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Modeling on the kinetics of an EPDM devulcanization in an internal batch mixer using an amine as the devulcanizing agent

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Abstract

The use of amines and the application of mechanical force (shear) in rubber devulcanization have been reported in the literatures. In this paper, the devulcanization of ethylene propylene diene rubber (EPDM) is conducted in a Brabender batch mixer using hexadecylamine (HDA) as the devulcanizing agent. Considering the complexity of the compound and the limitations of the analyses techniques for crosslinked systems, an engineering approach to model a devulcanization process of EPDM material is proposed. An engineering kinetic model has been derived by fitting a large number of experimental data with several models based on simple kinetic considerations. Rate determining parameters such as temperature, shear rate, reactant concentrations and time are included in the model. The model obtained covers all the phenomena happening during the devulcanization, without distinguishing them on the molecular level.

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Keywords: Computation; Kinetics; Modelling; Processing; Recycling; Rubber

1. Introduction

In 2002, the world's rubber consumption was up to 18 million tons, comprised of 41% natural rubber (NR) and 59% synthetic rubber (SR). Among these SRs, EPDM (ethylene propylene diene rubber) ranks as the third largest SR after styrene butadiene rubber (SBR) and butyl rubber (BR), contributing about 12% and 17% of world and European SR production respectively (Burridge, 2003).

EPDM was first introduced in the USA in a limited commercial quantity in 1962. Although its commercial production began only in 1963, currently EPDM is the fastest growing general-purpose elastomer (ca. 3–4% per year, Burridge, 2003). This fact is due to EPDM's excellent properties, especially its ozone resistance and its ability to be highly loaded by filler. Therefore, the utilization of EPDM can be found in a wide range of applications. An example in the automotive application can clearly indicate the importance of EPDM. About 3% of the total weight of a vehicle corresponds to non-tire rubber

products, namely weather-strips, hoses, vibration insulators and miscellaneous parts and about one-half by weight of this non-tire rubber is constituted by EPDM (Fukumori et al., 2002).

The earlier methods of handling rubber wastes, such as incineration, pyrolysis and landfill have ended up with ecological and environmental quality problems. Nevertheless, most of the scrap is still utilized for heat, yet very little is utilized for re-claimed rubber, which is the ideal recycling destination. Concerning the value and the importance of EPDM in the rubber world, a comprehensive study on an effective recycling technology for EPDM is indispensable.

Due to its vulcanized character, an EPDM rubber product cannot be readily recycled by melting. A more elaborate recycling technique is needed. Before a vulcanized rubber can be plasticized, the three-dimensional network structure of the vulcanizate has to be cleaved, which can take place at the cross-link sites or in the main chain (backbone). The main chain scission creates shorter polymer chains and causes a deterioration of the mechanical properties as compared to those of the virgin rubber, while cross-link scission results in polymers in their original form. Therefore, the three-dimensional network breakdown (the so-called devulcanization) is preferably selective at the cross-linking positions.

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Fig. 1. Different possible pathways involved in the devulcanization of a rubber network (Verbruggen et al., 1999).

Table 1
Bond energies of the three crosslink types (C–C, C–S, S–S) (Olmsted III and Williams, 1997)

Type of vulcanizates	Type of bonds to be broken	Energy required (kJ/mol)
Sulfur vulcanizate	–C–S–	310
	–S–S–	270
Peroxide vulcanizate	–C–C–	370

EPDM has a different reactivity towards devulcanization particularly from NR vulcanizates when treated with aromatic disulfides, due to differences in structure of the polymer chain and the cross-link sites. If the same devulcanization conditions are applied to EPDM rubber as used for NR, hardly any devulcanization were observed (Verbruggen et al., 1999).

Sverdrup (1970) proposed possible reaction pathways, which may occur during devulcanization of NR using diphenyldisulfide (see Fig. 1). The thermal devulcanization process leads to scission of the sulfur-cross-links as well as main-chain scission. In either case, diaryl-disulfide acts as a quenching agent for the radicals formed to prevent the recombination. Depending on the chemical characteristics of the rubber backbone, the balance between the two competing reactions differs greatly.

The mechanistic differences in the recycling chemistry of EPDM and NR have been explored by Verbruggen et al. (1999). They showed that sulfur-cured EPDM in general needs far more strenuous conditions than NR to be devulcanized. However, EPDM is less apt to main-chain scission relative to NR. The lower reactivity of EPDM towards disulfide compared to NR is the result of higher cross-link densities and a higher percentage of more stable monosulfidic cross-links in EPDM (Verbruggen et al., 1999). As can be seen in Table 1, the energy needed to break monosulfidic cross-links is higher than the energy needed to break the polysulfidic cross-links.

Mouri et al. (2000) proposed a devulcanization reaction mechanism under shear field, depicted in Fig. 2. It is believed that the polysulfidic and disulfidic bonds are converted initially by the action of heat into monosulfidic bonds and release low-molecular sulfide compounds (such as hydrogen sulfide, sulfur dioxide and carbon disulfide). These monosulfidic bonds are then broken under shear force. Subsequently, the remaining

sulfur atoms in the broken sulfur cross-links react with neighboring H-atoms to form a stable state (low-reactivity sulfur functional groups).

Earlier work on devulcanization reaction under a shear field was done by Fukumori et al. (2002). They proposed another perspective of the phenomena within the devulcanization process. As shown in Fig. 3, the difference in the elastic constant between 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 $\frac{1}{2}$, as shown in Fig. 3(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. Generally, it is understood that the mechanical behavior of cross-linked rubber may be mainly controlled by the entropic term in the strain energy. In contrast with this entropic deformation behavior, 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 Fig. 3(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 cross-link 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.

The preceding work from van Duin et al. (2003) on the effectiveness 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 (van Duin et al., 2003). The devulcanization process at high temperatures is assumed to have a radical character, and amines might facilitate this reaction. The work of van Duin et al. has shown that among different kinds of amines investigated (e.g. primary, secondary, tertiary, aromatic, benzylic and heterocyclic amines), only the amines with an α -H atom are effective as devulcanization agent. It was also shown that the use of these amines reduced the cross-link density mainly by cross-link scission (van Duin et al., 2003).

This paper presents the first part of a research project on a continuous devulcanization process, with the main focus on estimation of the effect of operating conditions on the degree of conversion. The molecular kinetic model of devulcanization is still under investigation at the moment. Both the action of a devulcanizing agent towards the cross-links in an EPDM compound and the mechanism of the mechanochemical reaction are not exactly known. The main reason for this is the

Fig. 2. Mechanism of cross-linking breakdown reaction proposed by Mouri et al. (2000).

Fig. 3. Breakdown of cross-links in high shear flow: (a) model for network chain; (b) deformation of the network chain (particularly S-S bonds) by shearing (Fukumori et al., 2002).

number of components contained 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 any how obvious that the cross-link density ($\equiv$ the amount of cross-links per gram rubber $\equiv$ [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 cross-link 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 studied further.

2. Experimental part

2.1. Materials and equipments

Waste vulcanized EPDM was supplied by Hertel B.V. from their production line for building profiles, and ground to particles less than 1 cm in size by Rubber Resources. The EPDM

compound was vulcanized using 8.6:1 accelerator:sulfur ratio, which is typical for efficient (EV) sulfur-curing system. This curing system leads to the formation of mostly mono-sulfidic bonds (Klingensmith et al., 1997). 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 17 000 was used to calibrate the Brabender.

A Brabender batch mixer (Plastic-corder PL2000) was used to perform the devulcanization reaction of EPDM. 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

2.2.1. Mooney viscosity

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

2.2.2. Cross-link density

The presence of cross-links hinders the dissolution of the rubber in an organic solvent: the rubber matrix takes up the solvent into its network and swells. The extent of swelling is dependent on the cross-link density of the rubber, given by the Flory–Rehner equation (Flory, 1950).

Table 2
Experimental scheme for the kinetic investigation of the devulcanization reaction

Series	Twall (°C)	RPM	[HDA] mol/g rubber	[Oil] %wt	Remarks
1	225	80	3×10^{-4}	5	To determine the effect of temperature on rate constants
2	230				
3	240				
4	250				
5	260				
6	270				
7	225	90			To determine the effect of shear on rate constants
8	250				
9	270				
10	225	100			
11	250				
12	270				
13	225	110			
14	250				
15	270				
16	225	120			
17	250				
18	270				
19	225	40			
20	225	60			

The sample was immersed in decaline for 3 days until it reached equilibrium swelling and subsequently 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 cross-link density among the other swelling agents (e.g. benzene, cyclohexane, etc.) (Dikland et al., 1993). The weight of the swollen sample and the weight of the dried sample are used to calculate the relative decrease of cross-link density ([Xlink]) during the process by using the cross-link density calculations in Reference (Flory, 1950).

2.2.3. 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 i.d. and 30 m length) was used.

First, the rubber sample was extracted in a known amount of hexane for at least 2 days, an extraction time long enough for the remaining HDA in the rubber samples to dissolve. Then, four parts of the extract were mixed with one part of the internal standard (IS) solution (0.5% decane in hexane) and analyzed in the GC.

A calibration chart was made by measuring the spectrum of several HDA and 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.

2.3. Experiments

2.3.1. Experimental scheme

The devulcanization process conducted in this study was based on the mechanism proposed by Mouri et al. (2000) and van Duin et al. (2003) using a shearing machine and HDA as the devulcanization agent. The devulcanization was performed in a Brabender batch mixer under shear stress generated by the rotating mixing heads and at high temperature supplied by an electrical heater.

The experiments were conducted at rotor speeds varying from 40 to 120 rpm and wall temperatures from 235 to 285 °C. This temperature range was chosen because it is reported to be the range in which HDA effectively cleaves the cross-links within EPDM rubber (van Duin et al., 2003). 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 2).

2.3.2. 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 (1967), was carried out. The calibration resulted in the following conversion between the shear rate and rotation speed of the Brabender:

$$\dot{\gamma} = 0.6754S \quad (\text{s}^{-1}). \quad (1)$$

Shear rate is included in the model, since it is known 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. Unfortunately, it is neither possible nor convenient to run the machine at constant shear force, which means adjusting the rotation speed with respect to the change in viscosity throughout the process.

3. Results

3.1. Screening experiments

The screening experiments were carried out to find the optimum initial concentrations of devulcanizing agent and oil, and the preparation procedure to obtain acceptable devulcanized product and reproducibility. The optimum way to introduce HDA into the reaction mixture is also investigated: i.e., by direct addition, by initially grinding the HDA before premixing, and by adding alcohol (96% ethanol, technical quality) to dissolve the HDA in order to improve the mixing. As the devulcanization reaction proceeds, cross-link density decreases, resulting in a lower measurable Mooney viscosity. Mooney viscosity was used in the screening experiments as an early indication of the degree of devulcanization.

The screening experiments resulted in an optimum devulcanization process for an initial concentration of 3×10^{-4} mol HDA/g rubber and 5%-wt oil. Further increase of the concentration of HDA or oil did not give significant additional decrease in Mooney viscosity. The best preparation procedure for the blend is grinding HDA before adding it to the rubber, together with some alcohol to aid the premixing. The blend is continuously rotated in a tumble-mixer for 4 days before it is ready to be processed in the Brabender.

3.2. Decrease in cross-link 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 cross-link density in time when processing the rubber without any addition of devulcanization agent. The results of the experiments in this condition are given in Fig. 4. Without addition of HDA, the cross-link 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.

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

3.3. The model

Not enough information is found in literature to derive an applicable kinetic model of EPDM devulcanization using amine

Fig. 4. Cross-link density–time profile during EPDM devulcanization in the Brabender mixer without HDA.

as a function of shear rate. However, the following informations are available:

- (1) 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.
- (2) HDA reacts with the sulfur bridges to yield a decross-linked product (van Duin et al., 2003).

Based on these informations and of very simple kinetics 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 (Fig. 5) by looking for the one that can give constant reaction orders and minimum sum of squares deviation from the experimental data.

The result of such screening procedure is the following:

$$-\frac{d[\text{Xlink}]}{dt} = k_1(T, \dot{\gamma}) \cdot [\text{Xlink}]^a [\text{HDA}]^b + k_2(T, \dot{\gamma}) \cdot [\text{Xlink}]^c, \quad (2)$$

$$-\frac{d[\text{HDA}]}{dt} = k_3(T, \dot{\gamma}) \cdot [\text{Xlink}]^a [\text{HDA}]^b + k_4(T, \dot{\gamma}) [\text{HDA}]^d. \quad (3)$$

The temperature, shear rate, concentration of the devulcanization agent, cross-link density and the devulcanization time are the parameter that undoubtedly determine the degree of decross-linking. 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 cross-link density, the devulcanization agent concentration and time are explicitly entailed in the model.

It is commonly understood that for the reaction of two substrates, the reaction rate coefficients are related by a constant ratio (ξ), the so-called stoichiometric coefficient, according to

Fig. 5. Modeling procedure.

the following scheme:

$$r = -\frac{d[\text{Xlink}]}{dt} = \frac{-d[\text{HDA}]/dt}{\xi} \quad (4)$$

In an attempt to see if such a stoichiometric coefficient between HDA and the cross-links can be extracted from the

kinetic data, the values of k_3 are plotted against the values of k_1

$$\xi = \frac{-d[\text{HDA}]/dt}{-d[\text{Xlink}]/dt} = \frac{k_3(T, \dot{\gamma}) \cdot [\text{Xlink}]^a \cdot [\text{HDA}]^b}{k_1(T, \dot{\gamma}) \cdot [\text{Xlink}]^a \cdot [\text{HDA}]^b} \quad (5)$$

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.

Fig. 6. Effect of temperature on k_1 at different shear rates. Fig. 7. Effect of temperature on k_2 at different shear rates.

Hence, it is fair to state that this value can be considered to be the stoichiometric coefficient between the HDA reacting and the cross-links 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:

$$k_3 = \xi \cdot k_1. \quad (6)$$

3.4. 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 the temperature will soften the polymer, lower the stress and reduce the rate of energy input at a given shear rate, hence the chain ruptures (Porter and Casale, 1987). The final effect of the temperature increase is the sum of its effect on both reactions. The temperature effects are illustrated in Figs. 6–8.

Increasing the shear rate at constant temperature, the mechanical energy (torque) applied is higher, as is shown in the following relation (Blyler and Daane, 1967):

$$M \sim \dot{\gamma}^n \sim S^n, \quad (7)$$

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 cross-link ruptures. This in turn might accelerate the chemical reaction rate between HDA and cross-links, since the mechanochemical reaction might facilitate the chemical reaction by mechanically rupturing the cross-links. The effects of shear rate on the k 's are plotted in Figs. 9–11.

A model for the rate constants was 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 the

Fig. 8. Effect of temperature on k_4 at different shear rates. Fig. 9. Effect of shear rate on k_1 at different temperatures.

Fig. 10. Effect of shear rate on k_2 at different temperatures. Fig. 11. Effect of shear rate on k_4 at different temperatures.

following equation:

$$k = k_0 \cdot \dot{\gamma}^p \exp\left(\frac{-Ea}{RT}\right). \quad (8)$$

The fitting results of the rate constants with this model are shown in Figs. 12–14 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 Eq. (8).

Finally, the engineering kinetic model for the EPDM compound studied is now complete with its dependencies on the temperature and shear rate, as listed in Table 3.

3.5. The model validation

The final model using the parameters listed in Table 6 was verified with the data from three different series. The validation results are shown in Figs. 15–17. 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 that comprises of the chemical reaction of HDA and cross-links, 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 bars. 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 still 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.

Fig. 12. Fitting result of k_1 with the model $k_1 = k_{01} \cdot \dot{\gamma}^{p1} \exp(-Ea_1/RT)$.

Fig. 13. Fitting result of k_2 with the model $k_2 = k_{02} \cdot \dot{\gamma}^{P_2} \exp(-Ea_2/RT)$.

Fig. 14. Fitting result of k_4 with the model $k_4 = k_{04} \cdot \dot{\gamma}^{P_4} \exp(-Ea_4/RT)$.

Table 3
Model parameters

Equation	Parameters
$-\frac{d[\text{Xlink}]}{dt} = k_1(\dot{\gamma}, T) \cdot [\text{Xlink}]^a \cdot [\text{HDA}]^b + k_2(\dot{\gamma}, T) \cdot [\text{Xlink}]^c$	$a = 4.93$
	$b = 0.61$
	$c = 8.34$
$-\frac{d[\text{HDA}]}{dt} = k_3(\dot{\gamma}, T) \cdot [\text{Xlink}]^a \cdot [\text{HDA}]^b + k_4(\dot{\gamma}, T) \cdot [\text{HDA}]^d$	$d = 7$
$k_1 = k_{01} \cdot \dot{\gamma}^{P_1} \exp(-Ea_1/RT)$	$\xi = 1.1069$
$k_2 = k_{02} \cdot \dot{\gamma}^{P_2} \exp(-Ea_2/RT)$	$k_{01} = 6.4951 \times 10^{18}$
$k_3 = \xi \cdot k_1$	$P_1 = 1.8114$
$k_4 = k_{04} \cdot \dot{\gamma}^{P_4} \exp(-Ea_4/RT)$	$Ea_1 = 73194 \text{ J/mol}$
	$k_{02} = 1.3628 \times 10^7$
	$P_2 = 7.3821$
	$Ea_2 = 153818.1 \text{ J/mol}$
	$k_{04} = 1.3566 \times 10^9$
	$P_4 = 5.5002$
	$Ea_4 = 127711.5 \text{ J/mol}$

Fig. 15. Model validation with experimental data ($T = 235\text{ }^{\circ}\text{C}$, 40 rpm). Fig. 16. Model validation with experimental data ($T = 265\text{ }^{\circ}\text{C}$, 100 rpm). Fig. 17. Model validation with experimental data ($T = 285\text{ }^{\circ}\text{C}$, 120 rpm).

4. Discussion

Taking a look at the resulting model (Eqs. (2) and (3)), both equations contain two terms on the right side. It is fair to say that

Table 4

Temperature influence on the rate constants at certain shear rates

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

$$\frac{\Delta k}{\Delta T} = \frac{k(T_2) - k(T_1)}{(T_2 - T_1)k(T_1)} 100\%.$$

these second terms represent other reactions happening during the devulcanizations, besides the main devulcanization reaction between the cross-link 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 Eqs. (2) and (3) represent the reaction of amine with the sulfur bridges (phenomenon 1). The second term in Eq. (2) may correspond to the oxidative scission of the sulfur bridges (phenomenon 4). The second term in Eq. (3) 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 paper.

4.1. 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 (Eq. (8)).

The increase of the rate constants per one-centigrade temperature increase at various shear rates are listed in Table 4. It can be seen that the increase of k_1 is higher at a given higher shear rate. As it is mentioned earlier, raising the temperature significantly increases the chemical reaction rate between HDA and the cross-links. On the other hand, the temperature increase also reduces the mechanochemical reaction rate. This corresponds to the theory proposed by Bueche (1960). The breaking tension of a bond is a function of $(\eta \cdot \dot{\gamma} / \rho) M_e^{0.5}$. An increase in temperature will result in a large decrease in η and minor changes in ρ 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

Table 5
Shear rate influence on the rate constants at certain temperatures

$\dot{\gamma}$ (s^{-1})	T ($^{\circ}\text{C}$)	$\Delta k_1/\Delta \dot{\gamma}$ (%)	$\Delta k_2/\Delta \dot{\gamma}$ (%)	$\Delta k_4/\Delta \dot{\gamma}$ (%)
27.02–40.52	235	5.55	151.93	4.89
40.52–54.03	235	4.17	49.09	102.56
54.03–81.05	235	2.36	78.34	1131.89

$$\frac{\Delta k}{\Delta \dot{\gamma}} = \frac{k(\dot{\gamma}_2) - k(\dot{\gamma}_1)}{(\dot{\gamma}_2 - \dot{\gamma}_1)k(\dot{\gamma}_1)} 100\%.$$

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 cross-links (k_1).

The role of shear is significant when handling high molecular weight polymers, such as EPDM, under shear force. The shear force applied by the mixer heads causes stretching of the EPDM matrix, which in turn results in network breakdown. The mechanical energy applied to the EPDM matrix is converted from viscous to elastic, i.e. from thermal dissipation towards molecular energy storage. The capability of absorbing and storing mechanical energy depends on the molecular weight, molecular weight distribution, crystallinity and temperature (Vasile, 2000). This energy storage first leads to changes in supramolecular structure, then to molecular bond rotations, chain orientation and elongation, bond bending and extension, and ultimately to the rupture of the chemical bonds (Porter and Casale, 1987). If the EPDM matrix stress limit is exceeded, network breakdown will occur.

As the cross-link density decreases, the chain length decreases and the chain stability of the EPDM matrix increases (Porter and Casale, 1987). Consequently, the affectivity of the shear force upon the EPDM matrix decreases through the devulcanization. Therefore, the decrease in the cross-link density is very fast during the first minutes, and then it gradually slows down and finally reaches a plateau where the decrease in cross-link density with time is insignificant (equilibrium).

As shown in Table 5, increasing the shear rate within the range of 54–81 s^{-1} at 235 $^{\circ}\text{C}$ resulted in a less significant increase in k_1 than increasing it within the shear range of 27–54 s^{-1} . This result corresponds to the fact that the mechanical energy applied should be sufficient to create high tension between the cross-links, leading to bond ruptures. This energy contributes to the dissociation of the sulfidic cross-link bonds. Once the energy applied exceeds the stress limit of the cross-link bonds, its further increase would give less significant effect on k_1 .

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, the values of k_2 and k_4 are also lower than the value of 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.

4.2. Competition between the reaction terms

The values of the kinetic parameters obtained from this research can be seen in Table 3. The activation energies for each

reaction are calculated according to Eq. (6). The activation energy for the reaction between HDA and the cross-links (Ea_1) is derived to be 73.19 kJ/mol. Deuri and Bhowmick (1987) reported the values for thermal desulfurization of polysulfidic cross-links 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 cross-link scission and main-chain scission might occur.

The activation energy in the k_2 and k_4 terms, mainly related to the oxidative scissions (Ea_2) and the HDA evaporation (Ea_4), are found to be 153 and 127 kJ/mol (Table 3). Compared to these values, the activation energy of the HDA reaction with cross-links is lower. The activation energy is the minimum energy that must be overcome by the reacting molecules before the reaction will occur (Fogler, 1992). Considering this definition, it can be concluded that the reaction between HDA and cross-links has a higher tendency (selectivity) to occur than the second-term reactions in Eqs. (2) and (3). 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 concurs with the expectation that the main reaction between HDA and cross-links should dominate other 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 .

5. 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. 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 Eq. (3) 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 cross-links (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 cross-links.

Since the model is derived based on a basic kinetic/engineering assumption, showing the relation between all the relevant parameters in a devulcanization process, the structure of the model and, especially, the modeling procedure might apply for other devulcanization processes, where shearing action and devulcanization agent are also used as in this study.

Notation

A	Arrhenius constant
a, b, c, d, e	reaction orders in Eqs. (2), (3), (9), dimensionless
Ea	activation energy according to Arrhenius equation, kJ/mol
[HDA]	concentration of devulcanizing agent, mol/g rubber
K	elastic constant, dimensionless
k_1, k_2, k_3, k_4, k_5	rate constants in Eqs. (2), (3), (9)
M	torque, N m
M_e	molecular weight between entanglements, g/mol
r	reaction rate in Eq. (4), Mol/(g s)
S	rotation speed of Brabender rotor in rpm
SSE	sum of square error, dimensionless
t	time, s
T	temperature, K or °C
[Xlink]	concentration of cross-links in EPDM matrix, mol/g rubber
<i>Greek letters</i>	
$\dot{\gamma}$	shear rate, s ⁻¹
η	viscosity, Pa.s
ξ	stoichiometric ratio for the reaction between HDA and cross-links (see Eq. (5)), dimensionless
τ	shear stress, N/m ²

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