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# Turning Vulcanized Natural Rubber into a Self-Healing Polymer: Effect of the disulfide/polysulfide Ratio

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## ABSTRACT

A self-healing sulfur vulcanized natural rubber (NR) is here reported using the common ingredients in a traditional NR formulation. The dynamic character of the di- and poly-sulfide bonds naturally present in covalently crosslinked rubbers was found to be responsible for the healing ability and the full recovery of mechanical properties at moderate temperatures provided the material was employed in a non-fully cured starting state. Results show that a compromise between mechanical performance and healing capability can be reached by tailoring the amount of sulfur, the crosslinking density and the disulfide/polysulfide ratio. The healing efficiency was found to depend on the post-curing storage time, the time between damage creation and re-establishment of mechanical contact, and the actual healing time. Furthermore, a dedicated Electron Spin Resonance (ESR) test allowed establishing the underlying healing principle based on temperature-induced free sulfur radicals. The main observations presented here can serve as the basis for the design and preparation of other self-healing polymers with long term durability based on di-/poly-sulfide bridges and other reversible moieties.

**Key words:** vulcanized natural rubber; degree of curing; self-healing; disulfides; polysulfides; elastomer; time dependence; ESR.

## INTRODUCTION

Elastomers are used in a variety of applications such as seals, bladders or tires. While these materials can sustain large deflections with little or no permanent deformation, elastomers can still fail through fracture and fatigue processes. In existing elastomers, the development of deformation induced damage is cumulative and damage once formed will not disappear at later stages. Self-healing materials seek to enhance the long term durability of a structure by effectively removing any local micro-, meso- or sometimes even macro- damage which occurs throughout its service life, either through autonomous damage activated processes or by an external trigger.

Conventional vulcanized natural or synthetic rubbers do not have such a self-healing capability as they derive their excellent and stable mechanical properties from the creation of a stable covalently bonded three-dimensional molecular network. Earlier research in the field of self-healing synthetic rubbers focussed on the deployment of supramolecular chemistry concepts,<sup>1-3</sup> where dynamic non-covalent bonds are the key healing component in the polymer system. Xiang *et al*<sup>4</sup> showed an effective catalyst (CuCl<sub>2</sub>) for triggering healing in sulfur crosslinked polybutadiene rubber (BR). Once activated, the CuCl<sub>2</sub>-based catalyst enables disulfide metathesis of disulfide and polysulfide bonds at 110 °C, thereby restoring the mechanical properties once the temperature stimulus is stopped. A similar catalyzed approach was followed using a copper methacrylate (MA-Cu) catalyst<sup>5</sup> to promote the disulfide metathesis reaction in vulcanized chloroprene rubber (CR). A different approach involves the inclusion of ionic groups in the elastomer backbone targeting at an ionic domain rearrangement after energy input and equilibration time leading to macroscopic healing. Carboxylated nitrile butadiene rubber (XNBR) is an example of such ionomeric elastomers. Nellesen *et al*<sup>6</sup> found that non-vulcanized XNBR could have a 50% restoration of its original tensile strength, whereas the restoration ratio dropped to 15% for fully cured material. Also, Das *et al*<sup>7</sup> converted bromobutyl rubber (BIIR) into a highly elastic material with some self-healing capabilities by the inclusion of reversible ionic associates that exhibit physical crosslinking ability.

Despite the potential function of natural rubber (NR) latex as an autonomous self-repairing material,<sup>8</sup> it is still very challenging to turn vulcanized natural rubber (NR) into a self-healing material. In an attempt to develop self-healing NR, researchers have mainly focused on epoxidized natural rubber (ENR), taking advantage of the polar nature of the oxirane groups present in the rubber backbone. Self-healing of low molecular weight ENR slightly vulcanized with dicumyl peroxide was investigated by Rahman *et al*,<sup>9-11</sup> following damage under different experimental conditions (high-energy impact or tear test). The self-healing was attributed to small chain inter-diffusion processes. Imbernon *et al*<sup>12</sup> reported a reprocessable (*i.e.* healable under non-ambient conditions) ENR using dithiobutyric acid as a crosslinker in presence of 1,2-dimethylimidazole acting as a catalyst. More recently, Chen *et al*<sup>13</sup> described a self-healing supramolecular NR obtained by the inclusion of zinc dimethacrylate (ZDMA) as ionic crosslinking moieties.

In a recent publication we introduced the possibility of developing self-healing NR based on a modification of the crosslinking process in traditional NR vulcanized formulations<sup>14</sup> and the research to be presented here aims to have a closer look at the role of sulfur in creating a self-healing ability in a NR. Sulfur is the most widely used vulcanization agent in rubber technology for curing polydiene rubbers including NR. Even though it is still a matter of debate, it is believed that sulfur reacts through a radical mechanism<sup>15-20</sup> with rubber chains creating sulfur crosslinks of different lengths (mono-, di- and poly-sulfide bonds), pendant side groups, and cyclic sulfides.<sup>21, 22</sup> The low reaction efficiency, in addition to the long time required to complete the vulcanization process, are the reasons why sulfur vulcanization requires activators (*e.g.* an activator complex constituted by an inorganic metal oxide such as

ZnO and a fatty acid such as stearic acid) and accelerants (*e.g.* N-cyclohexylbenzothiazole-2-sulphenamide, CBS). Accelerated sulfur vulcanizations are usually classified as conventional (CV), semi-efficient (semi-EV) and efficient (EV), depending on the accelerant/sulfur ratio (A/S) usually ranging between 0.1-0.6 (for CV), 0.7-2.5 (for semi-EV) and 2.5-12 (for EV).<sup>23</sup> Although the chemistry of the process is not completely understood, the consequences for the network structure are well described, *e.g.* an increase of the A/S ratio reduces the length of the sulfur bridges and increases the number of crosslinks.

The cleavage of disulfide bonds under various stimuli like heat, light or redox conditions<sup>24-29</sup> leads to temporary local mobility of the polymer and offers the potential of the renewal of crosslinks across damaged surfaces by exchange reactions<sup>14, 30</sup>, *i.e.* offers the potential of self-healing. Hence, the present work focusses on the effect of the amount and nature of sulfide linkages in NR containing varying amounts of sulfur and various disulfide/polysulfide ratio's, on the final mechanical properties and (tensile strength) healing efficiencies. Given the dynamic nature of the sulfide bonds not properly incorporated in the crosslinked network, we study also the effect of time (storage time after curing, time between creation of the crack and manual restoration of contact across the crack and actual healing time) on mechanical properties and healing efficiency. Electron Spin Resonance is used to demonstrate the role of free sulfur radicals. Raman spectroscopy is used to determine the disulfide/polysulfide ratio.

## EXPERIMENTAL

### Materials

Conventional (CV) sulfur-cured natural rubber (NR) compounds were prepared according to recipes widely reported in the literature.<sup>23, 31, 32</sup> Table 1 shows the three compositions in phr (parts per hundred rubber in weight) processed in this study. The accelerant/sulfur ratio (A/S) was kept constant at 0.2 and the sulfur crosslinking agent content increased in the order  $CV_1 < CV_2 < CV_3$ .

For the compounding NR mainly consisting of *cis*-1,4-polyisoprene chains (*cis*-PI) was kindly supplied by *Wurfbain B.V* under the trade name RSS3. The commercial grade vulcanizing additives were used as-received. Mixing was performed in an internal mixer (*Plasticorder 350S, Brabender*) with a chamber volume of 390 ml, a filling factor of 0.8 and following a 2-step mixing protocol: (1) NR, ZnO and SA were mixed for 6 min; (2) after 24 h, CBS and S were added and mixed for 4 min. Both mixing steps were done at 50 °C and 70 rpm.

The crosslinking process was followed using a Rubber Process Analyzer (*RPA2000, Alpha Technologies*) at curing temperature  $T_c = 150$  °C, frequency 0.833 Hz and 2.79% strain for 45 min, monitoring the torque variation as function of time. The compounds were then vulcanized in a laboratory press (*Wickert*) at 150 °C for different curing times leading to 50% ( $t_{50}$ ) and 90% ( $t_{90}$ ) of the maximal torque as derived from the corresponding curing curves. Samples were cut out from press-cured sheets to perform damage and healing tests. As-produced samples were optically homogeneous and free of bubbles or other defects.

**Table 1.** NR compound recipes in phr (parts per hundred rubber in weight).<sup>23, 31, 32</sup>

Ingredient	Composition (phr)		
	CV <sub>1</sub>	CV <sub>2</sub>	CV <sub>3</sub>
NR	100	100	100
Zinc oxide (ZnO)	5	5	5
Stearic acid (SA)	1	1	1
N-cyclohexylbenzothiazole-2-sulphenamide (CBS)	0.14	0.26	0.5
Sulfur (S)	0.7	1.3	2.5

## Material characterization

**Crosslinking density.** The average mass of network chains between crosslinks (crosslinking density,  $\nu$  [ $\frac{\text{mol}}{\text{g}}$ ]) was determined on the basis of solvent-swelling measurements in toluene by application of the Flory–Rehner equation<sup>33</sup> and assuming the formation of tetra-functional crosslinks during the vulcanization reaction (see Supporting information S1).

**Raman spectroscopy.** Raman spectroscopy tests were performed using a Raman InVia reflex microscope (*Renishaw*) with an acquisition time of 1 min. The spectral region from 400 to 1800  $\text{cm}^{-1}$  was collected using a laser with an excitation line of 785 nm. Three spectral bands were chosen: S-S stretching ( $\nu_{\text{s-s}}=500 \text{ cm}^{-1}$ ), C-S stretching ( $\nu_{\text{c-s}}=650 \text{ cm}^{-1}$ ), and C=C stretching ( $\nu_{\text{c=c}}=1590 \text{ cm}^{-1}$ ). The peak area was calculated using a peak analyzer tool from Origin<sup>®</sup>, the baseline was subtracted and the peak fitted to a Gaussian fit.

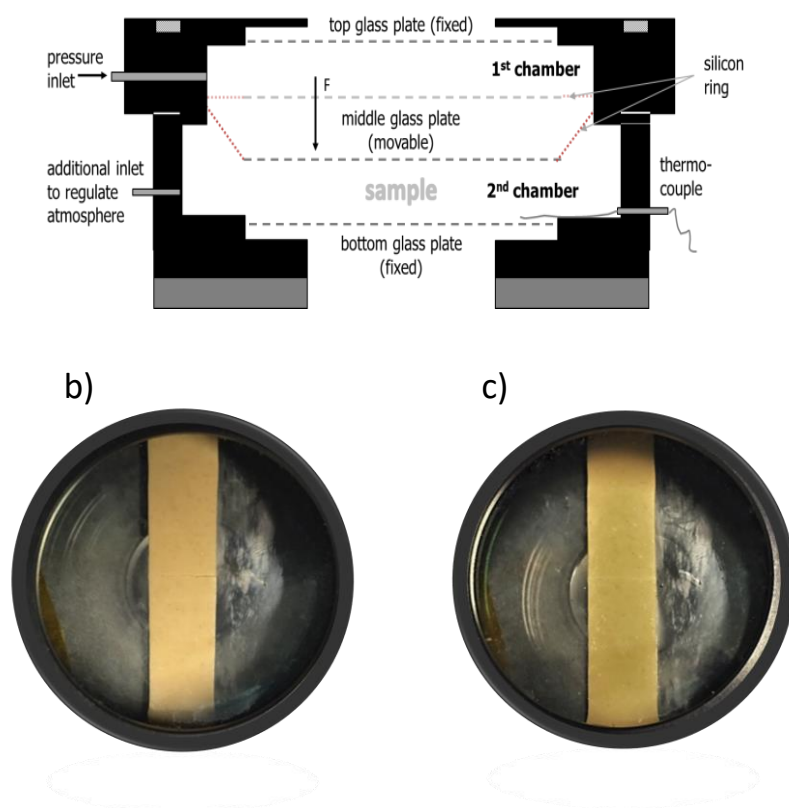
**Electron spin resonance spectroscopy (ESR).** ESR spectroscopy was performed on a spectrometer (*Bruker ECS-106*) equipped with temperature control and data acquisition systems. All the spectra were recorded at 70 °C, 9.44 GHz, 2.01 Gauss modulation amplitude, and 5.05 mW microwave power.

**Tensile testing.** Rectangular samples (10 x 70 x 2 mm) were used for uniaxial tensile testing. Tests were done on a universal mechanical testing machine (*Instron model 3365*) equipped with a 1 kN load cell. Samples were stretched until failure at a constant crosshead speed of 1 mm/s at room temperature. Stress at break (ultimate stress), strain at break (ultimate strain) and instantaneous modulus were determined in order to mechanically characterize the NR compounds and to evaluate their healing efficiency.<sup>34</sup> Data reported represent the average value from at least three samples.

## Healing procedure

**Home-built healing set-up.** A new home-built device (healing cell) for observing and assessing the healing process of self-healing polymers under well-defined conditions (temperature, clamping pressure, and surrounding gas atmosphere) was used. The healing cell

is a two chamber set-up as shown in Figure 1a). The sample is placed in the lower chamber (2<sup>nd</sup> chamber). By applying compressed air in the upper chamber (1<sup>st</sup> chamber), the middle (movable) glass plate is pushed onto the sample. The application of pressure transferred from the upper chamber to the sample by the glass plate results in lateral expansion of the sample and the generation of a contact pressure across the cut interface during healing. Due to the use of optical quality glass plates, the closure of the crack gap can be monitored optically during the healing process.



**Figure 1.** a) Schematic drawing of the set-up and working principle of the healing cell; b) photograph of NR cut sample inside the healing cell; c) photograph of healed NR sample inside the healing cell. After healing, the sample has physical integrity although the crack between the two cut surfaces remains visible.

**Mechanical healing.** Conventional tensile testing is one of the most important methods of polymer testing. In the particular case of elastomers, tensile testing is one of the basic tests for the quantitative characterization of *strength* and *deformability*, which are often described as “ultimate properties”. Hence conventional quasi-static tensile tests on pristine and healed samples were performed. Macroscopic damage was introduced to rectangular samples by manually making a straight cut along the width using a fresh scalpel blade. Within five minutes after cutting, the rectangular damaged samples were carefully positioned inside the healing cell between the two glass plates such that the cut surfaces were in seemingly optimal initial contact (see Figure 1b). Based on earlier work<sup>14, 24, 26, 27</sup> the cut samples were healed at 70 °C and 1 bar for 7 h. The combination of a rapid restoration of contact across the interface

and a long healing time at the optimal temperature should lead to the highest healing efficiencies and set the upper limit.

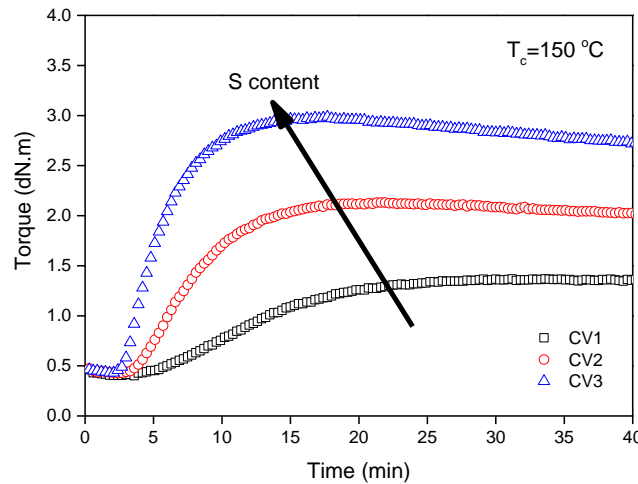
After removal from the healing cell, the samples were equilibrated at RT for at least 30 minutes before they were tensile tested according to the procedure described above. A schematic representation can be seen in Supporting information S2. The healing efficiency was calculated as the ratio between the tensile strength for healed and pristine specimens according to equation (1):

$$\text{Healing efficiency [\%]} = \frac{\sigma_b^{\text{healed}}}{\sigma_b^{\text{pristine}}} \times 100 \quad (1)$$

## RESULTS AND DISCUSSION

### Characterization of vulcanized NR

**Chemical characterization.** The vulcanization process of the three rubber compositions is shown in Figure 2. The curves show the relationship between the physical resistance of the material to shear (measured as torque) and the curing time thereby offering a rather complete picture of the overall crosslinking kinetics of the rubber compounds.



**Figure 2.** Rheometric curves of NR compounds with different sulfur content, cured at  $T_c=150$  °C.

The most relevant parameters deduced from the curing curves are summarized in Table 2 and show the well-known fact that a higher sulfur content leads to a higher  $S_{max}$  indicating higher degree of crosslinking.

**Table 2.** Curing characteristics of NR compounds vulcanized at  $T_c=150$  °C.

Compound	$t_{s2}$ <sup>*</sup> (min)	$t_{50}$ <sup>**</sup> (min)	$t_{90}$ <sup>**</sup> (min)	$S_{min}$ <sup>***</sup> (dN.m)	$S_{max}$ <sup>***</sup> (dN.m)
CV1	5.99	11.71	20.69	0.402	1.373
CV2	4.34	7.32	13.16	0.422	2.134
CV3	3.22	5.05	9.79	0.428	2.987

\* induction time before onset of vulcanization; \*\* times at which 50% and 90% of the maximal torque increase are reached; \*\*\* initial and the maximal torque.<sup>30,31</sup>

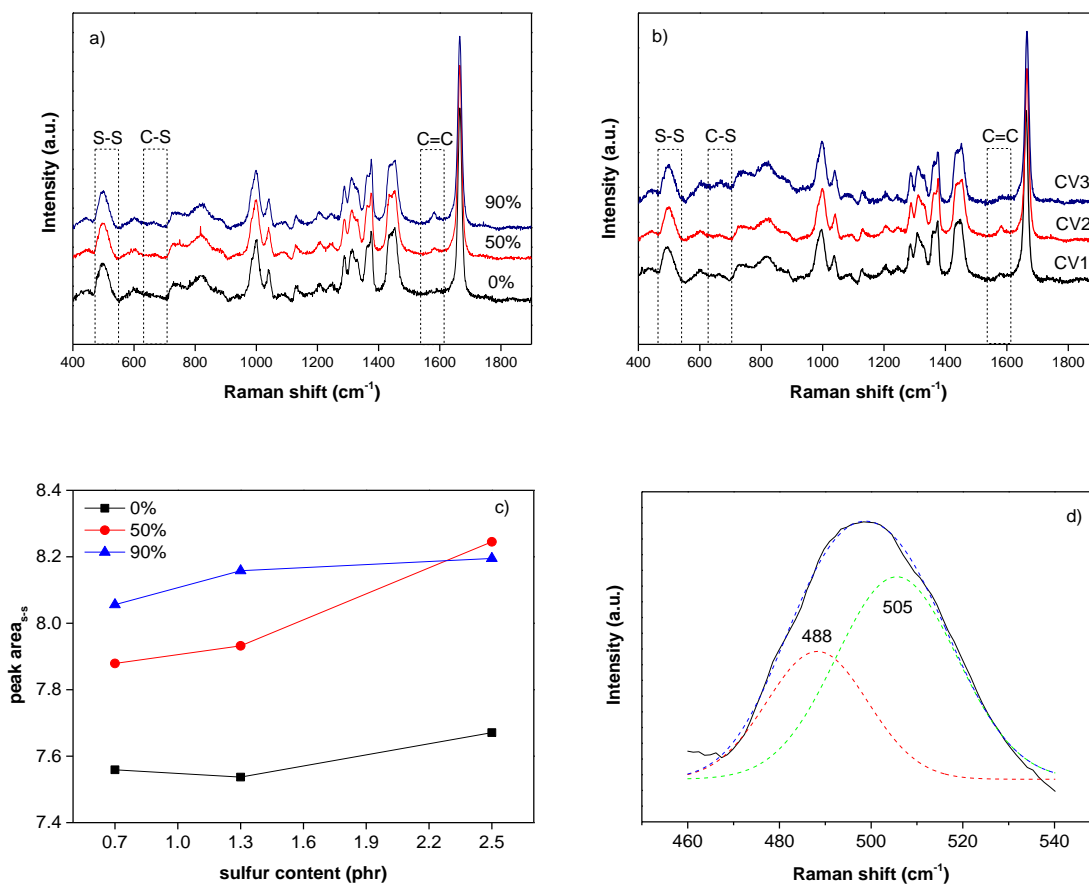
Table 3 shows the calculated values of crosslinking density based on swelling tests for the different compositions and the two curing times. An increase in crosslinking density with sulfur content (CV1<CV2<CV3) and to a lesser degree with curing time (50 < 90% curing time) can be observed. From a macroscopic phenomenological point of view, the rubber vulcanization reaction results in the random introduction of sulfur crosslinks between polyisoprene polymer chains building up a three-dimensional network. Hence, the results obtained are in agreement with reported dependencies.<sup>35</sup>

**Table 3.** Crosslinking density of NR compounds as function of curing time.

Compound	Curing time (%)	Swelling ratio, 1/Q	Crosslinking density, $\nu \times 10^{-4}$ (mol/g)
CV1	50	0.124	2.53± 0.02
	90	0.136	2.70± 0.01
CV2	50	0.192	3.50± 0.04
	90	0.197	3.46± 0.01
CV3	50	0.259	4.08± 0.03
	90	0.265	4.13± 0.06

The results of the Raman spectroscopy measurements aimed to unveil possible changes in the disulfide/polysulfide ratio with the sulfur content and curing time are shown in Figure 3. A weak new band at around 1582 cm<sup>-1</sup> typically assigned to dialkenyl sulfides<sup>36</sup> appears with increasing curing time (Figure 3a). This variation suggests that new crosslinks generate a shift in the  $\nu_{c=c}$  band frequency in carbon-carbon double bonds adjacent to these sites.<sup>36</sup> The crosslinking process is further confirmed by the appearance of a second low intensity band at around 650 cm<sup>-1</sup> characteristic of C-S bonds.<sup>37</sup> A more prominent Raman band near 500 cm<sup>-1</sup> lies in the interval characteristic of S-S stretching.<sup>26, 27</sup> Figure 3c clearly shows the evolution of this peak area with increasing sulfur content and curing time.





**Figure 3.** Raman spectra of NR compounds: a) CV2 cured at different times; b) different curing systems at 90% curing time; c) 500 cm<sup>-1</sup> peak area, and d) representative deconvolution of band at 500 cm<sup>-1</sup>.

Previous studies using Raman spectroscopy to monitor crosslinking in NR<sup>36, 38, 39</sup> have always been focussed on peaks at 1550 and 1750 cm<sup>-1</sup> linked to conjugated dienes and trienes. As far as we are aware in the rubber literature no attention has been paid to the S-S stretching region (450-550 cm<sup>-1</sup>). However, researchers working on proteins claim that this S-S band pattern is informative yet complex to analyze as it involves the overlapping peaks connected to different S-S linkages. They state that the molecular environment (solvent, neighbouring bonds, degree of substitution of attached carbons, etc.) affects the S-S bridges and dynamics.<sup>40-42</sup> As an example, Enescu *et al*<sup>40</sup> studied the role of protein structure in the reactivity of the four disulfide bridges of lysozyme. They report that for the *cis-cis* conformation a shoulder at 487 cm<sup>-1</sup> is observed with a 5% participation of the S-S stretching mode, while Scheraga *et al*<sup>41</sup> report S-S stretching frequencies in the same range for strained aliphatic disulfides. Brown *et al*<sup>42</sup> report bands at 502-503 cm<sup>-1</sup> assigned to polysulfides in sulfur-amine solutions.

In a further attempt to analyze the type of S-S bridges available in the different rubber formulations as function of the curing time and sulfur content, the 500 cm<sup>-1</sup> band was deconvoluted. Such an approach allows for the detection of the individual contributions of di-

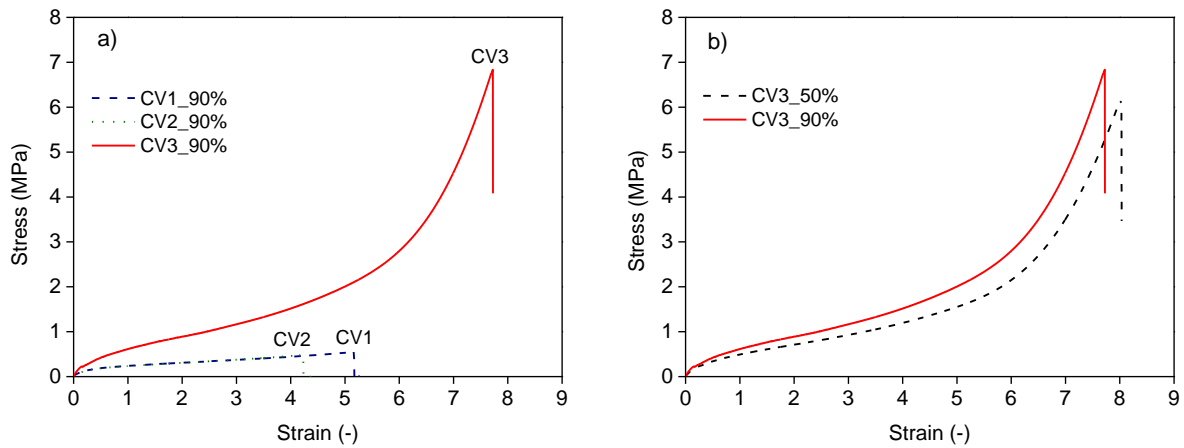
and poly-sulfide linkages in the rubber network structure. Following reported peak-assignments on proteins research (Table 4) the recorded peak was deconvoluted assuming two contributions ( $\sim 488\text{ cm}^{-1}$  and  $\sim 505\text{ cm}^{-1}$  assigned to disulfide and polysulfide fractions, respectively) (see Figure 3d). The area under the curve corresponding to the characteristic Raman bands is expected to be proportional to the respective bonds concentration.<sup>40</sup>

**Table 4.** Deconvolution results of the  $500\text{ cm}^{-1}$  Raman band for NR compounds at different curing degrees and sulfur content to identify disulfide and polysulfide contributions.

Compound	Curing degree (%)	Peak area		Peak area (%)		disulfide/polysulfide ratio
		488 $\text{cm}^{-1}$	505 $\text{cm}^{-1}$	488 $\text{cm}^{-1}$	505 $\text{cm}^{-1}$	
		(disulfide)	(polysulfide)	(disulfide)	(polysulfide)	
CV1	50	2.54±0.05	4.21±0.06	37.63	62.37	0.60±0.02
	90	2.79±0.09	5.77±0.37	32.59	67.41	0.48±0.05
CV2	50	2.28±0.08	4.18±0.14	35.29	64.71	0.55±0.04
	90	1.73±0.04	4.97±0.11	25.82	74.18	0.35±0.02
CV3	50	2.09±0.26	6.15±0.04	25.36	74.64	0.34±0.04
	90	1.78±0.14	5.55±0.24	24.28	75.72	0.32±0.04

According to rubber theory, conventional (CV) systems, just like the ones prepared in this study, predominantly lead to polysulfides.<sup>23, 43-46</sup> On this basis, the assignment of peaks and trends in Table 4 seems reasonable. As expected, more polysulfide than disulfide linkages can be detected with higher sulfur contents (from CV1 to CV3). The somewhat unexpected trend with the curing time (50 vs. 90%) for all samples can be explained by the shortening of polysulfides (leading to di- and mono-) concurrently taking place with the formation of additional crosslinks during the maturing stage of the curing process.<sup>47</sup> The crosslinking process therefore seems to overlap with the polysulfide shortening.

**Mechanical characterization.** Figure 4 shows the stress-strain curves for the 90%–cured NR compounds (Figure 4a) and a representative curve on the effect of curing time (Figure 4b). The characteristic parameters for all the polymers are compiled in Table 5.



**Figure 4.** Stress-strain curves of NR compounds with different sulfur content (a) and different curing degree (b).

**Table 5.** Mechanical testing parameters of NR compounds in the as-prepared state (0 months) and after being stored at room temperature for 3 and 9 months.

Compound	Curing time (%)	Ultimate stress (MPa)			Ultimate strain (-)			Modulus (MPa)		
		0 months	3 months	9 months	0 months	3 months	9 months	0 months	3 months	9 months
CV1	50	0.51	0.81	1.03	4.83	4.05	3.98	0.19	0.19	0.19
	90	0.55	1.12	1.56	5.17	4.72	4.98	0.20	0.24	0.54
CV2	50	0.56	3.42	4.64	5.07	4.74	4.79	0.19	1.50	1.48
	90	0.48	3.10	5.17	4.23	3.79	4.20	0.25	1.69	1.59
CV3	50	6.21	7.57	-	8.03	5.38	-	2.45	2.50	-
	90	6.51	7.53	-	7.57	5.31	-	2.70	3.09	-

As can be seen in Figure 4 and Table 5 the rubber compounds become stiffer and the tensile strength increases with increasing sulfur content ( $CV1 < CV2 < CV3$ ) as well as with longer curing times (90%). On the one hand, while the CV3 system shows a strain-hardening behavior typical of fully cured NR, CV1 and CV2 compounds exhibit less strain-hardening suggesting a lower amount of strong interchain covalent bonds formed between sulfur and the rubber backbone. The latter systems are thus more prone to comply with the imposed stretching due to the higher mobility ensured by the lower amount of such bonds.<sup>32</sup> On the other hand, mechanical performance improves with curing time. This fact is directly correlated to the crosslinking density measurements (see Table 3) according to the well-known formula of the theory of rubber elasticity, in its simplest form:<sup>31</sup>

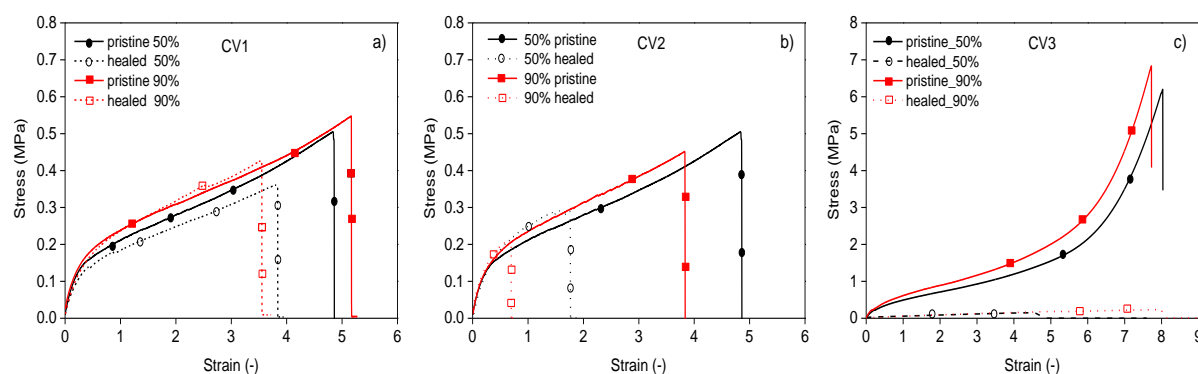
$$\sigma = RTv \left( \lambda - \frac{1}{\lambda^2} \right) \quad (2)$$

in which  $v$  is the number of crosslinks per  $\text{cm}^3$ ,  $\lambda$  is the extension ratio,  $R$  is the gas constant and  $T$  the absolute temperature.

The pristine 50% and 90%-cured NR compounds were also kept at room temperature for 9 months (so-called equilibrated compounds) and then mechanically tested. It was found that the ultimate stress and strain of CV1 and CV2 change considerably with time between 0 months and 3 months, evidencing the non-stable nature of such systems in the as-prepared non-fully cured state (see Table 5). Variations in properties of materials stored for 3 months and for 9 months are minimal suggesting quasi-equilibrium is reached upon 3 months storage. Between 0 and 3 months the ultimate stress increases and strain at break decrease, indicating that the labile and less stable bonds become more likely to react and set a permanent crosslinked network, resulting in higher mechanical performance and lower stretchability with time. In contrast, in the as-prepared state, the material is soft, highly stretchable, and dynamically unstable. Interestingly, the instantaneous modulus for the different polymer states under the specified testing conditions do not change significantly indicating that this parameter is clearly affected by the balance between reversible and irreversible bonds in the rubber network. Similar results were found by Gong *et al* with self-healing hydrogels.<sup>48</sup> For CV3 compounds, the increase in ultimate stress is negligible compared to the increase achieved by CV1 and CV2 compounds, confirming the more stable nature of the CV3 network in the as-prepared state.

## Quantification of macroscopic healing of vulcanized NR

**Effect of sulfur content and curing time.** Figure 5 shows the stress-strain curves of pristine and healed NR compounds at different curing stages. Healing, here understood as the disappearance of the cut and restoration of the mechanical integrity, was only observed for CV1 and CV2, in which the stress-strain curves for the healed materials almost overlap with their original stress-strain curves, resulting in a recovery of tensile stress of ~ 80% and ~ 60%, respectively. Such compounds appear to have a higher healing capability compared to the CV3 system, which showed no real healing but some form of surface sticking.

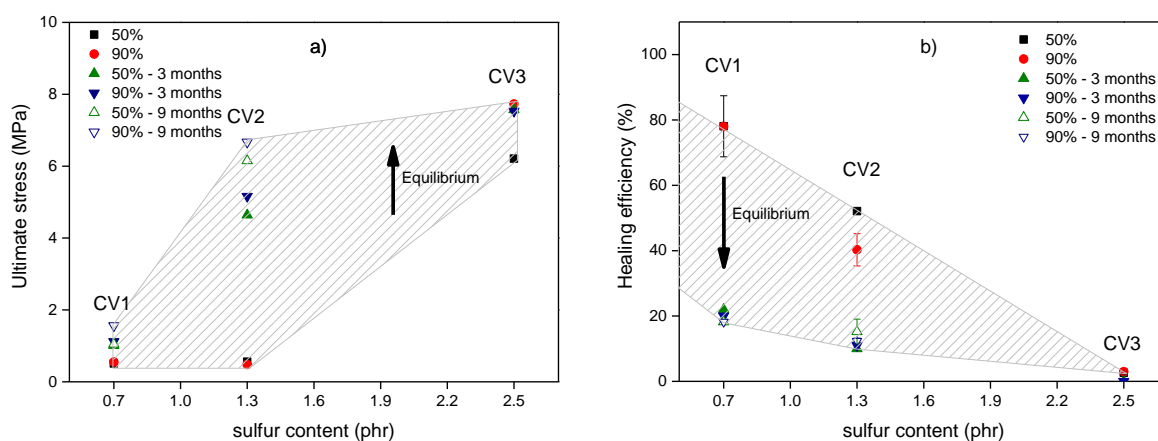


**Figure 5.** Stress-strain curves of pristine and healed samples for different sulfur content (CV1 (a), CV2 (b), CV3(c)) and curing degrees (50% and 90%).

As it can be seen in Figure 5 samples CV1 and CV2 almost fully recover their mechanical properties after macroscopic damage and thermal treatment. Such a result can be attributed to the high content of labile poly- and di-sulfides bridges and low crosslinking density allowing

for the rearrangement of the broken bonds at the healed interface. The almost full recovery can also indicate that only reversible bonds are broken during damage, and no breaking of primary chains takes place. Moreover, the crosslinking density of the healed samples is in the same range as for the pristine samples evidencing the recovery of the network, as previously reported by the authors.<sup>14</sup> Similar results were found by Balazs *et al*<sup>49</sup> in networks with multiple reformable bonds. CV3 on the other hand is a more stable and higher crosslinked network, making a full restoration of the interface not possible under the studied healing conditions. The results suggest the presence of a critical maximum crosslinking density allowing for some healing degree at the interface. Similarly, Rahman *et al.* reported a limit value of the swelling ratio ( $1/Q$ ) of 0.13 above which no self-healing takes place in epoxidized natural rubber (ENR) slightly vulcanized with peroxide.<sup>9, 11</sup> In our study, and ignoring the fact that peroxide-cured and sulfur-cured networks are different, the non-self-healing system CV3 has a swelling ratio (see Table 3) well above this critical ratio. Our data set is too sparse to determine the actual critical ratio for this NR system.

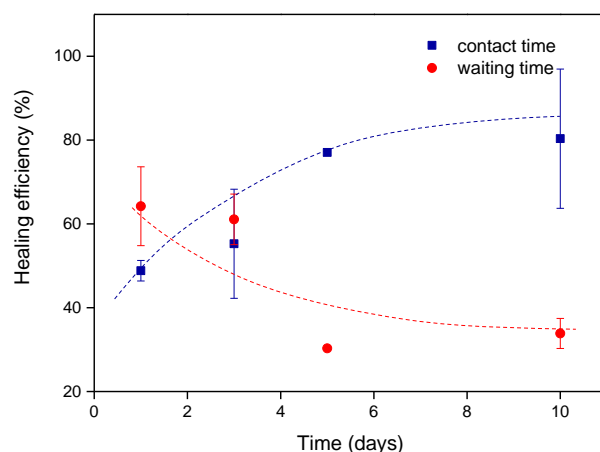
Figure 6 shows the ultimate stress and healing efficiency as a function of the sulfur content. Interestingly, there seems to be a correlation between the two opposing plots: low mechanical performance rubber systems show high healing capabilities and vice-versa. The dashed zone points out the region where a compromise can be established between the mechanical properties and the healing ability for this particular healing rubber case and testing protocol. At this stage it should be mentioned that the healing efficiency values reported here are test method dependent. The tensile test healing procedure as presented here is a common and easy protocol valid for samples comparison, although it has been demonstrated that for very deformable materials such as rubbers a fracture mechanical protocol yields more detailed insight in the various processes involved in healing.<sup>30, 50</sup>



**Figure 6.** a) Ultimate stress as function of sulfur content, curing degree and equilibration time; b) Healing efficiency calculated from tensile experiments as a function of sulfur content, curing degree and equilibration time.

**Effect of contact and waiting time on healing.** Additional healing experiments were carried out with the intention of unravelling the effect of wetting and surface contact area on healing and healing deactivation (*i.e.* time dependence). A first set of experiments consisted of

varying the contact time between two damaged surfaces at room temperature before imposing the thermal healing step (contact time series). In a second set, the two damaged surfaces were kept apart at room temperature before imposing the thermal healing treatment (waiting time series). Only CV2 material was used for these tests. CV1 was discarded due to its high healing efficiency in the as-prepared state, and CV3 due to its non-healing character. Both sets of samples were mechanically tested after the thermal healing treatment (70 °C, 7 h) in the healing cell. Figure 7 shows the corresponding healing efficiencies for both sets of experiments as function of contact and waiting time.



**Figure 7.** Healing efficiency for CV2 compounds as function of contact time (blue squares) and waiting time (red circles) at room temperature before thermal healing. All samples were tested after healing treatment at 70 °C for 7 h. Dashed lines are inserted to guide the eye.

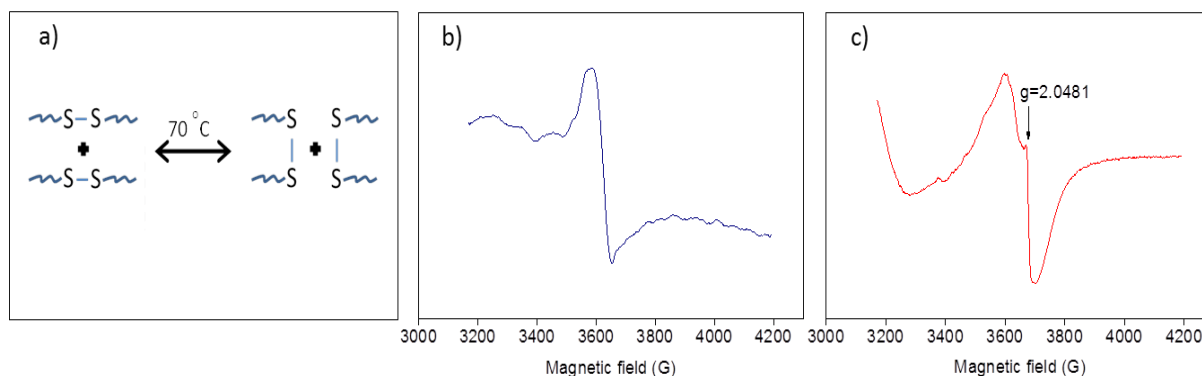
As it can be seen in Figure 7, higher contact times lead to higher healing efficiencies after thermal healing treatment. A possible explanation for the improved healing with room-temperature contact-time may rely on the improvement of the surface wetting (*i.e.* roughness disappearance). As we previously reported<sup>50</sup> higher healing degrees are obtained for lower roughness surfaces. Contact time therefore seems to play a key role in the balance between roughness disappearance (perfect contact) and chain interdiffusion kinetics at actual (sub) microscopic contact sites. The tests confirm that high healing is to be achieved when sufficient time is allowed for interface contact optimization as well as for the chemical re-shuffling reactions responsible for the healing.

A longer waiting time between cutting and recombining the surfaces seems to decrease the healing efficiency. Interestingly, the effect of waiting time in these polymers is lower than in H-bond based supramolecular polymers.<sup>51</sup> In the supramolecular system the deactivation has been assigned to bond lifetime of the supramolecular entity. In our system the healing efficiency is not affected during the first 3 days of storage at room temperature. While more dedicated tests need to be performed, the NR results seem to point at a free surface oxidation process and/or surface tension variation that decreases the possibility of wetting and chain diffusion promoted by disulfide bridges during the healing stage.

**Healing mechanism unraveling and role of di-/poly- sulfide bridges.** It is generally accepted that metathesis of disulfide bridges (Figure 8a) is responsible for healing in sulfur-based self-healing polymers.<sup>4, 5</sup> The underlying mechanism is presumed to be determined by the temperature-driven formation of sulfur radicals that bond to each other once the energetic stimulus is removed to form a new disulphide bridge, but this has not been demonstrated for self-healing NR systems. In order to probe the presence of free radicals and establish the underlying healing principle temperature dependent, ESR measurements were performed on the 90%-cured CV2 compounds. Figure 8b) and c) show the ESR spectra obtained at room temperature and at the optimal healing temperature of 70 °C.<sup>27</sup> The  $g$  tensor was calculated according to equation (3):

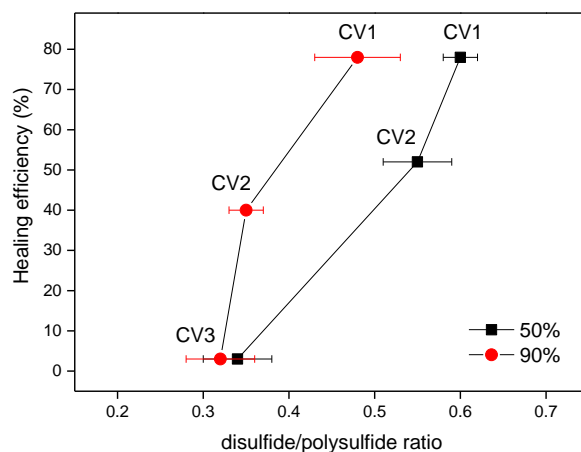
$$h\nu = g\beta B \quad (3)$$

where  $h$  is the Planck's constant,  $\nu$  is the frequency [MHz],  $\beta$  is the Bohr magneton and  $B$  the magnetic field [Gauss].<sup>52</sup> According to literature,<sup>20</sup> a  $g$  tensor value of 2.03-2.04 is expected for all type of polysulphanyl radicals  $R - S_n$  with  $n \geq 2$ , while allyl thiyl radicals  $R - S^{\cdot}$  are hardly observable in rubbery matrices above their glass transition temperature. Hence, the calculated value of  $g = 2.0481$  for the 70 °C spectrum can be regarded as evidence for the disulfide exchange reaction in CV2 compounds. Similar results were also obtained for other disulfide based healing systems developed in our group<sup>25, 27</sup> as shown in Supporting information S3, thereby confirming the hypothesis of radicals as responsible for the reversible reactions leading to macroscopic healing in sulfide-based healing polymers.



**Figure 8.** a) Disulfide exchange reaction scheme; b) ESR spectrum of 90%-cured CV2 compound at room temperature; c) ESR spectrum of 90%-cured CV2 compound at 70 °C.

While the role of the disulfides in healing is well accepted, the effect of the disulfide/polysulfide ratio on healing so far has received no attention. Figure 9 shows the healing efficiency as function of disulfide/polysulfide ratio obtained from Raman. The apparent trend for both curing degrees (50 and 90%) is that higher disulfide/polysulfide ratios lead to higher healing, with a ratio of 0.55 already giving efficiencies in the order of 50%. However, the limiting factor seems to be the sulfur content (CV1<CV2<CV3) and the degree of curing rather than the disulfide/polysulfide ratio.



**Figure 9.** Healing efficiency as function of disulfide/polysulfide ratio for different NR compounds at different curing times.

## CONCLUSIONS

In this research we have reported sulfur-cured NR compounds with mechanical self-healing capability and without the need of modifying conventionally used rubber formulations. We have demonstrated that the underlying disulfide metathesis healing mechanism is based on temperature-driven sulfur radical reactions. The study revealed that the ratio between di- and poly-sulfide bridges is an important mechanistic parameter, although other limiting factors on healing seem to be sulfur content, crosslinking density, post-curing storage time and contact time between damaged surfaces before healing treatment. A compromise between mechanical performance and healing capability can be potentially tailored depending on these parameters. The present work is a proof-of-concept study towards the development of a healing technology for possible future sustainable and long-term durability applications in the rubber industry.

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## ASSOCIATED CONTENT

S1. Determination of crosslinking density; S2. Tensile experiments on healed samples; S3. Electron spin resonance (ESR) measurements.



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