Development of a continuous process for EPDM devulcanization in an extruder
Sutanto, Poppy

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CHAPTER 3

MODELING THE KINETICS OF AN EPDM DEVULCANIZATION IN AN INTERNAL BATCH MIXER USING AN AMINE AS THE DEVULCANIZING AGENT

1. Introduction

This chapter focuses on the estimation of the effect of operating conditions on the degree of conversion during the devulcanization reaction. Unfortunately, the molecular kinetic model of devulcanization is not available in the literature. Both the action of a devulcanizing agent towards the crosslinks in an EPDM compound and the mechanism of the mechanochemical reaction are not exactly known. The main reason for this is the number of components present in rubber compounds. These components interfere with each other during the process and during the analysis, making it difficult to distinguish and exactly follow all the phenomena happening throughout the devulcanization. It is anyhow obvious that the crosslink density (≡ the amount of crosslinks per gram rubber = [Xlink]) is reduced and the devulcanizing agent is consumed during the devulcanization. Based on the reasons mentioned above, an engineering kinetic model is developed based on a study in a batch setup. The model studied here contains the main variables as the control and output parameters, i.e. temperature, shear rate and reactant concentrations (in this case: crosslink density and amine concentration).

Shortly, instead of studying the elementary kinetics of each component and combining them at the end to obtain a complete model, the opposite approach is used to study the kinetics of the system. A final kinetic model, which covers all the phenomena of devulcanization, is chosen out of several proposed models by selecting the one that gives the best agreement with a number of experimental data. From this final kinetic model, physical explanations of the model are proposed.

Earlier work on devulcanization reaction under a shear field was done by Fukumori et al. [1]. They proposed another perspective of the phenomena within the devulcanization process. The role of elastic constants has been considered as the
dominant one in a devulcanization. As shown in Figure 3.1, the difference in the elastic constant between the chemical bonds is much more significant than the difference in the bond energy. The elastic constant (K-value) for the S-S bonds is estimated to be about \( \frac{1}{30} \) of that for the C-C bonds, while the ratio of the bond energies is less than \( \frac{1}{5} \), as shown in Figure 3.1(a). Hence, simple heating in a pressure vessel would cleave both C-C and C-S or S-S bonds randomly, which in turn would lead to inferior physical properties of the reclaimed rubber. At extremely high shear stress, induced by kneading at high degree of filling in the reactor, most rubber molecules may become fully elongated to their limited extensibility. Under these conditions, the bonds having a lower elastic constant (the S-S bonds) may become more extended in comparison with bonds having higher elastic constant (the C-C bonds), as shown in Figure 3.1(b). This means that the elastic energy induced by high shearing may be particularly effective on the S-S bonds, causing a selective breakage at the crosslink sites.

Nevertheless, this selective breakage mechanism would be possible when the number of C-C bonds is almost equal to the number of C-S and S-S bonds. In practice, the number of C-C bonds in a rubber is much larger compared to the number of C-S and S-S bonds, leading to a higher chance in stretching C-C bond instead of C-S bond or S-S bond and accordingly unselective scission.

![Figure 3.1. Breakdown of crosslinks in high shear flow: (a) model for network chain; (b) deformation of the network chain (particularly S-S bonds) by shearing [1]](image)

The preceding work from Verbruggen et al. [2] on the effectivity of amine as devulcanization agent, shows an alternative to devulcanize EPDM rubbers with diphenyldisulfides. Amines are used for different purposes in rubbers, including the application as reclaiming agent. Several types of amine function as degradation stabilizers for plastics and coatings. Most degradation processes have a free radical character and these amines act as radical scavengers [2]. The devulcanization process at high temperatures is assumed to have a radical character and amines might facilitate this reaction. The work of Verbruggen showed that among different kinds of amines investigated (e.g. primary, secondary, tertiary, aromatic, benzyllic, and heterocyclic amines), only the amines with an \( \alpha \)-H atom are effective as devulcanization agent. It was also shown that the use of these amines reduced the crosslink density mainly by selective reaction of the former with the sulfur bridges [2].
Chapter 3: Modeling the Kinetics of an EPDM Devulcanization in an Internal Batch Mixer using an Amine as the Devulcanizing Agent

2. Materials and Methods

2.1. Materials & Equipments

Waste vulcanized EPDM was supplied by Hertel B.V. and ground to particles less than 1 cm in size by Rubber Resources. The vulcanized EPDM compound originates from the production line for building profiles. Hexadecylamine (HDA) from Acros was used as the devulcanization agent. Sunpar 150 oil from Sunoco B.V. was used as plasticizer in the process. Polyisobutene from Acros with a molecular weight below 17000 was used to calibrate the Brabender.

Devulcanization of EPDM was conducted in a Brabender batch mixer (Plastic-corder PL2000) in this research. The rotor speed and wall temperature of the mixing chamber were controlled. During the reaction, the torque and the temperature of the material were monitored as a function of time.

The premixing of the reaction substrates (EPDM rubber, HDA and oil) was conducted in a tumbling mixer.

2.2. Analytical Methods

Mooney Viscosity

The Mooney viscosity ML(1+4)100°C was measured using a Mooney MV2000 apparatus from Alpha Technologies.

Crosslink Density

The crosslink density was used as an indication of the extent of the devulcanization reaction. The presence of crosslinks hinders the dissolution of the rubber in an organic solvent: the rubber matrix takes up the solvent into its network and swells.

The sample was immersed in decaline for 3 days until it reached equilibrium swelling and subsequently was dried in a vacuum oven at 80°C until constant weight was reached. Decaline was used as the swelling agent, since it gives the highest accuracy in the measurement of EPDM crosslink density among the other swelling agents (e.g. benzene, cyclohexane, etc.) due to its low solvent-polymer interaction parameter with EPDM [3].

The weight of the swollen sample and the weight of the dried sample were used to calculate the relative decrease of crosslink density (\([X_{\text{link}}]\)) during the process. The apparent crosslink density was calculated using the Flory-Rehner equation as follows [4,5]:

\[
[X_{\text{link}}] = \frac{\ln(1-V_R) + V_R + \chi \cdot V_R^2}{V_S(0.5 \cdot V_R - V_R^{3/2})}
\]

where the interaction parameter of decalin-EPDM \(\chi\) is 0.121+0.278\(V_R\) [6].
Hexa-decyl Amine (HDA) Concentration

The concentration of HDA remaining after devulcanization was determined quantitatively by gas chromatography (GC). For this purpose, a gas chromatograph HP5890 series II equipped with HP-5 Capillary column (0.25 mm internal diameter and 30 m length) was used.

First, the rubber sample was extracted in a known amount of hexane for at least 2 days, which is enough to extract all the remaining HDA in the rubber sample. An extraction time longer than this does not give any increase in the amount of HDA dissolved. Then, 4 parts of the extract were mixed with 1 part of the internal standard solution (0.5% decane in hexane) and analysed in the GC.

A calibration chart was made by measuring the spectrum of several HDA and internal standard (IS) solutions in order to obtain a correlation between the ratio of HDA to IS area and the ratio of HDA to IS concentration. Using this correlation, the actual concentration of HDA in the extract and consequently in the devulcanized sample could be calculated.

3. Experiments

3.1. Experimental Scheme

The devulcanization process was conducted based on the devulcanization methods proposed by Mouri et al.[7] and Verbruggen et al. [2] using a shearing machine and hexadecylamine as the devulcanization agent. The devulcanization process performed in the Brabender batch mixer occurred under shear stress generated by the rotating mixing heads and by heat supplied by the electrical heater and generated by viscous dissipation.

The experiments were conducted at rotor speeds varying from 40 to 120 RPM and wall temperatures from 235°C to 285°C (Table 3.1). This temperature range was chosen because it has been reported to be the range in which HDA effectively cleaves the crosslinks within EPDM rubber [2]. The data obtained from varying temperature and rotation speed were used to generate the engineering model, which was used on a later stage to describe the kinetics of the devulcanization reaction as a function of temperature and shear rate.
Table 3.1. Experimental scheme for the kinetic investigation of the devulcanization reaction

<table>
<thead>
<tr>
<th>Series</th>
<th>( T_{\text{wall}} ) (°C)</th>
<th>RPM</th>
<th>[HDA] ( \text{mol/g rubber} )</th>
<th>[Oil] %wt</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>225</td>
<td></td>
<td>80</td>
<td></td>
<td>To determine the effect of temperature on rate constants</td>
</tr>
<tr>
<td>2</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>3</td>
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</tr>
<tr>
<td>7</td>
<td>225</td>
<td></td>
<td>3x10^{-4}</td>
<td>5</td>
<td>To determine the effect of shear on rate constants</td>
</tr>
<tr>
<td>8</td>
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<td></td>
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<td>9</td>
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<tr>
<td>20</td>
<td>225</td>
<td></td>
<td>60</td>
<td></td>
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</tr>
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</table>

3.2. Shear Rate Calibration in the Brabender

The Brabender constant had to be determined first in order to convert rotor speed into shear rate. Therefore, a calibration using polyisobutene as a Newtonian liquid, as described by Goodrich and Porter [8], was carried out. The calibration resulted in the following conversion between the shear rate and rotation speed of the Brabender:

\[
\dot{\gamma} = 0.6754 \cdot S \text{ [s}^{-1}] 
\]  

Shear rate is included in the model, as it is known from the screening experiments that devulcanization goes faster at higher rotation speeds. The reason is most commonly quoted as the shear force (which is related to the shear rate by a viscosity term), since energy is needed to deform the rubber matrix.

4. Results

4.1. Decrease in Crosslink Density without any Devulcanizing Agent

Although the results from the screening experiments showed that a devulcanization agent is necessary to devulcanize the rubber, it was interesting to see
the behavior of the measured crosslink density in time when processing the rubber without any addition of devulcanization agent. The results of the experiments in this condition are given in Figure 3.2. Without addition of HDA, the crosslink density decreased at much slower rate compared to when HDA was present. Besides, it was also observed that the devulcanization without HDA cannot reach the point at which the rubber starts to melt. This implies that the use of a devulcanizing agent is essential to devulcanize the EPDM rubber studied.

![Crosslink density-time profile during EPDM devulcanization in the Brabender mixer without HDA](image)

Figure 3.2. Crosslink density-time profile during EPDM devulcanization in the Brabender mixer without HDA

The plots show that the decrosslinking rate decreases with time along with the decrease of crosslink density. This is a reasonable tendency, since breaking the rubber network becomes more difficult when the amount of the remaining bonds to be broken is less.

4.2. The Model

Not enough information is found in literature to derive an applicable kinetic model of EPDM devulcanization using amine as a function of shear rate. However, the following informations are available:

- Devulcanization happens even without the presence of HDA, i.e. only by the action of temperature and shearing, even if the conversion is sensibly lower
- HDA reacts with the sulfur bridges to yield a decrosslinked product [2].

Based on this information and of very simple kinetic considerations, several models can still be proposed due to the fact that the exact mechanism is unknown. We
performed a screening of several proposed models (Figure 3.3) by looking for the one that can give constant reaction orders and minimum sum of squares deviation from the experimental data.

![Figure 3.3. Modeling procedure](image-url)
The following models for decrosslinking rate and HDA consumption were found as the result of the screening procedure:

$$\frac{-d[Xlink]}{dt} = k_1(T, \gamma) \cdot [Xlink]^a \cdot [HDA]^b + k_2(T, \gamma) \cdot [Xlink]^c$$  

$$\frac{-d[HDA]}{dt} = k_3(T, \gamma) \cdot [Xlink]^a \cdot [HDA]^b + k_4(T, \gamma) \cdot [HDA]^d$$

The temperature, shear rate, concentration of the devulcanization agent, crosslink density and the devulcanization time are the parameters that undoubtedly determine the degree of decrosslinking. Therefore, they are all included in the final model. Shear rate and temperature are incorporated in the rate constants ($k$’s), given that the shear rate indicates the intensity of the mechanical force applied and the temperature affects the physical properties of the material. The crosslink density, the devulcanization agent concentration, and time are explicitly entailed in the model.

It is commonly understood that for the reaction of two components, the reaction rate coefficients are related by a constant ratio ($\xi$), the so-called stoichiometric coefficient, according to the following scheme:

Crosslinks + $\xi$HDA $\rightarrow$ Product

$$r = -\frac{d[Xlink]}{dt} = -\frac{d[HDA]}{dt} \xi$$  

(5)

In an attempt to see if such a stoichiometric coefficient between HDA and the crosslinks can be extracted from the kinetic data, the values of $k_3$ are divided by the values of $k_1$ according to:

$$\xi = \frac{-\frac{d[HDA]}{dt}}{-\frac{d[Xlink]}{dt}} = \frac{k_3(T, \gamma) \cdot [Xlink]^a \cdot [HDA]^b}{k_1(T, \gamma) \cdot [Xlink]^a \cdot [HDA]^b}$$  

(6)

The result shows that by dividing $k_3$ by $k_1$ from every run, an almost constant number of 1.1 is obtained, with an error of 0.063 at 95% level of confidence.

Hence, it is fair to state that this value can be considered to be the stoichiometric coefficient between the HDA reacting and the crosslinks cleaved. For the rest of the discussion, $k_3$ will then be represented by $k_1$, since $k_3$ is related to $k_1$ by a constant ratio:

$$k_3 = \xi \cdot k_1$$  

(7)

4.3. Model for the Rate Constants

Increase of temperature results in a higher kinetic constant according to the Arrhenius equation due to the higher kinetic energy of the molecules. Contrary to that, the temperature affects the elasticity and viscosity of the polymer and accordingly the bond-rupture mechanism in the case of the mechanochemical reaction. Increasing temperature will soften the polymer, lower the stress and reduce the rate of energy
input at a given shear rate, hence the chain ruptures [9]. The final effect of the temperature increase is the sum of its effect on both reactions. The temperature effects are illustrated in Figure 3.4-3.6.

Figure 3.4. Effect of temperature on $k_1$ at different shear rates

Figure 3.5. Effect of temperature on $k_2$ at different shear rates
Increasing the shear rate at constant temperature, the mechanical energy (torque) applied is higher, as is shown in the following relation [10]:

\[ M \sim \dot{\gamma}^n \sim S^n \tag{8} \]

where \( M \) is the torque, \( \dot{\gamma} \) is the shear rate, \( S \) is the rotation speed, and \( n \) is a constant.

Consequently, higher shear rate results in more severe crosslink ruptures. This in turn might accelerate the chemical reaction rate between HDA and crosslinks, since the mechanochemical reaction might facilitate the chemical one by stretching out the crosslinks. The effects of shear rate on the \( k \)'s are plotted in Figure 3.7-3.9.

Figure 3.6. Effect of temperature on \( k_4 \) at different shear rates

Figure 3.7. Effect of shear rate on \( k_1 \) at different temperatures
A model for the rate constants can now be derived, by including the effects of temperature and shear rate. The effect of temperature can be represented well by an Arrhenius equation, while that of the shear rate by an allometric equation, according to:

\[
k = k_0 \gamma^p \exp\left(\frac{-E_a}{RT}\right)
\]  

(9)

The fitting results of the rate constants with this model are shown in Figure 3.10-3.12 for \( k_1 \), \( k_2 \), and \( k_4 \), respectively. They all show a very good agreement between the rate constants and the model shown in equation (9).
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Figure 3.10. Fitting result of $k_1$ with the model $k_1 = k_0 \cdot \gamma^p \cdot \exp(-E_a / RT)$

Figure 3.11. Fitting result of $k_2$ with the model $k_2 = k_0 \cdot \gamma^p \cdot \exp(-E_a / RT)$
Figure 3.12. Fitting result of $k_4$ with the model $k_4 = k_0_4 \cdot \gamma^{p_4} \cdot \exp(-E_{a_4}/RT)$

The engineering kinetic model for the EPDM compound studied is now complete with its dependencies on the temperature and shear rate. The values of the parameters derived from the whole modeling procedure are listed in Table 3.2. As can be seen in table 3.2, the reactions orders found are not whole numbers and larger than 1. This shows that the reactions studied are not elementary ones due to the presence of other components (as well as the possible interactions between them) in the rubber compound.

<table>
<thead>
<tr>
<th>Table 3.2. Model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
</tr>
<tr>
<td>$-\frac{dVe}{dt} = k_1(\dot{\gamma},T).Ve^a.HDA^b + k_2(\dot{\gamma},T).Ve^c$</td>
</tr>
<tr>
<td>$-\frac{dHDA}{dt} = k_3(\dot{\gamma},T).Ve^a.HDA^b + k_4(\dot{\gamma},T).HDA^d$</td>
</tr>
<tr>
<td>$k_1 = k_0_1 \cdot \dot{\gamma}^p_1 \cdot \exp(-E_{a_1}/RT)$</td>
</tr>
<tr>
<td>$k_2 = k_0_2 \cdot \dot{\gamma}^p_2 \cdot \exp(-E_{a_2}/RT)$</td>
</tr>
<tr>
<td>$k_3 = \xi_2 k_1$</td>
</tr>
<tr>
<td>$k_4 = k_0_4 \cdot \dot{\gamma}^p_4 \cdot \exp(-E_{a_4}/RT)$</td>
</tr>
<tr>
<td>$k_{0_2} = 1.3628 \cdot 10^7$</td>
</tr>
<tr>
<td>$P_2 = 7.3821$</td>
</tr>
<tr>
<td>$E_{a_2} = 153818.1 \text{ J/mol}$</td>
</tr>
<tr>
<td>$P_4 = 5.5002$</td>
</tr>
</tbody>
</table>
4.4. The Model Validation

The final model using the parameters listed in Table 3.2 was verified with the data from three different series. The validation results are shown in Figures 3.13-3.15. They all show a good agreement with the data. It means that this model can adequately describe the kinetics of the devulcanization reaction of EPDM and HDA under shear. This comprises the chemical reaction of HDA and crosslinks, the mechanochemical and the side reactions (i.e. the oxidative scission and HDA evaporation) in the range of processing conditions studied.

However, the model is less accurate in describing the HDA consumption, which is shown in the larger error. This error is especially significant in the first minutes of the devulcanization reaction. During these first minutes of reaction, the conversion of HDA is still low and some of the HDA might be remaining on the chamber wall of the Brabender mixer, which is impracticable to be collected quantitatively. This loss of HDA is very difficult to be measured and it gives lower values of the HDA analyzed.

![Figure 3.13. Model validation with experimental data (T= 235°C, 40 rpm)](image-url)
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![Graph](image_url)

Figure 3.14. Model validation with experimental data (T= 265°C, 100 rpm)

![Graph](image_url)

Figure 3.15. Model validation with experimental data (T= 285°C, 120 rpm)

5. Discussions

Taking a look at the resulting model (Equations (3) and (4)), both equations contain two terms on the right side. It is fair to say that the second terms represent other reactions happening during the devulcanizations, besides the main
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devulcanization reaction between the crosslink and HDA. The possible phenomena that may take place during the devulcanization process are listed as follows:

1. reaction of amine with the sulfur bridges
2. evaporation of the amine
3. adsorption/desorption of the amine on carbon black
4. oxidative scission of the sulfur bridges
5. oxidative scission of the main chains
6. oxidation of the amine

It must be emphasized here that most probably these phenomena are not elementary reactions and therefore complex reaction paths are involved. In spite of this, the proposed model is able to acceptably account for all these processes, although it does not explain what happens on a molecular scale. The first (main) term in equation (3) and (4) represents the reaction of amine with the sulfur bridges (phenomenon 1). The second term in equation (3) may correspond to the oxidative scission of the sulfur bridges (phenomenon 4). The second term in equation (4) may account for the oxidation, evaporation, and adsorption/desorption of the amine (phenomena 2, 3, and 6). The detailed study of these phenomena is out of the scope of this thesis.

5.1. Effect of Temperature and Shear Rate on Rate Constants

Both the temperature and shear rate affect the devulcanization reaction studied significantly. Therefore, simulations were prepared to study their influences on the rate constants by using the equation obtained for $k's$ (equation 9).

The increase of the rate constants per degree temperature at various shear rates are listed in Table 3.3. It can be seen that the increase of $k_1$ is higher at a given higher shear rate. As it has been mentioned earlier, raising the temperature significantly increases the chemical reaction rate between HDA and the crosslinks. On the other hand, the temperature increase also reduces the mechanochemical reaction rate. This corresponds to the theory proposed by Bueche [11], who formulated the breaking tension of a bond as a function of viscosity, shear rate, density, and the molecular weight between entanglements $M_e$:

$$\text{Breaking tension} \sim \frac{\eta \dot{\gamma}}{\rho} M_e^{0.5} \quad (10)$$

An increase in temperature will result in a large decrease in $\eta$ and minor changes in $\rho$ and $M_e$. If a higher fraction of bond rupture is expected, this opposite effect of the temperature increase must be compensated by an increase of $\dot{\gamma}$. Therefore, raising the temperature at higher shear rates results in less negative impact on the bond rupture rate. Consequently, it results in a higher increase in the reaction rate constant between HDA and crosslinks ($k_1$).
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Table 3.3. Temperature influence on the rate constants at certain shear rates

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>$\Delta k_1/\Delta T$ (%)</th>
<th>$\Delta k_2/\Delta T$ (%)</th>
<th>$\Delta k_4/\Delta T$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.03</td>
<td>6.81</td>
<td>49.81</td>
<td>794.43</td>
</tr>
<tr>
<td>60.79</td>
<td>7.21</td>
<td>47.57</td>
<td>193.09</td>
</tr>
<tr>
<td>67.54</td>
<td>7.36</td>
<td>54.80</td>
<td>39.11</td>
</tr>
<tr>
<td>74.29</td>
<td>7.91</td>
<td>51.22</td>
<td>50.56</td>
</tr>
<tr>
<td>81.05</td>
<td>8.41</td>
<td>48.57</td>
<td>14.09</td>
</tr>
</tbody>
</table>

\[
* \frac{\Delta k_i}{\Delta T} = \frac{k_i(T_2) - k_i(T_1)}{(T_2 - T_1) \cdot k_i(T_1)} \cdot 100\%
\]

The role of shear is significant when handling high molecular weight polymers, such as EPDM, under shear force. The latter, applied by the mixer heads, causes stretching of the EPDM matrix, which in turn results in network breakdown. When the EPDM matrix stress limit is exceeded, network breakdown will occur.

As the crosslink density decreases, the network becomes looser and the chain stability of the EPDM matrix increases [9]. Consequently, the effectiveness of the shear force upon the EPDM matrix decreases throughout the devulcanization. Therefore, the decrease in the crosslink density is very fast during the first minutes, and then it gradually slows down and finally reaches a plateau where the decrease in crosslink density with time is insignificant (equilibrium).

As shown in Table 3.4, increasing the shear rate within the range of 54 - 81 s$^{-1}$ at 235°C resulted in a less significant increase in $k_1$ than increasing it within the shear range of 27 - 54 s$^{-1}$. This difference might correspond to the critical mechanical energy value required to break the network. The energy applied should be sufficient to create high tension between the crosslinks, leading to bond ruptures. This energy contributes to the dissociation of the sulfidic crosslink bonds. Once the energy applied exceeds the stress limit of the crosslink bonds, its further increase would give less significant effect on $k_1$.

Table 3.4. Shear rate influence on the rate constants at certain temperatures

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>$T$ (°C)</th>
<th>$\Delta k_1/\Delta \dot{\gamma}$ (%)</th>
<th>$\Delta k_2/\Delta \dot{\gamma}$ (%)</th>
<th>$\Delta k_4/\Delta \dot{\gamma}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.02-40.52</td>
<td>235</td>
<td>5.55</td>
<td>151.93</td>
<td>4.89</td>
</tr>
<tr>
<td>40.52-54.03</td>
<td>235</td>
<td>4.17</td>
<td>49.09</td>
<td>102.56</td>
</tr>
<tr>
<td>54.03-81.05</td>
<td>235</td>
<td>2.36</td>
<td>78.34</td>
<td>1131.89</td>
</tr>
</tbody>
</table>

\[
* \frac{\Delta k_i}{\Delta \dot{\gamma}} = \frac{k_i(\dot{\gamma}_2) - k_i(\dot{\gamma}_1)}{(\dot{\gamma}_2 - \dot{\gamma}_1) \cdot k_i(\dot{\gamma}_1)} \cdot 100\%
\]

The increases in $k_2$ and $k_4$ seem to be higher with increasing temperature and shear rate, compared to the increase in $k_1$. However, their real values are lower than $k_1$. Therefore, the increases of $k_2$ and $k_4$ can be neglected compared to the $k_1$ increase, regarding their contribution to the total devulcanization reaction rate.
Figures 3.16 and 3.17 summarize the influences of temperature and shear rate on the $k_1$, which is the rate constant of the main reaction term.

![Diagram of chemical and mechanical reactions](image)

**Figure 3.16. Incremental change of $k_1$ with temperature**

![Diagram of chemical and mechanical reactions](image)

**Figure 3.17. Incremental change of $k_1$ with shear rate**

### 5.2. Competition between the Reaction Terms

The values of the kinetic parameters obtained from this research can be seen in Table 3.2. The activation energies for each reaction are calculated according to equation (9). The activation energy for the reaction between HDA and the crosslinks ($E_a$) is derived to be 73.19 kJ/mol. Deuri and Bhowmick [12] reported the values for thermal desulfurization of polysulfidic crosslinks in various grades of EPDM vulcanizates to be in the range of 60-85 kJ/mol in air and 95 kJ/mol in nitrogen environment. The value of the activation energy obtained in this research seems to be within this range, although in the devulcanization reaction conducted, not only polysulfidic, but also disulfidic and monosulfidic crosslink scission and main chain scission might occur.

The activation energy in the $k_2$ and $k_4$ terms, mainly related to the oxidative scissions ($E_{a2}$) and the HDA evaporation ($E_{a4}$), are found to be 153 and 127 kJ/mol (Table 3.2). Compared to these values, the activation energy of the HDA reaction with crosslinks is lower. The activation energy is the minimum energy that must be overcome by the reacting molecules before the reaction can occur [13]. Considering this definition, it can be concluded that the reaction between HDA and crosslinks has a higher tendency to occur than the second-term reactions in equations (3) and (4). This can also be seen from the value of $k_1$, which is much higher than $k_2$ and $k_4$ at corresponding temperature and shear rate. This result agrees with the expectation that the main reaction between HDA and crosslinks should dominate over side reactions (degradation, evaporation, etc.) in order to prevent deterioration in the mechanical
properties and to achieve an effective devulcanization process. This low extent of degradation is also in agreement with the fact that EPDM material has an excellent resistance against the oxidation process. Due to the higher activation energy, the rate of oxidative scission and HDA evaporation are also more sensitive towards temperature effect. This can be seen in the higher increase of $k_2$ and $k_4$ with temperature increase, compared to the increase of $k_1$.

6. Conclusions

A complex process such as devulcanization can be represented by an engineering kinetic model, where the effects of the dominant parameters on the process are studied and formulated in a practical engineering equation.

The model includes all the phenomena that occur during the devulcanization process, but it is not possible to distinguish them on a molecular level. This is also the reason why the reaction orders obtained from this kind of engineering equation are large and fractional. According to the validation results, the model is able to predict the decrease of the reactants quite adequately.

Although the kinetic model derived here is not an elementary model, the results can give an idea about the reaction profiles and will be useful for designing a reactor and can give a contribution to further research on the devulcanization kinetics. The rate constant of the second term of equation (4) is much smaller in comparison with that of the first term. This means that the rate of side reactions involving HDA is much lower than the reaction rate between HDA and crosslinks (at the HDA concentration studied), which is an advantage to the process since the HDA can be optimally used for the main reaction with the crosslinks.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Arrhenius constant</td>
</tr>
<tr>
<td>$a, b, c, d$</td>
<td>reaction orders in equation (3), (4)</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy according to Arrhenius equation (kJ/mol)</td>
</tr>
<tr>
<td>$[\text{HDA}]$</td>
<td>concentration of devulcanizing agent (mol/g rubber)</td>
</tr>
<tr>
<td>$k_1, k_2, k_3, k_4$</td>
<td>rate constants in equation (3), (4)</td>
</tr>
<tr>
<td>$K$</td>
<td>elastic constant</td>
</tr>
<tr>
<td>$M$</td>
<td>torque (N.m)</td>
</tr>
<tr>
<td>$M_c$</td>
<td>molecular weight between entanglements (g/mol)</td>
</tr>
<tr>
<td>$r$</td>
<td>reaction rate in equation (5) (mol/(g.s))</td>
</tr>
<tr>
<td>$S$</td>
<td>speed of rotation of brabender rotor (rpm)</td>
</tr>
<tr>
<td>$\text{SSE}$</td>
<td>sum of square of the error</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (K or °C)</td>
</tr>
<tr>
<td>$V_R$</td>
<td>volume fraction of rubber in swollen gel</td>
</tr>
</tbody>
</table>
Chapter 3: Modeling the Kinetics of an EPDM Devulcanization in an Internal Batch Mixer using an Amine as the Devulcanizing Agent

\[ V_s \] molar volume of the solvent \[ m^3/mol \]

\[ [\text{Xlink}] \] crosslink density \[ mol/g \]

\[ \gamma \] shear rate \[ s^{-1} \]

\[ \eta \] viscosity \[ Pa.s \]

\[ \tau \] shear stress \[ N/m^2 \]

\[ \xi \] stoichiometric ratio for the reaction between HDA and crosslinks (see equation (7)) -

\[ \chi \] Flory-Huggins parameter -

References