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Modelling a continuous devulcanization in an extruder

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Abstract

An engineering kinetic model is applied to EPDM devulcanization in an extrusion process. Parameters that were included in the model are crosslink density, devulcanizing agent concentration, time, shear rate, and temperature. The extruder is considered as a series of plug flow and stirred tank reactors. The residence time is calculated using solid flow or liquid flow model, depending on the degree of decrosslinking. The model can accurately predict the decrosslinking degree inside the temperature boundary defined by the applied experimental conditions. Outside this boundary, the effect of chemical degradation on the measured conversion becomes more significant.

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Keywords: Modelling; Reactive extrusion; Rubber recycling; Devulcanization; EPDM rubber; Amine devulcanization agent

1. Introduction

EPDM is the fastest growing elastomer among the synthetic rubbers since its introduction in 1963 (Burridge, 2003, 2005; Noordermeer, 1993). It represents 7% of the world rubber consumption and it is the most widely used non-tyre rubber. This is generally due to its excellent ozone resistance as compared to natural rubber and its synthetic counterparts (isoprene rubber/IR, styrene butadiene rubber/SBR, and butadiene rubber/BR). Besides, EPDM can also be extended with fillers and plasticizers to an extremely high level and still give good processability and properties in its end products, which is a matter of price advantage. Moreover, it has an outstanding oxygen and ozone resistance, good electrical properties, little moisture adsorption, excellent resistance to weathering and chemicals, a good compression set, and a very good dynamic fatigue resistance. The main use of EPDM (over a third of its global output) (Burridge, 2005) is in automotive applications such as profiles, hoses, and seals, in building and construction as profiles, roofing foil, and seals, in cable and wire as insulation and jacketing. EPDM is also used in blends with general-purpose rubbers to improve the ozone and weathering resistance in products such as in cover strips and thermoplastic material used for exterior automotive applications (bumpers and panels) (Noordermeer,

1993). Contrary to the other rubber parts of cars, namely tires, EPDM rubber has received much less attention concerning the recycling issue.

Toyota developed a technology for continuously reclaiming EPDM rubber within a short time (10 min) using a twin-screw reactive extruder (Mouri et al., 2000a,b,c; Sato, 1999; Suzuki et al., 1998). The continuous devulcanization processing using the extruder was made possible by optimizing the various conditions, which include the reaction temperature, screw geometry, and rotational speed, and the amounts of additives such as devulcanizing agent and reclaiming oil. The rubber material was typically cut into pieces passing 10 mm sieve and fed into the extruder. Oil and devulcanizing agent were added to the rubber in a weight ratio of 20:6:1 (rubber/oil/devulcanizing agent), and the mixture was swollen for at least 24 h at room temperature. The twin-screw extruder (TSE) used was 1.2 m long, with an output capacity of 5–20 kg/h. The screws had a diameter of 30 mm and rotated up to 500 rpm. The rubber temperature was increased quickly to the devulcanization temperature of 300 °C during the process. A temperature within the range of 280–330 °C was claimed to be most preferable for sulphur vulcanized EPDM, while the shear stress applied was preferred to be between 1 and 15 MPa (Matsushita et al., 1999).

The previous work of van Duin et al. (2003) has shown the effectivity of amine as devulcanization agent. Amines are used for different purposes in rubbers, including the application as reclaiming agent. Several types of amine function as degradation

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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 showed 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 crosslink density mainly by crosslink scission (van Duin et al., 2003).

The novel aspect of the current research is the combination of shearing and the use of α -H aliphatic amines as devulcanizing agent to obtain revulcanizable EPDM rubbers and the modelling of the process. In order to achieve a feasible EPDM devulcanization, the process parameters in the extruder, such as the shear stress, the temperature, and the screw configuration, have to be optimized. For this optimization, a satisfactory model for the process in the TSE is required, which in turn necessitates the development of a kinetic model on EPDM devulcanization reaction. An engineering type of kinetic model was derived for this purpose. A suitable screw configuration and operating conditions for the continuous system were designed using this engineering kinetic model.

The engineering kinetic model derived previously (Sutanto et al., 2006) was applied to the continuous system. All the parameters studied (shear rate, crosslink density, temperature, time, and devulcanization agent concentration) have positive influence on the devulcanization (conversion) rate.

A self-wiping co-rotating extruder was used for this study. It is considered as a continuous reactor, composed of stirred tank and plug flow reactors in series. The residence time is calculated based on the flow rate, the rotation speed of the screws, and the back flow rate. By knowing the residence time of the material in the reactor and the shear rate applied to it in each screw section, the degree of conversion (degree of decrosslinking) can be calculated. The calculated crosslink densities of the material leaving the extruder were compared with the experimental ones to validate the model.

2. Materials and equipments

2.1. Materials

The material used here was an efficient vulcanized EPDM compound containing Keltan 4703, 110 phr carbon black, and an accelerator:sulphur ratio of 8.6:1; the same material was used to derive the engineering kinetic equations in the reference (Sutanto et al., 2006). The rubber was cut into crumbs of smaller than 1 cm by a rubber shredder. Hexadecylamine from Acros and Sunpar 150 oil were used in the process.

Crosslink density was measured by immersing in decaline for 3 days until equilibrium swelling is reached and subsequently drying the swollen sample 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 (Dikland et al., 1993).

The weight of the swollen sample and the weight of the dried sample were used to calculate the relative decrease of crosslink density ($[Xlink]$) during the process. The apparent crosslink density was calculated using the Flory–Rehner equation as follows (Kim and Lee, 2000; Sombatsompop and Kumnuantip, 2003):

$$[Xlink] = \frac{\ln(1 - V_R) + V_R + \chi \cdot V_R^2}{V_S(0.5 \cdot V_R - V_R^{1/3})},$$

where the interaction parameter of decaline–EPDM χ is $0.121 + 0.278 \cdot V_R$ (Dikland, 1992).

2.2. Equipments

A co-rotating TSE from APV Baker with a length of 1.25 m and screw diameter of 5 cm was used for this research. The amine used in this research has a melting point above the room temperature (38–47 °C). Therefore, it was decided to feed the hexadecylamine as a liquid, by preheating it in a jacketed vessel and pumping it as a liquid into the extruder.

3. Modelling concept

Modelling of a process in an extruder is a matter of calculating the effects of all the extrusion parameters on the conversion. Fig. 1 shows the initially suggested modelling scheme for the devulcanization process studied. Barrel temperature, screw configuration, feed rate, screw speed, and die resistance are the control parameters, the values of which can be set. The other parameters in Fig. 1 are dependent directly or indirectly on the control ones.

In a common modelling procedure, the values of the dependent parameters can be calculated by dividing the extruder in smaller segments, for example, 2.5 cm segments, as was chosen in the present case. The length of a segment is adjusted as a function of the reaction speed: a shorter segment for a faster reaction rate and the other way around. Since the conversion within a segment is assumed to be very low, the structure of the material will not change drastically and hence its physical properties can be assumed as constant over each segment.

The physical properties of the material are determined by the degree of conversion, which is dependent on the reaction time, concentrations, and process conditions (in this case temperature and shear rate). The phase of the material (solid/liquid), heat transfer coefficient, density, viscosity, heat capacity, and friction coefficient between the rubber and the channel walls are the physical properties considered here. These are used in a segment for calculating the degree of conversion and subsequently the physical properties of the succeeding segment.

The key of this modelling method is that all the physical properties must be measurable, which is unfortunately not the case in a devulcanization process. The main problems in determining the physical properties were encountered in the friction coefficient and viscosity measurement. The friction coefficient

Fig. 1. Initial extruder modelling scheme (+: positive effect, -: negative effect).

Fig. 2. The modelling concept of the simplified extrusion model.

was difficult to measure since the devulcanization process causes particle size modification and phase transition. The viscosity of the devulcanized rubber was hard to measure, especially at low degree of conversion and when the material is unstable (it recrosslinks during the measurement). During the devulcanization, the material is gaining back its fluidity. This transition is not sharp: when the rubber is not fully devulcanized, it consists of solid vulcanizate particles and devulcanizate melt. This in turn disturbs the viscosity measurement, giving instability during the test. Shortly, the viscosity term is only available after a certain degree of conversion is reached, which is not always the case when the feed rate, hence the residence time, is varied.

Due to the restrictions in the modelling system as presented in Fig. 1, a simpler method was proposed, considering the extruder as a series of shearing reactors. By calculating the shear rate

of each screw type and the residence time in each reactor and inserting them in the model derived in the reference (Sutanto et al., 2006), the degree of conversion (in terms of crosslink density and HDA concentration) can be calculated.

The new modelling scheme is depicted in Fig. 2, with the parameters in the grey boxes as the control variables. Thus, the screw configuration, screw speed, the reaction temperature, and feed rate are the control variables studied. The screw configuration, screw speed, and feed rate altogether determine the residence time in the extruder. The shear rate is determined by the screw speed and screw geometry.

4. Calculations of the parameters

From the kinetic model obtained from batch experiments, two parameters are necessary to be calculated and included in

the model in order to calculate the final conversion, i.e. the residence time and the shear rate.

Before discussing the equations used in the extruder modelling, several assumptions are introduced:

1. Leakage flow is negligible, considering the high viscosity of rubber. In most part of the extruder, the EPDM is in solid phase as rubber crumbs, which turns into a highly viscous melt form after devulcanization reaches certain critical decrosslinking degree.
2. The whole extruder is divided into two sections: solid flow section and liquid flow section. The length of each section varies for each experiment, depending on the devulcanization rate at various experimental conditions. From the batch experiments, it has been observed that a minimum conversion of 65% is required for this material to be considered as liquid. At conversion values (decrosslinking degree) higher than this, the rubber is macroscopically homogeneous. Therefore, 65% conversion is selected as the phase transition point. Solid flow model is thus applied from the feeding point until the point where the decrosslinking degree is below 65%, and liquid flow model for the rest of the extruder length. The assumption of a critical degree of conversion is a common method in the kinetic influenced rheology (Malkin and Kulichikhin, 1996).
3. Newtonian flow is assumed since the exact flow behaviour during the devulcanization process is unknown. Newtonian flow was also assumed in the shear rate calculation in the batch system in a Brabender (Sutanto et al., 2006) when deriving the engineering kinetic model. Since the essence of the extrusion modelling is to apply similar operating conditions as in the Brabender, taking the same assumption for the extrusion process seems reasonable.

Calculation for the extruder process was performed according to the procedure in Fig. 3. In the screw sections where no axial mixing takes place and therefore a plug flow was assumed, the calculation was done per segment of 2.5 cm by first calculating the residence time and shear rate in that section, and then introducing them into the kinetic model to obtain the degree of conversion. From the degree of conversion, the corresponding HDA concentration and crosslink density at the end of each segment were calculated. These values were taken as initial ones in the calculation for the succeeding segment. On the other hand, the conversion in the screw sections where axial mixing occurs and therefore continuous stirred tank reactor (CSTR) was assumed was performed without dividing the section into segments (Fig. 4).

4.1. Shear rate

Shear rate ($\dot{\gamma}$) is dependent on the screw geometry and rotation speed (N) according to the following equations (Goffart et al., 1996; VanderWal et al., 1996):

1. For 90° kneading elements:

$$\dot{\gamma} = 24.56 + 0.42 \cdot (10^6 Q - 0.005) - 0.072 \cdot \ln(2 \cdot 10^5 Q) \cdot (60N - 25) + 0.98 \cdot (60N - 25). \quad (1)$$

Fig. 3. Calculation procedure for modelling the conversion in the extruder.

2. For pressure build-up elements:

$$\dot{\gamma} = 4.8N - 10^4 Q. \quad (2)$$

4.2. Residence time

The residence time of a material in a continuous reactor can be simply calculated when the filled (effective) volume of the reactor (V_R) and the flow rate (Q) is known, according to

$$\tau = \frac{Q}{V_R} \quad (3)$$

and

$$V_R = V \cdot f, \quad (4)$$

where V is the reactor volume and f is the degree of fill.

The reactor volume is calculated for each screw type, using the following relation:

$$V = A_l \cdot l. \quad (5)$$

A_x is the crosssectional area of the gap between the screw and the barrel (Booy, 1978,1980) as depicted in Fig. 4:

$$A_l = (k_b - 2k_s) \cdot R_s^2, \quad (6)$$

Fig. 4. Crosssection of a pair of co-rotating screws with two tips (Booy, 1980).

$$k_b = 2 \cdot (\pi - \psi) + \frac{C_L}{R_s} \cdot \sin \psi, \quad (7)$$

$$k_s = n \cdot \left\{ \psi \cdot \left(\frac{C_L}{R_s} \right)^2 - \frac{C_L}{R_s} \cdot \sin \psi + \frac{\alpha}{2} \cdot \left[\left(\frac{C_L}{R_s} \right)^2 - 2 \cdot \frac{C_L}{R_s} + 2 \right] \right\}, \quad (8)$$

$$\cos \psi = \frac{C_L}{2R_s}. \quad (9)$$

The degree of fill of the extruder is dependent on the screw configuration, feed rate, and screw speed. In a transporting screw element, the degree of fill is calculated by

$$f = \frac{Q}{Q_{D,\max}}. \quad (10)$$

4.2.1. Solid model

The rubber waste is added as rubber crumbs into the extruder by means of a hopper. The rubber crumbs behave as solid particles in the extruder; they do not attach to the channel walls

like in the case of viscous liquid transport and hence the gravitational force plays an important role.

The differences in solid flow model and liquid flow model are in the calculation of the volumetric flow rate Q and the maximum drag flow capacity $Q_{D,\max}$. For solid section, Eq. (3) becomes

$$t = \frac{Q}{V_R} = \frac{Q_{\text{solid}}}{V_{\text{section}} \cdot f} = \frac{Q_{\text{solid}}}{A_l \cdot dl \cdot f}, \quad (11)$$

where dl is the length of the segment (2.5 cm).

Q_{solid} is determined by the rubber feed rate and the density. Considering the rubber is in the solid phase, the volumetric flow rate of the rubber bed (Q_{solid}) was calculated using the bulk density of the rubber crumb (ρ_{bulk}):

$$Q_{\text{solid}} = \frac{\dot{M}}{\rho_{\text{bulk}}}. \quad (12)$$

4.2.2. Liquid model

For the liquid section, Eq. (3) becomes

$$t = \frac{Q}{V_R} = \frac{Q_{\text{liquid}}}{V_{\text{section}} \cdot f} = \frac{Q_{\text{liquid}}}{A_l \cdot dl \cdot f}. \quad (13)$$

The volumetric rubber flow rate Q_{liquid} is calculated using the density of the rubber:

$$Q_{\text{liquid}} = \frac{\dot{M}}{\rho_{\text{rubber}}}. \quad (14)$$

The degree of fill in Eq. (10) is calculated by using the maximum drag capacity for liquid flow:

$$Q_{D,\max} = 0.5m \cdot H \cdot W \cdot V_z \cdot f_D, \quad (15)$$

$$V_z = \pi \cdot N \cdot D_s \cdot \cos \varphi, \quad (16)$$

$$\varphi = \tan^{-1} \left(\frac{t_s}{2\pi R_s} \right), \quad (17)$$

where H is the height of the channel, W is the width of the channel, t_s is the screw thread, m is the number of parallel channels calculated using the following equation (Booy, 1980):

$$m = 2 \cdot n_s - 1 + \frac{\alpha \cdot n_s}{\pi} \quad (18)$$

with n_s as the number of screws and α the tip angle in radians. The f_D in Eq. (15) is the geometrical correction factor for drag flow, calculated numerically using the method described by Booy (1980). The drag flow coefficient is necessary to correct the volume of the screw channel due to its curvature.

Kneading sections with 90° stagger angle and -45° stagger angle (which are applied in this study) have no positive pumping action and therefore their degree of fill is always 1. The material is pushed through these sections by the preceding pressure build-up elements.

At the end of the pumping zone at the extruder exit, the die provides resistance to the flow according to Eq. (20); therefore,

back flow occurs in this last zone.

$$\dot{\gamma}_{\text{die}} = 32 \cdot \frac{Q}{\pi D_{\text{die}}^3}, \quad (19)$$

$$\Delta P_{\text{die}} = 4 \cdot \mu \cdot \dot{\gamma}_{\text{die}} \cdot \frac{L_{\text{die}}}{D_{\text{die}}^2}. \quad (20)$$

The presence of back flow increases the degree of fill by reducing the drag capacity of the screw. The back flow is formulated as

$$Q_p = Q_D - Q, \quad (21)$$

$$\frac{dp}{dz} = Q_p \cdot \frac{12 \cdot \mu}{m \cdot W \cdot H^3 \cdot f_p}. \quad (22)$$

The f_p is the geometrical correction factor for pressure flow, calculated using the method described by Booy (1980). The length of fully filled part is calculated as follows:

$$L_{ff} = \frac{P_{\text{die}}}{dp/dz}. \quad (23)$$

The degree of fill of the screw zone is

$$f = \frac{Z_{ff}}{Z_{\text{zone}}} + \left(1 - \frac{Z_{ff}}{Z_{\text{zone}}}\right) \cdot \frac{Q}{Q_D}. \quad (24)$$

Since the pressure drop is calculated in down-channel direction z (see Fig. 5), the degree of fill is also calculated in the same direction by converting the length of the pumping zone

into the l (screw axial) direction:

$$Z_{\text{zone}} = \frac{l_{\text{zone in } l \text{ direction}}}{\sin \varphi}. \quad (25)$$

The residence time in this pumping zone is then calculated by substituting Eq. (25) into Eq. (4) and subsequently Eq. (3). Therefore, the residence time is increased by the occurrence of back flow.

4.3. Conversion

The conversion is calculated forwards, from the inlet point to the exit point. The reaction rate is calculated as a function of the residence time and the shear rate in the corresponding section, using Eqs. (1)–(3) and their parameters in Table 1 (Sutanto et al., 2006). The resulting crosslink density and HDA concentration are used for the calculation of the succeeding section.

$$-r_{\text{Xlink}} = -\frac{d[\text{Xlink}]}{dt} = k_1(T, \dot{\gamma}) \cdot [\text{Xlink}]^a [\text{HDA}]^b + k_2(T, \dot{\gamma}) \cdot [\text{Xlink}]^c, \quad (26)$$

$$-r_{\text{HDA}} = -\frac{d[\text{HDA}]}{dt} = k_3(T, \dot{\gamma}) \cdot [\text{Xlink}]^a [\text{HDA}]^b + k_4(T, \dot{\gamma}) \cdot [\text{HDA}]^d. \quad (27)$$

The extruder is considered as a series of CSTRs and PFRs. The screw sections where back flow occurs, namely in the mixing section (+45° followed by −45° stagger angle) and in the pumping zone before the die, are considered as a CSTR and conversion is calculated directly for the whole section, while the rest of the extruder is considered as a PFR where calculation is done per segment. Mass balance equations derived for steady-state reactors (Levenspiel, 1972), where the accumulation in the reactor is zero, are applied and rearranged into the following equations:

1. The conversion in a plug flow section is calculated using Eqs. (28) and (29) by solving them simultaneously (and numerically):

$$t = -\int_{[\text{Xlink}]_i}^{[\text{Xlink}]_o} \frac{d[\text{Xlink}]}{r_{\text{Xlink}}}, \quad (28)$$

$$t = -\int_{[\text{HDA}]_i}^{[\text{HDA}]_o} \frac{d[\text{HDA}]}{r_{\text{HDA}}}. \quad (29)$$

2. The conversion in a CSTR is calculated using Eqs. (30)–(31). This calculation assumes that the outgoing HDA concentration and crosslink density are equal to the concentration inside the reactor.

$$t = \frac{[\text{Xlink}]_i - [\text{Xlink}]_o}{-r_{\text{Xlink}}}, \quad (30)$$

$$t = \frac{[\text{HDA}]_i - [\text{HDA}]_o}{-r_{\text{HDA}}}. \quad (31)$$

Fig. 5. z is the down-channel direction and l is the direction along the screw axis.

Table 1
Engineering kinetic 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 $	$a = 4.93$
	$b = 0.61$
	$c = 8.34$
$-\frac{d[\text{HDA}]}{dt} = k_3(\dot{\gamma}, T) \cdot [\text{Xlink}]^a \cdot [\text{HDA}]^b + k_4(\dot{\gamma}, T) \cdot $	$d = 7$
	$\xi = 1.1069$
$k_1 = k_{01} \cdot \dot{\gamma}^{P_1} \cdot \exp(-Ea_1/RT)$	$k_{01} = 6.4951 \times 10^{18}$
$k_2 = k_{02} \cdot \dot{\gamma}^{P_2} \cdot \exp(-Ea_2/RT)$	$P_1 = 1.8114$
$k_3 = \xi \cdot k_1$	$Ea_1 = 73194 \text{ J/mol}$
	$k_{02} = 1.3628 \times 10^7$
	$P_2 = 7.3821$
	$Ea_2 = 153818.1 \text{ J/mol}$
$k_4 = k_{04} \cdot \dot{\gamma}^{P_4} \cdot \exp(-Ea_4/RT)$	$k_{04} = 1.3566 \times 10^9$
	$P_4 = 5.5002$
	$Ea_4 = 12711.5 \text{ J/mol}$

5. Experimental procedures

5.1. Modelling the residence time vs. screw configuration

From Eqs. (28)–(31) it is obvious that the residence time plays an important role in the degree of conversion. Residence time in the extruder is influenced by screw configuration, screw speed, and throughput. Since changing the screw configuration is not a convenient method to vary the residence time, it has been optimized by doing simulations in the beginning; the same configuration was used for the rest of experiments. Variation of residence time between the experiments could be obtained by varying the throughput and the screw speed.

Residence time in the extruder can be increased by using more screws with smaller pitch angle, i.e. smaller transporting capacity. Kneading elements at 90° stagger angle do not have transport capacity. The material passing these kneading elements is pushed to down-channel direction by the preceding transport element. Therefore, the length of the kneading sections should not be too long in order to prevent too high torque, which will disturb the extruder operation.

For the designing purpose of the screw configuration, the problem was simplified to transport of rubber material without taking into account the conversion, phase transformation, and back flow.

Simulation has been done in order to compare the residence time obtained by several screw configurations. Since the devulcanization process proceeds slowly, configuration with the longest possible residence time was chosen for the extruder experiments. The kneading sections with 90° stagger angle were spread along the extruder, with pressure build-up elements between them to provide pushing action on the material to pass the non-transporting kneading sections.

5.2. Experimental scheme

Experiments in the extruder were carried out by varying the rotation speed, rubber flow rate, and barrel temperature. The

rotation speed was varied between 50 and 200 rpm, set temperature between 250 and 300 °C, and rubber flow rate 3–7 kg/h.

6. Results and discussions

6.1. Viscosity values

In a common modelling procedure for polymer processing, the viscosity is calculated as a function of shear, temperature, and molecular weight. The devulcanization reaction involves a phase transition, from solid rubber crumbs into melt. The fact that this phase transition is a result of the reaction complicates the viscosity modelling even more. The viscosity can only be measured (still very roughly) after a certain degree of decrosslinking is reached, the point where the rubber starts to flow.

The apparent viscosity values in this research were approximated by measuring the die pressure at various flow rates, and using them in Eqs. (19) and (20). The viscosity values found from the experiments were not accurate due to the presence of two phases in the devulcanizate (solid rubber crumb with viscous devulcanizate) as can be seen in Fig. 6. Fig. 6(a) shows the plot of apparent viscosity against shear rate at two temperatures. The plot shows a negligible effect of shear rate on the apparent viscosity values; this in turn supports the Newtonian flow assumption taken. Fig. 6(b) shows a more significant tendency of the apparent viscosity values with respect to the degree of conversion (assigned as the measured crosslink density), although the spread is still too wide to derive an appropriate model.

As it has been observed during the modelling, the viscosity term apparently does not have significant influence in the degree of fill. Substituting Eqs. (20) and (21) in Eq. (22), the viscosity terms are eliminated. In practice, viscosity variation might take place in the screw zones and hence will influence the pressure build-up profile due to the non-isoviscous flow (Eqs. (22) and (23)). This viscosity variation might occur due to the difference in the temperature profile, degree of conversion, and non-Newtonian flow.

Fig. 6. Apparent viscosity: (a) as a function of shear rate and (b) as a function of [crosslink].

Fig. 7. Predicted decrosslinking degrees vs. experimental values.

Fig. 8. Results of extrapolation of the model to 300 °C set temperature.

6.2. Model validation

The result of the extrusion modelling is presented in Fig. 7; the predicted decrosslinking degrees are plotted against the measured ones from the experiments within the range of temperature in the batch experiments (225–285 °C set temperature) at shear rate of 50–217 s⁻¹, respectively. The crosslink density is measured in decaline, and the corresponding decrosslinking degree is calculated as

$$\text{decrosslinking degree} = \frac{XL_0 - XL_{\text{end}}}{XL_0} \cdot 100\%. \quad (32)$$

The result shows a nice agreement, giving a standard error of 4%. The standard error of estimate is defined as (Holman and Gajda, 1989)

$$\text{standard error} = \sqrt{\frac{\sum (\text{decrosslinking degree}_{\text{exp}} - \text{decrosslinking degree}_{\text{model}})^2}{n_{\text{exp}} - 2}} \quad (33)$$

with n_{exp} as the number of experiments.

Unfortunately, when the kinetic model was applied to an extended operating temperature (300 °C), the measured

conversions are much higher than the predicted values (see Fig. 8). This is likely due to the significant degradation, which was not observed in the batch experiments due to the limitation in the Brabender operating temperature. Degradation is more likely to occur at higher temperature, resulting in main chain breakage and therefore in lower values of the measured crosslink density. Analysis in the GPC (Fig. 9) of a devulcanizate from an experiment at 300 °C, 50 rpm, and 3.5 kg/h rubber feed rate shows a decrease of MW to half of its original value (23 000 vs. 58 000 g/mol, respectively). The measured crosslink density of this sample is 6.1×10^{-5} mol/g rubber, compared to its predicted value of 1.2×10^{-4} mol/g rubber. Although it is tempting to draw a conclusion that the 100% difference in the crosslink density measured is caused by the 50% decrease of the

average MW, a more quantitative approach, which is outside the scope of this research, would be needed to completely explain this.

Fig. 9. GPC result of a sample from 300 °C set temperature, 50 rpm, and 3.5 kg/h feed rate.

7. Conclusions

Modelling a devulcanization process in an extruder needs a number of simplifications due to the unavailability of physical properties data, especially the viscosity. Taking into account the simplifications and assumptions used here, the model can predict the conversion in the extruder quite well.

Extrapolating the experimental conditions to a higher temperature and higher shear rate did not give a good agreement, due to the occurrence of phenomena that were not observed when deriving the engineering kinetic model. However, these observed deviation can be easily, although only qualitatively, explained by taking into consideration the degradation of the rubber at high temperature.

The analysis on the devulcanizate does not show any significant amount of degradation product. The molecular weight of the devulcanizate is around 40% lower than the molecular weight of the virgin material, indicating less than one scission per polymer chain of the sol fraction.

The successful continuous devulcanization process modelling shows that the extruder operating conditions can resemble the operating conditions in the batch system to attain the same shear and residence time.

Notation

C_L	centreline distance between the screw axes, m
f	degree of fill, dimensionless
f_D	geometrical correction factor for drag flow, dimensionless

f_P	geometrical correction factor for pressure flow, dimensionless
H	height of the channel, m
[HDA]	concentration of HDA in the rubber, mol HDA/g rubber
m	number of parallel channels, dimensionless
$\dot{M}$	mass flow rate, kg/s
n	number of screw tips, dimensionless
N	rotation speed, rps
Q	volumetric flow rate, m ³ /s
$Q_{D,max}$	maximum drag flow capacity, m ³ /s
R_b	barrel radius, m
R_s	outside radius of the screw, m
t	residence time, s
t_s	screw lead, m
V	reactor volume, m ³
V_R	filled reactor volume, m ³
W	width of the channel, m
[Xlink]	crosslink density, mol/g rubber

Greek letters

$\dot{\gamma}$	shear rate, s ⁻¹
μ	viscosity, Pa s
τ	shear stress, Pa
φ	helix angle at R_s , rad

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References

- Booy, M.L., 1978. Geometry of fully wiped twin-screw equipment. *Polymer Engineering and Science* 18, 973–984.
- Booy, M.L., 1980. Isothermal flow of viscous-liquids in corotating twin screw devices. *Polymer Engineering and Science* 20, 1220–1228.
- Burridge, E., 2003. EPDM. *European Chemical News* 15.
- Burridge, E., 2005. EPDM. *European Chemical News* 82, 16.
- Dikland, H., 1992. Coagents in peroxide vulcanisations of EP(D)M rubber. Thesis/Dissertation, University of Twente.
- Dikland, H.G., Hulskotte, J.M., van der Does, L., Bantjes, A., 1993. Interactions of various liquids with EPDM peroxide vulcanizates cures in the presence of coagents. *Polymer Bulletin* 30, 477–480.
- Goffart, D., VanderWal, D.J., Klomp, E.M., Hoogstraten, H.W., Janssen, L.P.B.M., Breyse, L., Trolez, Y., 1996. Three-dimensional flow modeling of a self-wiping corotating twin-screw extruder. 1. The transporting section 3. *Polymer Engineering and Science* 36, 901–911.
- Holman, J.P., Gajda Jr., W.J., 1989. *Experimental Methods for Engineers*. McGraw-Hill Book Co., New York.
- Kim, J.K., Lee, S.H., 2000. New technology of crumb rubber compounding for recycling of waste tires. *Journal of Applied Polymer Science* 78, 1573–1577.
- Levenspiel, O., 1972. *Chemical Reaction Engineering*. Wiley, New York.
- Malkin, A.Ya., Kulichikhin, S.G., 1996. *Rheokinetics*. Huethig & Wepf Verlag, Germany.
- Matsushita, M., Mouri, M., Okamoto, H., Sato, N., Suzuki, Y., Owaki, M., Suzuki, N., Nakashima, K., Honda, H., Yoshida, T., Takeuchi, K., 1999. European Patent 0931809 A2.
- Mouri, M., Okamoto, H., Matsushita, M., Honda, H., Nakashima, K., Takeuchi, K., Suzuki, Y., Owaki, M., 2000a. De-vulcanisation conditions and mechanical properties of re-vulcanised rubber for EPDM. Continuous reclamation of rubber by shear flow reaction control technology (part II). *International Polymer Science and Technology* 27, T/23–T/28.
- Mouri, M., Sato, N., Okamoto, H., Matsushita, M., Honda, H., Nakashima, K., Suzuki, Y., Owaki, M., 2000b. Continuous devulcanisation by shear flow stage reaction control technology for rubber recycling. Part 3. Study of the devulcanisation process for EPDM. *International Polymer Science and Technology* 27, T/12–T/16.
- Mouri, M., Sato, N., Okamoto, H., Matsushita, M., Honda, H., Nakashima, K., Takeuchi, K., Suzuki, Y., Owaki, M., 2000c. Continuous devulcanisation by shear flow stage reaction control technology for rubber recycling. Part 4. Devulcanisation mechanism for EPDM. *International Polymer Science and Technology* 27, T/17–T/22.
- Noordermeer, J.W.M., 1993. Ethylene–propylene elastomers. In: Kirk, R.E., Othmer, D.F., Grayson, M. (Eds.), *Kirk–Othmer Concise Encyclopedia of Chemical Technology*. Wiley Interscience, New York.
- Sato, N., 1999. Paper presented at the International Rubber Conference (IRC) Proceeding. Seoul, South Korea.
- Sombatsompop, N., Kumnuantip, C., 2003. Rheology, cure characteristics, physical and mechanical properties of tire tread reclaimed rubber/natural rubber compounds 1. *Journal of Applied Polymer Science* 87, 1723–1731.
- Sutanto, P., Laksmana, F., Picchioni, F., Janssen, L.P.B.M., 2006. *Chemical Engineering Science* 61, 6442–6453.
- Suzuki, Y., Owaki, M., Mouri, M., Sato, N., Honda, H., Nakashima, K., 1998. Recycling technology using a twin screw reactive extruder for vulcanized EPDM rubber. *Toyota Technical Review* 48, 53–57.
- van Duin, M., Noordermeer, J.W.M., Verbruggen, M.A.L., van der Does, L., 2003. Patent Application Number US2003013776.
- VanderWal, D.J., Goffart, D., Klomp, E.M., Hoogstraten, H.W., Janssen, L.P.B.M., 1996. Three-dimensional flow modeling of a self-wiping corotating twin-screw extruder. 2. The kneading section. *Polymer Engineering and Science* 36, 912–924.