

# Understanding the Effects of Cross-Linking Density on the Self-Healing Performance of Epoxidized Natural Rubber and Natural Rubber

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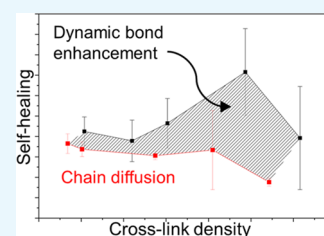


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Supporting Information

**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 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. Epoxidized 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 and sulfur to provide realistic models of commercial rubber formulations is described, and a cross-linking density of  $5 \times 10^{-5} \text{ mol cm}^{-3}$  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 rubber. The material has high elasticity, high tensile strength, and low heat build-up; however, it also has low oil resistance and gas permeability.<sup>1,2</sup> Epoxidation of NR to create epoxidized natural rubber (ENR) improves these disadvantageous properties while retaining many of the positive properties of NR.<sup>1,3</sup> ENR exists commercially in two forms, ENR25 and ENR50, which contain 25 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.<sup>2,3</sup>

In this context, ENR has a range of applications from adhesives to tires and other automotive parts.<sup>2,4</sup> While its chemical and mechanical properties have been examined for more than 40 years,<sup>5–7</sup> 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<sup>8,9</sup> and for self-healing applications.<sup>10–15</sup> Self-healing of polymeric materials is a highly desirable property and is defined as the capability of a material to recover from physical damage.<sup>16,17</sup>

ENR can be cured using the same established chemistries as NR and other rubbers, typically sulfur or dicumyl peroxide

(DCP) cures.<sup>4</sup> 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.<sup>18,19</sup> In addition to these curing methods in common with NR, it has also been demonstrated that ENR can be cured with dicarboxylic acids<sup>20–23</sup> or with zinc acrylate *via* an oxa-Michael reaction.<sup>24</sup> 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.<sup>23</sup> 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%.<sup>12</sup> Self-healing was achieved through dynamic disulfide bridges which have a low bond dissociation energy that promotes a disulfide metathesis reaction.

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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 Hernández *et al.*, and it was concluded that while the ratio was important to the self-healing performance, the main limiting factor was the sulfur content as the samples with lower sulfur content reached higher self-healing performance despite similar ratios as other samples.<sup>25</sup>

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.<sup>10</sup> 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 the 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 the cross-linking density and self-healing performance has not been examined in elastomers. Here, we examine self-healing in ENR and NR compounded with different curing systems in 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 SECTION

ENR (Ekoprena, 50 mol % epoxidation) was received from the Tun Abdul Razak Research Centre (TARRC). NR (SMR CV60) was received from Corrie MacColl. Sulfur-cured and 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.<sup>10,25</sup> The commercial grade vulcanizing additives were used as received. Tables 1–4 show the master batches created in this

**Table 1. ENR Sulfur-Cured Compound Formulations in Parts per Hundred Rubber in Weight (phr)**

ingredient	composition (phr)				
	S1	S2	S3	S4	S5
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

study. The amount of cross-linking agent increases with the compound number. 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 mixer of 78 cm<sup>3</sup> 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 s prior to adding cure chemicals (including ZnO and 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  $T_{90} + 5$  min. Testing was conducted at 160 °C for 30 min following ASTM D5289. Samples were cut out of press-cured sheets to perform tensile testing and healing tests.

## MATERIAL CHARACTERIZATION

**Cross-Linking Density.** The cross-linking density in mol cm<sup>-3</sup> was evaluated through swelling of the cured compounds in toluene according to ASTM D471-12 and using the Flory–Rehner equation (see the Supporting Information).

**Dynamic Mechanical Analysis.** Temperature evolution of both storage and loss moduli of cured rubber blends were measured using a TA Instruments dynamical mechanical analyzer in a compression configuration. Samples were cut from the cured rubber sheets and were submitted to a 3 °C min<sup>-1</sup> ramp (single frequency 1 Hz, amplitude 20 μm). The temperature ranged from -30 to 30 °C for ENR samples and -70 to -10 °C for NR samples. See the Supporting Information for NR rubber sample data.

**Fourier Transform Infrared Spectroscopy.** Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer 100 Fourier transform spectrometer fitted with an ATR accessory. Spectrum data were analyzed using the OPUS software. Spectra were recorded in the wavenumber range 4000–400 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup> and 24 scans. See the Supporting Information for NR sample spectra and full spectra for ENR samples.

**Tensile Testing.** The mechanical properties of the NR 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 machine equipped with a Laserscan 200 instrument and a 500 N static load cell. The samples were stretched until failure at an extension rate of 500 ± 50 mm min<sup>-1</sup> under room temperature and humidity conditions. The 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 five samples for this characterization. See the Supporting Information 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 h at 120 °C to heal. The samples were equilibrated at room temperature for 30 min before tensile testing. The data reported represents the median of three samples. The self-

**Table 2. ENR DCP-Cured Compound Formulations**

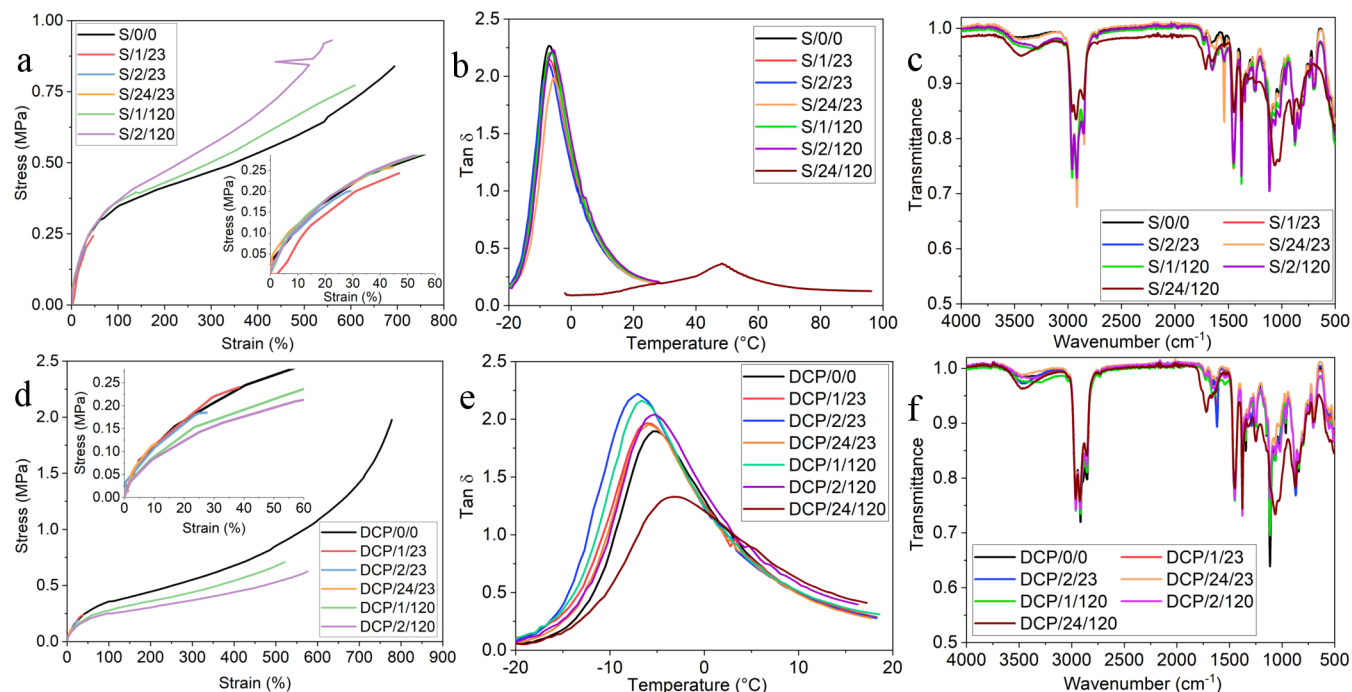
ingredient	composition (phr)						
	D1	D2	D3	D4	D5	D6	D7
ENR	100	100	100	100	100	100	100
DCP	0.3	0.5	1.0	1.5	2.0	2.7	3.4

Table 3. NR Sulfur-Cured Compound Formulations

ingredient	composition (phr)								
	S1	S2	S3	S4	S5	S6	S7	S8	S9
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)						
	D1	D2	D3	D4	D5	D6	D7
NR	100	100	100	100	100	100	100
DCP	0.3	0.5	0.8	1.0	1.5	2.0	2.6



**Figure 1.** Sulfur-cured ENR: (a) tensile properties; inset—magnified initial region; (b) tan  $\delta$  curves; (c) IR spectra. DCP-cured ENR: (d) tensile properties; inset—magnified initial region; (e) tan  $\delta$  curves; (f) IR spectra. Key: curative/SH time (hours)/SH temperature ( $^{\circ}\text{C}$ ) (e.g. S/2/120 represents a sulfur cure for 2 h at 120  $^{\circ}\text{C}$ ). See the [Supporting Information](#) for tensile data for 24/120.

healing ability was calculated as the ratio of the ultimate tensile strength of the healed samples to the pristine samples as in eq 1

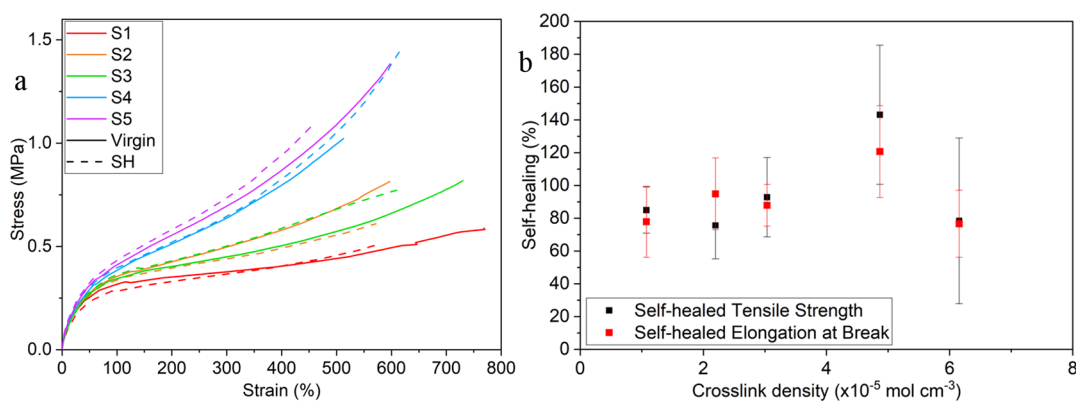
$$\text{Self-healing ability (\%)} = \frac{\sigma_b^{\text{healed}}}{\sigma_b^{\text{pristine}}} \times 100 \quad (1)$$

**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.<sup>26–29</sup> Initially for each rubber, 0.2 g of rubber was swollen in toluene for 72 h, and the cross-link density was 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 h 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 h 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 the [Supporting Information](#) for results of reductive swelling.

## RESULTS AND DISCUSSION

**Cross-linked 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 h at room temperature and 1, 2 and 24 h at 120  $^{\circ}\text{C}$ . The results of these initial self-healing tests, together with dynamic mechanical analysis (DMA) and IR data, can be seen in [Figure 1](#) and [Tables S1 and S2](#) (see [Supporting Information](#)).



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

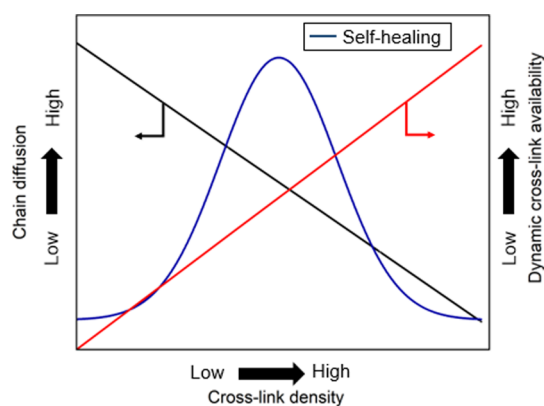
Samples are indicated by curative/self-healing time (hours)/self-healing temperature (°C), for example, S/2/120 represents a sulfur cure for 2 h at 120 °C. These results reveal that there is no significant self-healing at room temperature for either curing system, even after 24 h. The tensile strength is recovered in the S-cured ENR by only approximately 30% at room temperature and in DCP-cured ENR by 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.<sup>30–34</sup> The S-cured samples show that the self-healing after 1 h 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 h, the samples exposed for 24 h suffer deleterious effects similar to those seen in thermal oxidation studies of ENR.<sup>35</sup> 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.<sup>35</sup> 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  $\text{cm}^{-1}$ , as well as a carboxyl peak at 1700 and 3400  $\text{cm}^{-1}$  for hydroxyl groups. These peaks are also present in the IR spectrum of DCP-cured ENR for 24 h (Figure 1f). Consistent with this interpretation, broadening and shifting of the  $\tan \delta$  peak is also observed in Figure 1e.

From these data, self-healing for 1 h at 120 °C was examined to further probe the self-healing mechanism. A range of sulfur-cured ENR samples were prepared with varying sulfur contents (ENR S1–S5, Table 1). The cross-linking density was calculated using the Flory–Rehner equation (via swelling in toluene), resulting in values from  $1.1 \times 10^{-5}$  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 efficiently occurs within 1 h of healing at 120 °C, facilitating recovery of the entanglements.

Figure 2b highlights that a maximum in self-healing performance occurs at a 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 monosulfidic 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,<sup>10,12,25,36</sup> 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: as cross-link density increases, chain 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 the self-healing of rubbers, a range of DCP-cured ENR samples were prepared (Table 2) in which the carbon–carbon cross-links are



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

not dynamic and cannot, therefore, reform (Figure 4). This should demonstrate the autonomic behavior of cross-linked

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

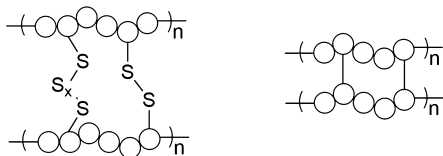


Figure 4. Dynamic and static cross-links investigated in this work.

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 indicates that chain diffusion, which decreases as the 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 observed at a lower cross-linking density in this work than in the study by Cheng *et al.*<sup>12</sup> After reductive swelling experiments, a sulfur-cured ENR sample partially dissolved, but the majority was retained as a gel suggesting the presence of monosulfidic cross-links (Table S11, Supporting Information) which are known to hinder chain diffusion.<sup>26–29</sup> As Cheng *et al.* employed disulfide cross-linkers in their work, these monosulfidic 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 FT-IR 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 the 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 FT-IR spectra across the range of sample studies suggests that the self-healing performance is not influenced by changes in hydrogen-bonding characteristics of the system (Figure 7).

**Cross-linked NR.** Samples were prepared with NR to explore the generality of the relationship between the 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 NR shows little discernible 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, Supporting Information). 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 that reported in this work by using conditions of 70 °C

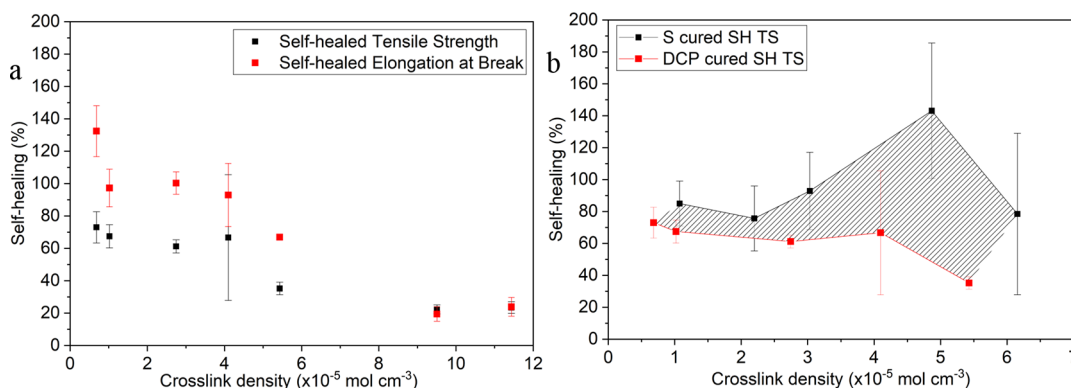


Figure 5. (a) Self-healing of tensile properties in DCP-cured ENR D1–D7 compounds after 1 h at 120 °C; (b) isolation of the contribution to self-healing from dynamic cross-links in sulfur-cured ENR.

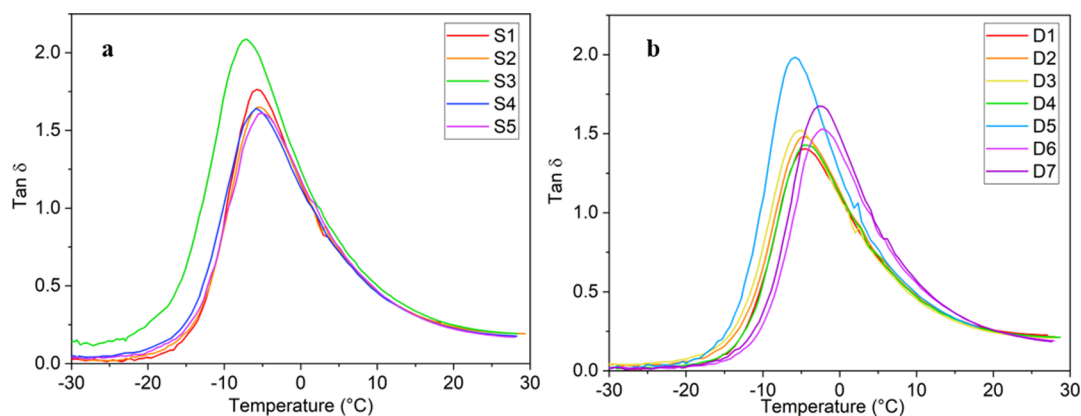


Figure 6. Tan  $\delta$  data from DMA for ENR samples. (a) S1–S5 and (b) D1–D7.

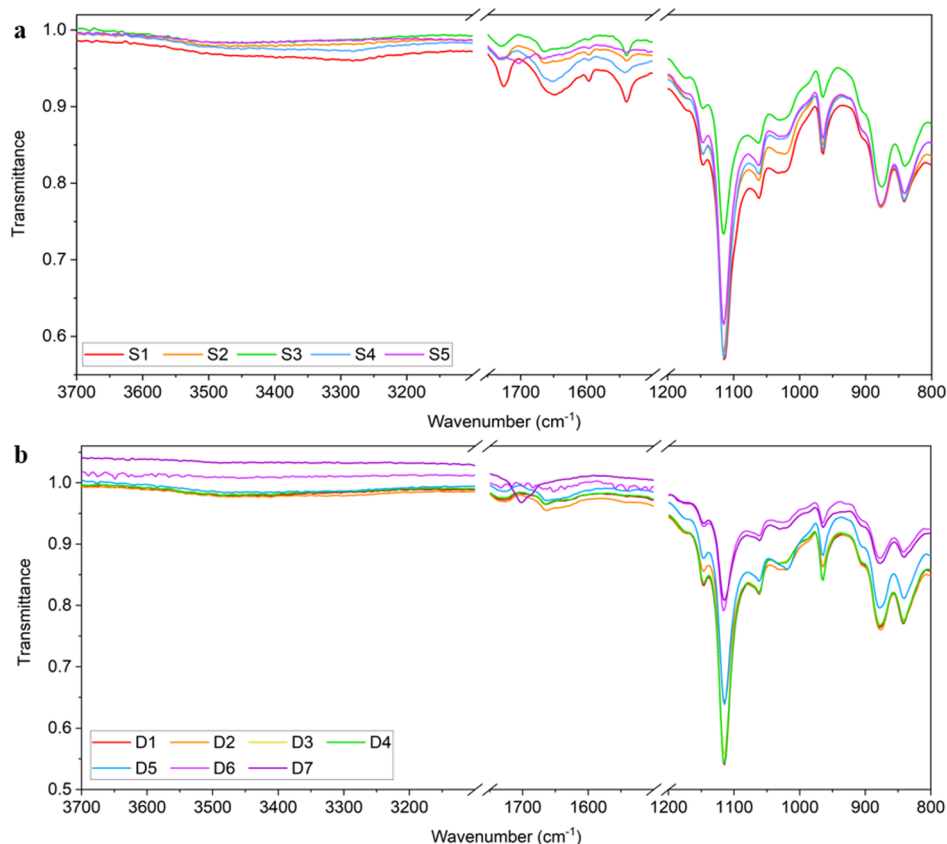


Figure 7. FT-IR spectra of ENR samples. (a) S1–S5 and (b) D1–D7. Spectra cut to show regions of polar groups: 3500–3200  $\text{cm}^{-1}$  (hydroxyl), 1750–1600  $\text{cm}^{-1}$  (carboxyl), 1100–1000  $\text{cm}^{-1}$  (ether), and 900–800  $\text{cm}^{-1}$  (epoxide).

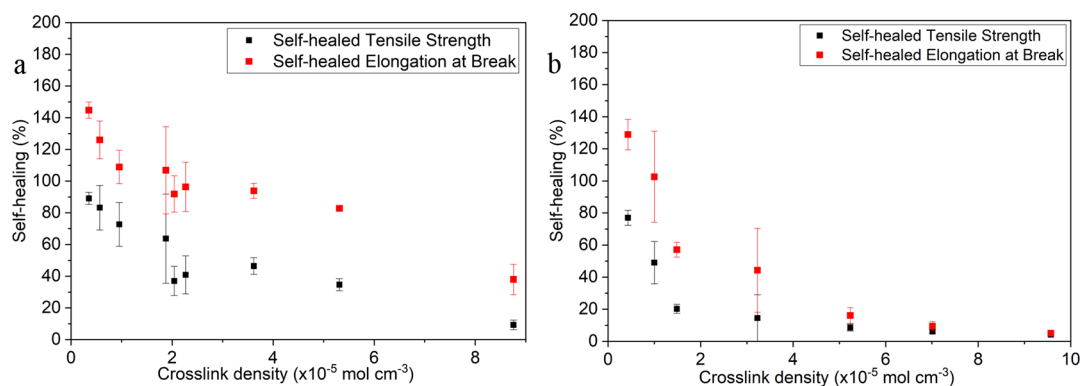
for 7 h.<sup>25</sup> This highlights that different conditions yield different absolute values of self-healing and that this should be taken into account when assessing the application of a self-healing rubber product.

## CONCLUSIONS

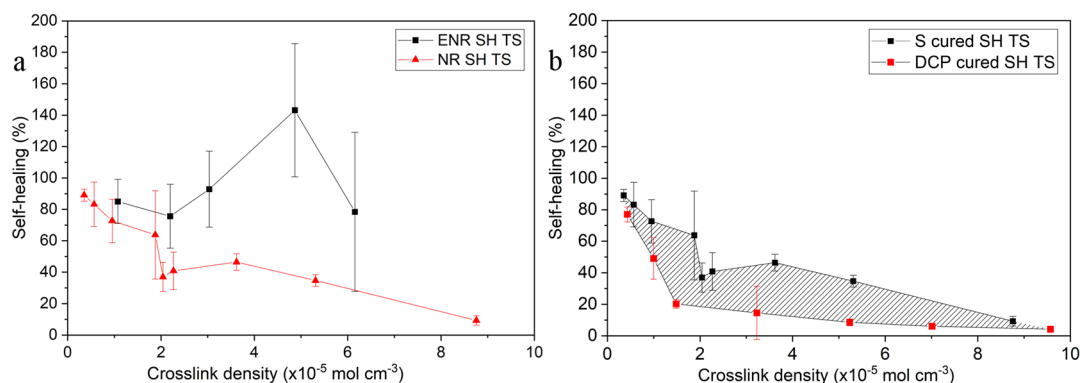
This work compared the self-healing of dynamic cross-links (sulfur-cured) and static cross-links (DCP-cured) in ENR and NR. Materials were prepared with a range of cross-linking densities, leading to the demonstration of a direct relationship between cross-link density and self-healing performance. Thus, 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 NR, 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.



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



**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.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c00971>.

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

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### Author Contributions

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

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

S, sulfur; DCP, dicumyl peroxide; SH, self-healed; ENR, epoxidized natural rubber; NR, natural rubber; TS, Tensile strength

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