



Citation for published version:

Boden, J, Bowen, CR, Buchard, A, Davidson, MG & Norris, C 2022, 'Understanding the Effects of Cross-Linking Density on the Self-Healing Performance of Epoxidized Natural Rubber and Natural Rubber', *ACS OMEGA*, vol. 7, no. 17, pp. 15098-15105. <https://doi.org/10.1021/acsomega.2c00971>

DOI:

[10.1021/acsomega.2c00971](https://doi.org/10.1021/acsomega.2c00971)

Publication date:

2022

Document Version

Peer reviewed version

[Link to publication](#)

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Understanding the effects of cross-linking density on self-healing performance of epoxidised natural rubber and natural rubber

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Keywords: Self-healing; epoxidised natural rubber; natural rubber; cross-linking density.

ABSTRACT: The demand for self-healing elastomers is increasing due to the potential opportunities such materials offer in reducing down-time and cost through extended product lifetimes and the reduction of waste. However, further understanding of self-healing mechanisms and processes is required in order to develop a wider range of commercially applicable materials with self-healing properties. Epoxidised natural rubber (ENR) is a derivative of polyisoprene. ENR₂₅ and ENR₅₀ are commercially available materials with 25 and 50 mol % epoxidation, respectively. Recently, reports of the use of ENR in self-healing materials have begun to emerge. However, to date, there has been limited analysis of the self-healing mechanism at the molecular level. The aim of this work is to gain understanding of the relevant self-healing mechanisms through systematic characterization and analysis of the effect of cross-linking on the self-healing performance of ENR and natural rubber (NR). In our study, cross-linking of ENR and NR with dicumyl peroxide (DCP) and sulfur to provide realistic models of commercial rubber formulations is described and a cross-linking density of 5×10^{-5} mol cm⁻³ in sulfur-cured ENR is demonstrated to achieve a healing efficiency of 143 % for the tensile strength. This work provides the foundation for further modification of ENR, with the goal of understanding and controlling ENR's self-healing ability for future applications.

INTRODUCTION

Natural rubber (NR), a renewable resource derived from *Hevea Brasiliensis*, has mechanical properties that are generally superior to those of synthetic rubbers. The material has high elasticity, high tensile strength and low heat build-up, however it also has low oil resistance and gas permeability.^{1,2} Epoxidation of NR to create epoxidised natural rubber (ENR) improves these disadvantageous properties, whilst retaining many of the positive properties of NR.^{1,3} ENR exists commercially in two forms, ENR₂₅ and ENR₅₀, which contain 25 mol % and 50 mol % respectively of epoxy groups on the cis-1,4-isoprene backbone. Due to the presence of these epoxy groups, ENR is also more polar than NR, which increases its compatibility with more polar components such as silica with the additional benefit of enabling a variety of secondary modifications.^{2,3}

In this context, ENR has a range of applications from adhesives to tires and other automotive parts.^{2,4} While its chemical and mechanical properties have been examined for more than 40 years,⁵⁻⁷ it has yet to realize its full potential as a commercial elastomer. However, recently there has been an increasing interest in ENR for tires in electric vehicles as it has much potential for low rolling resistance materials^{8,9} and for self-healing applications.¹⁰⁻¹⁵

Self-healing of polymeric materials is a highly desirable property and is defined as the capability of a material to recover from physical damage.^{16,17}

ENR can be cured using the same established chemistries as NR and other rubbers, typically sulfur or dicumyl peroxide (DCP) cures.⁴ The poor ageing characteristics of ENR cured with sulfur, due to acid-catalyzed ring-opening of the epoxides to form ether cross-links, can be offset with the addition of a suitable base.^{18,19} In addition to these cure methods in common with NR, it has also been demonstrated that ENR can be cured with dicarboxylic acids²⁰⁻²³ or with zinc acrylate via an oxa-Michael reaction.²⁴ These curing methods avoid the drawback of the sulfur cure and also afford the possibility of introducing different chemical functionalities via the structure of the cross-linker.

As an example, Imbernon *et al.* incorporated a disulfide bond using dithiodibutyric acid as a cross-linker.²³ This allowed the material to regain most of its mechanical properties after reprocessing, creating an ENR with the ability to be partially recycled. Cheng *et al.* took this further by employing a mixture of diamine and dicarboxylic curing agents that contained disulfide bridges, thus producing a self-healing ENR that could achieve a self-healing efficiency of 98 %.¹² Self-healing was

achieved through dynamic disulfide bridges which have a low bond dissociation energy that promotes a disulfide metathesis reaction.

Self-healing can also be achieved with sulfur cure systems. The ratio of dynamic disulfidic/polysulfidic cross-links was investigated in sulfur cured NR by Hernandez *et al.* and it was concluded that while the ratio was important to the self-healing performance, the main limiting factor was sulfur content as the samples with lower sulfur content reached higher self-healing performance despite similar ratios as other samples.²⁵

It is established that ENR has self-healing properties. For example, Rahman *et al.* determined by ballistic testing that self-healing could occur autonomically in ENR that was lightly cross-linked with DCP.¹⁰ This was proposed to be due to the synergistic effect of chain interdiffusion and polar interactions. Consequently, ENR₅₀ was found to self-heal at a higher wt % DCP than ENR₂₅ as it has a greater amount of polar interactions. It was observed that once the cross-linking density increases above a certain value the material can no longer self-heal. Thus, to develop useful materials, a compromise must be achieved between maintaining good mechanical properties (that requires a high cross-linking density) and imparting self-healing ability (which is limited by cross-linking density).

These literature examples all compare the self-healing performance against the cure system or cure ingredient content. However, to our knowledge, the direct relationship between cross-linking density and self-healing performance of ENR has not been examined in elastomers. Here we examine self-healing in ENR and NR compounded with different curing systems at a range of cross-linking densities to determine whether there is a relationship between self-healing performance and cross-link density and to estimate the extent of this interaction relative to the autonomic self-healing behavior of ENR.

EXPERIMENTAL

Epoxidised natural rubber, Ekoprena, 50 mol % epoxidation, was received from the Tun Abdul Razak Research Centre (TARRC). Natural rubber (SMR CV60) was received from Corrie McColl. Sulfur cured and dicumyl peroxide (DCP) cured ENR and NR were prepared according to formulations reported in the literature using low lead ZnO, stearic acid 1890, 300 mesh Sulfur and Luperox DC40.^{10,25} The commercial grade vulcanizing additives were used as received. Tables 1-4 shows the master batches created in this study. The cross-linking agent increases from rubber X1. Formulations were chosen to achieve a low cross-linking density in order to isolate the effects of dynamic cross-links between sulfur and DCP cured rubber and therefore accelerants were not added to sulfur compounds. Compounds were produced using a HAAKE Rheomix OS/610 of 78 cm³ chamber volume with Banbury style rotors set at 40 °C and 60 rpm. In all cases the mixing cycle was as follows: the rubber was masticated for 30 seconds prior to adding cure chemicals (including ZnO & Stearic Acid for sulfur cure). The batch was dumped after 3 min total mixing time. The cure characteristics of

the compounds were determined using a rheometer (Alpha Technologies MDR 2000) with a cure time of T₉₀ + 5 minutes. Testing was conducted at 160 °C for 30 minutes following ASTM D5289. Samples were cut out of press-cured sheets to perform tensile testing and healing tests.

Table 1 ENR Sulfur-cured compound formulations in parts per hundred rubber in weight (phr)

Ingredient	Composition (phr)				
	S ₁	S ₂	S ₃	S ₄	S ₅
ENR	100	100	100	100	100
Zinc Oxide (ZnO)	5	5	5	5	5
Stearic acid (SA)	1	1	1	1	1
Sulfur (S)	0.3	0.5	0.8	1.0	1.6

Table 2 ENR DCP-cured compound formulations

Ingredient	Composition (phr)						
	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇
ENR	100	100	100	100	100	100	100
Dicumyl peroxide (DCP)	0.3	0.5	1.0	1.5	2.0	2.7	3.4

Table 3 NR Sulfur-cured compound formulations

Ingredient	Composition (phr)								
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉
NR	100	100	100	100	100	100	100	100	100
ZnO	3	3	3	3	3	3	3	3	3
SA	1	1	1	1	1	1	1	1	1
S	0.8	1.1	1.6	2.1	2.7	3.2	3.8	4.3	4.9

Table 4 NR DCP-cured compound formulations

Ingredient	Composition (phr)						
	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇
NR	100	100	100	100	100	100	100
DCP	0.3	0.5	0.8	1.0	1.5	2.0	2.6

Material Characterization

Cross-linking density The cross-linking density in mol cm⁻³, was evaluated through swelling of the cured compounds in toluene according to ASTM D471-12 and using the Flory-Rehner equation (see Supporting Information, SI).

Dynamic Mechanical Analysis (DMA) Temperature evolution of both storage and loss moduli of cured rubber blends were measured using a TA Instruments Dynamical Mechanical Analyzer (DMA), in a compression configuration. Samples were cut from the cured rubber sheets and were submitted to a 3 °C min⁻¹ ramp (single frequency 1 Hz, amplitude 20 μm) The temperature ranged from -30°C to 30 °C for ENR samples and -70 °C to -10 °C for NR samples. See SI for NR rubber samples data.

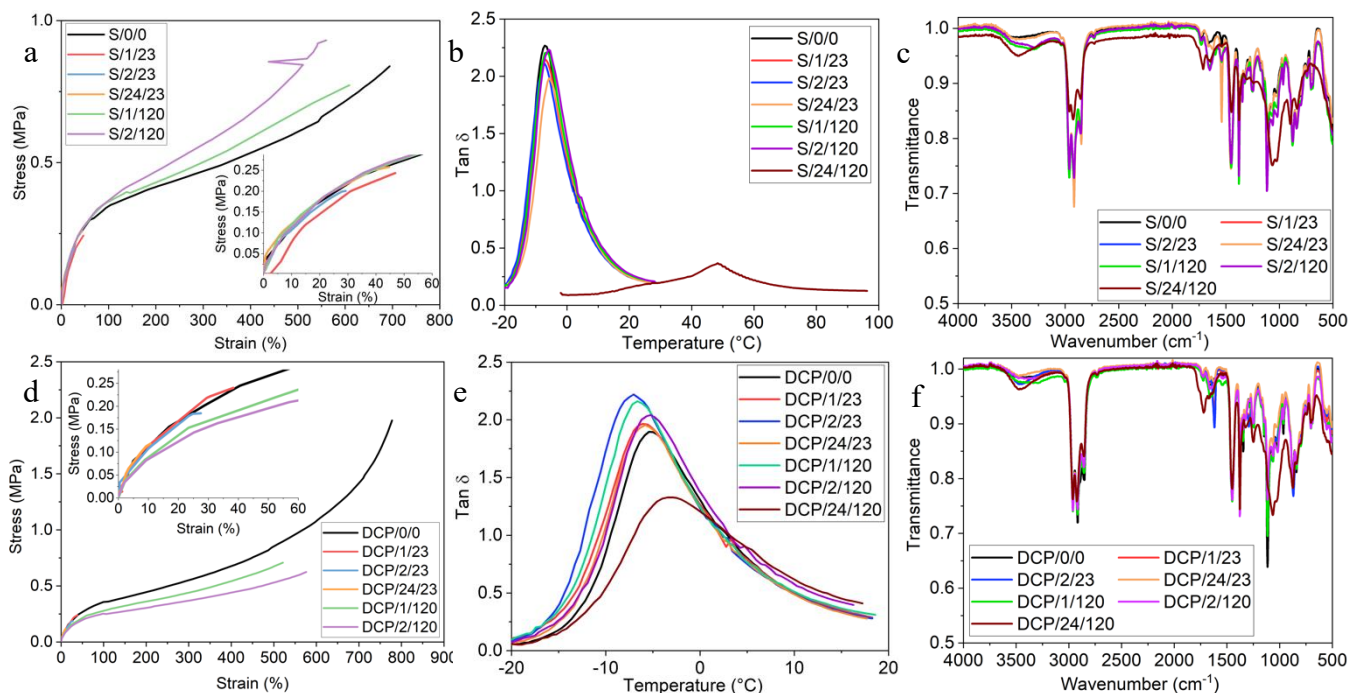


Figure 1 Sulfur-cured ENR: a) Tensile properties; insert – magnified initial region; b) Tan δ curves; c) IR spectra. DCP-cured ENR: d) Tensile properties; insert– magnified initial region; e) Tan δ curves; f) IR spectra. Key: Curative/ SH time (hours)/ SH temperature ($^{\circ}\text{C}$) (e.g. S/2/120 represents a sulfur cure for two hours at 120 $^{\circ}\text{C}$). See SI for tensile data for 24/120.

Fourier Transform Infra-Red Spectroscopy (FT-IR)

FTIR spectra were recorded on a Perkin Elmer 100 Fourier transform spectrometer fitted with an ATR accessory. Spectrum data was analyzed using the OPUS software. Spectra were recorded in the wavenumber range 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} , and 24 scans. See SI for NR sample spectra and full spectra for ENR samples.

Tensile testing The mechanical properties of the natural rubber samples were determined with static uniaxial tensile tests. Dumbbells were cut using a Type 2 ISO-37 die and their thickness and width were measured. Static uniaxial tensile tests were carried out on a Lloyd instruments LR5K plus equipped with a Laserscan 200 instrument and 500 N static load cell. The samples were stretched until failure at an extension rate of 500 mm min^{-1} +/- 50 mm min^{-1} under room temperature and humidity conditions. Ultimate tensile strength and ultimate strain at break were recorded in order to characterize the samples and evaluate the self-healing abilities. Data reported represents the median of 5 samples for this characterization. See SI for tensile testing results for DCP-cured ENR and S- and DCP- cured NR.

Self-healing Samples were cut with a clean scalpel and then gently pressed together to establish contact and left for 1 hour at 120 $^{\circ}\text{C}$ to heal. The samples were equilibrated at room temperature for 30 minutes before tensile testing. Data reported represents the median of three samples. Self-healing ability was calculated as the ratio of the ultimate tensile strength of the healed samples to the pristine samples as in Equation (1):

$$\text{Self-healing ability (\%)} = \frac{\sigma_b^{\text{healed}}}{\sigma_b^{\text{pristine}}} \times 100 \quad (1)$$

Reductive swelling It is possible to determine the various concentrations of polysulfidic, disulfidic and monosulfidic cross-links present within a sulfur cured rubber by exposure to thiols.^{26–29} Initially for each rubber, 0.2 g of rubber was swollen in toluene for 72 hours and the cross-link density calculated, as previously discussed. To then cleave the polysulfidic cross-links, a new sample of 0.2 g of rubber was exposed to 0.2 M solution (10 mL) of 2-propanethiol in piperidine under argon for 6 hours at 25 $^{\circ}\text{C}$, after which the solvent was removed *in vacuo* and the rubber was dried to constant weight. The cross-link density after cleavage was then determined as before. In order to cleave both polysulfidic and disulfidic cross-links, another 0.2 g was treated with 1 M (10 mL) 1-hexanethiol in piperidine under argon for 48 hours at 25 $^{\circ}\text{C}$. The solvent was then removed *in vacuo* and the rubber was dried to constant weight. The cross-link density after cleavage was then determined as before. See SI for results of reductive swelling.

RESULTS AND DISCUSSION

Cross-linked Epoxidised Natural Rubber (ENR) Two master batches of ENR with 0.8 wt % sulfur and 2.0 wt % DCP were manufactured. Dumbbells cut out of these materials were then subjected to self-healing testing at different temperatures and times with a minimum of three samples for each test. The conditions selected to enable comparison of self-healing across a range of materials and cross-linkers were as follows: 1, 2 and 24 hours at room temperature and 1, 2 and 24 hours at 120 $^{\circ}\text{C}$. The results of these initial self-healing tests, together with DMA and IR

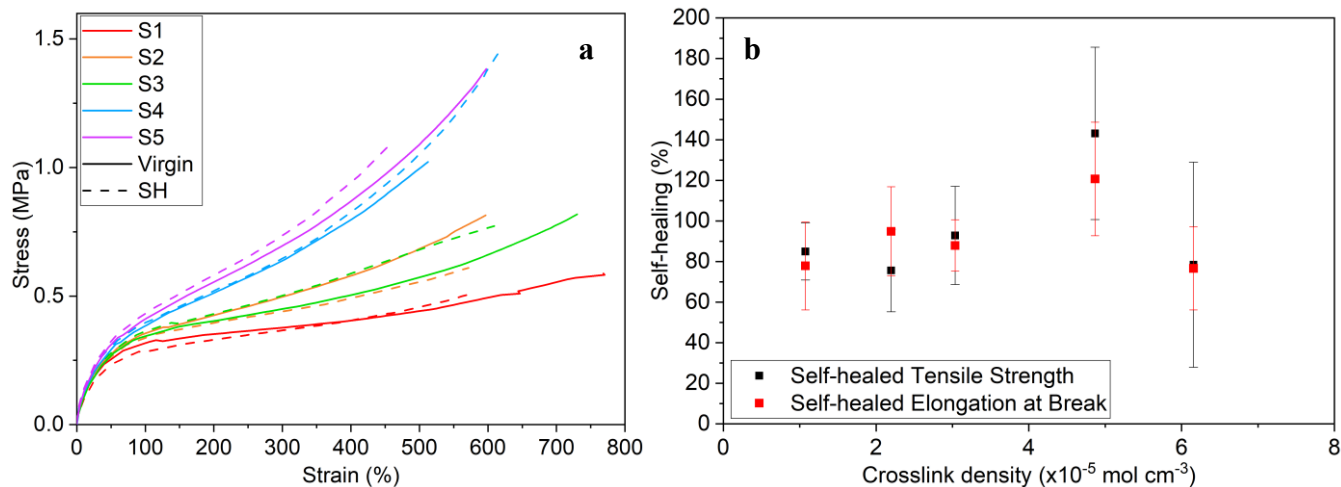


Figure 2 a) Tensile properties and b) self-healing versus cross-link density of ENR S1-S5 compounds after 1 hour at 120 °C. Key = virgin (solid line) and self-healed (SH) (dashed line).

data, can be seen in Figure 1 and Table S1 & S2 (see SI). Samples are indicated by curative/ self-healing time (hours)/ self-healing temperature (°C), e.g. S2/120 represents a sulfur cure for two hours at 120 °C. These results reveal that there is no significant self-healing at room temperature for either curing system, even after 24 hours. The tensile strength is recovered in the S-cured ENR by only approximately 30 % at room temperature, and in DCP-cured ENR to approximately 10 %. Meanwhile elongation at break recovery is very low at about 5 % in both systems.

However, heating at 120 °C has a dramatic effect on the self-healing ability. At this temperature both the hydrogen bonding and dynamic disulfide bridges should be disrupted and the polymer chains are free to flow past each other, allowing for chain interdiffusion and bond reformation.³⁰⁻³⁴ The S-cured samples show that the self-healing after 1 hour is markedly improved, with a tensile strength recovery of 93 % and elongation at break recovery of 88 %. Increases for DCP-cured ENR can also be observed, but to a lesser extent. Although the high temperature method has positive effects over 1 and 2 hours, the samples exposed for 24 hours suffer deleterious effects similar to those seen in thermal oxidation studies of ENR.³⁵ It has been reported that at 120 °C acid-catalyzed ring-opening of the epoxides results in the ENR becoming more brittle and stiff through introduction of ether, carboxylate and hydroxyl functionalities.³⁵ This is most clearly reflected in the broad $\tan \delta$ peak shifted to high temperatures in Figure 1b, which supports a large increase in the cross-link density due to the formation of new ether bonds. Ether peaks are present in the IR spectrum in Figure 1c at 1050 cm^{-1} , as well as a carboxyl peak at 1700 cm^{-1} and 3400 cm^{-1} for hydroxyl groups. These peaks are also present in the IR spectrum of DCP-cured ENR for 24 hours (Figure 1f). Consistent with this interpretation, a broadening and shifting of the $\tan \delta$ peak is also observed in Figure 1e.

From these data, self-healing for 1 hour at 120 °C was examined to further probe the self-healing mechanism. A range of sulfur-cured ENR samples were prepared with

varying sulfur content (ENR S1-S5, Table 1). The cross-linking density was calculated using the Flory-Rehner equation (via swelling in toluene), resulting in values from $1.1 \times 10^{-5} \text{ mol cm}^{-3}$ to $6.2 \times 10^{-5} \text{ mol cm}^{-3}$. Self-healing performance remains high for all samples (>76%, see Table S4) as revealed by tensile testing (Figure 2a), which indicates that chain interdiffusion is efficiently occurring within the one hour of healing at 120 °C, facilitating recovery of the entanglements.

Figure 2b highlights that a maximum in self-healing performance occurs at cross-link density of approximately $5 \times 10^{-5} \text{ mol cm}^{-3}$, suggesting that good material properties do not always need to be compromised to achieve high levels of self-healing performance. Self-healing values greater than 100 % are reported because of the introduction of mono-sulfidic bonds during heating in the self-healing process. This was confirmed by reductive swelling experiments which will be discussed later in this work. The relationship between cross-linking density and self-healing performance has been discussed previously,^{10,12,25,36} but to our knowledge the direct control of cross-link density to maximize self-healing performance has not been explored explicitly for elastomers. Self-healing efficiency is affected by the ability of polymer chains (and therefore broken cross-links) to diffuse across a cut and also by the availability of broken cross-links to enable a cross-link to reform. These two factors are competing: for increasing cross-link density, diffusion decreases, whereas the availability of broken cross-links increases. Therefore, a maximum self-healing efficiency is observed for a level of cross-link density at which these two competing factors balance (Figure 3). The level of cross-linking required for optimum self-healing efficiency will depend on the nature of the elastomer and the dynamic bond as well as on the conditions of self-healing.

To further clarify the role of dynamic cross-links in self-healing of rubbers, a range of DCP-cured ENR samples were prepared (Table 2) in which the carbon-carbon cross-links are not dynamic and cannot, therefore, reform

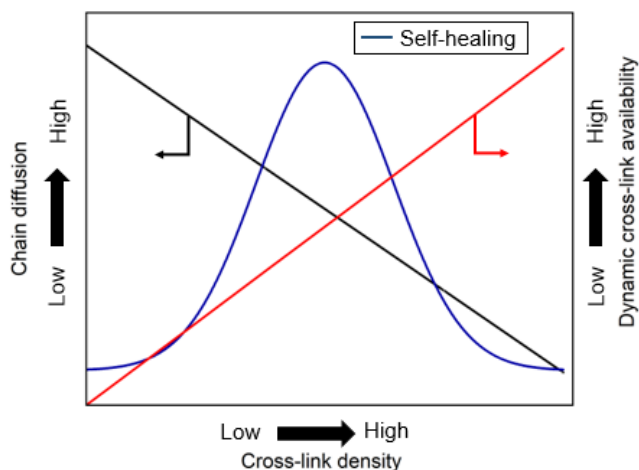


Figure 3 Qualitative representation of the competing factors that produce a maximum in the self-healing performance of rubbers cured with dynamic cross-links.

(Figure 4). This should demonstrate the autonomic behavior of cross-linked ENR, thereby allowing the additional contribution of dynamic sulfur cross-links to be estimated. As expected, the DCP-cured ENR shows a steady decrease in self-healing performance with increasing cross-link density with no significant maximum observed at intermediate cross-link density (Figure 5a); this is in contrast to the behavior described above for sulfur cured ENR (Figure 2b). This highlights that chain diffusion, which decreases as cross-link density increases, is the only contribution to self-healing (black line, Figure 3). Figure 5b highlights the different behavior between these two cross-linking systems and provides an estimate of the underlying self-healing ability (red line) and therefore the contribution to self-healing of dynamic cross-links in the sulfur system (shaded region). This supports the relationship described in Figure 3, highlighting that it is possible to optimize self-healing through cross-link density to achieve better materials.

The maximum for self-healing in sulfur-cured ENR was

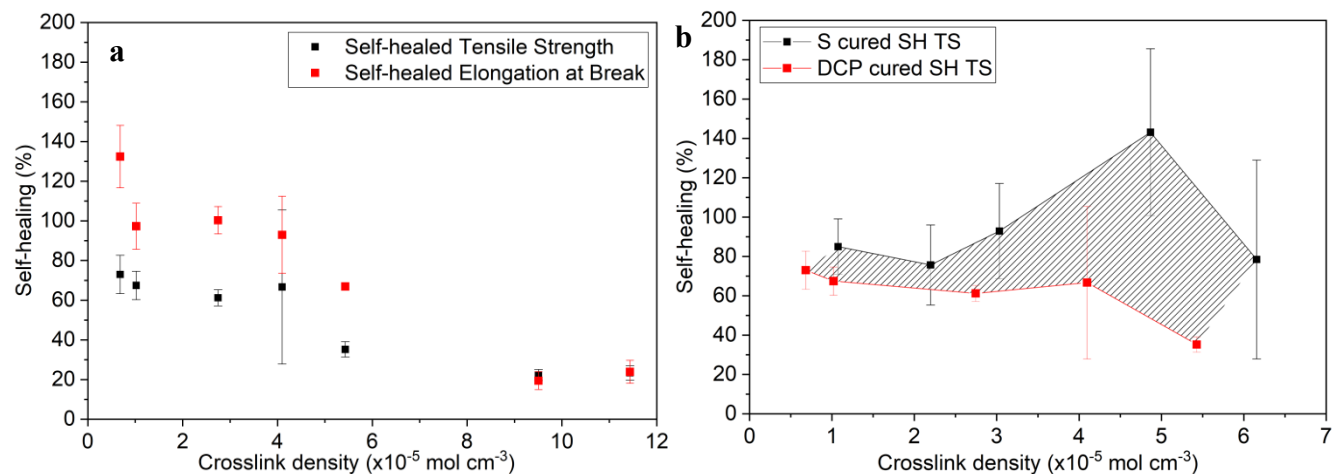


Figure 5 a) Self-healing of tensile properties in DCP-cured ENR D1-D7 compounds after 1 hour at 120 °C; b) isolation of the contribution to self-healing from dynamic cross-links in sulfur-cured ENR.

Dynamic sulfur cross-links Static C-C cross-links

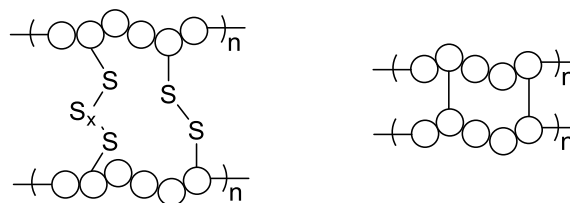


Figure 4 The dynamic and static cross-links investigated in this work

observed at a lower cross-linking density in this work than Cheng *et al.*¹² After reductive swelling experiments a sulfur-cured ENR sample partially dissolved, but the majority was retained as a gel suggesting the presence of mono-sulfidic cross-links (Table S11, S1) which are known to hinder chain diffusion.²⁶⁻²⁹ As Cheng *et al.* employed disulfide cross-linkers in their work, these mono-sulfidic cross-links could explain the difference in cross-link density for the peak of maximum self-healing between these works. They also explain why self-healing values >100% are reported (Figure 2b) as the presence of these cross-links results in higher tensile strengths than in the virgin samples.

Further characterization of the systems described was carried out by DMA and FTIR spectroscopy. It is interesting to note that while the self-healing performance is dependent upon the cross-link density, there is little variation in the viscoelastic properties across the range of samples investigated (Figure 6). This suggests that $\tan \delta$ is not a useful parameter for predicting self-healing performance and techniques that reveal the cross-link density of a sample more directly, such as double quantum NMR spectroscopy or swelling as in this analysis, are more appropriate predictors of self-healing performance. Similarly, little variation in FTIR spectra across the range of samples studies suggests that the self-healing performance is not influenced by changes in hydrogen bonding characteristics of the system.

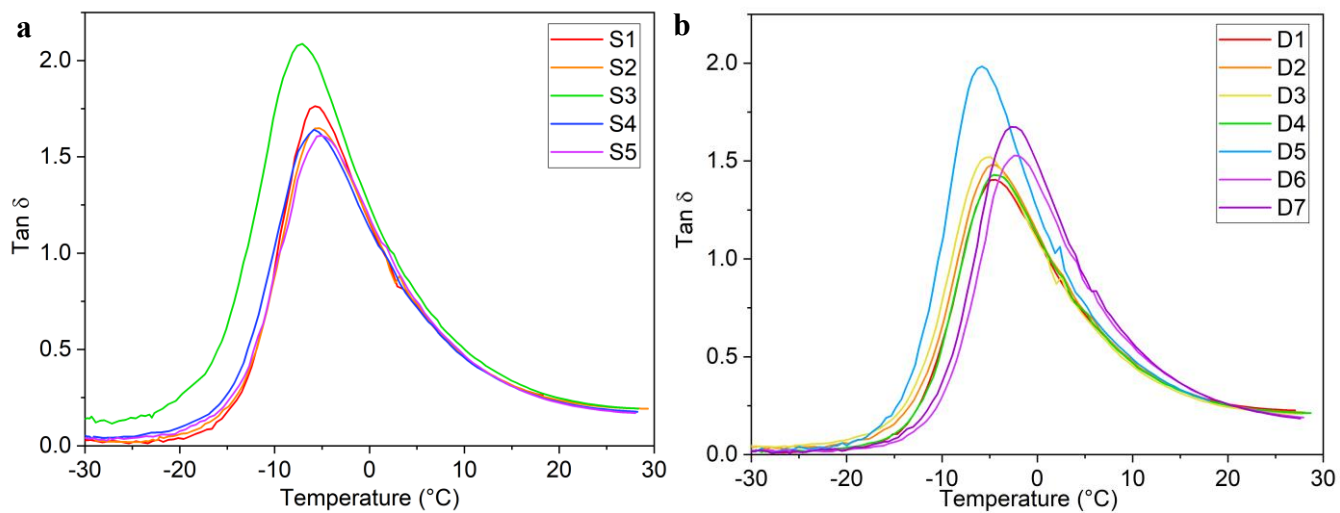


Figure 6 Tan δ data from DMA for ENR samples a) S1–S5 and b) D1–D7.

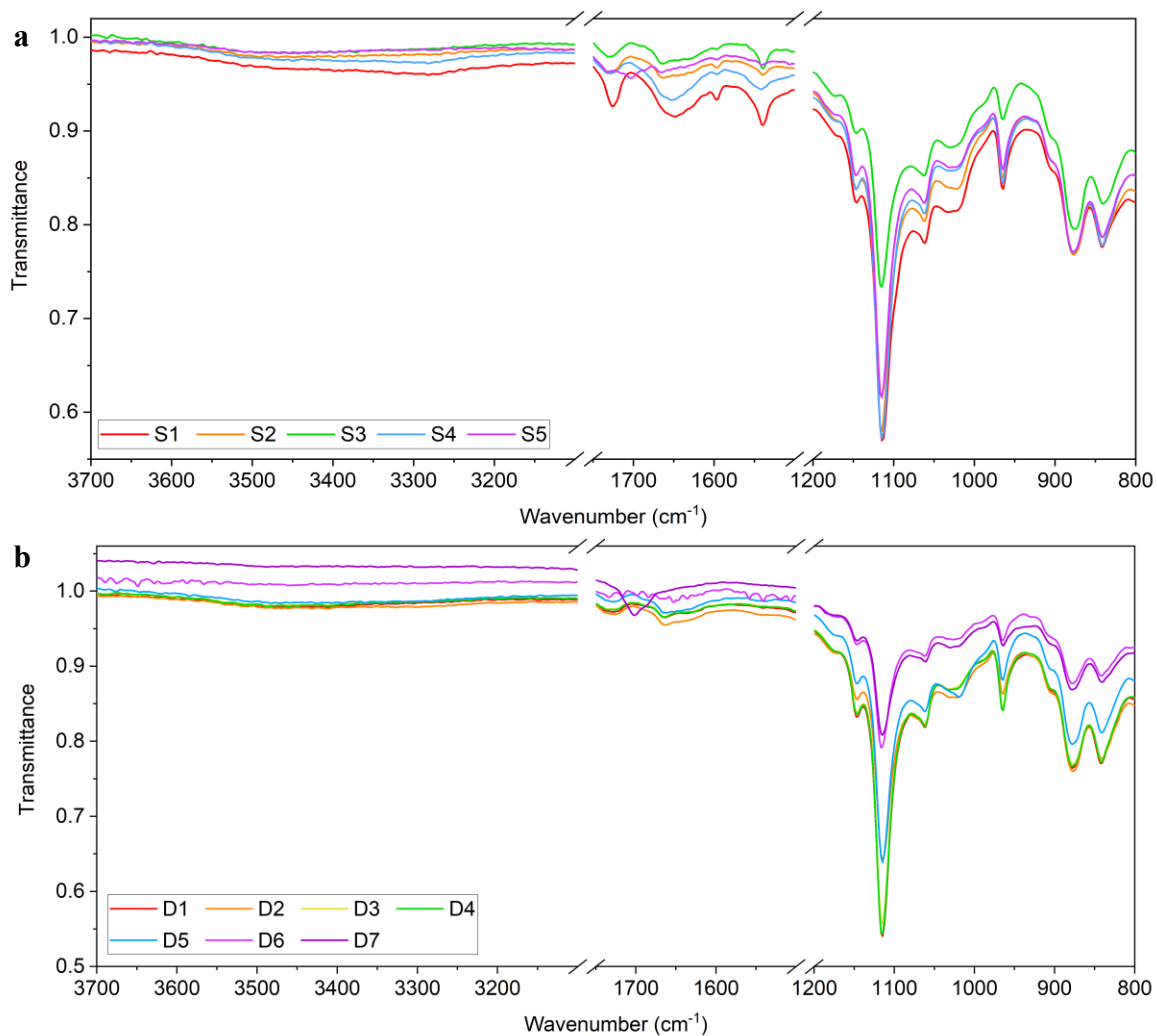


Figure 7 FT-IR spectra of ENR samples a) S1–S5 and b) D1–D7. Spectra cut to show regions of polar groups: 3500–3200 cm⁻¹ (hydroxyl), 1750–1600 cm⁻¹ (carboxyl), 1100–1000 cm⁻¹ (ether) and 900–800 cm⁻¹ (epoxide)

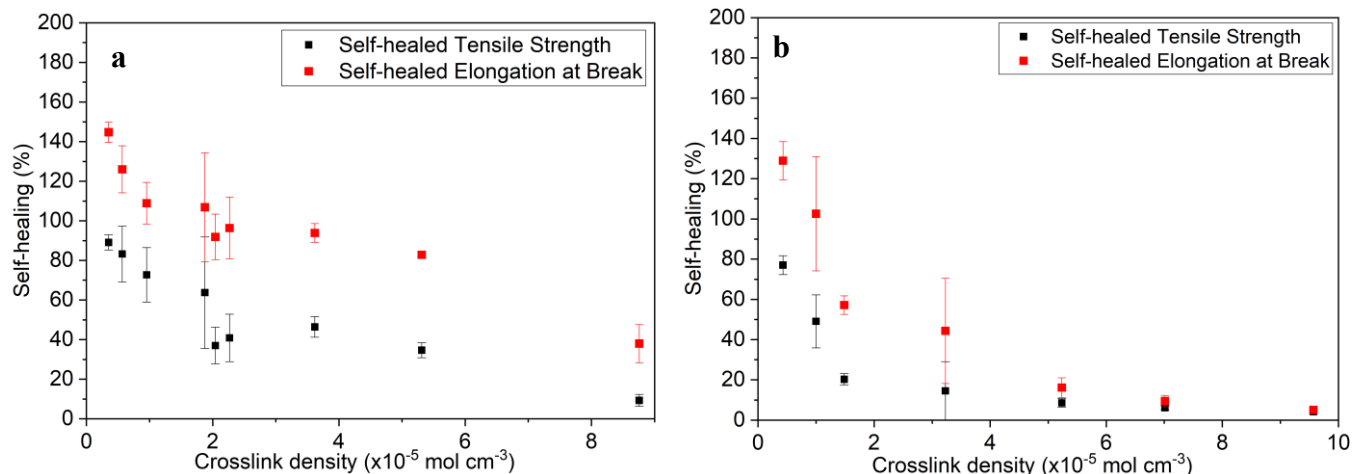


Figure 8 Self-healing of tensile properties after 1 hour at 120 °C in a) sulfur-cured NR (S₁–S₉); b) DCP-cured NR (D₁–D₇)

Cross-linked Natural Rubber (NR) Samples were prepared with NR to explore the generality of the relationship between cross-link density and self-healing performance. As for ENR, two sets of samples were prepared; sulfur-cured NR (S₁–S₉, Table 3) and DCP-cured NR (D₁–D₇, Table 4). Figure 8 shows a decrease in self-healing performance for sulfur-cured NR as well as for DCP-cured NR across the range of cross-link densities examined. Indeed, the DCP-cured natural rubber shows little discernable self-healing ability across a wide range of cross-linking densities. Self-healing in DCP-cured NR can only occur via chain diffusion and this is limited to low cross-link densities. As highlighted in Figure 9a, the decrease for the sulfur-cured NR samples is in contrast to the results for S-cured ENR, for which a distinct maximum in self-healing performance was apparent. The lack of a maximum is proposed to be due to reduced chain diffusion dominating the self-healing performance in NR (Figure 3). Despite there being no obvious maximum in the self-healing performance, a plot comparing S- and DCP- cured NR does reveal an enhancement in self-healing

performance due to the dynamic cross-linking of the former (Figure 9b). Although at very low and very high cross-link densities the two systems are similar, at intermediate values, a significant contribution to self-healing performance due to the dynamic sulfur cross-links can be discerned.

Reductive swelling experiments were carried out on a sulfur-cured NR sample (Table S₁₁, S₁). This sample fully dissolved after treatment with 1-hexanethiol suggesting that it only contained polysulfidic and disulfidic linkages. As no monosulfidic cross-links are present, this suggests that the self-healing performance seen in Figure 8a is the best that can be achieved with sulfur-cured NR under these conditions. However, Hernández *et al.* achieved self-healing of 80 % with sulfur-cured NR at higher cross-link density values than reported in this work by using conditions of 70 °C for 7 hours.²⁵ This highlights that different conditions yield different absolute values of self-healing and that this should be taken into account when assessing the application of a self-healing rubber product.

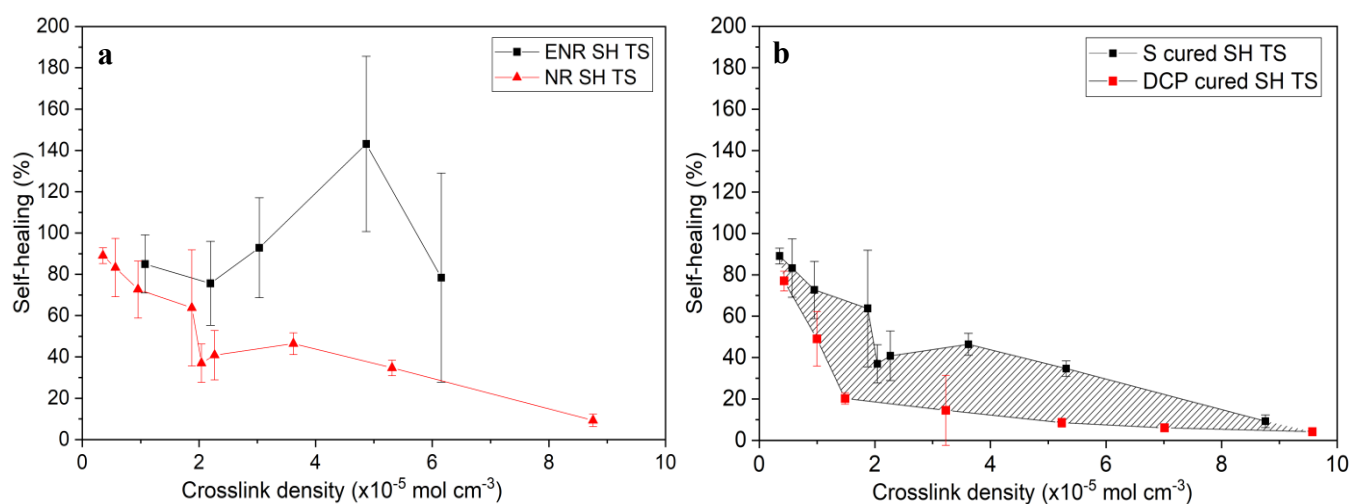


Figure 9 a) Comparison of the self-healing performance for sulfur-cured ENR and sulfur-cured NR; b) Isolation of the contribution to self-healing from dynamic cross-links in sulfur-cured NR .

Conclusions

This work has compared self-healing of dynamic cross-links (sulfur-cured) and static cross-links (DCP-cured) in epoxidised natural rubber (ENR) and natural rubber (NR). Materials were prepared with a range of cross-linking densities, leading to the demonstration of a direct relationship between cross-link density and self-healing performance. Thus, the ability to directly influence self-healing performance through variation of the cross-link density was demonstrated. This is a rare example of control of self-healing properties in elastomers. Comparison of the dynamic and static cure systems over the same cross-link density range revealed an enhancement of self-healing due to dynamic cross-linking and enabled the contribution of this effect to self-healing performance to be estimated. Sulfur-cured ENR was also shown to have superior self-healing performance relative to sulfur-cured NR under the conditions tested.

Although the focus of this work has been on natural rubber, we highlight the importance of control over cross-linking density in achieving the optimal balance between mechanical properties and self-healing performance of cross-linked polymers in general. These results contribute to the growing understanding of self-healing processes for future application of sustainable materials in both academic and industrial contexts.

ASSOCIATED CONTENT

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All authors have given approval to the final version of the manuscript.

Funding Sources

Funding for this research was supported jointly by the EPSRC and by Artis.

ACKNOWLEDGMENT

James Boden would like to acknowledge Antonio Cerdán and Martyna Pichla for compounding the materials within this work and Alison Jones for performing the tensile testing. Also thanks to Dr Vincent Coveney for helpful discussions.

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ABBREVIATIONS

S – sulfur, DCP – dicumyl peroxide, SH – self-healing, ENR – epoxidized natural rubber, NR – natural rubber.

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Swelling and cross-link density measurement, additional characterization data and tensile properties of compounds and reductive swelling results.

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