video extensometer.

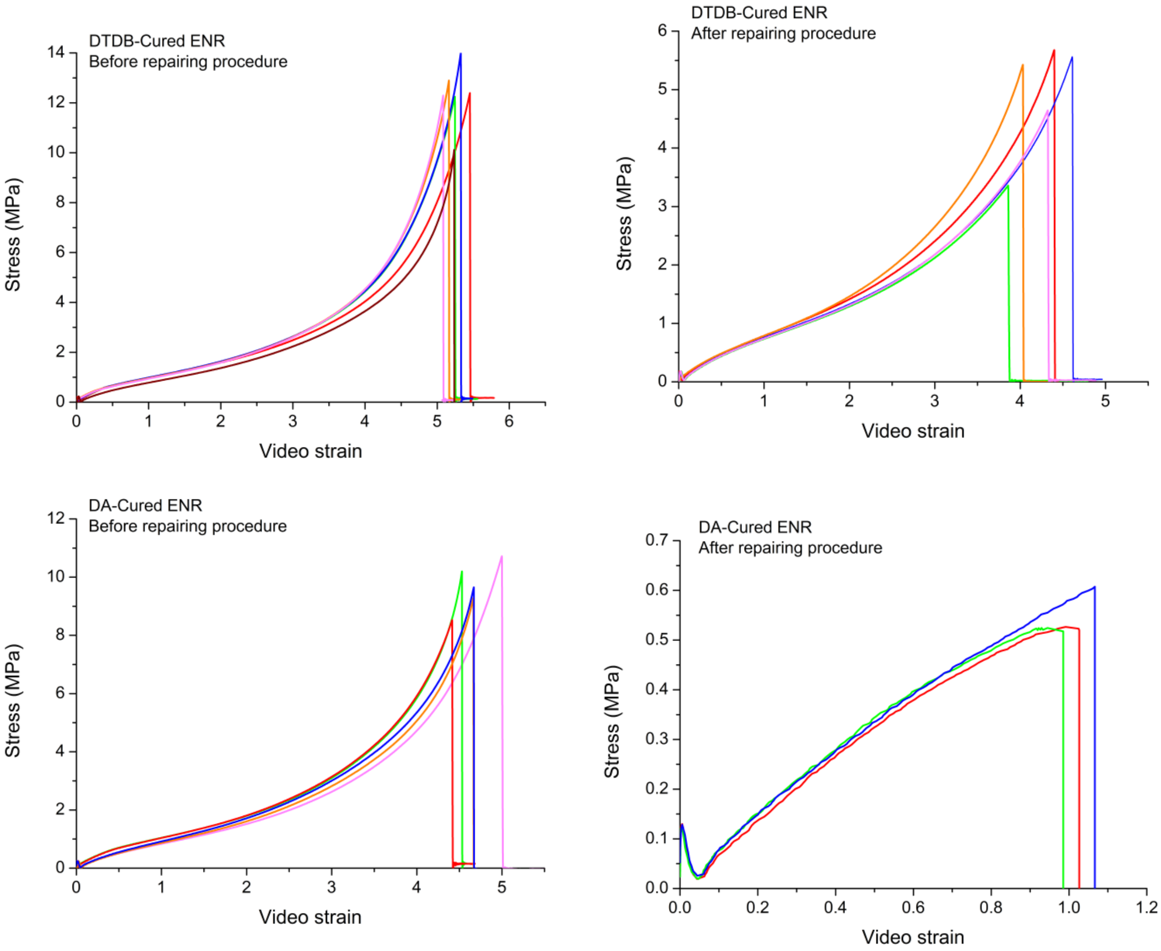

Figure S2. Stress-strain profiles of the specimen before and after reprocessing (up: DTDB-cured material, down: DA-cured)

On these curve, we can see the good reproducibility of the experiment. To calculate the ultimate tensile properties we took an average number of stress and strain at break on all tested specimens.

3- Swelling experiment

Toluene was used as a good solvent of ENR for swelling experiments. Swelling behavior of DTDB-cured material was studied before and after reprocessing. A piece of each material (virgin 1.6 x 5.23 x 5.34 mm and reprocessed 2.16 x 5.04 x 5.15 mm) was left in toluene for a few days and the weight was followed over time. After a few hours, the weight remained constant indicating that the samples reached their equilibrium swelling. The swelling ratio Q is plotted against time on Figure S3. Q is defined as $= \frac{m_s - m_u}{m_u}$, m_s and m_u being the swollen and unswollen mass of the sample.

The swelling ratio of the DTDB-cured ENR is very similar before and after reprocessing meaning that the density of crosslinks in the two networks is almost the same.

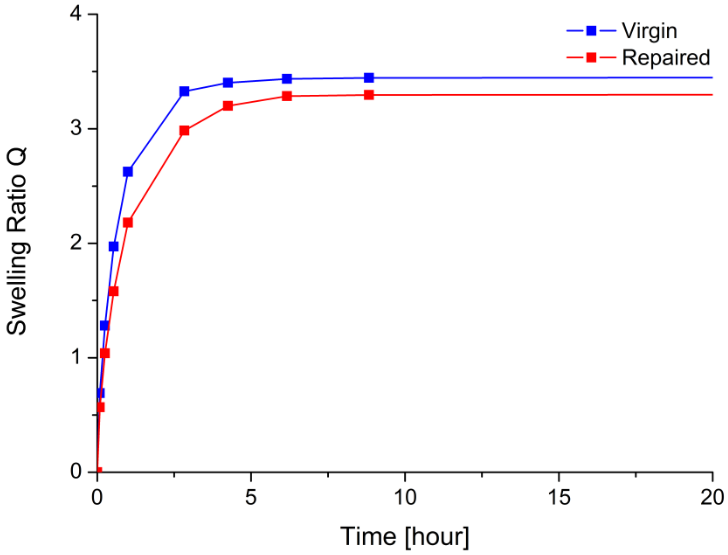

Figure S3. Swelling behaviour of the material

4- Study of the dissolved DTDB-cured network in reductive conditions

By using reductive conditions, disulfide links can be broken into thiols. It causes very large swelling of the disulfide-containing network that weakens the material a lot. Under magnetic stirring, the piece of rubber finally dissolves. But, the material obtained after swelling is degraded. Indeed, ^{1}H-NMR indicated that the chemistry of the material is the same (epoxidized polyisoprène, see Figure S4), but gel permeation chromatography showed much shorter chains than in initial ENR ($M_w \approx 10000$-20000 g.mol^{-1} instead of almost 10^6 g.mol^{-1} for virgin ENR).

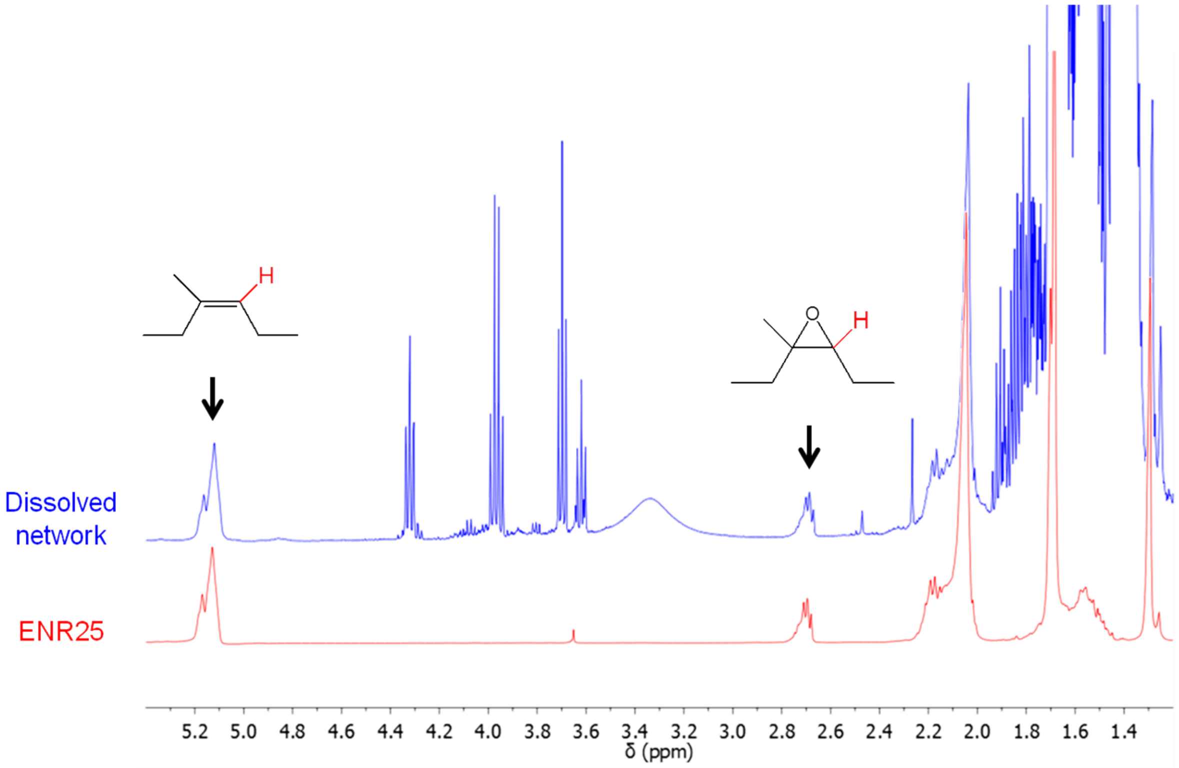

Figure S4. ^{1}H-NMR superposition of ENR25 in red and the dissolved material in blue

This NMR was done on a piece of DTDB-cured network that was dissolved in THF with the presence of water and a very large excess of TBP (to accelerate the dissolving process). When dissolved, the material was filtered and the solvent was completely evaporated. On the blue curve of Figure S4, the peaks of TBP appeared (a mix of its native form and oxidized form) because of the large excess. By comparing to the spectrum of pure ENR25 (in red), one can see that the characteristic peaks of ENR25 are present in the good ratio, confirming that the ENR structure is not altered (olefinic proton at 5.1 ppm and proton of the epoxy ring around 2.7 ppm).

5- Determination of Young's Modulus

Young's modulus of DTDB-cured ENR was also determined using tensile measurements. For a better reproducibility, rectangular specimens were used. The specimen (5 x 30 mm) were cut in a film of the tested material (width was around 1.6 mm for the virgin cured sample and 2 mm for the reprocessed one). For this test, the strain speed was fixed at 10 min^{-1} which corresponds approximately to a crosshead speed of 200 mm.min^{-1} because the effective length of the specimens was around 20 mm in each case. The corresponding curves are given on Figure S5.

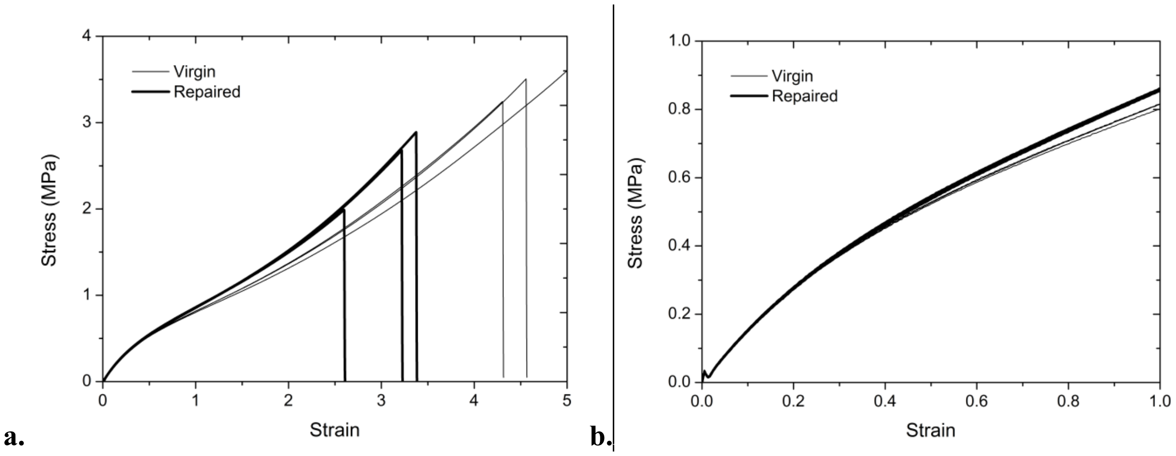

Figure S5. Tensile test for the determination of Young's Modulus on DTDB-cured ENR
(**a**. Stress-strain profile, **b.** Zoom.)

The beginning of the curves is very reproducible so we did only three measurements for each material. Considering that the Young's modulus is the slope of the stress/strain curve at low strain, it is possible to deduce from these measurements that E = 1.6 MPa for the virgin sample and E = 1.5 MPa for the reprocessed one. However E can also be found by another method that should be somehow more precise. For a uniaxial tensile test, the affine model gives the stress σ in function of the elongation ratio λ :

$$\sigma = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

The Young's modulus can thus be obtained by plotting

$$\frac{\sigma}{\lambda + \frac{1}{\lambda^2}} = f(\lambda)$$

which is a constant K at low strains. In this case the Young's modulus is taken as $E = 3K$ (indeed for rubbers, the Poisson's coefficient is 0.5 which gives $E = 3G$). With this second method, Young's moduli were found to be respectively 1.67 and 1.66 MPa with an error of only about ±0.02 MPa.

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