

Quantifying and comparing the selectivity for crosslink scission in mechanical and mechanochemical devulcanization processes

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ABSTRACT: Devulcanization processes have potential to increase the economic value of ground tire rubber (GTR) derived from waste tires, although the chemistry of the devulcanization process is still poorly understood. This article presents a method, based on sol extraction and swelling measurements, for quantifying the selectivity for crosslink scission over main chain scission, and applies it to extrusion-based mechanical and mechanochemical devulcanization processes at various operating conditions. The mechanochemical devulcanization process, using diphenyl disulfide and process oil, resulted in a higher selectivity for crosslink scission than the mechanical devulcanization process. Furthermore, it was shown that the process oil, along with lower reaction temperature, in the mechanochemical devulcanization process was responsible for the increased selectivity, rather than the presence of diphenyl disulfide.

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INTRODUCTION

The problem of the accumulation of waste tires is receiving increased attention in the 21st century as a result of environmental concerns as well as the economic undesirability of discarding the valuable materials still present in tires at the end of their useful life.^{1,2} Attempts at recovering value from waste tires include combustion for energy recovery, pyrolysis (recovery of fuel or valuable chemicals),³ and devulcanization for material recycling.⁴ While energy recovery and typical fuel-recovery pyrolysis processes only recover a small amount of value from the high-value materials that go into the production of tires, devulcanization processes aim to recover more value by closed-loop recycling of rubber instead of downcycling.^{2,4}

The difficulty associated with recycling the rubber, comprising the majority of a waste tire's mass, is linked to the stability of the thermoset rubber network structure produced during vulcanization. Devulcanization processes aim to revert the thermoset rubber in waste tires into a secondary raw material that is thermoplastic in nature, and can be devulcanized into useful products. Devulcanization is an ideal case of rubber reclamation in which only the crosslinks of the network are broken, thus preserving the length of the original rubber polymer molecules.⁴ However, in practice, most devulcanization processes result in some extent of carbon-carbon (C-C) bond scission—thereby shortening the polymer molecules—which leads to degradation of the mechanical properties of the devulcanized rubber.⁴ Gener-

ation of recycled rubber that retains the mechanical properties of the original vulcanizate (tensile strength, elastic modulus, etc.) upon devulcanization, requires minimization of the shortening of the primary polymer chains by maximizing the selectivity toward sulfur-crosslink scission.

Various technologies have been developed in an attempt to generate high quality reclaimed rubber in an economically viable process. Some of the most commonly reported reclaiming technologies include mechanical,^{5–8} mechanochemical,^{9–12} thermal,¹³ ultrasonic,^{14–16} and microbial^{17,18} processes. Of particular interest in this study are the mechanical and mechanochemical devulcanization processes, both of which are defined by the mechanical shearing of ground tire rubber (GTR) at elevated temperatures. The distinction between mechanical and mechanochemical devulcanization is the addition of reclaiming agents to the GTR in the latter process, prior to mechanical shearing. The most prominent reclaiming agents for application to GTR are various disulfides dispersed in various oils.^{9–12} The advantage of using reclaiming agents is that the process can be conducted at lower temperatures and shorter reaction times are required,⁹ as well as apparent improvements in the selectivity for crosslink scission.⁴

Horikx's theory¹⁹ has been used widely in the devulcanization literature^{8,9,12,20,21} as a method for indicating the selectivity for crosslink scission during a devulcanization process. Horikx's theory describes the relationship between the sol fraction and

Table I. CCD of the Mechanical Devulcanization Experiments

Run	Barrel temperature (°C)	Screw speed (rpm)
M1	175	55
M2	190	37
M3	190	73
M4	225	30
M5	225	55
M6	225	80
M7	260	37
M8	260	73
M9	275	55
M10	225	55
M11	225	55
M12	225	55

the relative decrease in crosslink density of a crosslinked polymer network in two limiting cases of network breakdown: random scission of C—C bonds in the polymer chains and scission of the crosslinks. Therefore, a plot of experimental data against the limiting curves indicates the preference of a devulcanization process for C—C scission or crosslink scission based on the relative proximity of experimental points to the limiting curves.

The present study focuses on estimation of the sol fraction and crosslink density of reclaimed GTR for the purpose of further analysis by Horikx's theory. While there are newer methods for determining the crosslink density,^{22–24} swelling measurements were used in this study since they are still widely used in literature and have been shown to be consistent with NMR methods when the Kraus correction²⁵ is taken into account.²² Based on refined measurement methods for estimating the sol fraction of the polymer component of GTR, a quantitative selectivity parameter (based on Horikx's theory) is proposed for crosslink scission in devulcanization processes. This selectivity parameter is applied to both mechanical and mechanochemical devulcanization at various process conditions in a single screw extruder. The resulting analysis provides evidence of varying selectivity between different devulcanization processes and reaction conditions.

EXPERIMENTAL

Materials

GTR was supplied by Dawhi Rubber Recycling (Germiston, South Africa), consisting of (steel- and fibre-free) truck tire rubber ground to a particle size of 20 mesh (841 μm). Distillate Aromatic Extract (DAE) process oil was supplied by H&R Group (Durban, South Africa). Diphenyl disulfide (DPDS) of 99% purity was sourced from Sigma Aldrich (Schnellendorf, Germany). Acetone and toluene of 99.5 and 99.8% purity, respectively, were sourced from Kimix (Cape Town, South Africa).

Devulcanization Processes

All devulcanization experiments were conducted in a Brabender PLE-651 Plasti-Corder single screw extruder with a screw diameter of 19 mm and an L/D ratio of 25:1, equipped with a heated

6 mm strand die. The feedstock in all experiments was fed into the extruder using a screw conveyor set to feed at a rate of 3.6 kg/h. Both mechanical and mechanochemical devulcanization were conducted using the same equipment, using the procedures described below.

Mechanical Devulcanization. The mechanical devulcanization experiments consisted of feeding the GTR into the extruder operating at varying screw speed and barrel temperature, as summarized in Table I. A central composite design (CCD) was selected for the experimental design in order to allow response surface models (RSM) to be fitted to the experimental data within a minimal number of experimental runs. The experimental domain consisted of temperatures ranging from 175 to 275 °C and screw speeds from 30 to 80 rpm, based on typical values investigated by previous authors.^{5–8} For each experimental run, the process was operated for 10 minutes to reach steady state before samples were collected for analysis.

Mechanochemical Devulcanization. The feedstock for mechanochemical devulcanization was prepared by premixing the GTR, DAE (100 g/kg_{GTR}), and varying amounts of DPDS. A CCD was selected for the experimental design, using temperatures of 150–220 °C and DPDS concentrations of 5–30 g/kg_{GTR} as indicated in Table II. The experimental domain was chosen based on literature values.^{9,12,26,27} The premixed feedstock was allowed to rest for 30 minutes before beginning the experiment in order to allow the GTR to absorb the mixture of DPDS and DAE.²⁶ During mechanochemical devulcanization, the screw speed was kept constant at 30 rpm in order to keep the number of experimental runs to a feasible limit. Also the mechanochemical devulcanization experiments were allowed to run for 10 min to ensure steady state operation before collecting samples for analysis.

Characterization

Thermogravimetric Analysis. A proximate analysis of the GTR was performed by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC 1 thermal analyzer. The TGA program was set to ramp at 10 °C/min with isothermal segments at 110 °C (10 min), 275 °C (30 min), 600 °C (10 min), and 750 °C

Table II. CCD of the Mechanochemical Devulcanization Experiments

Run	Barrel temperature (°C)	DPDS (g/kg _{GTR})
C1	150	17.5
C2	160	8.70
C3	160	26.3
C4	185	5.00
C5	185	17.5
C6	185	30.0
C7	210	8.70
C8	210	26.3
C9	220	17.5
C10	185	17.5
C11	185	17.5
C12	185	17.5

(10 min), with values in brackets indicating the duration of the isothermal segments. A nitrogen flow of 100 mL/min was used from the beginning of the analysis until the end of the isothermal segment at 600 °C, after which the atmosphere was switched to oxygen flowing at 100 mL/min.

Solvent Extraction and Swelling Procedure. Samples of GTR and reclaimed rubber were weighed (m_{sample}) to a sample size of approximately 0.6 g before being enclosed in filter paper and subjected to Soxhlet extraction in acetone for 18 h in order to remove the majority of the soluble low molecular weight compounds. The samples were allowed to dry overnight in a fume hood and weighed again (m_{dry1}). The dried samples were then placed in toluene at room temperature for 72 h, with the toluene being replaced with fresh toluene every 24 h in order to ensure equilibrium swelling and maximum extraction of the residual soluble compounds and polymer fragments. The swollen samples were removed from the toluene and gently dabbed with absorbent paper to remove excess toluene between crumb particles and then weighed (m_{swollen}) before being dried in a vacuum oven overnight at 60 °C to constant weight (m_{dry2}). Measurements were conducted in triplicate in order to account for measurement error, which was found to be typically around 5% for both sol fraction and crosslink density measurements. Measurement errors have been indicated with error bars in Figures 6 and 7.

Sol Fraction. The gel fraction g is defined as the mass fraction (–) of the insoluble network material resulting from a network-forming polymerization or crosslinking process,²⁸ while the sol fraction s is the mass fraction of soluble polymer material, according to eq. (1)^{19,29}:

$$s = 1 - g \quad (1)$$

The majority of authors in the devulcanization field estimate the sol fraction as the soluble mass fraction of the GTR, according to eq. (2)^{7,8,10,21,27,30,31}:

$$s = \frac{m_{\text{sample}} - m_{\text{dry2}}}{m_{\text{sample}}} \quad (2)$$

Equation (2) usually results in an overestimate of the sol fraction since it does not account for the soluble non-rubber components in GTR such as process oils added during compounding. Some authors account for the extractable non-rubber components in GTR and reclaimed rubber by extracting them by Soxhlet extraction with acetone and then employing eq. (3)²⁰:

$$s = \frac{m_{\text{dry1}} - m_{\text{dry2}}}{m_{\text{dry1}}} \quad (3)$$

While eq. (3) accounts for the error due to the acetone-soluble components of the GTR, it fails to account for the presence of insoluble non-rubber components in GTR, such as carbon black.

Shi *et al.*¹² estimated the mass of the soluble portion of the rubber as the mass removed by the toluene extraction ($m_{\text{sol}} = m_{\text{dry1}} - m_{\text{dry2}}$) and then estimated the mass of the insoluble portion of the rubber (m_{gel}) by TGA of the dry sample after

swelling in toluene. The sol fraction was then determined according to eq. (4)¹²:

$$s = \frac{m_{\text{sol}}}{m_{\text{sol}} + m_{\text{gel}}} \quad (4)$$

An inherent assumption in the method of Shi *et al.* is that a perfect separation of the soluble non-rubber and rubber components is achieved by extraction in acetone and toluene, respectively.

In this article a mass balance approach is followed, similar to that of Shi *et al.*,¹² but without assuming perfect separation of rubber and non-rubber components, according to eq. (5):

$$s = \frac{m_{\text{sample}}(1 - e_N) - m_{\text{dry2}}}{m_{\text{polymer}}} \quad (5)$$

where m_{polymer} is the mass of the rubber polymers (g) in the sample before extraction with acetone and toluene, and e_N is the mass fraction (–) of extractable non-rubber components. The mass fraction (–) of extractable non-rubber components in the GTR was calculated according to eq. (6), assuming the sol fraction of the highly crosslinked polymer network of the initial GTR to be negligible by comparison to the extractable non-rubber compounds^{19,29}:

$$e_N = \frac{m_{\text{sample}} - m_{\text{dry2}}}{m_{\text{sample}}} \quad (6)$$

It was further assumed that no carbon black or ash was removed from samples during the solvent extraction procedures, which was confirmed by TGA to be a valid assumption.

Crosslink Density. The crosslink density of the rubber network was calculated by the swelling method using the Flory–Rehner equation³² in the mass-basis form given by Horikx¹⁹:

$$v_e = \frac{V_{R0} + \chi V_{R0}^2 + \ln(1 - V_{R0})}{\rho_R \underline{V}_S \sqrt[3]{V_{R0}}} \quad (7)$$

where v_e is the number of elastically effective network chains (commonly referred to as the crosslink density) per unit mass of the polymer network (mol/g), V_{R0} is the volume fraction (–) of the polymer in the swollen gel phase of the sample, χ is the Flory–Huggins interaction parameter [assumed to be 0.39 for toluene in natural rubber (NR), since the rubber in truck tires is predominantly NR],^{20,33} ρ_R is the density of the rubber polymer (assumed to be 920 kg/m³),²⁰ and \underline{V}_S is the molar volume of toluene (1.06×10^{-4} m³/mol).⁵

While the Flory–Rehner equation is useful for determining the crosslink density of unfilled networks, the presence of carbon black fillers in GTR restricts the swelling of the rubber network resulting in an error in the volume fraction of rubber in the swollen network.²⁵ Therefore, the actual volume fraction (V_{R0}) to be used in eq. (7) was calculated using the equation proposed by Kraus²⁵:

$$\frac{V_{R0}}{V_R} = 1 - \frac{\phi[3c(1 - \sqrt[3]{V_{R0}}) + V_{R0} - 1]}{1 - \phi} \quad (8)$$

where ϕ is the volume fraction (–) of the carbon black in the dry sample after swelling (assuming a density of 1850 kg/m³ for the filler)²⁰ and c is a correlation parameter (–) depending

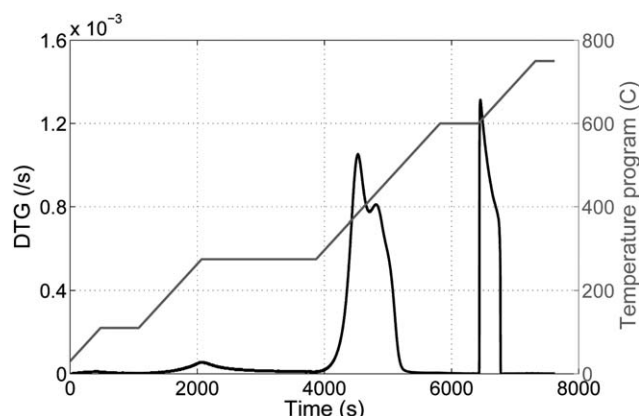


Figure 1. DTG trace generated from a sample of GTR using the specified temperature–time program with isothermal segments at 110, 275, 600, and 750 °C.

only on the type of filler. A value of $c=1.17$ has been used for GTR from truck tires.^{20,31} The apparent volume fraction of rubber in the swollen network (V_R) was calculated according to eq. (9):

$$V_R = \frac{m_R}{m_R + m_S \frac{\rho_R}{\rho_S}} \quad (9)$$

where m_R is the mass of rubber polymer in the swollen gel phase, calculated by mass balance, m_S is the mass of solvent taken up by the sample at equilibrium swelling, and ρ_S is the density of the swelling solvent (870 kg/m³ for toluene).⁵

The relative decrease in crosslink density was calculated according to eq. (10):

$$X = 1 - \frac{v_{e2}}{v_{e1}} \quad (10)$$

Horikx Analysis. Horikx's equations describe two limiting cases of network breakdown: random C—C bond scission and crosslink scission. In the case of random C—C bond scission, the relationship between the relative decrease in crosslink density (X) and the final sol fraction is described by eq. (11)¹⁹:

$$X_C = 1 - \frac{(1 - \sqrt{S_C})^2}{(1 - \sqrt{s_1})^2} \quad (11)$$

where X_C is the relative decrease in crosslink density in the case of C—C bond scission, s_1 is the sol fraction (–) of the rubber in GTR before devulcanization, and S_C is the theoretical sol fraction of the rubber at the corresponding value of X_C . Due to the difficulty of obtaining a precise experimental measurement of the initial sol fraction, s_1 was estimated according to eq. (12)¹⁹:

$$s_1 = \frac{(2 + \gamma_1) - (\gamma_1^2 + 4\gamma_1)^{0.5}}{2\gamma_1} \quad (12)$$

where γ_1 is the crosslinking index (–) of the rubber network in the GTR before devulcanization. The crosslinking index represents the average number of crosslinks per polymer molecule, and is calculated according to eq. (13)¹⁹:

$$\gamma = Mv_e + 2 \quad (13)$$

where M is the number-average molecular weight (g/mol) of the original polymer chains before the crosslinking process. Due to the difficulty of determining M for GTR, the initial number-average molecular weight of the rubber was assumed to be $M=200,000$ g/mol based on reports of M for masticated NR.^{9,19}

For selective crosslink scission, the relationship between the relative decrease in crosslink density and the sol fraction after devulcanization is described by eq. (14)¹⁹:

$$X_X = 1 - \frac{\gamma_2(1 - \sqrt{S_X})^2}{\gamma_1(1 - \sqrt{s_1})^2} \quad (14)$$

where X_X is the relative decrease in crosslink density in the case of crosslink scission, S_X is the theoretical sol fraction of the rubber at the corresponding value of X_X , and γ_1 and γ_2 represent the crosslinking index (–) before and after devulcanization, respectively.

RESULTS AND DISCUSSION

GTR Characterization

The composition of GTR was estimated by proximate analysis, performed using TGA. The TGA data, shown in Figure 1, allowed the determination of the mass fractions of moisture, volatiles, fixed carbon and ash in the GTR, as summarized in Table III.

The mass fraction of carbon black was assumed to be equal to the mass fraction of the fixed carbon (~ 0.299), as has been done previously.^{5,15,20} The volatiles fraction of the proximate analysis was comprised mostly of the rubber network and volatile non-rubber components,³⁴ although a reliable quantitative distinction between rubber and non-rubber components could not be obtained through TGA.

The polymer fraction of the GTR was approximated as the remaining mass of the GTR after accounting for the extractable non-rubber components, carbon black and ash, according to eq. (15):

$$w_p = 1 - e_N - w_{CB} - w_{ash} \quad (15)$$

where w_p , w_{CB} , and w_{ash} are the mass fractions (–) of the polymer, carbon black, and ash, respectively. The mass composition of the GTR is summarized in Table IV.

The crosslink density of the rubber network in the GTR was found to be $v_{e1} = 117 \times 10^{-6}$ mol/g using the Flory–Rehner

Table III. Proximate Analysis of the GTR used in this Study, Compared with Measurements by Other Authors

Component	Mass fraction (–)		
	This work	Mangili <i>et al.</i> ²⁰	Tao <i>et al.</i> ⁷
Moisture	0.005	0.009	Included in volatiles
Volatiles	0.634	0.624	0.64
Fixed carbon	0.299	0.300	0.30
Ash	0.063	0.072	0.06

Table IV. Composition of GTR used for the Basis of Analysis of Reclaimed Rubber

Component	Mass fraction (–)		
	This work	Mangili et al. ²⁰	Tao et al. ⁷
Extractable non-rubber (e_N)	0.076	0.094	0.06
Polymer (w_P)	0.562	0.530	0.58
Carbon black (w_{CB})	0.299	0.300	0.30
Ash (w_{ash})	0.063	0.072	0.06

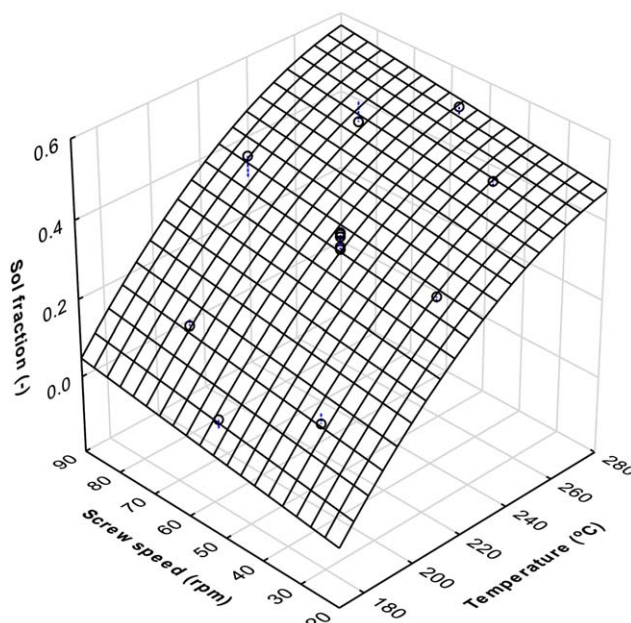
equation with Kraus correction.^{19,25} The corresponding sol fraction of the rubber at this crosslink density was calculated to be $s_1 = 0.00144$ using eq. (12), thus supporting the assumption of negligible sol fraction when calculating the composition of the GTR.

Sol Fraction of Reclaimed Rubber

The sol fractions for the samples from each experimental run were calculated using eq. (5) with the values in Table IV. It should be noted that the mass fractions in Table IV were corrected in order to account for the additives used in the mechanochemical devulcanization experiment by assuming that all of the DAE and the majority of the DPDS were extracted along with other soluble compounds.⁹

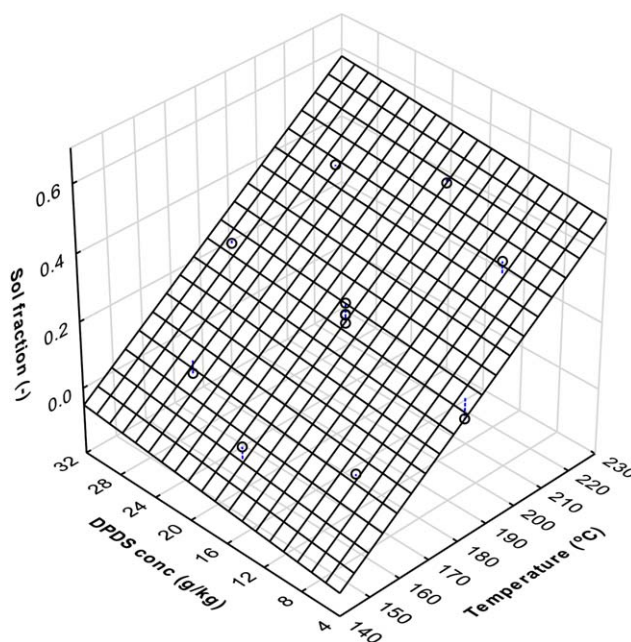
The sol fraction in reclaimed rubber from the mechanical devulcanization process increased strongly with increasing barrel temperature, with the gradient tapering off at higher temperatures (Figure 2). The gradient tapering could reflect an expected tangential approach to the theoretical maximum sol fraction of unity, although the data seems to reflect a tangential approach to a much lower sol fraction (~ 0.6). Alternatively, the gradient tapering could also be due to the devolatilization of non-rubber components at high extrusion temperatures (>260 °C), as suggested by TGA data in Figure 1. The peak in the DTG at temperatures from 220 to 275 °C is probably due to devolatilization of the extractable non-rubber components, since the moisture is removed at around 100 °C and typical rubber polymers present in GTR have been shown to devolatilize at temperatures beyond 300 °C.³⁵ While the TGA data suggests that the rubber polymers are stable up to 300 °C, the shearing forces and oxygen present in the extruder could also result in polymer degradation and burning at temperatures below 300 °C. Therefore, the measured sol fractions of samples extruded at high temperatures (>260 °C) are expected to be erroneously low, due to devolatilization of extractable non-rubber components, resulting in e_N being overestimated in the sol fraction analysis. Previous reports²⁷ have also noted a tapering gradient of sol fraction with increasing temperatures above 240 °C.

While mechanical devulcanization showed a tapering gradient of increasing sol fraction with increasing temperature, mechanochemical devulcanization did not show the same tapering behavior within the experimental domain (Figure 3). The absence of the tapering behavior in the case of mechanochemical devulcanization is consistent with the postulation of devolatilization of non-rubber components at high temperatures in

**Figure 2.** Sol fraction (–) of samples from the mechanical devulcanization experiments.

mechanical devulcanization, since the highest temperature used in mechanochemical devulcanization was 220 °C, at which point there appears to be negligible devolatilization shown by the DTG data in Figure 1.

The sol fraction increased strongly with increasing temperature during mechanochemical devulcanization, while the effect of the DPDS concentration on the sol fraction was considerably weaker, as seen in Figure 3. Previous reports confirm the strong

**Figure 3.** Sol fraction (–) of samples from the mechanochemical devulcanization experiments.

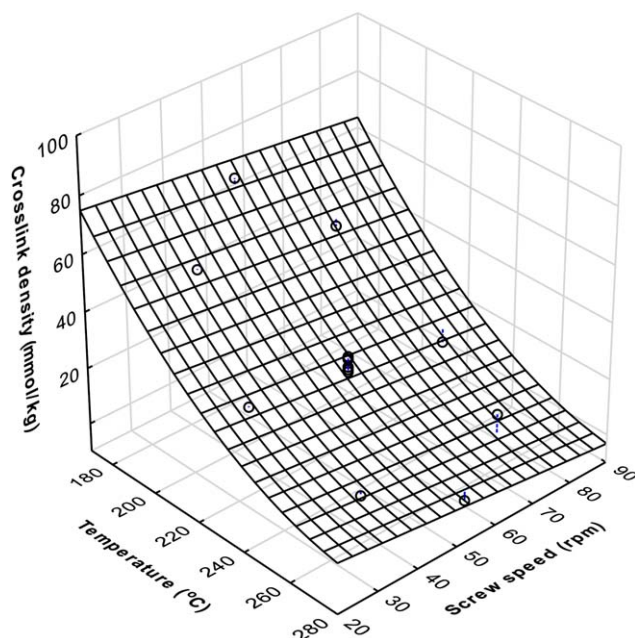


Figure 4. Crosslink density (mmol/kg) of samples from the mechanical devulcanization experiments.

influence of process temperature on the sol fraction of rubber reclaimed by the mechanochemical method.¹² Others have shown either a weak increase in the sol fraction with increasing disulfide concentration,⁹ or unclear effects of varying disulfide concentration.¹⁰

Crosslink Density of Reclaimed Rubber

Crosslink density results for the mechanical and mechanochemical devulcanization processes are given in Figures 4 and 5,

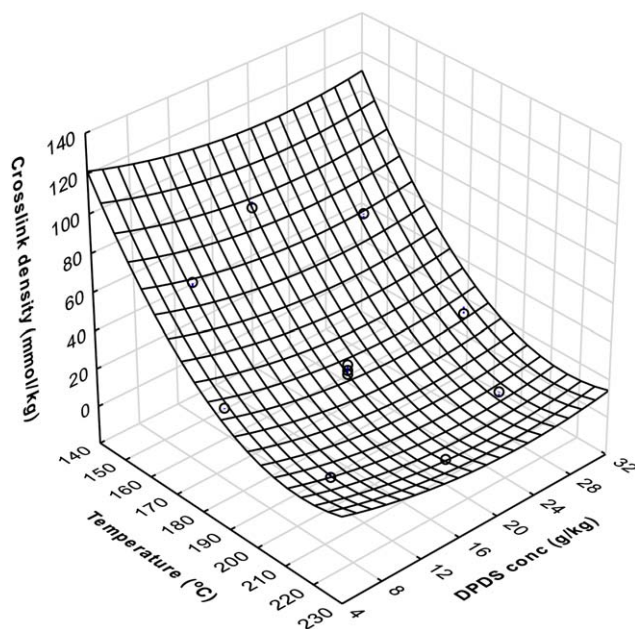


Figure 5. Crosslink density (mmol/kg) of samples from the mechanochemical devulcanization experiments.

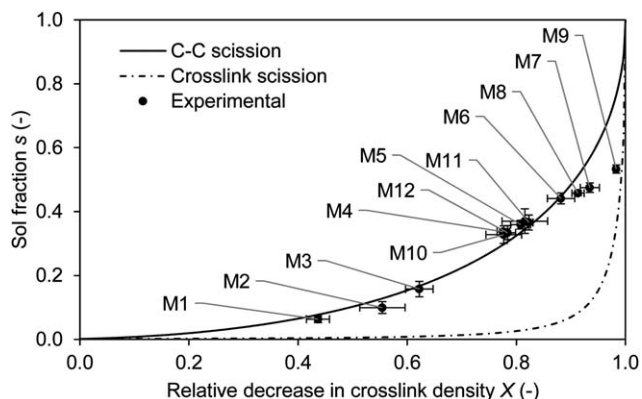


Figure 6. Horikx plot of data from the mechanical devulcanization experiment.

respectively. Increasing the barrel temperature of the extruder strongly reduced the crosslink density of the gel fraction of the reclaimed rubber product, in both the mechanical and the mechanochemical devulcanization. Higher screw speeds also resulted in lower crosslink density of the product in mechanical devulcanization, although the effect of screw speed was weak in comparison to the temperature effect. Previous studies^{6,7} using twin screw extruders have found the effect of screw speed on crosslink density to be stronger than that observed in this study, which is attributed to differences in shearing effects between single- and twin-screw extruders.³⁶ In the case of mechanochemical devulcanization, the DPDS concentration had a weak effect on the crosslink density of the product, which has been reported previously,⁹ despite the proposed benefits of disulfide inclusion on the selectivity for crosslink scission.^{4,9}

Horikx Analysis

The Horikx plots for the mechanical and mechanochemical devulcanization are presented in Figures 6 and 7, respectively. Mechanochemical devulcanization clearly shifted the data in the Horikx plot toward the crosslink scission curve, suggesting an improvement in the selectivity for crosslink scission in comparison to the mechanical devulcanization process. Such an increase in selectivity for crosslink scission would better preserve the

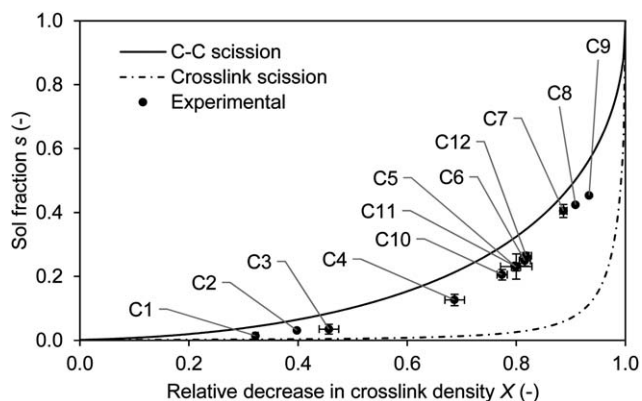


Figure 7. Horikx plot of the data from the mechanochemical devulcanization experiment.

Table V. Valid Correlation Range for the Kraus Correction Compared with Experimental Measurements

Sample	
M1	0.28
M2	0.30
M3	0.32
M4	0.40
M5	0.41
M6	0.47
M7	0.50
M8	0.48
M9	0.56
Valid range ²⁵	0–0.45

length of the polymer chains,¹⁹ thus yielding recycled rubber with better physical properties.^{12,37}

The three experimental points representing a very high level of network breakdown in the case of mechanical devulcanization (M7, M8, and M9) appear to suggest improved selectivity for crosslink scission because they lie closer to the crosslink scission curve. This apparent increase in selectivity was probably a result of the devolatilization behavior under these experimental conditions ($T > 260$ °C), as suggested by the increasingly significant devolatilization rate at $T > 260$ °C shown in the TGA data in Figure 1. It was also noted that the three points in question lay outside of the Kraus correction's correlation range,²⁵ as shown in Table V, which was expected to result in significant errors in the calculated crosslink density. Further research into the range of validity of Kraus' correction for reclaimed rubber will be required for application to cases involving this high level of network breakdown.

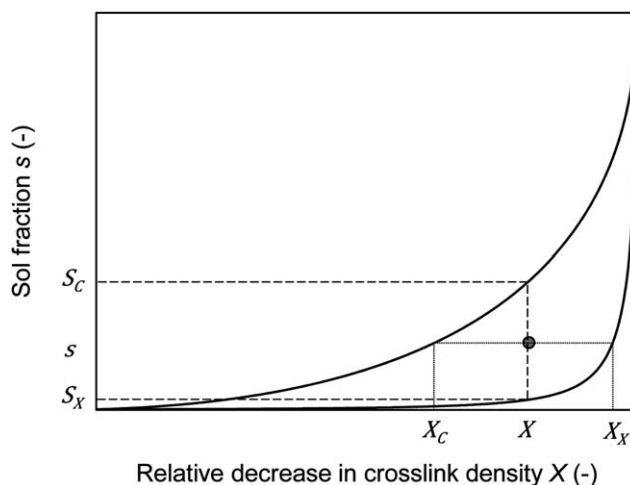
Quantification of Selectivity

Definition of Selectivity Parameters. The Horikx plots in Figures 6 and 7 gave a qualitative indication of the improved selectivity of the mechanochemical devulcanization process over the mechanical devulcanization process, by interpretation of the graphical data. In order to permit quantitative comparison of the variation of the selectivity as influenced by process parameters, quantitative selectivity parameters are developed based on Horikx's equations. Two possible approaches are considered: defining the selectivity parameter in the sol fraction (vertical) direction or in the crosslink density (horizontal) direction, as shown in Figure 8.

The sol fraction selectivity parameter (K_S) was defined using the value of the measured sol fraction (s) relative to the predicted sol fractions of the limiting cases (C—C scission and crosslink scission) at the measured crosslink density, according to eq. (16):

$$K_S = \frac{S_C - s}{S_C - S_X} \quad (16)$$

where S_C and S_X are the theoretical sol fractions for random C—C scission and selective crosslink scission, respectively, as a function of the measured relative decrease in crosslink density.¹⁹

**Figure 8.** Derivation of the selectivity parameters.

Therefore, the crosslink scission line of the Horikx plot corresponds to $K_S = 1$ while the C—C scission line corresponds to $K_S = 0$.

The selectivity parameter in the crosslink density direction (K_X) was defined using the measured decrease in crosslink density (X) relative to the corresponding values predicted by Horikx analysis at the same value of the measured sol fraction (s), according to eq. (17):

$$K_X = \frac{X - X_C}{X_X - X_C} \quad (17)$$

where X_C and X_X are the theoretical values of the relative decrease in crosslink density for C—C scission and crosslink scission, respectively, at the measured value of the sol fraction. Therefore, as in the case of K_S , the crosslink scission line corresponds to $K_X = 1$ and the C—C scission line corresponds to $K_X = 0$.

The overall selectivity parameter is then defined according to eq. (18):

$$K = \frac{K_S + K_X}{2} \quad (18)$$

The constants used for the calculation of the selectivity parameters in this study are reported in Table VI.

Comparison of Selectivity Parameters. Due to the uncertainty in the sol fraction and crosslink density measurements of some of the mechanical devulcanization experiments due to the devolatilization and errors in the Kraus correction, runs M7, M8,

Table VI. Initializing Values Used for Calculation of the Selectivity Parameters

Parameter	Value (unit)	Comment
M	200,000 (g/mol)	Molecular weight of rubber polymer before vulcanization
v_{e1}	117 (mmol/kg)	Initial crosslink density
γ_1	25.4	Initial crosslinking index
s_1	0.00144	Initial sol fraction

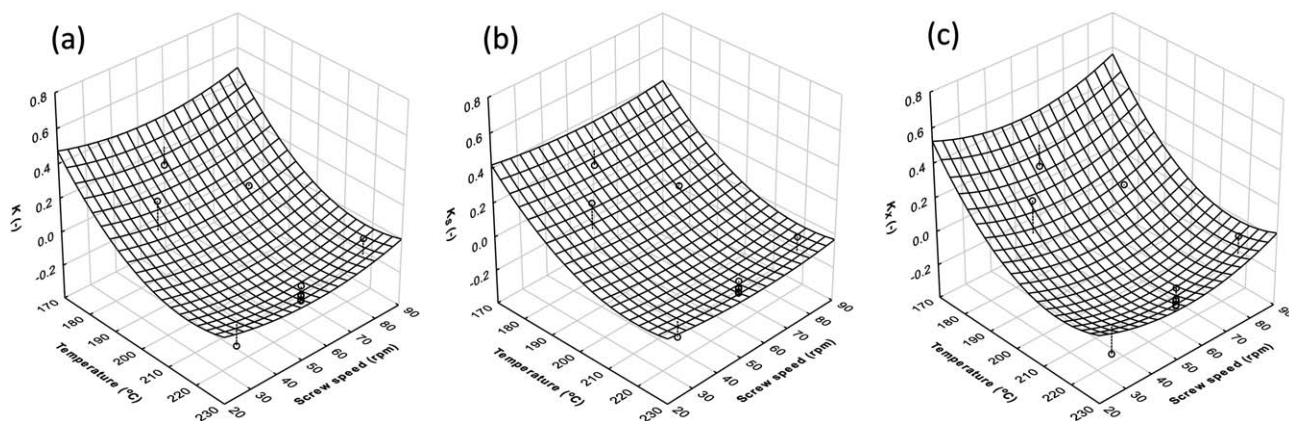


Figure 9. Selectivity plots over the mechanical devulcanization experimental domain, including the overall selectivity parameter K (a), vertical selectivity parameter K_S (b), and horizontal selectivity parameter K_X (c).

and M9 were excluded from further analysis. The selectivity plots over the experimental domain of the mechanical devulcanization experiments (Figure 9) showed a trend of decreasing selectivity with increasing temperature. No clear conclusion could be drawn on the effect of screw speed on the selectivity for crosslink scission. While all three selectivity parameters (K_S , K_X , and K) led to the same conclusion, K_X appeared to be more sensitive to experiment and measurement errors, as evidenced by the wide scatter of the data points in Figure 9(c).

Figure 10 shows that there was no significant variation of any of the selectivity parameters with varying DPDS concentration in the mechanochemical devulcanization experiments, although the selectivity decreased sharply with increasing reaction temperature. Shi *et al.*¹² investigated the performance of a mechanochemical devulcanization process in a two-roll mill at low temperature (<40 °C) and high temperature (180 °C). Their results showed a clear increase in the selectivity for crosslink scission at the lower temperature according to a Horikx plot, and those results are corroborated by the quantitative results in Figure 10.

The weak effect of both the screw speed and DPDS concentration on the selectivity parameters suggested that the temperature was the most important factor determining the selectivity for crosslink scission. Therefore, the lower temperatures

employed in mechanochemical devulcanization could account for part of the improved selectivity in comparison to mechanical devulcanization, although Figure 11 shows that there is still a higher selectivity in the case of mechanochemical devulcanization at comparable temperatures.

An increase in the concentration of DAE in the GTR fed to the extruder (0–150 g/kg_{GTR}), in the case of mechanochemical devulcanization without DPDS, was found to increase the selectivity for crosslink scission (Figure 12). Previous authors²⁶ have noted an increase in selectivity for crosslink scission when increasing the amount of oil used in a mechanochemical devulcanization process, which was attributed to an improvement in the dispersion of DPDS within the rubber network by the presence of increasing amount of process oil. The results in Figure 12 demonstrated that higher oil concentrations increased the selectivity for crosslink scission even in the absence of DPDS.

The higher selectivity for crosslink scission achieved when swelling the rubber with process oil could lead to superior mechanical properties of reclaimed rubber, due to better preservation of the molecular weight of the polymer chains.^{12,37} However, process oil added to GTR during devulcanization will remain in the reclaimed rubber, and may have a negative impact on the mechanical performance of the reclaimed rubber upon

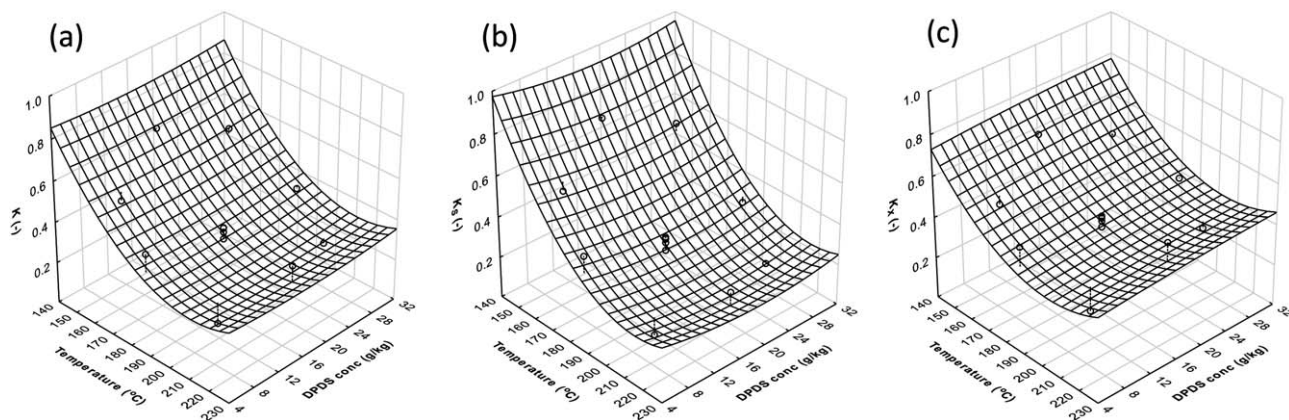


Figure 10. Selectivity plots over the mechanochemical devulcanization experimental domain, including the overall selectivity parameter K (a), vertical selectivity parameter K_S (b), and horizontal selectivity parameter K_X (c).

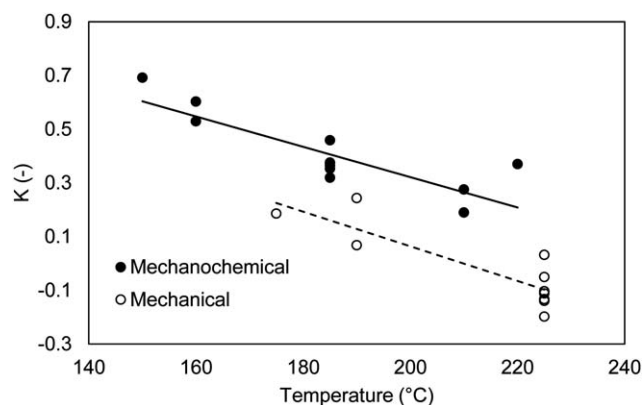


Figure 11. Difference in selectivity parameter between mechanical and mechanochemical devulcanization at comparable temperatures.

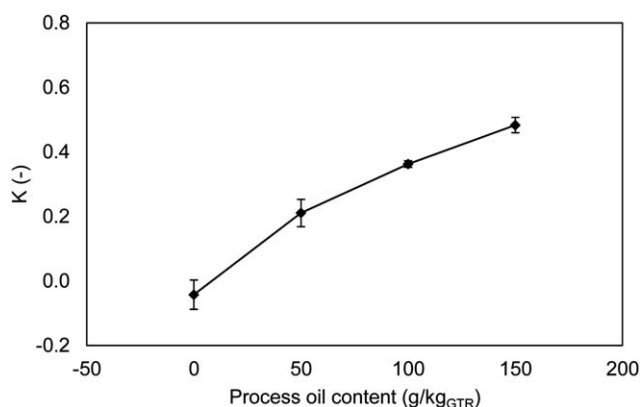


Figure 12. Variation of the selectivity parameter for mechanochemical devulcanization in the absence of DPDS with varying process oil content at constant temperature (200 °C) and screw speed (30 rpm).

revulcanization. If the swelling effect of the DAE on the rubber, rather than direct chemical reaction, is responsible for the increased selectivity for crosslink scission, then mechanical devulcanization processes employing supercritical CO₂ swelling could be expected to achieve excellent selectivity without the potential disadvantage of excess process oil remaining in the reclaimed rubber.²⁰

CONCLUSIONS

This study has shown the applicability of a selectivity parameter, K , based on Horikx's analysis of bond scissions in polymer networks, for quantifying the selectivity for crosslink scission in various devulcanization processes and conditions. The application of the selectivity parameter has shown that higher temperatures in the mechanical and mechanochemical devulcanization processes result in lower selectivity for crosslink scission, while the concentration of DPDS seems to have no significant effect on the selectivity for crosslink scission. Furthermore, it has been shown that a higher concentration of process oil added to the rubber feedstock prior to devulcanization causes a significant increase in the selectivity for crosslink scission. The effect of process oil on the selectivity for crosslink scission could account for the increased selectivity observed in the mechanochemical

process over the mechanical process, since the only other differences between the processes—DPDS concentration and screw speed—appeared to have no effect on the selectivity parameter. Further application of the selectivity parameter to the problem of characterizing reclaimed rubber could help with developing a clearer understanding of the relationship between the properties of reclaimed rubber and the performance of vulcanizates containing reclaimed rubber.

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REFERENCES

- Adhikari, B.; De, D.; Maiti, S. *Prog. Polym. Sci.* **2000**, *25*, 909.
- Ferrer, G. *Resour. Conserv. Recy.* **1997**, *19*, 221.
- Danon, B.; van der Gryp, P.; Schwarz, C. E.; Görgens, J. F. J. *Anal. Appl. Pyrol.* **2015**, *112*, 1.
- Myhre, M.; Saiwari, S.; Dierkes, W.; Noordermeer, J. *Rubber Chem. Technol.* **2012**, *85*, 408.
- Bilgili, E.; Arastoopour, H.; Bernstein, B. *Powder Technol.* **2001**, *115*, 277.
- Maridass, B.; Gupta, B. R. *Polym. Test.* **2004**, *23*, 377.
- Tao, G.; He, Q.; Xia, Y.; Jia, G.; Yang, H.; Ma, W. *J. Appl. Polym. Sci.* **2013**, *129*, 2598.
- Yazdani, H.; Karrabi, M.; Ghasmi, I.; Azizi, H.; Bakhshandeh, G. R. *J. Vinyl Addit. Technol.* **2011**, *17*, 64.
- Rajan, V. V.; Dierkes, W. K.; Joseph, R.; Noordermeer, J. W. M. *J. Appl. Polym. Sci.* **2007**, *104*, 3562.
- De, D.; Maiti, S.; Adhikari, B. *J. Appl. Polym. Sci.* **1999**, *73*, 2951.
- Zhang, X.; Lu, C.; Liang, M. *J. Polym. Res.* **2008**, *16*, 411.
- Shi, J.; Jiang, K.; Ren, D.; Zou, H.; Wang, Y.; Lv, X.; Zhang, L. *J. Appl. Polym. Sci.* **2013**, *129*, 999.
- Winkelmann, H. A. *Ind. Eng. Chem.* **1926**, *18*, 1163.
- Isayev, A. I.; Chen, J.; Tukachinsky, A. *Rubber Chem. Technol.* **1995**, *68*, 267.
- Yun, J.; Oh, J. S.; Isayev, A. I. *Rubber Chem. Technol.* **2001**, *74*, 317.
- Hong, C. K.; Isayev, A. I. *J. Appl. Polym. Sci.* **2001**, *79*, 2340.
- Li, Y.; Zhao, S.; Wang, Y. *Polym. Degrad. Stabil.* **2011**, *96*, 1662.
- Bredberg, K.; Persson, J.; Christiansson, M.; Stenberg, B.; Holst, O. *Appl. Microbiol. Biotechnol.* **2001**, *55*, 43.
- Horikx, M. M. *Rubber Chem. Technol.* **1956**, *29*, 1166.

20. Mangili, I.; Collina, E.; Anzano, M.; Pitea, D.; Lasagni, M. *Polym. Degrad. Stabil.* **2014**, *102*, 15.
21. Formela, K.; Cysewska, M.; Haponiuk, J. *Polimery* **2014**, *59*, 170.
22. Dibbanti, M. K.; Mauri, M.; Mauri, L.; Medaglia, G.; Simonutti, R. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42700.
23. Heuert, U.; Knörger, M.; Menge, H.; Scheler, G.; Schneider, H. *Polym. Bull.* **1996**, *37*, 489.
24. Saalwachter, K. *Prog. Nucl. Magn. Reson. Spectrosc.* **2007**, *51*, 1.
25. Kraus, G. *J. Appl. Polym. Sci.* **1963**, *7*, 861.
26. Saiwari, S.; Dierkes, W. K.; Noordermeer, J. W. M. *Kaut. Gummi Kunst.* **2013**, *66*, 20.
27. Si, H.; Chen, T.; Zhang, Y. *J. Appl. Polym. Sci.* **2013**, *128*, 2307.
28. Alemán, J. V.; Chadwick, A. V.; He, J.; Hess, M.; Horie, K.; Jones, R. G.; Kratochvíl, P.; Meisel, I.; Mita, I.; Moad, G.; Penczek, S.; Stepto, R. F. T. *Pure Appl. Chem.* **2007**, *79*, 1801.
29. Charlesby, A. *Proc. R. Soc. London. Ser. A: Math. Phys. Sci.* **1954**, *222*, 542.
30. Mangili, I.; Lasagni, M.; Anzano, M.; Collina, E.; Tatangelo, V.; Franzetti, A.; Caracino, P.; Isayev, A. I. *Polym. Degrad. Stabil.* **2015**, *121*, 369.
31. Mangili, I.; Lasagni, M.; Huang, K.; Isayev, A. I. *Chemom. Intell. Lab. Syst.* **2015**, *144*, 1.
32. Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521.
33. Danon, B.; Görgens, J. *Thermochim. Acta* **2015**, *621*, 56.
34. Zanchet, a.; Carli, L. N.; Giovanela, M.; Crespo, J. S.; Scuracchio, C. H.; Nunes, R. C. R. *J. Elastom. Plast.* **2009**, *41*, 497.
35. Danon, B.; Mkhize, N. M.; van der Gryp, P.; Görgens, J. F. *Thermochim. Acta* **2015**, *601*, 45.
36. van Zuilichem, D. J.; Stolp, W.; Janssen, L. P. B. M. *J. Food Eng.* **1983**, *2*, 157.
37. Flory, P. J. *Chem. Rev.* **1944**, *35*, 51.