

**COMPARATIVE INVESTIGATION OF THE  
DE-VULCANIZATION PARAMETERS OF TIRE RUBBERS**

**By S. Saiwari, W.K. Dierkes\* and J.W.M. Noordermeer.  
Department of Elastomer Technology and Engineering,  
University of Twente, 7500AE Enschede, the Netherlands**

**Presented at the Fall 182nd Technical Meeting of the  
Rubber Division of the American Chemical Society, Inc.  
Cincinnati, OH  
October 9-11, 2012**

**ISSN: 1547-1977**

**\*Speaker**

# **COMPARATIVE INVESTIGATION OF THE DE-VULCANIZATION PARAMETERS OF TIRE RUBBERS**

By

S. SAIWARI, W.K. DIERKES AND J.W.M. NOORDERMEER\*.

DEPARTMENT OF ELASTOMER TECHNOLOGY AND ENGINEERING,  
UNIVERSITY OF TWENTE, 7500AE ENSCHEDE, THE NETHERLANDS

\*Corresponding author. Ph: +31 (0)53 489 2529; Fax: + 31 (0)53 489 2151;  
email: J.W.M. Noordermeer@utwente.nl

## **ABSTRACT**

The optimal process conditions for a high ratio of de-vulcanization to polymer degradation have been investigated for tire rubbers: SBR, BR, NR and CIIR. These polymers all show their own particular breakdown characteristics. The temperature dependence of the breakdown mechanism was investigated by measuring sol fractions and crosslink densities. For SBR and BR, the highest reduction in crosslink density was found at a temperature of 220°C, together with a moderate increase in sol content. According to the Horikx theory, which correlates sol fraction and decrease in crosslink density, this is the result of a high degree of crosslink scission. Higher process temperatures result in a lower decrease in crosslink density due to recombination of active chain fragments. NR and CIIR show different

behaviour. Breakdown of NR in this temperature range results in an almost complete destruction of the polymer network; crosslink density is reduced to almost zero and the sol fraction is close to 100%. The same result is found for CIIR at higher temperatures. Although different rubbers react via other de-vulcanization mechanisms, the best de-vulcanization conditions for whole passenger car tire material are optimized.

## INTRODUCTION

Rubber is a very durable material, in particular tire rubber, and this poses a major challenge for recycling. For end-of-life tires, incineration is currently the most important outlet, impeding the re-use of this valuable raw material in new rubber products. A considerable share of material recycling can only be achieved if tire material can be used in real recycling loops: tires back into tires.

Passenger car tire material is a blend of different polymers: styrene butadiene rubber (SBR), butadiene rubber (BR), natural rubber (NR) and isobutylene isoprene rubber (IIR), with the main component being SBR. Each polymer has its own specific function in tires and all show their own particular degradation and de-vulcanization characteristics. Therefore, the optimal process conditions for a high ratio of de-vulcanization to polymer degradation have to be balanced not only for the main component: SBR, but also for BR, NR and IIR.

Within this study, the above mentioned polymers were de-vulcanized and investigated concerning their tendency for crosslink versus main chain scission, with the lead polymer being SBR. The balance of crosslink to polymer scission is crucial for the quality of the recycled material, and it can be shifted by using a de-vulcanization aid, which chemically enhances crosslink scission or suppresses main chain scission. Diphenyldisulfide (DPDS), which was reported to be an effective de-vulcanization chemical<sup>1-3</sup>, was used as de-vulcanization aid in this investigation. Furthermore, de-vulcanization was done under nitrogen atmosphere and the de-vulcanized material was quenched in liquid nitrogen immediately after the process in

order to suppress the reaction of radicals or other reactive species in the de-vulcanizate with oxygen or with other reactive species<sup>4</sup>. In this paper, the mechanisms behind the breakdown processes of the different elastomers are discussed, and the best de-vulcanization conditions for whole passenger car tire material are elaborated.

## **EXPERIMENTAL**

### **MATERIALS**

The SBR type used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of treated distillate aromatic extract (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. The BR (cis-1,4 polybutadiene) grade Buna CIS 132 was produced by nickel catalysis; it is a stereospecific polybutadiene with high cis-1,4 content, obtained from Dow Chemical, Germany. Its Mooney viscosity ML(1+4) measured at 100°C was 45 MU. The butyl rubber was a halogenated grade, CIIR (chlorinated butyl rubber), obtained from Lanxess, Germany. The Mooney viscosity ML(1+4) measured at 100°C was 38 MU. Natural rubber was TSR20 (Technically Specified Rubber) with a Mooney viscosity ML(1+4) measured at 100°C of 80 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives, sulfur and N-tert-butyl-2-benzothiazylsulfenamide (TBBS), were obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for

extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. TDAE oil used as processing oil for the devulcanization was supplied by Hansen&Rosenthal, Germany. Diphenyldisulfide (DPDS) used as devulcanization aid was obtained from Sigma-Aldrich, Germany.

## PREPARATION OF DE-VULCANIZATES

*Mixing and vulcanization.*- Gum rubbers were first compounded according to the formulations shown in Table I. For this investigation, no fillers were added in order to facilitate the analysis of the material. The cure characteristics were measured using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170 °C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for  $t_{c,90} + 5$  minutes in a Wickert WLP1600 laboratory compression molding press at 170 °C and 100 bar, into 2 mm thick sheets.

*Grinding.*- The vulcanized rubber sheets were subsequently ground in a Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

*De-vulcanization.*- Thermo-chemical de-vulcanization was performed batchwise in an internal mixer (Brabender Plasticorder PL-2000), having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used, and the chamber temperature was 220 °C. After adding ground rubber and TDAE oil (5 phr) into the mixer, the DPDS (30 mmol/100 g compound) was added. The de-vulcanization was carried out under nitrogen

atmosphere at 2 different temperatures: 220 °C and 260 °C. The de-vulcanization time was 5 minutes. After de-vulcanization, the material was taken out of the internal mixer and directly quenched into liquid nitrogen.

## CHARACTERIZATION OF THE DE-VULCANIZATES

*Rubber soluble fraction.*- The soluble (Sol) and insoluble (Gel) fractions of the reclaimed materials were determined by extraction in a Soxhlet apparatus. The vulcanized and de-vulcanized samples were extracted initially for 48 hrs in acetone in order to remove low molecular polar substances like remains of accelerators and curatives, followed by an extraction for 72 hrs in THF to remove the apolar components: oil and non-crosslinked polymer residues or soluble polymer released from the network by the de-vulcanization process. The extraction was followed by drying the samples in a vacuum oven at 40 °C and determining the weight loss until constant weight. The sol fraction was defined as the sum of the soluble fractions in acetone and THF. Correction for the oil contained in the original SBR was made. The gel fraction was calculated by the following equation:

$$\text{Gel fraction} = 1 - \frac{\text{weight of rubber dissolved in solvents}}{\text{weight of pure rubber in the compound}} \quad (1)$$

*Crosslink density.*- The extracted samples were subsequently swollen in toluene for 72 hrs at room temperature. The weight of the swollen vulcanizates was

measured after removal of surface liquid with absorption paper. The crosslink density was calculated according to the Flory-Rehner<sup>5</sup>, Equations 2 and 3:

$$v_e = \frac{v_r + \chi v_r^2 + \ln(1 - v_r)}{V_s (0.5 v_r - v_r^{1/3})} \quad (2)$$

with

$$v_r = \frac{m_r}{m_r + m_s (\rho_r / \rho_s)} \quad (3)$$

where:

$v_e$  = crosslink density per unit volume;

$v_r$  = polymer volume fraction of the swollen sample;

$V_s$  = solvent molar volume;

$m_r$  = mass of the rubber network;

$m_s$  = weight of solvent in the sample at equilibrium swelling;

$\rho_r$  = density of the rubber;

$\rho_s$  = density of the solvent;

$\chi$  = Flory-Huggins polymer-solvent interaction parameter (0.37 for the system

SBR/toluene<sup>6,7</sup>, 0.34 for the system BR/toluene<sup>8,9</sup>, 0.39 for the system NR/toluene<sup>10</sup>

and 0.56 for the system CIIR/toluene<sup>11</sup>)

## RESULTS AND DISCUSSION

### DE-VULCANIZATION OF SBR

The sol fractions and crosslink densities of the remaining gel as a function of the de-vulcanization temperature of the SBR de-vulcanizates (D-SBR) are depicted in Figure 1. Principally, the increase of the rubber sol fraction and decrease of crosslink density indicate the extent to which the rubber network is broken. Thermo-chemical de-vulcanization of sulfur-cured SBR using DPDS as de-vulcanization aid shows initially an increase of the rubber soluble fraction with increasing de-vulcanization temperature, but for very high temperatures in the range of 260 °C the sol fraction decreases again. Furthermore, at a temperature of 260 °C a significant increase in crosslink density is observed as well. Basically, DPDS as de-vulcanization agent was added in order to scavenge radicals formed during the reclaiming process and thus avoid secondary reactions of the polymer parts. However, at high de-vulcanization temperatures, i.e. 260 °C, an extensive generation of reactive radicals occurs. These lead to formation of new inter- and intramolecular bonds<sup>12</sup> resulting in a decrease of the rubber sol fraction and renewed increase in crosslink density.

A useful tool to further understand the de-vulcanization mechanism is the method developed by Horikx<sup>13</sup>: the rubber sol fraction of the de-vulcanizates and the crosslink density of the rubber gel fractions are correlated. Horikx derived a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in crosslink density, as a result of either

main-chain scission or crosslink breakage. This treatment of polymer degradation can equally well be applied to rubber reclaiming, where also a mix of main-chain scission and crosslink breakage takes place. When main-chain scission takes place, the relative decrease in crosslink density is given by:

$$1 - \frac{v_f}{v_i} = 1 - \left[ \frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2} \right] \quad (4)$$

where  $s_i$  is the soluble fraction of the rubber network before degradation or reclaiming,  $s_f$  is the soluble fraction of the reclaimed vulcanizate,  $v_i$  is the crosslink density of the network prior to treatment and  $v_f$  is the crosslink density of the reclaimed vulcanizate. For pure crosslink scission, the soluble fraction is related to the relative decrease in crosslink density by:

$$1 - \frac{v_f}{v_i} = 1 - \left[ \frac{\gamma_f \left(1 - s_f^{1/2}\right)^2}{\gamma_i \left(1 - s_i^{1/2}\right)^2} \right] \quad (5)$$

where the parameters  $\gamma_f$  and  $\gamma_i$  are the average number of crosslinks per chain in the insoluble network after and before reclamation, respectively. The values for  $\gamma_f$  and  $\gamma_i$  are determined as described by Verbruggen<sup>14</sup>. Figure 2 gives a graphical representation of Equations 4 and 5. The curves in this figure correspond to the situation where only main chains are broken (solid curve) and where only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is

generated until most of the crosslinks are broken; only then the long chains can be removed from the network. In the case of main-chain scission, sol is produced at a much earlier stage, because random scission of the polymers in the network results in small loose chains, which can easily be removed.

The experimentally determined sol fractions of de-vulcanized SBR as depicted in Figure 1 at 2 different de-vulcanization temperatures, 220 °C and 260 °C as a function of the relative decrease in crosslink density are shown in Figure 3. A de-vulcanization temperature of 220 °C results in a shift of the data point to the right hand side of the graph, which indicates an increase in sol fraction and large decrease of crosslink density compared to the untreated SBR. However, a further increase of the de-vulcanization temperature to 260 °C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This indicates inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is increased rather than decreased with increasing treatment temperature. All data points are rather close to the line of crosslink scission: This is the dominant breakdown process under these conditions for this polymer.

#### DE-VULCANIZATION OF BR

The sol fraction and crosslink density of BR de-vulcanizates (D-BR) as a function of de-vulcanization temperature are shown in Figure 4. A de-vulcanization temperature of 220 °C results in a significant increase in sol fraction and a decrease in crosslink density; the values of the material de-vulcanized at 260 °C show values in-

between. The sol fraction of BR de-vulcanizates as a function of the relative decrease in crosslink density according to Horikx<sup>13</sup> is shown in Figure 5. At a de-vulcanization temperature of 220 °C, all experimental data are situated above the line of main-chain scission with about 45% decrease in crosslink density compared to untreated BR; the data points of BR de-vulcanizates at a de-vulcanization temperature of 260 °C are closer to the line of main-chain scission but at a much lower relative decrease in crosslink density. This means that a de-vulcanization temperature of 220 °C is more effective than a temperature of 260 °C, as the percentage of soluble polymer is higher and the final crosslink density is lower. However, a considerable amount of main chain scission occurs in both cases, as the sol content is rather high.

The differences in the de-vulcanization behavior at the two different de-vulcanization temperatures may be attributed to the complexity of the degradation mechanism of the polybutadiene based polymer<sup>15-19</sup>. Degradation of polybutadiene and other butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer<sup>20</sup>. In a degradation process network breakdown occurs, but at the same time network recombination takes place. The degradation mechanisms are schematically depicted in Figure 6. Basically, two reactions can occur during degradation of polybutadiene:

- Chain scission and formation of inactive molecules;
- Formation of active chain segments.

Chain scission occurs when breaking of the C-C bonds (carbon-carbon bonds) in the polymer chains is accompanied by hydrogen transfer<sup>2</sup>, and results in chemically

inactive polymer segments with a lower molecular weight. The formation of active bond fragments presumably takes place when hydrogen transfer is not possible. Both, hydrogen transfer as well as radical scavenging by the de-vulcanization aid of the active chain fragments are apparently more effective at a de-vulcanization temperature of 220 °C, leading to a higher sol fraction and a lower crosslink density compared to a temperature of 260 °C. For this polymer, the devulcanization temperature should be as low as possible.

#### DE-VULCANIZATION OF NR

The sol fraction and crosslink density of NR de-vulcanizates as a function of the de-vulcanization temperature are shown in Figure 7. Almost 100% sol fraction of NR de-vulcanizates (D-NR) is observed at both de-vulcanization temperatures, 220 °C and 260 °C. Moreover, the crosslink densities of the de-vulcanizates treated at these temperatures are reduced to almost zero. This indicates that breakdown of NR in this temperature range results in an almost complete destruction of the NR network.

It was reported<sup>2</sup> before that the NR vulcanizate network can strongly be decreased in crosslink density at temperatures above 170 °C. Moreover, DPDS was reported<sup>1-3</sup> to be an effective de-vulcanization aid for NR. Temperature is the main governing factor and addition of DPDS can significantly enhance the effects. The sol fraction of NR de-vulcanizates as a function of the relative decrease in crosslink density according to Horikx<sup>13</sup> is shown in Figure 8. As can be seen, the data points for NR de-vulcanizates reach the joint top point of both lines, main-chain and crosslink

scission: This material is completely soluble; no network connections are remaining between the polymer molecules. Both NR de-vulcanizates had a very low viscosity and showed tacky behavior, another indication of a complete breakdown of the network. For this polymer, the de-vulcanization temperature is not critical within this temperature range, as long as the polymer chains stay intact. The simplified reaction scheme proposed for breaking an NR network by using DPDS is shown in Figure 9.

#### DE-VULCANIZATION OF CIIR

Figure 10 shows the changes in sol fraction and crosslink density of CIIR de-vulcanizates as a function of de-vulcanization temperature. The relative decrease in crosslink density is shown in Figure 11. An increase in sol fraction with increasing de-vulcanization temperature was observed: the sol fractions were about 36% and more than 95% after de-vulcanization of CIIR at 220 °C and 260 °C, respectively. Consequently, the de-vulcanized CIIR at 260 °C had a very low viscosity and showed tacky behavior. However, in terms of crosslink density it was found that there was no significant decrease at a de-vulcanization temperature of 220 °C. It can clearly be noticed from Figure 11 that all experimental data are situated above the line of main-chain scission and at less than 10% decrease in crosslink density compared to untreated CIIR. They are clustered at the left hand side which indicates that the crosslink density of the treated rubber is more or less the same as the crosslink density of the untreated one. This may be attributed to a de-vulcanization mechanism which is not uniform and homogeneously distributed throughout the rubber particles, and for

which the validity of the Horikx plot is limited. The two different de-vulcanization mechanisms, uniform and non-uniform, are schematically depicted in Figure 12<sup>21</sup>.

A limitation of the Horikx representation is, that it assumes homogeneous breakdown of the vulcanized network throughout the particles (A). However, the results for de-vulcanized CIIR at 220°C indicate a different mechanism: peeling off of the outer layers of the particles, while the inner cores of the particles stay more or less untreated at constant crosslink density (B). This inhomogeneity causes in actual practice a lower decrease in crosslink density at a particular sol fraction, than would have been obtained for homogeneous breakdown.

## CONCLUSIONS

SBR, BR, NR and CIIR react according to different de-vulcanization mechanisms. BR behaves more or less the same as SBR: it shows chain recombination with increasing de-vulcanization temperatures. Using a de-vulcanization temperature of 220 °C leads to a decrease in crosslink density for at least 45% in case of BR and 65% in case of SBR compared to original vulcanizates. For NR, the network is easily broken down with a treatment temperature higher than 170 °C, but it is a combination of polymer and crosslink scission. Therefore, it is necessary to keep the de-vulcanization temperature as low as possible to prevent the destruction of the NR molecular chain and to shift the balance to crosslink scission. CIIR acts differently from the other types of rubber: The network breakdown is enhanced by increasing the de-vulcanization temperature within the temperature window used in this study. However, at lower

temperatures, the breakdown is not uniformly distributed throughout the particles; for a uniform breakdown a higher temperature has to be used. Taking all these factors into consideration, a good compromise for the de-vulcanization conditions for all types of rubber can be proposed. For the best de-vulcanization of tire rubbers, it is necessary to keep the de-vulcanization temperature as low as possible for an efficient devulcanization, a high ratio of crosslink to main chain scission, and a homogenous breakdown of the vulcanized network. The main processing parameter is temperature, however it has an adverse effect on these three characteristics.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from RecyBEM B.V., the Netherlands. The technical support and supply of rubber and chemicals for this research by ApolloVredestein is also highly appreciated.

## REFERENCES

- <sup>1</sup> V.V. Rajan, W.K. Dierkes, R. Joseph, and J.W.M. Noordermeer, *J. Appl. Polym. Sci.*, **102**, 4194 (2006).
- <sup>2</sup> V.V. Rajan, W.K. Dierkes, J.W.M. Noordermeer, and R. Joseph, *RUBBER CHEM. TECHNOL.*, **78**, 855 (2005).
- <sup>3</sup> A.R. Jalilvand, I. Ghasemi, M. Karrabi, and H. Azizi, *Progr. Rubber. Plast. Recycling Techn.*, **24**(1), 33 (2008).

- <sup>4</sup> S. Saiwari, W.K. Dierkes, and J.W.M. Noordermeer, paper # 82, presented at a meeting of the Rubber Division, ACS, Oct. 11-13., 2011, Cleveland (OH, USA).
- <sup>5</sup> P.J. Flory, *J. Am. Chem. Soc.*, **63**, 3096 (1941).
- <sup>6</sup> S.C. George, K.N. Ninan, and S. Thomas, *Polym. Compos.*, **7**, 343 (1999).
- <sup>7</sup> S.L. Abd-El-Messieh and K.N. Abd-El-Nour, *J. Appl. Polym. Sci.*, **88**, 1613 (2003).
- <sup>8</sup> W.L. Hergenrother, *J. Appl. Polym. Sci.*, **16**, 2611 (1972).
- <sup>9</sup> W.O.Parker, A. Ferrendo, D. Ferri, and V. Canepari, *Macromolecules*, **40**, 5787 (2007).
- <sup>10</sup> M. Kojima, A. Tosaka, and Y. Ikeda, *Green Chem.*, **6**, 84 (2004).
- <sup>11</sup> J.T. Sunil and R. Joseph, *Int. J. Polym. Mat.*, **56**, 743 (2007).
- <sup>12</sup> “Thermal Degradation of Organic Polymers”, S.L. Madorsky, ed., Interscience Publishers, New York, U.S., 1964.
- <sup>13</sup> M.M. Horikx, *J. Polym. Sci.* **19**, 445 (1956).
- <sup>14</sup> M.A.L. Verbruggen, L. van der Does, J.W.M. Noordermeer, M. van Duin, and H.J. Manuel, *RUBBER CHEM. TECHNOL.*, **72**, 731 (1999).
- <sup>15</sup> R.N. Hader and D.S. le Beau, *Industrial and Engineering Chemistry*, **43(2)**, 250 (1951).
- <sup>16</sup> V. Yu Levin, S.H. Kim, and A.I. Isayev, *RUBBER CHEM. TECHNOL.*, **70**, 120 (1997).
- <sup>17</sup> J. Choi and A.I. Isayev, *RUBBER CHEM. TECHNOL.*, **84**, 55 (2011).
- <sup>18</sup> A.I. Isayev, S.H. Kim and W. Feng, *RUBBER CHEM. TECHNOL.*, **78**, 606 (2005).

- <sup>19</sup> J.S. Oh, A.I. Isayev, and E. von Meerwall, RUBBER CHEM. TECHNOL., **77**, 745 (2004).
- <sup>20</sup> M.D. Sarkar, P.G. Mukunda, P.P. De, and A.K. Bhowmick, RUBBER CHEM. TECHNOL., **70**, 855 (1997).
- <sup>21</sup> K.A.J. Dijkhuis, I. Babu, J.S. Lopullissa, J.W.M. Noordermeer and W.K. Dierkes, RUBBER CHEM. TECHNOL., **81**, 190 (2008).

## CAPTIONS TO FIGURES

FIG. 1.– Sol fraction and crosslink density of SBR de-vulcanizates versus de-vulcanization temperatures

FIG. 2.– Random main chain scission and crosslink scission curves in a Horikx plot.

FIG. 3.– Relative decrease in crosslink density versus sol fraction of SBR de-vulcanizates

FIG. 4.– Sol fraction and crosslink density of BR de-vulcanizates versus de-vulcanization temperatures

FIG. 5.– Relative decrease in crosslink density versus sol fraction of BR de-vulcanizates

FIG. 6.– Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers.

FIG. 7.– Sol fraction and crosslink density of NR de-vulcanizates versus de-vulcanization temperatures

FIG. 8.– Relative decrease in crosslink density versus sol fraction of NR de-vulcanizates

FIG. 9.– Simplified reaction scheme proposed for the de-vulcanization of natural rubber by DPDS<sup>2</sup>

FIG. 10.– Sol fraction and crosslink density of CIIR de-vulcanizates versus de-vulcanization temperatures

FIG. 11.– Relative decrease in crosslink density versus sol fraction of CIIR de-vulcanizates

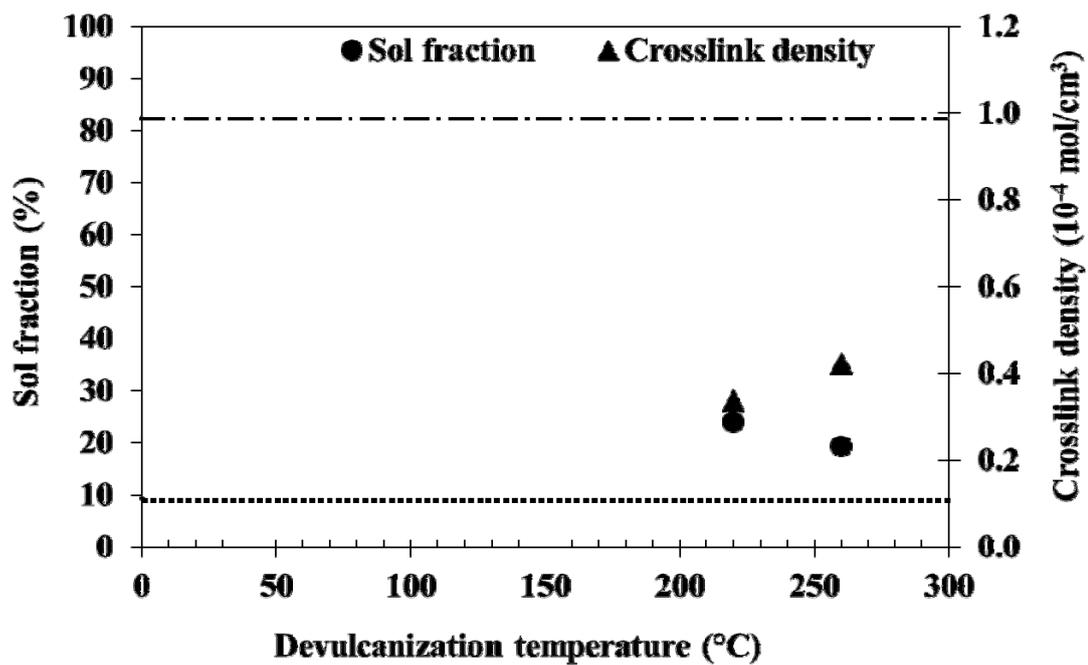
FIG. 12.– Schematic representation of two different de-vulcanization mechanisms,  
A: Homogeneous de-vulcanization and B: Inhomogeneous de-vulcanization<sup>21</sup>.

TABLE I. FORMULATIONS OF THE RUBBER COMPOUNDS

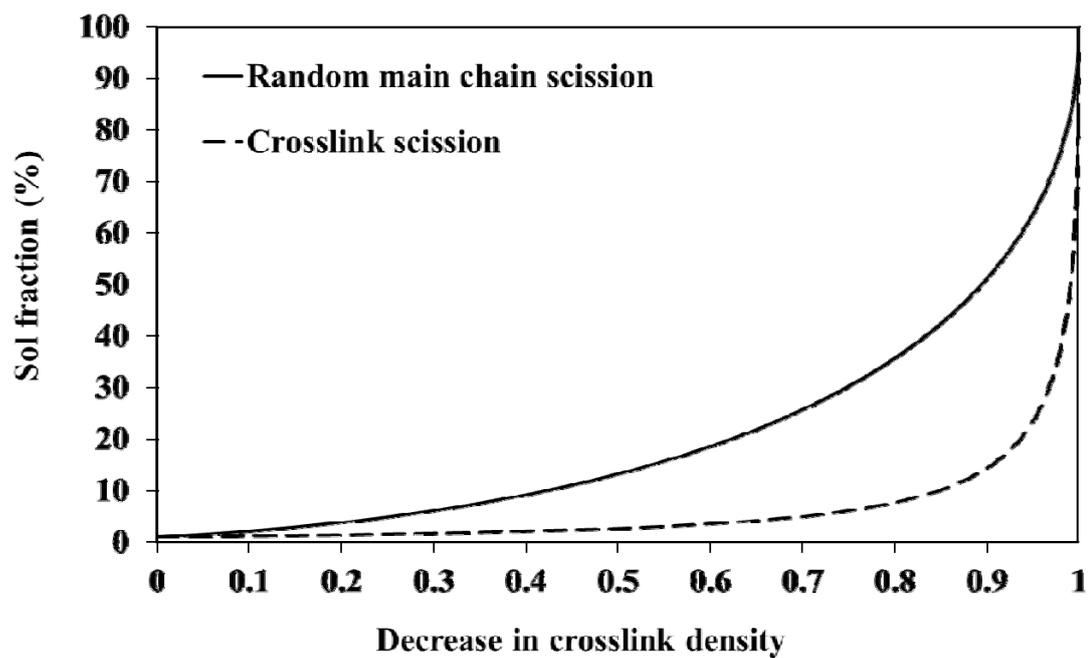
Ingredient	Phr			
SBR	100	-	-	-
BR	-	100	-	-
NR	-	-	100	-
CIIR	-	-	-	100
ZnO	4.13	3.00	3.00	3.00
Stearic acid	2.06	2.00	1.00	2.00
Sulfur	2.75	2.00	2.00	0.50
TBBS*	1.38	1.00	1.00	-
MBTS**	-	-	-	1.00

\* TBBS: N-tert-butyl-2-benzothiazyl sulfenamide

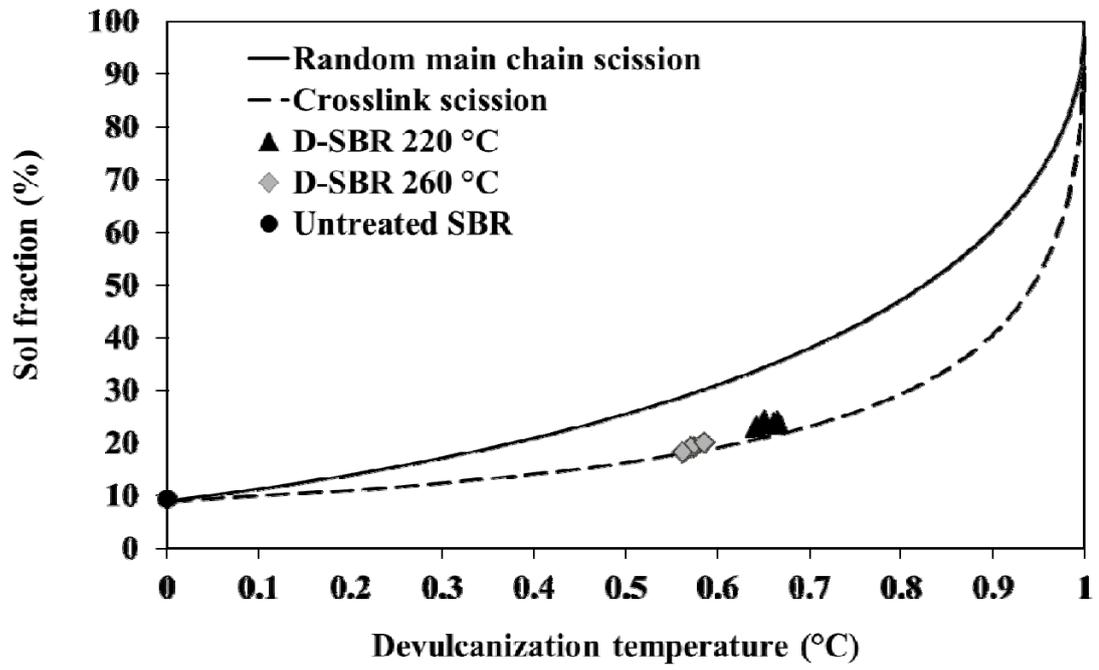
\*\* MBTS: Merceptobenzothiazyl disulfide



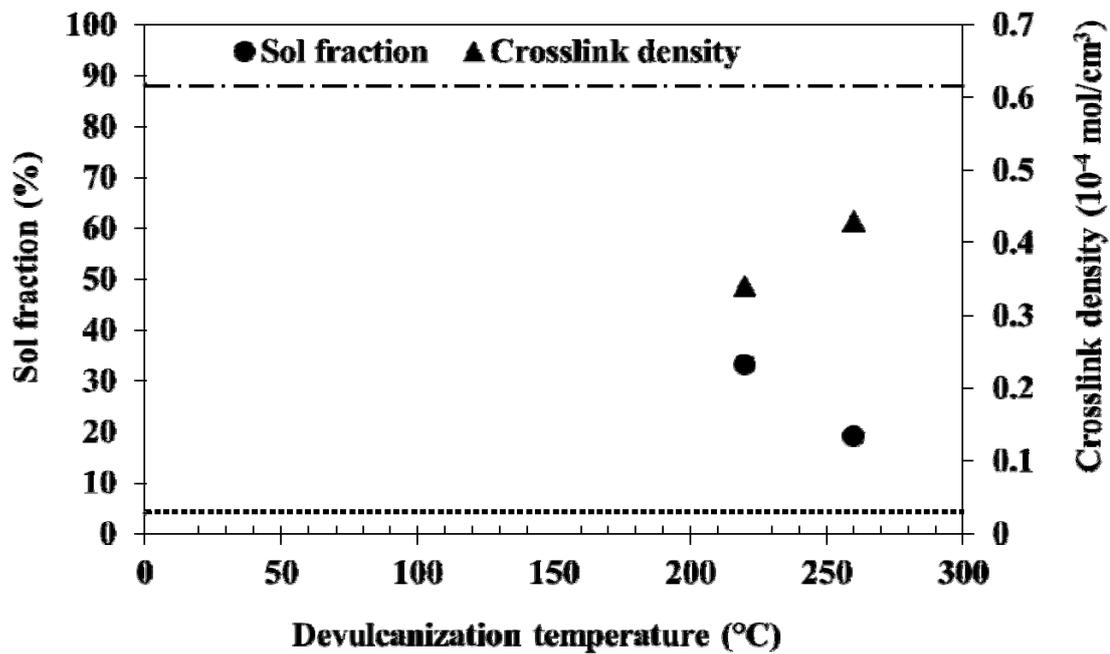
**Figure 1.** Sol fraction and crosslink density of SBR de-vulcanizates versus de-vulcanization temperature; (.....): Sol fraction of untreated SBR vulcanizate; (- - -): Crosslink density of untreated SBR vulcanizate.



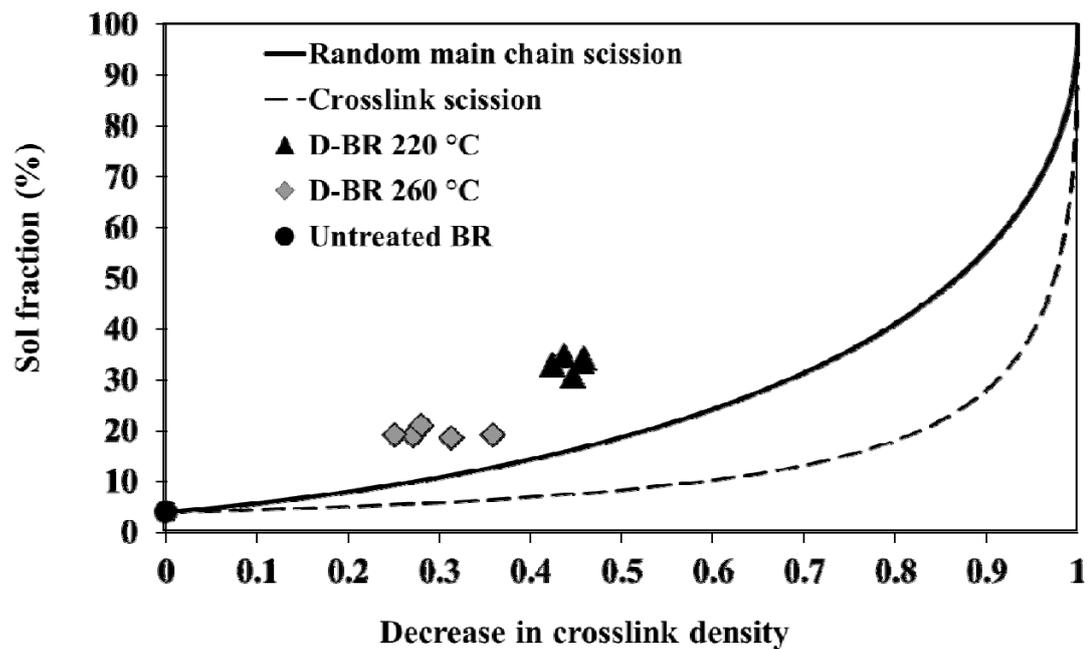
**Figure 2** Random main chain scission and crosslink scission curves in a Horikx plot



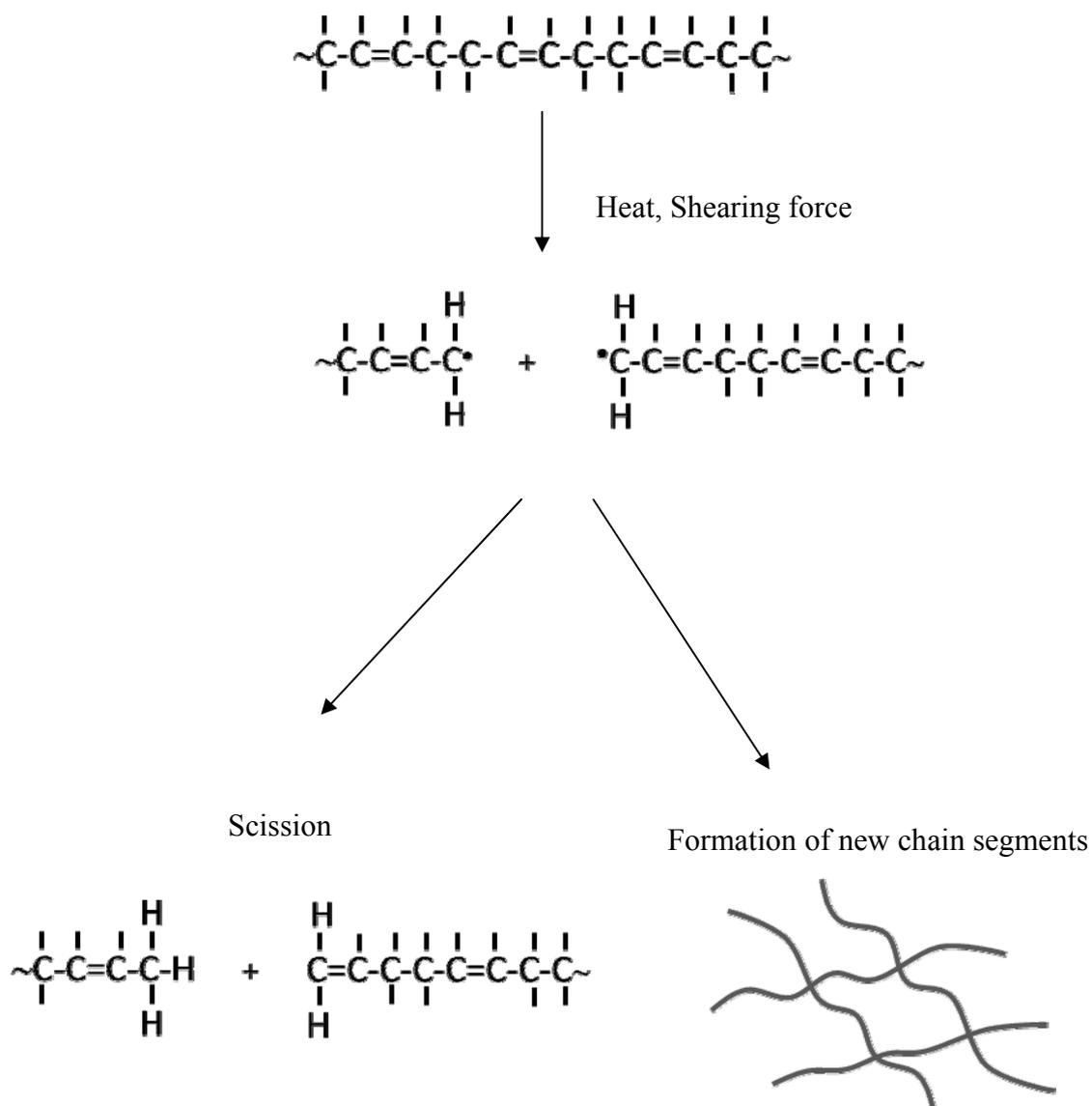
**Figure 3.** Relative decrease in crosslink density versus sol fraction of SBR de-vulcanizates



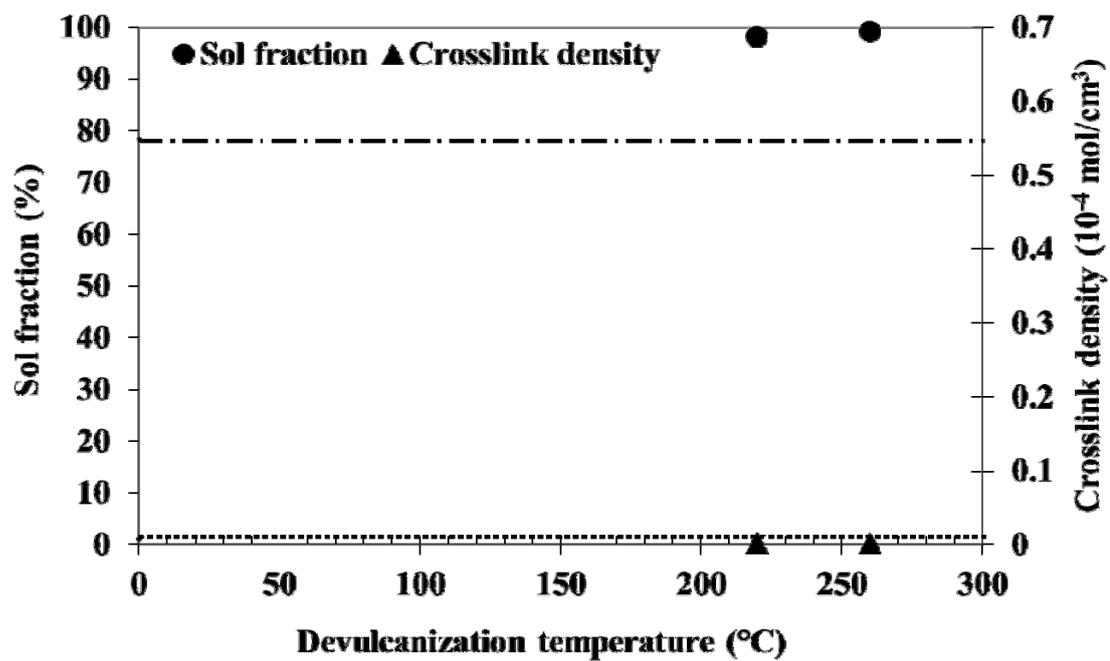
**Figure 4.** Sol fraction and crosslink density of BR de-vulcanizates versus de-vulcanization temperature; (.....): Sol fraction of untreated BR vulcanizate; (- - -): Crosslink density of untreated BR vulcanizate.



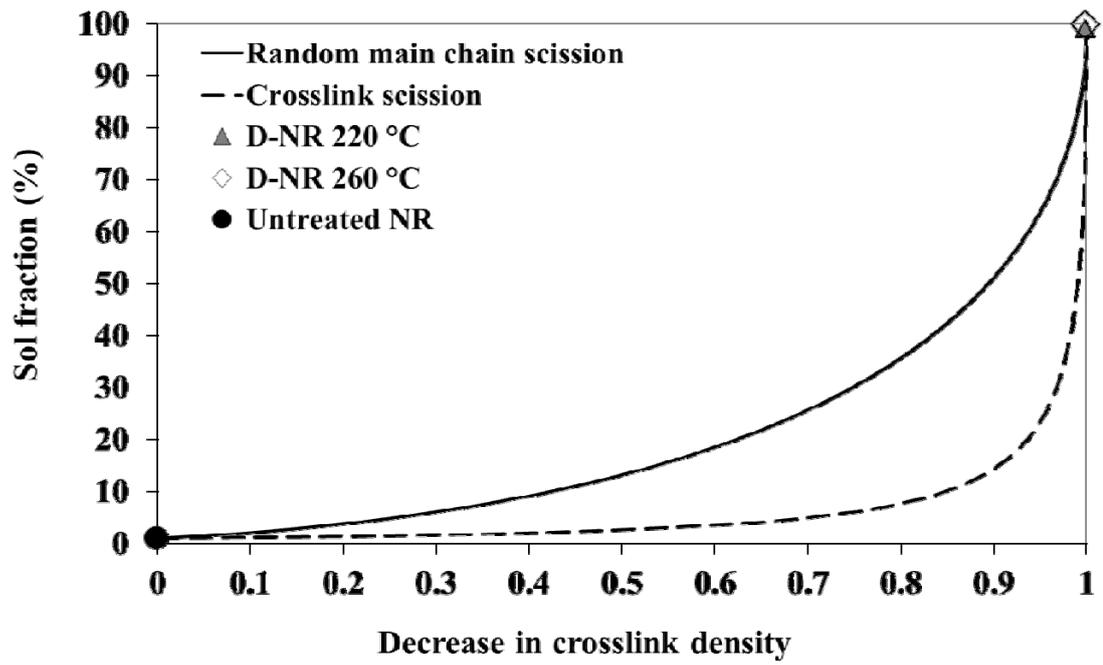
**Figure 5.** Relative decrease in crosslink density versus sol fraction of BR de-vulcanizates



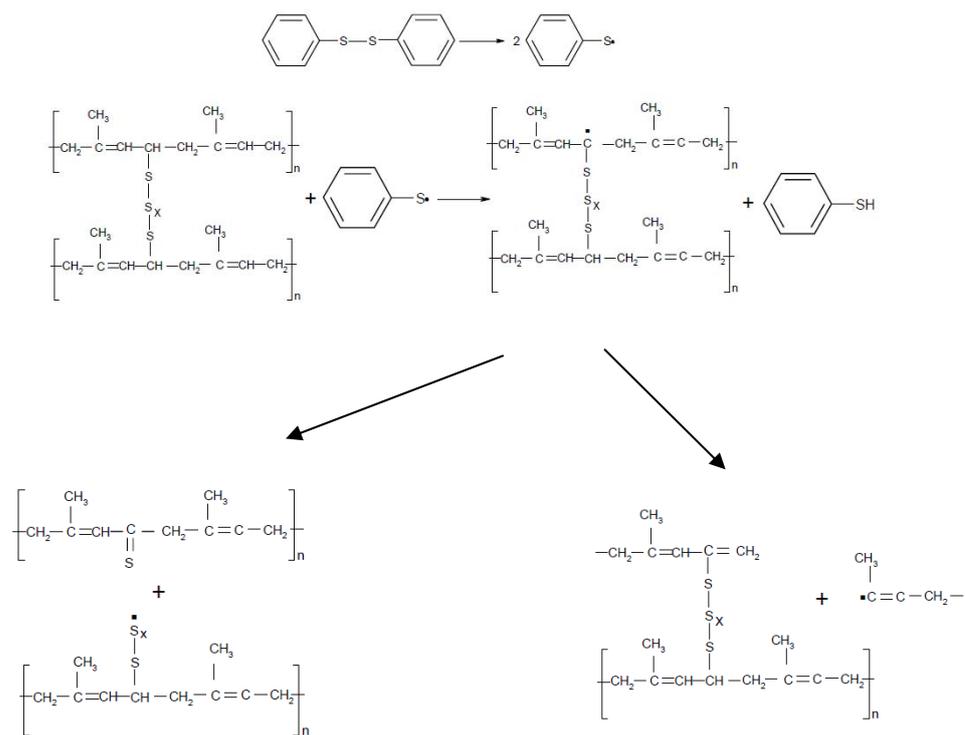
**Figure 6.** Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers.



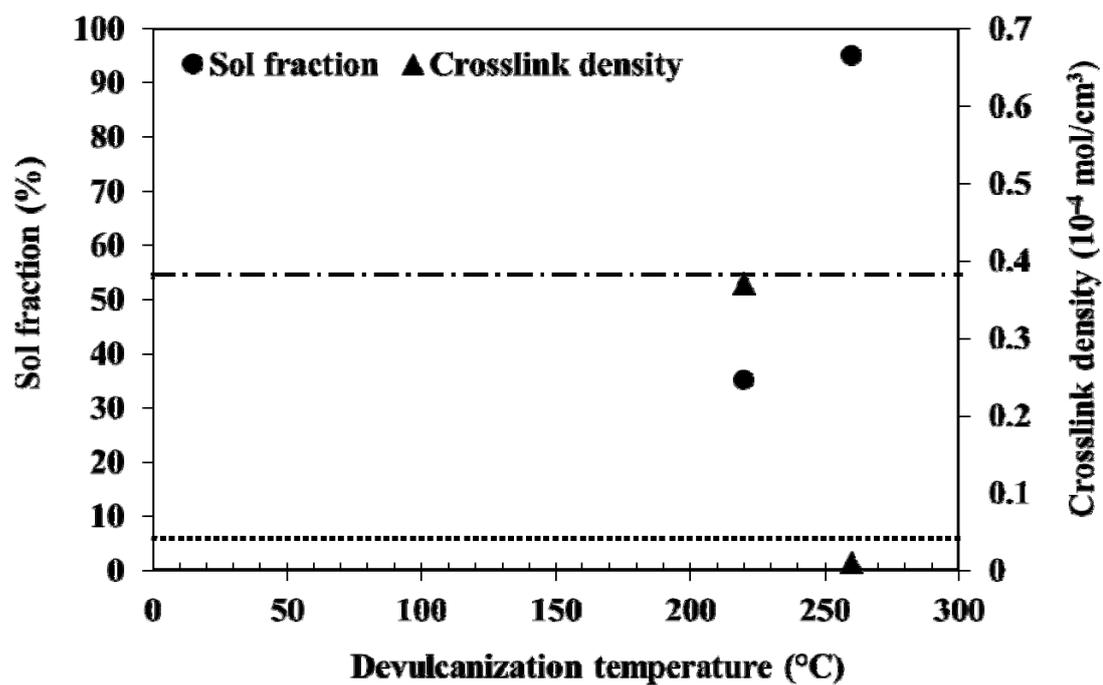
**Figure 7.** Sol fraction and crosslink density of NR de-vulcanizates versus de-vulcanization temperature; (.....): Sol fraction of untreated NR vulcanizate; (- · - ·): Crosslink density of untreated NR vulcanizate.



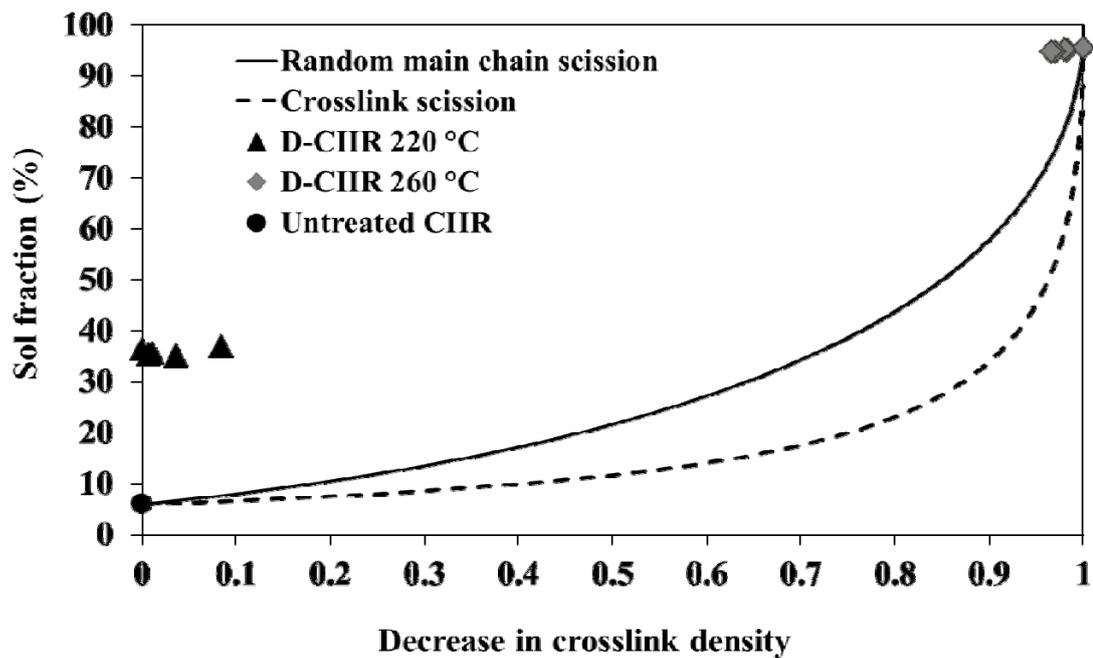
**Figure 8.** Relative decrease in crosslink density versus sol fraction of NR de-vulcanizates



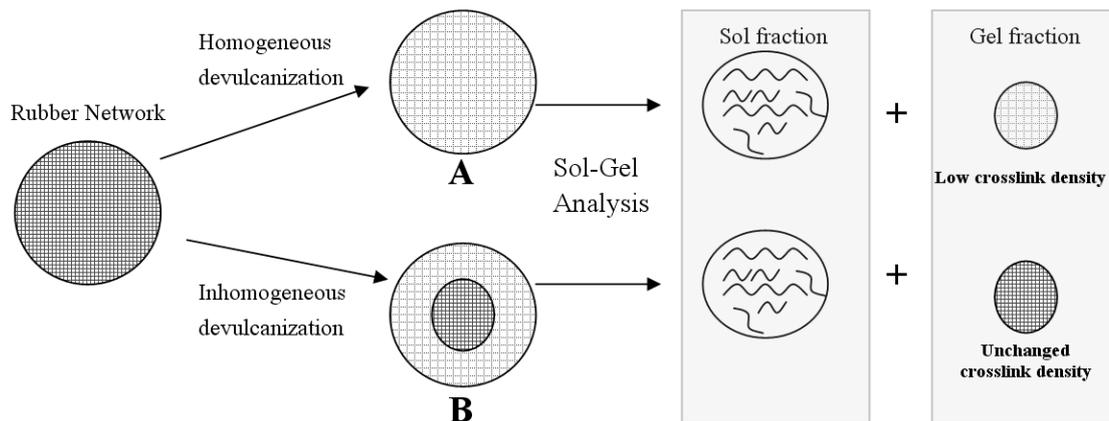
**Figure 9.** Simplified reaction scheme proposed for the de-vulcanization of natural rubber by DPDS<sup>2</sup>



**Figure 10.** Sol fraction and crosslink density of NR de-vulcanizates versus de-vulcanization temperature; (.....): Sol fraction of untreated CIIR vulcanizate; (- · - ·): Crosslink density of untreated CIIR vulcanizate.



**Figure 11.** Relative decrease in crosslink density versus sol fraction of CIIR de-vulcanizates



**Figure 12.** Schematic representation of two different de-vulcanization mechanisms, A: Homogeneous de-vulcanization and B: Inhomogeneous de-vulcanization<sup>21</sup>.