EXPERIMENTAL VALIDATION OF THE CHARLESBY AND HORIKX MODELS APPLIED TO DE-VULCANIZATION OF SULFUR AND PEROXIDE VULCANIZATES OF NR AND EPDM

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ABSTRACT

The theoretical model developed by Charlesby to quantify the balance between cross-links creation of polymers and chain scission during radiation cross-linking and further modifications by Horikx to describe network breakdown from aging were merged to characterize the balance of both types of scission on the development of the sol content during de-vulcanization of rubber networks. There are, however, disturbing factors in these theoretical considerations vis-à-vis practical reality. Sulfur- and peroxide-cured NR and EPDM vulcanizates were de-vulcanized under conditions of selective cross-link and random main-chain scissions. Cross-link scission was obtained using thiol-amine reagents for selective cleavage of sulfur cross-links. Random main-chain scission was achieved by heating peroxide vulcanizates of NR with diphenyldisulfide, a method commonly employed for NR reclaiming. An important factor in the analyses of these experiments is the cross-linking index. Its value must be calculated using the sol fraction of the cross-linked network before de-vulcanization to obtain reliable results. The values for the cross-linking index calculated with sol-gel data before de-vulcanization appear to fit the experimentally determined modes of network scission during de-vulcanization very well. This study confirms that the treatment of de-vulcanization data with the merged Charlesby and Horikx models can be used satisfactorily to characterize the de-vulcanization of NR and EPDM vulcanizates. [doi:10.5254/rct.16.83776]

INTRODUCTION

To find the proper solutions for the enormous amounts of end-of-life rubber articles, in particular, for tires, there is a steady increase in technologies being developed for recycling of rubber. Overviews of the great variety of methods available are described in Beckman et al.1 and Myhre et al.2 They demonstrate the diversity of approaches that can be used with differing levels of success. The technologies already being employed or being developed range from grinding the waste rubber and reusing it in a powdery form in new, virgin rubber compounds3,4 to pyrolysis of the rubber to turn it into a gas, an oil, and a black-char fraction with the aim of reusing the char fraction in new rubber articles.5,6

The rubber recycling processes, which are often called reclaiming, commonly involve shearing of the vulcanizates at elevated temperatures. The shearing action causes primarily main-chain scission, similar to the mastication of virgin NR.7 In some cases, chemicals are used to aid in the de-vulcanization reaction. In addition, the elevated temperature may cause degradation reactions, which lead to both random and cross-link scissions. Although reclaiming of NR with these recycling processes has occurred for many years, their application to EPDM has proven more difficult. EPDM requires more strenuous de-vulcanizing conditions than NR does.8–10 To interpret the differences in behavior between NR and EPDM during de-vulcanization, it is important to know whether those differences are due to the different chemical structures of the main chains of the polymers—unsaturated vs fully saturated—or to the types of cross-links. Information about the relative amounts of random scission vs cross-link scission is needed to understand these differences.

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A method of investigating whether random or cross-link scission has the main role during de-vulcanization can be based on the amount of soluble polymeric material generated, a so-called sol-gel analysis. Charlesby developed the sol-gel analysis in his study of the balance between cross-linking and chain scission during irradiation of polymers. Horikx assumed that those relationships could also be employed to model the development of the sol fraction in a cross-linked polymer network being subjected to a degradation process, such as aging. The Horikx model expresses the relative decrease in network chain density as a function of the sol fraction and the cross-link index for vulcanizate breakage under random or cross-link scission conditions.

A comparison of experimental data for de-vulcanized products with the data generated from the Horikx model provides a tool to judge which of the two mechanisms prevails in the absolute amount of scission. The approach by Horikx was further elaborated on in the doctoral thesis of the first author to assess the balance between random and cross-link scission for a de-vulcanization process. As this method finds broader acceptance, it may be used for other elastomers than the NR and EPDM mentioned, such as SBR, BR, and isobutylene-isoprene rubber; therefore, the objective of the present study was to more thoroughly evaluate the applicability of the equations derived for vulcanizate breakdowns under conditions of random or cross-link scission for rubber de-vulcanization. An experimental verification of the equations derived from Horikx was necessary because certain assumptions made in the model of vulcanizate disintegration are not always met. The model equations were derived for networks built of polymers with a Poisson molecular mass distribution. However, the assumption that the original molecular mass distribution of a polymer could be described with a Poisson distribution is often not valid. Therefore, in the present study, the equations were experimentally verified for three polymers with varying molecular weight distributions: NR and two EPDM polymers. Further, the network chain density in the Horikx model equations is only for the chemical cross-link density. The Flory-Rehner equation is commonly used to assess the cross-link density of polymers by equilibrium swelling, providing values for the chemical network chain density without accounting for network imperfections, such as entanglements. In practice, however, all vulcanizates have network imperfections. The particular choice of the Flory-Rehner equation might, therefore, influence the results. In addition, the polymer–solvent interaction parameter χ employed in the Flory-Rehner equation is commonly determined experimentally, and its value can vary from one experimental study to another. To evaluate the consequences thereof, equilibrium swelling is performed in n-heptane on samples of sulfur Vulcanized ethylidene–norbornene-containing EPDM (ENB-EPDM), and the network chain density is subsequently calculated with four different values of χ taken from literature.

The applicability of the Horikx model is experimentally verified by de-vulcanization under conditions for which it is certain that only random scission or only cross-link scission can occur. For selective scission of sulfur cross-links, the treatment of sulfur vulcanizates with thiol-amine reagents is employed because sulfur cross-links are broken by the action of these reagents exclusively, and no main chain scission occurs. This holds true for both NR and EPDM vulcanizates. Random scission occurs during breakage of NR peroxide vulcanizates because both cross-links and the main chains contain carbon–carbon cross-links, and the NR main chain is particularly sensitive to chain scission.

**MODEL THEORY**

A model description for sol-gel analysis of rubber networks during de-vulcanization can be constructed in two ways: (1) by considering the amount of soluble material generated by detachment of molecular fragments from a vulcanized network, whether via random or cross-link scission; or (2) by starting with a certain molecular mass distribution of soluble polymers, breaking them by chain scission, and then cross-linking them into a network and subsequently comparing...
that imperfect network with one constructed out of intact chains. Either way, this results in a certain amount of polymer molecules being soluble: the sol fraction and molecules inserted into the insoluble network called the gel fraction.

**CROSS-LINKING AND POLYMER SCISSION BY IRRADIATION (CHARLESBY)**

Charlesby\textsuperscript{11,12} treats polymers that are cross-linked by irradiation. Radiation cross-linking normally results in a situation in which the probabilities of cross-linking two polymer chains and of scission of the two monomeric units in a polymer chain both have a role, where $p$ is the probability of breaking a given bond linking two monomer units, and $q$ is the probability of creating a cross-link between two monomer units.

Based on the small probability $p$ of breaking a bond relative to the probability $q$ of forming a cross-link, Charlesby derived a series of equations for the sol and gel fractions during cross-linking, which are generally applicable, irrespective of the molecular mass distribution of the original polymers. The cross-linking index, that is, the average number of cross-links per original polymer molecule, as defined by Flory,\textsuperscript{21} is related to $\bar{M}_n$ by Eq. 1:

$$\gamma = \frac{q}{w} \frac{\bar{M}_n}{w}$$

where $\gamma$ is the cross-linking index, $\bar{M}_n$ is the average molecular mass of the original polymer, and $w$ is the molecular mass of a monomer in the polymer chain. $\bar{M}_n/w$ is the number of monomers in a “number average” original polymer molecule before cross-linking.

The cross-linking coefficient $\delta$, which is equal to the average number of cross-links per “mass average” polymer molecule is related to $\bar{M}_w$ by Eq. 2:

$$\delta = \frac{q}{w} \frac{\bar{M}_w}{w}$$

where $\bar{M}_w$ is the weight average molecular mass of the original polymer.

The gel and sol fractions during cross-linking are related to $q$ as shown in Eq. 3:

$$g = 1 - s = 1 - \frac{xN_x e^{-q\gamma x}}{\sum xN_x}$$

where $g$ is the gel fraction, $s$ is the sol fraction, $x$ is the number of monomers per primary polymer molecule, $N_x$ is the number of polymer molecules with $x$ monomer units, and $\sum xN_x$ is the total number of monomers included in all polymers within the sample.

Equation 3 can be further detailed if the molecular mass distribution for the primary polymer molecules is defined. From the examples given by Charlesby, two are detailed hereunder.

*Monodisperse Distribution.* — In this case, all primary molecules are the same mass. Because $x$ is then the same for all polymer molecules, it equals $\bar{M}_n/w$ and Eqs. 1 and 3 reduced as follows:

$$g = 1 - e^{-q\gamma x} = 1 - e^{-\gamma x}$$

$$s = e^{-\gamma x} = e^{[-\gamma(1-s)]}$$

These equations are implicit expressions for the gel and sol fractions. By numerical evaluation, $g$ can be expressed as a function of the cross-linking index $\gamma$. These are the same relationships as derived earlier by Flory,\textsuperscript{21} in a somewhat different form. Gel formation during cross-linking starts no earlier for this distribution than when $\gamma > 1$: the so-called gelpoint.
Poisson Distribution. — In a case of random network destruction by whatever process—oxidative breakdown, mechanical shearing, or de-vulcanization, including chain scission—it is commonly assumed that a Poisson-type molecular mass distribution of fragments is formed. To interpret the experimental results for de-vulcanization, it is, therefore, of value to see how the Charlesby model predicts gel and sol fractions for this molecular mass distribution. The Poisson distribution is defined as a special case of the Schultz-Flory distribution:

\[ N_x = Np(1 - p)^{x-1} \approx \frac{Np e^{-px}}{1 - p} \approx Np e^{-px} \quad \text{for } p \ll 1 \]  

(6)

where \( N \) is the total number of polymer molecules in the distribution. Based on this distribution, the following relationship for the sol fraction \( s \) and the gel fraction \( g \) is derived as follows:

\[ s = 1 - g = \frac{1}{(1 + \gamma - \gamma s)^{\frac{1}{2}}} \]  

(7)

Note that Charlesby defined the Poisson distribution here with the parameter \( p \), that is, the probability of breaking a given bond linking two monomers in an infinite chain broken at random, to form soluble polymers: the higher, \( p \), and the lower, the molecular mass. Commonly, for definitions of the Poisson distribution of polymers, the parameter \( p \) denotes the extent to which the polymerization reaction has proceeded. A simple consideration shows that \( p \) (according to Charlesby) equals \( \frac{1}{c_0} \) (the extent of polymerization reaction).

The approximations made in Eq. 6 only hold for a very small \( p \), which is normally the case if the primary chains or polymers detached from the network are still of reasonably high molecular mass. The implicit Eq. 7 for \( s \) can be made explicit to read as follows:

\[ s = \frac{(2 + \gamma) - \sqrt{\gamma^2 + 4\gamma}}{2\gamma} \]  

(8)

Other relationships derived for this Poisson distribution include

\[ \bar{M}_{gel} = \frac{\bar{M}_n(1 + \gamma - \gamma s)}{\gamma} \]  

(9)

and

\[ \gamma_{gel} = (1 + s)(1 + \gamma - \gamma s) \quad \text{for } \gamma > 0.5 \]  

(10)

where \( \bar{M}_{gel} \) is the average initial molecular mass of the molecules that were included in the gel, and \( \gamma_{gel} \) is the cross-linking index in the gel. Because the larger molecules are preferentially included in the gel, \( \bar{M}_{gel} \neq \bar{M}_n \) and \( \gamma_{gel} \neq \gamma \).

At this point, it is illustrative to see how the gel and the sol fractions depend on the cross-linking index \( \gamma \) for both molecular mass distributions: monodisperse and Poisson. The sol fraction starts to decrease and the gel fraction to increase at \( \gamma > 1.0 \) for the mono-disperse distribution, as originally derived by Flory.\(^{31}\) However, for the Poisson distribution the sol fraction already starts to decrease at \( \gamma > 0.5 \). For the Poisson distribution, it generally holds that \( \bar{M}_w: \bar{M}_n = 2:1 \). Therefore, both distributions can be merged to start gel formation at the cross-linking coefficient \( \delta = 1 \), as defined in Eq. 2. This stresses the fact that the larger molecules in the distributions are the first to be caught in the cross-linked network.

NETWORK BREAKDOWN (HORIKX)

Anticipating that network breakdown will lead to a Poisson distribution of molecular fragments, Horikx took Charlesby’s network—built from an original Poisson distribution before
cross-linking—and let it be broken again via two routes: random chain scission and selective scission of the cross-links. He treated a third case called directed chain scission at the nearest-neighbor sites to a cross-link, but this case is considered less relevant in the present context.

The question at this point is how much sol is formed as a function of the remaining cross-link density. As a measure of cross-link density, \( m_o \) is defined as the number of elastically effective polymer network chains per cubic centimeter of network, including the sol fraction, that is, before extraction of the sol. Inversely, \( \frac{1}{2} m_o \) equals the number of cross-links per cubic centimeter of network for tetrafunctional cross-links. Horikx defined the cross-link density \( m_o \) as the number of polymer network chains per gram of network. The difference between the two definitions involves the specific density of the network. It makes no difference for the treatment given here because the specific density drops out of the equations later on. Further, Horikx assumed that the number of network chains \( m_o \) was given by the chemically cross-linked chains only, excluding trapped entanglements. It is then evident that

\[
\gamma = \frac{v_o}{N}
\]  

where \( N \) is the number of primary molecules per cubic centimeter of polymer.

It follows from Eq. 9 that the number of primary molecules per gram of network is given by Eq. 12:

\[
N_{gel} = \frac{\gamma N}{1 + \gamma - \gamma s} = \frac{v_o}{1 + \gamma - \gamma s}
\]

By combining Eqs. 10, 11, and 12, the number of chains in the network: \( v_{o, gel} \) is given by Eq. 13:

\[
v_{o, gel} = \gamma_{gel} N_{gel} = v_o (1 + s)
\]

Combining Eqs. 7 and 12, the following relationship is obtained:

\[
N_{gel} = v_o \sqrt{s}
\]

According to Flory, the number of elastically effective polymer chains in the network \( v_e \), as determined by mechanical or gel measurements, requires a correction on \( v_o \) to account for dangling chain-ends given by Eq. 15

\[
v_e = v_o - 2N
\]

for tetrafunctional cross-links. It is this \( v_e \), which is determined via swelling using the well-known Flory-Rehner equation for tetrafunctional cross-links:

\[
v_e = -\frac{\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2}{V_s \left( \phi_2^{1/3} - \frac{1}{3} \phi_2 \right)}
\]

where \( v_e \) is the volume fraction of polymer in the swollen gel, \( V_s \) is the molar volume of the solvent, and \( \chi \) is the interaction parameter for the solvent–polymer system.

The number of elastically effective chains per cubic centimeter of network is then given by combining Eqs. 14 and 15:

\[
v_e = v_{o, gel} - 2N_{gel} = v_o (1 + s) - 2v_o \sqrt{s}
\]

or
Random Main Chain Scission. — During random main chain scission, the number of cross-links \( m_o \) remains constant, and soluble matter is created by randomly detaching small molecular fragments out of the network. By virtue of Eq. 11, \( \gamma \) decreases as much as \( N \) increases. If Eq. 18 is formulated before \( i \) and after \( f \), the network scission and the ratio of both are taken as the relative decrease in network chain density, then, \( \nu_o \) drops out of the equation, and the latter can be expressed as a function of the soluble fractions before and after scission:

\[
1 - \frac{\nu_f}{\nu_i} = 1 - \frac{(1 - \sqrt{s_f})^2}{(1 - \sqrt{s_i})^2}
\]

where \( s_i \) is the soluble fraction, \( \nu_i \) is the number of elastically effective network chains per cubic centimeter of the still untreated vulcanizate, and \( s_f \) and \( \nu_f \) correspond to the situation after the treatment.

Selective Crosslink Scission. — To determine the soluble fraction in the case of cross-link scission, \( N \) is taken as constant and \( \gamma \) decreases. In this case \( \nu_o = \gamma N \) does not drop out of the equation. The relative decrease in cross-link density is now dependent on the cross-link index \( \gamma \):

\[
\nu_e = \nu_o \text{gel} - 2N \text{gel} = \nu_o (1 - s^1/2)^2 = \gamma N(1 - s^1/2)^2
\]

The relation between the effective number of network chains before and after the treatment now reads as follows:

\[
1 - \frac{\nu_f}{\nu_i} = 1 - \frac{\gamma_f(1 - \sqrt{s_f})^2}{\gamma_i(1 - \sqrt{s_i})^2}
\]

with \( \gamma_i \) as the cross-linking index before treatment and \( \gamma_f \) as the cross-linking index after selective cross-link scission.

The determination of \( \gamma_i \) needs further detailing. Horikx used the measurement of the network chain density in the gel by equilibrium swelling, together with the value measured for \( \bar{M}_n \) with gel permeation chromatography (GPC), and Eq. 11 and \( N = \rho/\bar{M}_n \) to calculate \( \gamma_i \) as follows:

\[
\gamma_i = \frac{\bar{M}_n}{\rho}
\]

where \( \rho \) is the density. Another way to determine \( \gamma_i \) is by measuring the residual sol content immediately after vulcanization and then making use of Eq. 8. These two ways lead to differences, which will be further detailed in the experimental section.

Comparison of Eqs. 21 and 19 shows that Eq. 21 has the additional factor \( \gamma_f/\gamma_i \), which is always <1.0. Consequently, a particular sol fraction \( s_f \) corresponds to a higher \( 1 - \nu_f/\nu_i \) in the case of cross-link scission than it does in the case of random scission. Cross-link scission requires a far greater decrease in cross-link density to generate a specific amount of sol than does random scission.

In the present study, the actual de-vulcanization experiments are done on vulcanized samples from which the initial soluble fraction \( s_i \) has been extracted. The additional soluble fraction generated by the network breakage, therefore, has to be added to the initial soluble fraction to correspond with the \( s_f \) as defined by Horikx. To prevent confusion, we use the symbols \( s_i \) and \( s_f \)
for the Horikx definition and \( S_i \) and \( S_f \) (capital letters) for the experimental results, whereby \( s_i = S_i \) and \( s_f = S_i + S_f \). This requires a slight adjustment of Eqs. 19 and 21. The equivalent equations are, therefore,

\[
1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_i (1 - \sqrt{S_f + S_i})^2}{\gamma_i (1 - \sqrt{S_i})^2}
\]  

(23)

for cross-link scission, and

\[
1 - \frac{v_f}{v_i} = 1 - \frac{(1 - \sqrt{S_f + S_i})^2}{(1 - \sqrt{S_i})^2}
\]  

(24)

for random scission.

To construct theoretical curves for cross-link and random scission, the value of \( \gamma_f \) is lowered in small steps, and \( S_j \) is calculated with Eqs. 23 and 24, using the experimentally determined values for \( S_i \) and \( \gamma_f \).

### EXPERIMENTAL

**MATERIALS AND COMPOUND RECIPES**

The polymers used were NR (SIR 20, L. Wurfbain & Co., Haywards Heath, UK), ENB-EPDM (Keltan® 4802, DSM Elastomers BV, Heerlen, The Netherlands; 49 wt% (60 mole%) ethylene, 4.5 wt% (1.2 mole%) 5-ethylidene-2-norbornene; Mooney viscosity ML (1 + 4) 125 °C: 77; and HD-EPDM (Nordel® 1040, DuPont, Wilmington, DE, USA; 54 wt% (64.5 mole%) ethylene, 3 wt% (1.2 mole%) 1,4-hexadiene, Mooney viscosity ML (1 + 4) 125 °C: 39. They were compounded and vulcanized with conventional sulfur vulcanization systems.\(^{23,24}\) NR was also compounded with peroxide. The formulations employed are given in Table I.

The compounding ingredients used were zinc oxide (Merck, Kenilworth, NJ, USA), stearic acid (Merck), \( N \)-cyclohexyl-2-benzothiazole-sulfenamide (Perkacit CBS, Flexsys BV, Deventer, The Netherlands), mercapto-benzothiazole (Perkacit MBT, Flexsys BV), tetramethylthiuram disulfide (Perkacit TMTD, Flexsys BV), sulfur (Merck), and dicumylperoxide (DCP, 100% pure, Schuchardt, Göttingen, Germany).

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(uppercase letters) for the Horikx definition and \( S_i \) and \( S_f \) (capital letters) for the experimental results, whereby \( s_i = S_i \) and \( s_f = S_i + S_f \). This requires a slight adjustment of Eqs. 19 and 21. The equivalent equations are, therefore,
METHODS

Preparation of Compounds and Vulcanizates. — The compounds were mixed on a laboratory size two-roll mill (former Schwabenthan, Berlin, Germany) and vulcanized until $t_{90}$, as derived from rheometer testing in a Göttfert (Buchen, Germany) Elastograph at 140 °C and 160 °C for NR and EPDM, respectively. The samples used for the de-vulcanization were 0.5 g of a 0.3 mm thin film.

For determination of the molecular masses before vulcanization, compounds of NR, ENB-EPDM, and HD-EPDM—after milling but before vulcanization—were dissolved in toluene (p.a., Biosolve) or decahydronaphthalene (Merck, mixture of cis- and trans-isomers). The solutions were filtered to remove zinc oxide, and the polymers were precipitated in acetone. The molecular masses of the precipitated polymers were measured by GPC. Solutions of 10 mg/mL in tetrahydrofuran were filtered over 0.45 μm filters (Schleicher & Schuell, Dassel, Germany) and analyzed with Waters (Milford, MA, USA) styragel columns (pores 105, 104, 103, and $5 \times 10^{2}$ Å) with a flow rate of 1.47 mL/min. The intrinsic viscosity needed for calibration of the GPC was determined with a Viscotek H502 viscosimeter (Malvern Instruments, Malvern, UK) equipped with a refractive index detector (Waters 410).

A two-step extraction method was used to obtain the values for $S_i$. The vulcanizates were first extracted in a Soxhlet apparatus for 48 h with acetone to remove residues of the vulcanization ingredients and other nonpolymeric substances. Next, they were extracted for 72 h with tetrahydrofuran to remove un-cross-linked polymer. The procedure yields low molecular mass products, un-cross-linked polymer $S_i$ and extracted vulcanizate.

Equilibrium swelling was performed in an excess of solvent under a nitrogen blanket and with exclusion of light for 72 h. For EPDM vulcanizates, decahydronaphthalene was used as a solvent, with a polymer–solvent interaction parameter25 of $\chi = 0.121 + 0.278f_2$. The solvent for NR26,27 was toluene with $\chi = 0.378 + 0.071f_2$. The Flory-Rehner equation (Eq. 16) was used for the calculations of the network chain densities. A polymer–solvent combination for which four different interaction parameters were available from the literature was selected to determine whether the experimental results were influenced by the accuracy of the value assigned to the polymer–solvent interaction parameter $\chi$. This polymer–solvent combination was EPDM – n-heptane, and the interaction parameters used were $\chi = 0.44$, $\chi = 0.354 + 0.083f_2$, $\chi = 0.347 - 0.011f_2$, and $\chi = 0.34 + 0.22f_2$.25

Selective Cross-link Scission of Sulfur Vulcanizates with Thiol-Amine Reagents. — Vulcanizates, which varied in network chain density as well as in molecular mass distribution of the original polymer, were studied. For selective scission of cross-links, performed on sulfur vulcanizates, thiol-amine reagents were used. Reaction conditions were adjusted by varying the amounts and the reaction times of the thiol-amine reagents to obtain variations in the levels of scission of the sulfur cross-links. All vulcanizates were pre-swollen for 72 h in toluene. Next, 30 mL of 0.4M 2-propanethiol and 1M piperidine in toluene per gram of vulcanizate were added, and the vulcanizates were kept in this reagent for reaction times varying from 2 to 72 h. For more severe conditions of cross-link scission, 30 mL of 1M 1-dodecanethiol and 3M piperidine in toluene per gram of vulcanizate were added, and the vulcanizates were kept in this medium for a period of 168 h.

Random Network Scission of Peroxide Vulcanizates. — Experiments with NR peroxide vulcanizates were performed at 200 (±5) °C for 2 h in a reaction vessel flushed with nitrogen. To obtain different levels of random breakage of NR peroxide vulcanizates, they were heated with the recycling agent diphenyldisulfide (Acros > 98%) in varying quantities from 0 to $4.6 \times 10^{-4}$ mole/cm$^3$. The disulfide was brought into the previously extracted peroxide vulcanizates by swelling in a solution of the disulfide in tetrahydrofuran.

Analysis of Vulcanizates After Scission. — After network or cross-link breakage, the amount of newly formed extractable polymer $S_i$ was determined. Sulfur vulcanizates were extracted for 24 h in
petroleum ether and for 48 h in tetrahydrofuran after treatment with thiol-amine reagents. NR peroxide de-vulcanizates were first extracted with ethanol, to remove unreacted disulfide and some low molecular mass species formed during the high temperature treatment. $S_f$ was determined as the mass loss after extraction in a Soxhlet apparatus with tetrahydrofuran for 72 h.

RESULTS

SELECTIVE SCISSION OF CROSS-LINKS IN SULFUR VULCANIZATES WITH THIOL-AMINE REAGENTS

The Values of $\gamma_i$ to be Used for Interpretation of Crosslink Scission Experiments. — Table II shows the molecular masses of the original un–cross-linked polymers and $\nu_i$ for the sulfur vulcanizates before the cross-link scission experiments. The density of the vulcanizates was taken as $\rho = 0.95$ g/cm$^3$ for NR vulcanizates, and $\rho = 0.86$ g/cm$^3$ for the EPDM vulcanizates. As explained before, values of $\gamma_i$ are required for interpretation later in the de-vulcanization experiments because the relation between the soluble fraction generated in a polymer network and the scission of cross-links is strongly influenced by errors in $\gamma_i$. The values can be obtained in two ways. Charlesby derived a relation between $\gamma$ and the fraction in a cross-linked polymer sample that is still soluble (the sol fraction), as given by Eq. 7. When the experimentally determined value of $S_f$ is substituted in this equation, $\gamma_i$ can be derived. Horikx, however, did not determine the soluble fraction in the cross-linked polymer before degradation ($S_f$) because of the presence of low molecular mass residues of the vulcanization system. He, therefore, used Eq. 22 to calculate $\gamma_i$. Table II shows the data for sulfur vulcanizates with values for $\gamma_i$ according to Eqs. 7 and 22. Both methods (Charlesby and Horikx) for determining the value of $\gamma_i$ before network breakage result in rather different values. Either of these values can now be substituted in Eq. 23, to be compared with actual de-vulcanization results.

In Figures 1–4, experimental values of $S_f$ after selective cross-link scission of the three polymer sulfur vulcanizates with thiol-amine reagents are compared with $S_f$ as calculated with Eq. 23, with values for $\gamma_i$ taken from Table II and denoted by the dashed and dotted lines. The experimental data are in better agreement with values calculated with Eq. 23, if $\gamma_i$ is calculated according to Eq. 7 than according to Eq. 22. The higher values for $\gamma_i$ calculated with Eq. 22 result in theoretical fractions $S_f$ that are considerably lower than the experimental values. The reason for the poorer fit using Eq. 22 is, that for calculation of $\gamma_i$ values for $\bar{M}_n$ and $\nu_i$ have to be determined. With the experimental determination of these characteristics significant uncertainties are introduced. An error in the measurement of $\bar{M}_n$ with GPC (often more than 20%) might e.g. be caused by the presence of branching in the polymer. Both NR and EPDM contain long-chain branching, although in NR the polymer becomes more linear upon mastication. Ahagon compared GPC results with sol-gel analysis, by using partially pre-cross-linked liquid polyisoprene. $\bar{M}_n$ in the theory of sol-gel analysis is that of the unbranched linear polymer, while the one measured with GPC corresponds

<table>
<thead>
<tr>
<th></th>
<th>NR</th>
<th>ENB-EPDM</th>
<th>HD-EPDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{M}_n$, 10$^6$ g/mol</td>
<td>26 ± 3</td>
<td>7 ± 2</td>
<td>3 ± 0.4</td>
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<tr>
<td>$\bar{M}_w/\bar{M}_n$</td>
<td>2.4</td>
<td>2.5 ± 0.8</td>
<td>5.5 ± 0.6</td>
</tr>
<tr>
<td>$\nu_i$, 10$^{-4}$ mol/cm$^3$</td>
<td>0.73 ± 0.08</td>
<td>3.1 ± 0.1</td>
<td>1.85 ± 0.07</td>
</tr>
<tr>
<td>$S_f$, %</td>
<td>1.8 ± 0.3</td>
<td>0.97 ± 0.05</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>$\gamma_i$ according to Eq. 7</td>
<td>6.6</td>
<td>9.25 ± 0.03</td>
<td>3.0 ± 1</td>
</tr>
<tr>
<td>$\gamma_i$ according to Eq. 22</td>
<td>20</td>
<td>25 ± 8</td>
<td>6 ± 1</td>
</tr>
</tbody>
</table>
to the branched polymer. Branch points are equivalent to cross-links once embedded in the network structure. Therefore, when branching is present, $M_n$ as measured with GPC is higher than the real value for $M_n$ that should be substituted in Eq. (22), and consequently the calculated value for $\gamma_i$ is too high.

Another uncertainty is the initial network chain density: $v_i$, as obtained from equilibrium swelling experiments. While $v_i$ should only contain the network chain density that is the result of chemical cross-linking, the experimentally determined value for $v_i$ also contains the contribution of trapped physical entanglements. The amount of entanglements can under circumstances be high compared with the amount of chemical cross-links. In the present study, the NR vulcanizates probably have the highest ratio of entanglements to chemical cross-links: the ratio of the initial cross-linking index $\gamma_i$ calculated with Eq. (22) to $\gamma_i$ calculated with Eq. (7) is highest for NR. Moore

![Figure 1](image1.png)

**Fig. 1.** — Fraction of soluble polymer in a NR sulfur vulcanizate after treatment with thiol-amine reagent, pure cross-link scission, vs the relative decrease in network chain density.

![Figure 2](image2.png)

**Fig. 2.** — Fraction of soluble polymer after cross-link scission with thiol-amine of ENB-EPDM sulfur vulcanizates vs the relative decrease in network chain density, using equilibrium swelling in $n$-heptane with $\chi = 0.44$ (ref 28); $\Delta, \chi = 0.347 - 0.011 v$ (ref 30); $\nabla, \chi = 0.354 + 0.083 v$ (ref 29); and $\nabla, \chi = 0.34 + 0.22 v$ (ref 25).
and Watson compared chemical values of the amount of chemical peroxide cross-links with physical entanglements from equilibrium swelling.33 They found that a difference in network chain density was mainly due to an almost constant amount of trapped entanglements in the vulcanizates, the total network chain density being twice the chemical network chain density. The amount of trapped entanglements increased only slightly with increasing chemical cross-link density.

The fact therefore that the overall network chain density is composed of a constant factor due to entanglements and a variable chemical contribution, results in a relative value that is less accurate. The contribution of entanglements results in a higher $\frac{m_f}{m_i}$, or a lower relative decrease in network chain density after de-vulcanization. This can explain the deviation of the experimental points for NR from the calculated data in Figure 1, where $1-\frac{m_f}{m_i}$ is somewhat too low for the fractions of soluble polymer formed upon cross-link breakage.

**FIG. 3.** — Fraction of soluble polymer in an ENB-EPDM sulfur vulcanizate after treatment with thiol-amine reagent vs the relative decrease in network chain density.

**FIG. 4.** — Fraction of soluble polymer in a HD-EPDM sulfur vulcanizate after treatment with thiol-amine reagent vs the relative decrease in network chain density.
As to EPDM, Baldwin studied the concentration of entanglements in EPDM vulcanizates as a function of \( m \) using the method developed by Langley.\(^{34,35}\) Later, Langley and Polmanteer showed that the contribution of trapped entanglements to the Young’s modulus of a vulcanize is not a constant value, but increases when the concentration of chemical cross-links is increased until this contribution reaches a saturation level. The height of this level depends on polymer type and molecular mass.\(^{36}\) Baldwin showed that for EPDM vulcanizates the value for \( m \) at which all entanglements are trapped is approximately \( 2.3 \times 10^{-4} \text{ mol/cm}^3 \).\(^{34}\) The entanglement chain density contributes then to this value for approximately \( \gamma_i \). The values of \( \gamma_i \) for EPDM sulfur vulcanizates according to Eqs. (7) and (22) are in reasonable agreement with this: the value for \( \gamma_i \) calculated with Eq. (22) is approximately three times that for \( \gamma_i \) calculated with Eq. (7): Table II. Below this network chain density, however, the contribution of trapped entanglements decreases with the total chain density. As the use of the relative value \( 1 - \frac{m_f}{m_i} \) diminishes the influence of the entanglements, it is expected that the experimental and calculated data will be in better agreement.

The contribution of the entanglement chain density to the total network chain density is lower for HD-EPDM sulfur vulcanizates compared with ENB-EPDM vulcanizates: about one half of the total network chain density as indicated by the \( \gamma_i \) in Table II, assuming that the value for \( M_n \) measured with GPC is approximately correct. This is most probably the result of the fact that the overall network chain density is lower than for ENB-EPDM and therefore also the contribution of the trapped entanglements. The lower values of \( \gamma_i \) for HD-EPDM vulcanizates are the result of the lower \( M_n \) of the HD-EPDM polymer: Table II.

Sensitivity of the Horikx Model Treatment Toward the Values of the Polymer-Solvent Interaction Parameter. — In Figure 2 for ENB-EPDM sulfur vulcanizates treated with thiol-amine reagents and swollen in n-heptane, some deviation from the calculated curve is observed for higher decreases in network chain density. This depends on the value of \( \chi \) used in the calculation of the cross-link density with Eq. (16), as taken from different literature sources.\(^{25,28-30}\) Especially the dependence of \( \chi \) on \( \nu_r \) is a point of concern. With larger difference between \( \nu_f \) and \( \nu_r \), the relative decrease in network chain density is more influenced by this dependence on \( \chi \).

Effects of Molecular Mass Distribution Used for the Model Treatment. — \( M_n \) and \( M_w/M_n \) of the polymers are given in Table II. It was assumed in the theoretical treatment that the molecular mass distribution of the polymers before vulcanization was a Poisson distribution. In practice, the molecular mass distributions deviate. However, the deviations from the Poisson distribution apparently do not lead to a significant discrepancy between calculated and experimental values in the case of selective cross-link scission of EPDM as can be seen from the close fits in Figures 3 and 4.

For the NR network de-vulcanized by cross-link scission, there is also some difference between calculated and experimental values: Figure 1, which can be the result of deviations from the Poisson molecular mass distribution. If this were the case, however, these would also influence the experimental values for random scission: Figure 5. However, there the experimental values for random scission show a good fit to the calculated values: see next paragraph.

RANDOM NETWORK SCISSION OF PEROXIDE VULCANIZED NR

For peroxide cured NR, aging studies have shown that random chain scission occurs in an oxidative environment at high temperatures.\(^{37,38}\) Cross-links are attached directly to the polymer main chain: in the cross-links and in the polymer main chains the same type of saturated carbon-carbon chemical bonds are present. These cross-links are assumed to be randomly distributed throughout the vulcanize.\(^{33}\)

For the calculation of the relationship between \( S_f \) and \( 1 - \frac{\nu_f}{\nu_i} \) in the case of random scission according to Eq. (24), \( \nu_i \) and \( S_i \) are required. For the peroxide vulcanize of NR these values are
given in Table III. Figure 5 shows the relationship between experimental values of \( S_f \) and \( 1-\frac{v_f}{v_i} \) after de-vulcanization with diphenyldisulfide and those calculated with Eq. (24). The experimental values are in good agreement with the calculated ones. It indicates that the disintegration of the NR peroxide vulcanizates proceeds indeed by random scission, for which Eq. (24) can be used to determine the relationship between the fraction of soluble polymer and the relative decrease in network chain density.

In the case of random scission, \( \gamma_i \) does not occur in Eq. (24). This means that the influence of entanglements is smaller, as it has more influence on \( \gamma_i \) as calculated with Eq. (22) than on \( 1-v_f/v_i \). When random chain scission takes place, both removal of chemical cross-links and trapped entanglements from the vulcanizate occurs, because chain scission also leads to release of entanglements. Suh et al. compared the oxidative breakdown of NR peroxide vulcanizates cross-linked in solution to keep the amount of entanglements on a low level, with that of NR peroxide vulcanizates cross-linked in the bulk.\(^{39,40}\) Analysis of these vulcanizates with stress relaxation did show that the initial stress relaxation was higher for vulcanizates with entanglements, because of the higher decrease in the value of \( v_f \). However, \( 1-v_f/v_i \) as measured with equilibrium swelling, was almost the same for both types of vulcanizates, showing that the influence of entanglements on the latter is limited.

### Table III

<table>
<thead>
<tr>
<th>EXPERIMENTAL VALUES FOR NR PEROXIDE VULCANIZATE</th>
</tr>
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<tbody>
<tr>
<td>NR peroxide vulcanizate</td>
</tr>
<tr>
<td>( S_f, % )</td>
</tr>
<tr>
<td>( v_f, 10^{-4} \text{ mol/cm}^3 )</td>
</tr>
<tr>
<td>( \gamma_i ) according to Eq. 7</td>
</tr>
<tr>
<td>( \gamma_i ) according to Eq. 22</td>
</tr>
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</table>
DISCUSSION

There are several factors remaining which deserve critical discussion as they may have influenced the experimental validation of the present theoretical treatments.

RELEVANCE OF THE ASSUMPTIONS REGARDING THE MOLECULAR MASS DISTRIBUTION BEFORE CROSS-LINKING

Tanaka has shown that NR from Hevea trees has a bimodal molecular mass distribution, the ratio of low to high molecular mass being dependent on the age of the rubber tree. A study of Harmon and Jacobs showed a bimodal molecular mass distribution as well, developed during mill mastication of NR, even though the overall masses shifted to lower values. Consequently, the molecular mass distribution of masticated NR is certainly not a Poisson distribution. For EPDM it is well known that due to side-reactions via the unsaturated third monomers ethylidene norbornene and less so hexadiene, commonly a substantial amount of branching is obtained during polymerization, which definitely also disturbs the molecular mass distribution. In addition, a distribution skewed to low molecular masses is quite common. Therefore, to investigate the influence of the molecular mass distribution, three polymers that strongly differ in their distributions were used in the present study.

The model of Horikx generally assumes that the vulcanized polymers originated from a Poisson molecular mass distribution, and that upon random scission again a Poisson distribution is obtained. An alternative model of Dobson and Gordon, used by Yashin and Isayev to also model network break-down by de-vulcanization or random scission, assumes that the starting molecular mass distribution of the polymers is a Flory distribution. It remains a point of conjecture at this stage, if the fact that the network before network breakage was built from a polymer with either a Poisson or a Flory distribution, has a significant effect on the outcome of the de-vulcanization. Deviations from these assumptions might influence the relationship between the amount of soluble polymer and the change in cross-link density in a vulcanizate. However, the experimental results for the NR and the two EPDM polymers show that this effect is very limited, at least for the polymers employed in this study.

INFLUENCES OF NETWORK IMPERFECTIONS

Sulfur vulcanized rubbers are three-dimensional polymer networks in which the branching units or cross-link sites are commonly tetra-functional. In actual practice, such networks have imperfections such as dangling chain ends; cross-links are not all tetra-functional and entanglements are trapped during the cross-linking process. Deviations in the functionality of the cross-links are commonly neglected in sol-gel analyses. All these network imperfections can influence the analyses.

A point of criticism with respect to the Horikx as well as to the Gordon and Dobson models is, that they were developed in a time that people thought of rubber networks as more nicely defined than considered today. In later years it has become increasingly accepted, that imperfections exist in the networks for various reasons.

First, it has become evident that a rubber vulcanizate derives its mechanical properties not only from the chemical cross-links but also to a large extent from entanglements. It is common to include the effect of these entanglements in statistical theories only in a qualitative manner via the so-called trapping factor, first introduced by Langley. If indeed the contribution of trapped entanglements on the modulus of a rubber network is as high as sometimes 50%, their contribution to the swelling and consequent network chain density calculated on basis of such experiments sheds...
doubt on the results. The elastic behavior of mobile entanglements differs from that of localized cross-links, their contribution to elasticity being lower.\textsuperscript{51} Even so, a contribution of entanglements to the network chain density in the swollen state is often taken into account.\textsuperscript{56,57} Others assume that the contribution of trapped entanglements is not significant in the swollen state.\textsuperscript{58} This remains a subject of debate.

Second, the influence of dangling chain ends provides concern. The work of Andrady et al.\textsuperscript{59} is often quoted as representative for the influence of dangling chain ends on rubber network properties. To some extent this effect is included in the Horikx model by the correction made in Eq. (15). In the Gordon-Dobson model the dangling chain ends are taken care of by the simulation of building ‘branches on the tree’. We may therefore assume that the effect of these latter network imperfections is properly taken care of in both these models.

As a third point of consideration, it is increasingly realized that rubber networks cannot be considered as homogeneously cross-linked. There are strong indications that, dependent on the cross-linking system – sulfur, peroxide or radiation curing – the cross-link density on a nano-scale is inhomogeneously distributed within rubber networks.\textsuperscript{60–65} Upon swelling of such inhomogeneous networks, the solvent molecules will preferentially migrate into the loosely cross-linked regions rather than in the tightly cross-linked ones. For the same reason, it is obvious to expect that the accessibility of thiol-amine agents to cross-links will be greater in regions where the local cross-link density is lower. Consequently, the fragments released from the network, particularly by chemical cross-link scission, may be considered to preferentially consist of tightly cross-linked clusters. This is a factor outside the concept of the model descriptions given above.

CONSEQUENCES OF UNCERTAINTIES IN THE VALUES OF THE CROSS-LINKING INDEX AND NETWORK CHAIN DENSITY

Horikx already mentioned that the theoretical relation between the soluble fraction generated in a polymer network and the scission of cross-links is strongly influenced by variations in $\gamma$. The number of cross-links per polymer chain $\gamma$, is directly related to the network chain density and the number average molecular mass of the polymers before cross-linking.

Not only the measurement of the network chain density is subject to errors, but also an absolute determination of the number average molecular mass is difficult, especially when nonpolymeric soluble components are present. Because of this, $\gamma$ is commonly not very accurate when calculated with Eq. 22. Calculation of $\gamma$ with Eq. 7 leads to results that correlate much better with the experiment but may also add uncertainty when $S_i$ of the vulcanizate is difficult to measure. Especially in the case of sulfur vulcanizates, it can be difficult to separate residues of the vulcanization system and low molecular mass polymer species. This is a possible explanation for the small deviation of the results for cross-link scission in NR in Figure 1 from the calculated curve.

Another uncertainty in the determination of the network chain density with equilibrium swelling is the polymer–solvent interaction parameter $\chi$. The value for $\chi$ is experimentally determined, which, in itself, can give rise to errors. Rubber polymers are modified along their chains by the sulfur vulcanization system, and this supposedly results in a change in the interaction parameter $\chi$ with the vulcanization system and cure time.\textsuperscript{18,20} This can be another reason for the deviation in the results for the cross-link scission in NR from the calculated curve in Figure 1. For ENB-EPDM, Figure 2 shows that deviations in the value of $\chi$ can also result in slight discrepancies between the calculated curves and the experimental data.
APPLICABILITY OF THE MODELS TO NR AND EPDM

Referring to the previous discussion, it is now clear that the original molecular mass distribution of the polymers NR and EPDM used in the present study did not correspond to Poisson distributions. On the other hand, it looks like this had little bearing on the analyses.

All other considerations regarding network imperfections served to underline the potentially limited applicability of the models described in the paragraph on sol-gel analysis. Proper insight in the mere existence and consequences of these effects is still the subject of considerable debate and research. Attempts to include these in the model descriptions would have resulted in qualitative improvements and was not deemed worthwhile or possible under the present circumstances, especially because the experimental results fit the model descriptions surprisingly well after all.

CONCLUSIONS

In spite of all restrictions that were formulated around the assumptions needed for the combined Charlesby and Horikx models for network breakdown, the results of the de-vulcanization experiments confirm that the model did apply surprisingly well. By using selective scission of cross-links in sulfur vulcanizates, relationships between $S_f$ and $1 - \gamma_f/\gamma_i$ could be compared with those calculated according to the Charlesby–Horikx treatment. Experimental data were in agreement with those calculated for cross-link scission if $\gamma_i$ was calculated from the fraction of soluble polymer in the vulcanize before breakage. Calculation of $\gamma_i$ from the network chain density measured with equilibrium swelling resulted in higher values for $\gamma_i$, most probably caused by the fact that both entanglements as well as chemical cross-links were influencing equilibrium swelling.

The results from this study show that the method developed by Horikx based on the Charlesby model for analysis of the type of vulcanize breakage: random or cross-link scission, and further developed in the present monograph, can satisfactorily be used to quantify the de-vulcanization of NR and EPDM vulcanizates.

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