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EXPERIMENTAL INVESTIGATION AND IDENTIFICATION OF MATERIAL PARAMETERS FOR RUBBER BLENDS

This contribution gives an overview about new procedures for the parameter identification for the material characterisation of rubber blends. They are based on a Newton-Raphson procedure and a genetic algorithm. As basis serves an experimental investigation of the viscous properties of rubber blends by means of a capillary-viscometer. Because of simultaneous consideration of wall slippage, temperature and of the die swell, the proposed material characterisation is represented by a coupled system of nonlinear equations. Describing their solutions requires a numerical integration algorithm. For this purpose a generalized Newton-Raphson scheme has been adopted. The verification of the developed parameter identification was done by means of another approach which is based on a genetic algorithm.

1. Introduction

Capillary rheometry simulates polymer extrusion in a simplified way. It allows the characterisation of polymers by determination of the viscosity function and of the extrudate swell. As regards viscous properties, there is still a lack of constitutive characterisation of rubber blends. In this contribution new concepts are presented with respect to the computation of viscous properties without using common, partly questionable correction methods [9].

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The dimensioning of injection heads for the extrusion of rubber profiles is exclusively based on empiric knowledge of the non-linear flow behaviour of elastomers, basically of the so-called die swell. The swelling of the extrudate when emerging from a capillary is typical for non-Newtonian viscoelastic fluids. It relates to the elastic properties of rubber blends. Therefore, the experimental investigation and numerical treatment of the die swell is of high interest.

This was one of the motivations for starting a research project in the field of rubber blend technologies. The knowledge of the die swell is very important for the production of rubber profiles. Thus, the final goal of this project is the numerical prognosis concerning tools for the extrusion of rubber. The research work was done in co-operation with SEMPERIT Technische Produkte Ges.m.b.H. & Co KG which provides the rubber blends as well as the experimental devices.

This paper is structured as follows: In Chapter 2 a short description of the used experimental devices for the determination of the viscosity function and of the die swell of the rubber blends is given. In Chapter 4 the so far common material characterisation using different correction methods is summarised. Chapter 5 refers to the proposed new material characterisation. Because of the coupling between viscosity and shear strain rate and the consideration of die swell, an adaptation of an optimization method is required. The verification of the new material characterisation is given in Chapter 6 by comparing results of the different material characterisations methods. The paper will be completed by conclusions and some present research activities.

2. Materials and experimental investigations

The investigated materials are rubber blends used in industry, containing mainly EPDM (ethylene-propylene-diene-monomer) and carbon black in different compositions. So far four different rubber blends were investigated. These are used for window sealings, pipeline constructions and various parts of cars.

The used standard experimental device is a capillary-viscometer (GÖTTFERT Ges.m.b.H., Germany, see Figure 1 (a)). In this capillary-viscometer the melt is filled in a reservoir and pressed through a circular capillary with a certain stamp velocity v_i . The corresponding pressure p_i is measured in front of the capillary (see Figure 1 (b)). In order to characterise the investigated materials various experiments by means of this capillary-viscometer with different capillary lengths L , capillary radii R and extrudate temperatures T were performed. With one experiment the investigation of various stamp velocities v_i is possible. Therefore a vector notation for indicating different duty points i is used.

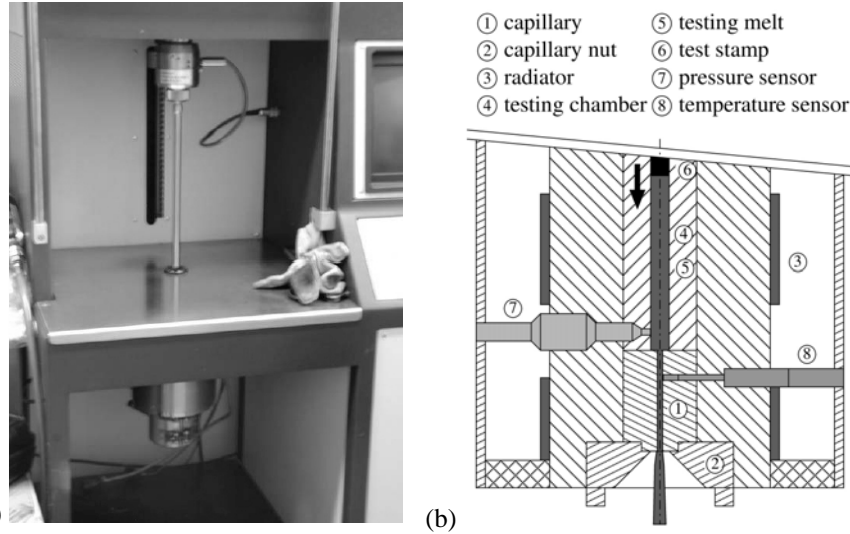


Figure 1 - Capillary-viscometer (a) situation at SEMPERIT (b) principle

In addition to the extrusion pressure p the die swell-area ratio χ of all experiments has been determined. For that purpose a so-called swell value measuring unit was used (see Figure 2 (a)). It measures the diameter by means of a laser beam with a wave-length of approximately 700 nm. In this contribution the dimensionless swell value χ_i represents a strand cross-sectional area ratio. For the validation of this measuring method a high speed camera has been used (see Figure 2 (b)), because the highest exit speed of the strand is about 1000 mm/s. Comparing these results leads to a successful validation of the swell value measuring tool [11].

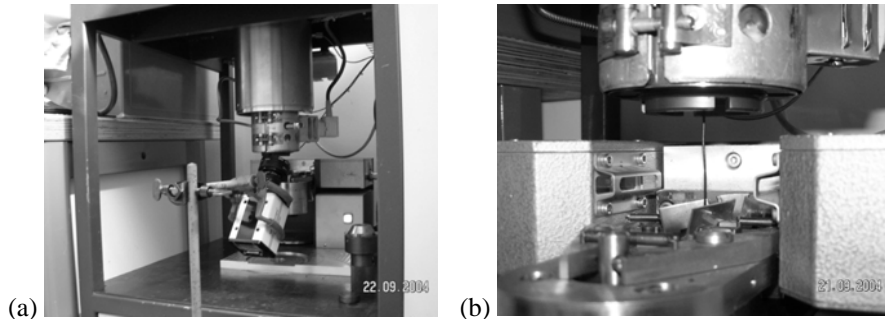


Figure 2 - Determination of the die swell by means of (a) a high speed camera and (b) a swell value measuring unit

The swell value is defined as follows:

$$\chi_i = \left(\frac{d_i}{D} \right)^2 \quad \text{with } i \in \{1, \dots, j\} \quad (1)$$

where d_i is the diameter of the measured strand and D is the diameter of the capillary. j is the total number of investigated duty points per experiment.

3. Constitutive characterisation using a power law

For the description of the pseudo-plastic material behaviour of rubber blends the power law by OSTWALD and DE WAELE described in [9] is used. Its application to the investigated rubber blends is possible for a common interval of the shear strain rate $\dot{\gamma}$. For the visualisation of the obtained results a distinction is drawn between the flow curve $\tau(\dot{\gamma})$ and the viscosity curve $\eta(\dot{\gamma})$ (see Figure 3), where τ is the shear stress at the wall of the capillary. The power law approximates the results from the experiments through a straight line in a double logarithmic scale as:

$$\eta_i = k \dot{\gamma}_i^{n-1} \Leftrightarrow \tau_i = k \dot{\gamma}_i^n \quad \text{with } i \in \{1, \dots, j\}, \quad (2)$$

where k is the consistency parameter in [Pasⁿ] and n is the dimensionless viscosity exponent. These parameters are determined by means of a Gaussian quadrature as:

$$n = \frac{j \sum_{i=1}^j \lg \tau_i \lg \dot{\gamma}_i - \sum_{i=1}^j \lg \tau_i \sum_{i=1}^j \lg \dot{\gamma}_i}{j \sum_{i=1}^j \lg^2 \dot{\gamma}_i - \sum_{i=1}^j \lg \dot{\gamma}_i \sum_{i=1}^j \lg \dot{\gamma}_i} \quad \text{and} \quad \lg k = \frac{1}{j} \left(\sum_{i=1}^j \lg \tau_i - n \sum_{i=1}^j \lg \dot{\gamma}_i \right), \quad (3)$$

where k corresponds to the viscosity at a shear strain rate of $\dot{\gamma} = 1 \text{ s}^{-1}$ and n describes the slope of the viscosity curve in the corresponding diagram.

The objective of the present material characterisation is to determine all required state variables which describe the flow situation of a die through a circular capillary. The use of circular capillaries has the disadvantage that the measurement of the pressure is performed before the capillary entry. Therefore, entrance and outlet pressure losses are not considered by such a measurement. This fact has to be considered in the material characterisation.

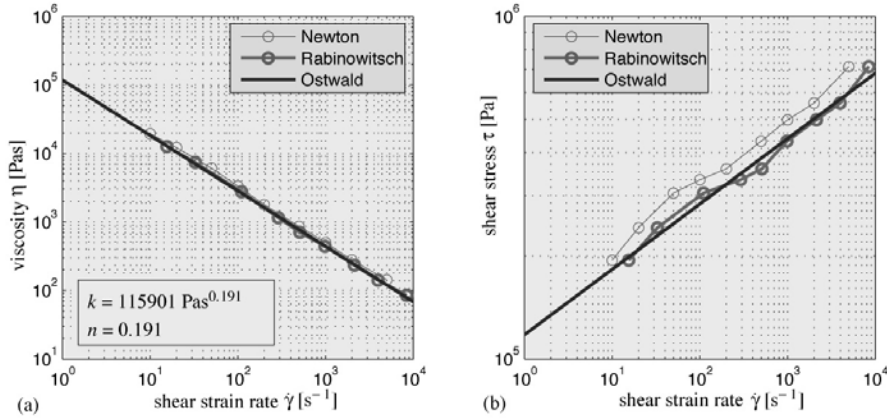


Figure 3 - Application of the power law for a viscosity curve and a flow curve

4. Former material characterisations

4.1 Pressure loss due to viscoelastic properties

Because of the viscoelastic behaviour of rubber a pressure reduction occurs when the melt is transferred from the reservoir to the capillary. In order to identify the pressure loss a plot of the measured pressure p over the corresponding L/R -ratio of the used capillary is performed. This plot is called as BAGLEY plot [2].

Figure 4 (a) shows such a BAGLEY plot for an investigated rubber blend and for four capillaries $L/D = 40/1, 20/1, 10/1$ and $5/1$ mm. The intersection of the straight lines with the ordinate yields the pressure loss $p_{E,i}$ for the corresponding stamp velocity v_i .

A disadvantage of this widely used graphical method is the fact that a minimum of two experiments are required to obtain the BAGLEY plot. With the determined pressure loss p_E the shear stress at the wall of the capillary can be calculated as:

$$\tau_i = \frac{(p_i - p_{E,i})R}{2L} \quad \text{with } i \in \{1, \dots, j\} \quad (4)$$

Furthermore, the BAGLEY pressure correction leads for some experiments to negative pressure losses p_E , which are physically not possible. To overcome this problem, GLEISSE [5] introduced an additional process parameter q . Thus, for every experiment positive pressure losses p_E are obtained. The latter approach leads to the problem that for not investigated materials the parameter q is unknown.

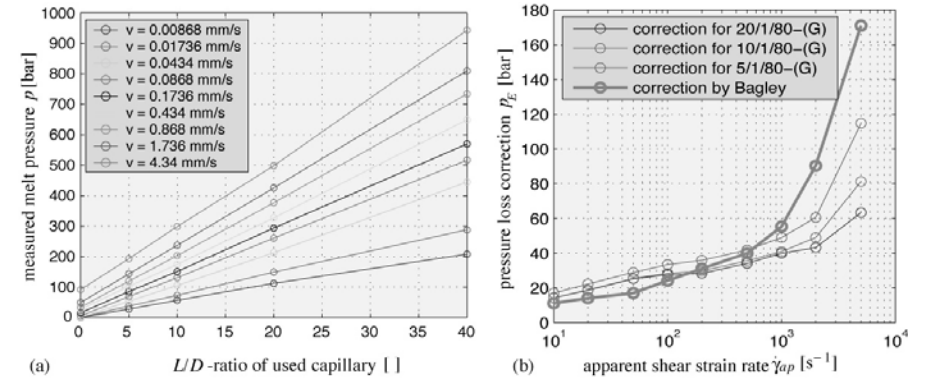


Figure 4 - (a) BAGLEY plot and (b) comparison of pressure losses for a rubber blend at a temperature $T = 100$ °C

Figure 4 (b) shows a comparison between the pressure losses p_E for the capillaries $L/D = 20/1, 10/1$ and $5/1$ mm which were obtained with the BAGLEY and the GLEISSE correction method for a chosen $q = 2.0$. For different capillaries the latter leads to different values for the pressure loss, especially at high shear strain rates.

4.2 Determination of the true shear strain rate

Due to the nonlinear coupling of the viscosity and the shear strain rate, the correction methods are necessary to determine the parameters of the power law according to (3). The following approach has to be chosen:

1. Newtonian material properties are assumed. The resulting physical values are called apparent and marked with a subscript “ ap ”.
2. The apparent values have to be transformed into true values using the correction method by RABINOWITSCH [13].

4.3 Consideration of wall slippage

The most important condition for using the described correction methods is the condition of adhesion for flow on the wall of the capillary. To check whether wall slippage occurs, a correction by MOONEY [10] has to be used. For that purpose, a plot of the reduced flow rate versus the reciprocal capillary radius is required. When obtaining straight lines for experiments with different capillary radii and constant L/D -ratios the wall slippage velocity $v_{G,i}$ corresponds to the slope of the obtained lines. As it can be seen from Figure 5 the correction method for the consideration of wall slippage fails for the investigated rubber blends. GEIGER [4] confirmed this problem for other rubber blends, too. Furthermore, the obtained velocities are not associated to the investigated duty points.

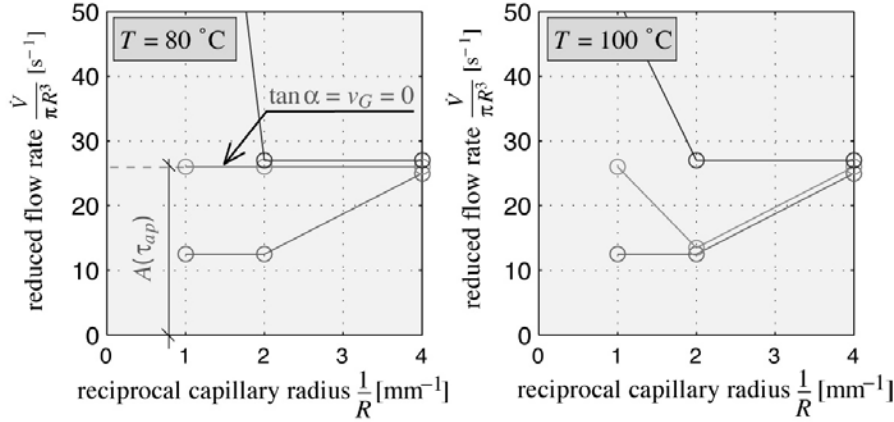


Figure 5 - MOONEY plot for a rubber blend for different temperatures

The described, common used correction methods are well suitable for polymers. The application for the investigated rubber blends, however, is not always reasonable. Therefore, a new material characterisation method for rubber blends is proposed which considers simultaneously the coupling of the viscosity and the shear strain rate as well as wall slippage.

4.4 Consideration of temperature

For polymers, it has been shown that the slope of viscosity curves for different temperatures does not change. Then the so-called time-temperature superposition can be used. For the investigated rubber blends a similar behaviour has been determined. The viscosity curve for a certain temperature can be obtained from a known viscosity curve which is valid for another temperature.

ARRHENIUS [1] explains the temperature dependence of the viscous properties by means of a change of the functional location of the molecular chains. The ratio of viscosities for different temperatures is defined as

$$\ln \frac{\eta(T_2)}{\eta(T_1)} = \frac{E_0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (5)$$

where E_0 is the material-specific activation energy in [J/mol] and $R = 9.314$ J/mol.K is the gas constant.

The consideration of the temperature by means of the WLF equation [15] is possible for the investigated rubber blends, too. This relationship explains the temperature dependence of the viscosity by the probability of changes of the functional location.

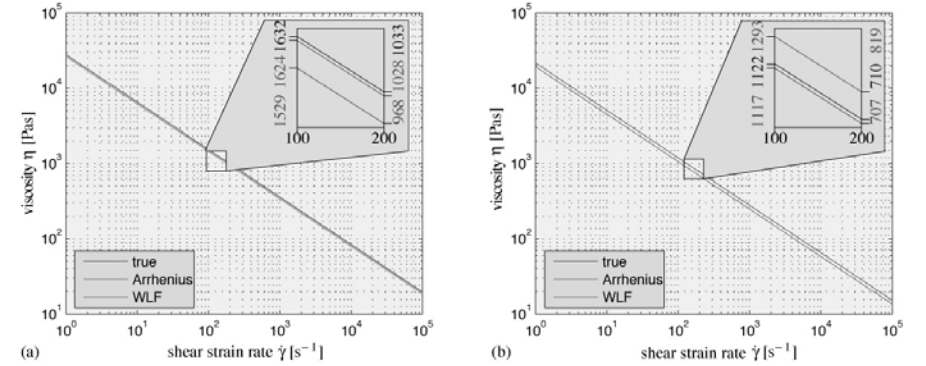


Figure 6 - Comparison of approaches for the time-temperature superposition

The ratio of viscosities for different temperatures is defined as

$$\ln \frac{\eta(T_2)}{\eta(T_1)} = - \frac{C_1 (T_2 - T_1)}{C_2 + (T_2 - T_1)}. \quad (6)$$

In the original equation C_1 and C_2 are constants. In the present context, C_1 and C_2 denote material parameters, because T_1 and T_2 are the investigated temperatures. Figure 6 shows the viscosity curves for (a) 100 °C and (b) 120 °C. Using the viscosity curve for 80 °C and the different approaches the corresponding viscosity curves are determined accurately.

5. New material characterisation

In order to improve the back calculation of the measured pressure of circular capillaries, additional experiments with slit capillaries have been performed. With this type of experiments the determination of the melt pressure p inside the capillary is possible [3]. This enables statements about the pressure losses p_E for circular capillaries. Consideration of these experiments in the material characterisation procedure reduces the coupled state variables for the capillary experiment. They are:

- the material parameters k and n of the power law, and
- the shear strain rate $\dot{\gamma}$ at the wall of the capillary.

If these state variables are known, the determination of the shear strain rate dependent viscosity is possible.

Because of the consideration of wall slippage and the coupling between viscosity and shear strain rate the resulting characterisation is represented by a coupled system of nonlinear equations. Describing their solution requires a numerical integration algorithm. This is achieved by means of two methods.

5.1 Generalized Newton-Raphson procedure

The concept of this scheme is explained in MÜLLNER et al. [12]. This iteration method requires for a certain number of unknown variables the same number of conditional equations. The variables are the parameters of the power law, k and n , and the shear strain rate $\dot{\gamma}$. Thus, the number of unknown variables is $j+2$. Furthermore the derivatives of the conditional equations are required. The power law constants are calculated using equation (3). The shear strain rate is computed as:

$$\dot{\gamma}_i = \sqrt[n]{\frac{(1-\alpha)p_i R}{2L}} \quad \text{with } i \in \{1, \dots, j\}, \quad (7)$$

where $0 < \alpha < 1$ considers the pressure loss due to the measuring of p_i before the capillary entry. α depends on the used circular capillary L/R . The three equations are collected in the residuum vector \mathbf{R} .

Furthermore, a starting state near the unknown solution is required. For this purpose the Newtonian shear strain rate is used:

$$\dot{\gamma}_{ap,i} = \frac{4v_i R_K^2}{R^3} \quad \text{with } i \in \{1, \dots, j\}, \quad (8)$$

where R_K is the radius of the reservoir. After approximately five iteration steps the coupled variables k , n and $\dot{\gamma}$ are determined with a satisfying accuracy. With the decoupled shear stress at the wall of the capillary

$$\tau_i = \frac{(1-\alpha)p_i R}{2L} \quad \text{with } i \in \{1, \dots, j\}, \quad (9)$$

the determination of the viscosity curve $\eta(\dot{\gamma})$ is possible.

5.2 Genetic algorithm

For the validation of the results obtained with the NEWTON-RAPHSON procedure an independent method is required. For this reason a genetic algorithm by HOLLAND [8] is used. Genetic algorithms are non-deterministic stochastic optimisation methods that utilize the theories of evolution and natural selection to solve a problem within a complex solution space. A detailed description of genetic algorithms can be found in GOLDBERG [6]. The goal of the algorithm is the determination of parameters which will be transformed into individuals. Such an optimisation step is called generation.

The quality, i.e., the fitness of each individual of a certain generation is described by the respective value of the fitness function f . The fitness is the inverse value of the sum over the squared deviations between measured swell

values $\chi_{sta,i}$ and computed swell values χ_i . Let j denote the number of investigated stamp velocities per filling of the test chamber of the capillary-viscometer. Then the fitness is computed as:

$$f = \left\{ \sum_{i=1}^j (\chi_i - \chi_{sta,i})^2 \right\}^{-1}. \quad (10)$$

For the computed swell values the onset by TANNER [14] is used. This onset has been enlarged by HAN [7] for finite-long capillaries. In order to make this law applicable for rubber blends, it is necessary to identify a material parameter δ . For $\delta = 8$ the original onset is obtained. Hence, the swell value is computed as:

$$\chi_i = \left(\frac{d_i}{D} \right)^2 = \left(1 + \frac{D}{L} \right)^2 \sqrt[3]{1 + \frac{\Delta\sigma_i^2}{\delta\tau_i^2}}. \quad (11)$$

In order to obtain an equation for the swell value which only depends on the unknown material parameters MÜLLNER et al. [11] developed the following onset for the swell value:

$$\chi_i = \left(\frac{d_i}{D} \right)^2 = \left(1 + \frac{D}{L} \right)^2 \sqrt[3]{1 + \frac{1}{\delta} \left(\frac{2}{\kappa^{n-2}} \frac{n-1}{n-2} \right)^2}. \quad (12)$$

In MÜLLNER et al. [11] five material parameters had to be determined. Due to additional experiments with slit capillaries the determination of the pressure factor q and the shift factor κ by means of the genetic algorithm is not required anymore.

The pressure factor q describes the pressure loss at the passage from the reservoir to the capillary according to GLEISSLE [5]. It is comparable to α defined in Section 5.1. The shift factor $\kappa = 2.154$ which is also required for the GLEISSLE correction has been determined by choosing a certain progression of stamp velocities v_i within an experiment. Details of these two parameters can be found in [11].

Thus, the number of unknown parameters which shall be optimised by means of the genetic algorithm can be reduced to three:

- the consistency factor k of the power law according to (2),
- the viscosity exponent n of the power law according to (2), and
- the swell parameter δ according to (11).

When the genetic algorithm is not able to improve the value of the fitness of an individual of the present generation, it stops after a specified number of generations. The obtained material parameters describe all state variables listed in Figure 7 for the investigated material.

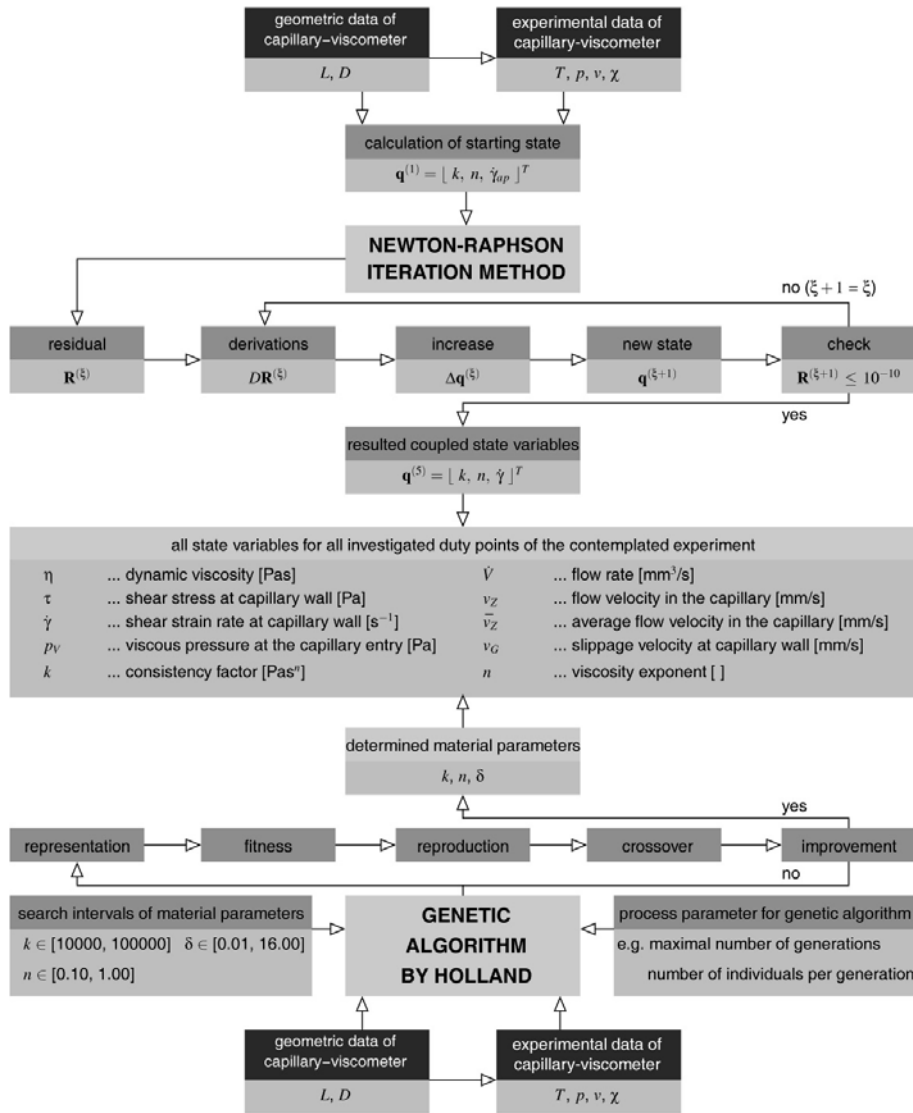


Figure 7 - Process chart for the new material characterisation methods

If the three material parameters are known the determination of the shear strain rate dependent viscosity is possible. The appearance of only two of the three material parameters in the main relationships of the genetic algorithm (10) leads to a challenging of the uniqueness of the obtained solution in the three-dimensional solution space $\{k, n, \delta\}$. Nevertheless, the obtained results are generally more reliable than those obtained by MÜLLNER et al. [11].

However, this method is used for validation only. Further studies on an optimum equation for the evaluation of the fitness for better parameter identification are in progress. This improvement can be achieved by means of an additional equation regarding another type of experiment.

Figure 7 shows the different approach for both material characterisation methods. Furthermore, all state variables of the corresponding experiment are listed. They can be used as input data for numerical simulations of rubber profiles made by extrusion.

6. Results and comparison

After the material parameters are obtained a detailed validation of these parameters has been done by computation of all state variables and a subsequent comparison with the results of the different material characterisations of Chapters 4 and 5.

Figure 8 (a) shows the viscosity curves for all three characterisation methods, where the thin lines mark the results from the experiment $L/D = 10/1$ mm at a temperature $T = 100$ °C and the thick lines are the average viscosity curves for the investigated rubber blend at a temperature $T = 100$ °C. The average viscosity curves are obtained on the basis of ten experiments with different capillaries. Consideration of wall slippage yields to smaller gradients of the viscosity curves. Minor deviations between the NEWTON-RAPHSON procedure and the genetic algorithm are a consequence of considering the die swell of rubber blends. Furthermore, the numerical difference of the power law constants between the shown single experiment and the average values are much larger for the conventional correction methods.

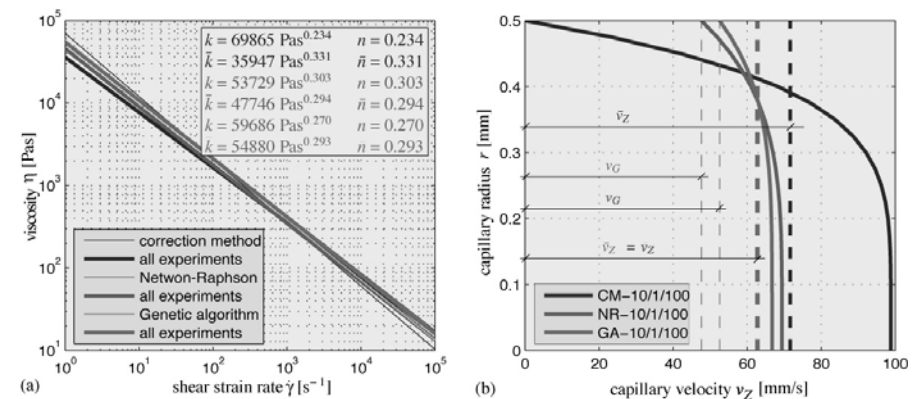


Figure 8 - Comparison (a) of the viscosity curves and (b) of the velocity profiles in a capillary for the experiment $L/D = 10/1$ mm at a temperature $T = 100$ °C

Figure 8 (b) shows the obtained velocity profiles in a capillary, where $r = 0$ describes the middle of the circular capillary and $r = 0.50$ mm marks the wall of the capillary. The average velocity \bar{v}_z is equal for both, the NEWTON-RAPHSON procedure and the presented version of the genetic algorithm. The obtained results fulfil the continuity condition between the reservoir and the capillary, whereas the average velocity obtained from the correction methods violates the continuity condition which refers to the flow rate:

$$\dot{V}_i = \underbrace{v_i R_K^2 \pi}_{\text{reservoir}} = \underbrace{\bar{v}_{z,i} R^2 \pi}_{\text{capillary}} . \quad (13)$$

Remarkable are the flat gradients of the velocity profiles which consider wall slippage. The wall slippage velocity $v_G^{(NR)}$ represents approximately 60 % of the maximum velocity obtained by means of the NEWTON-RAPHSON procedure. With the genetic algorithm a higher wall slippage velocity $v_G^{(GA)}$ is obtained.

7. Conclusions

It has been shown that for industrial used rubber blends the application of common correction methods is not reasonable. The mentioned correction methods are well suitable for polymers, however, for rubber blends certain application problems occur. The main condition for using these correction methods is the condition of adhesion of the flow on the wall of the capillary which is not adhered for the investigated rubber blends. The consideration of wall slippage using a correction method fails as well as the application of two different methods for the back calculation of the melt pressure because of the measurement before the capillary entry.

To solve these application problems for the investigated rubber blends two new procedures for the constitutive characterisation of rubber blends are proposed. The first one is based on the generalised NEWTON-RAPHSON procedure. The coupled state variables are determined by means of a non-linear equation system. This method considers wall slippage as well as the non-linear coupling of the viscosity and the shear strain rate. With the obtained state variables the calculation of the wall slippage velocity for every investigated duty point is possible.

The new method requires validation for the investigated blends. For this purpose a genetic algorithm is used. In order to obtain a fitness equation for the evaluation of various individuals, which are sets of unknown parameters, the consideration of the swelling of the material after the capillary entry is necessary. The different approach to the material characterisation leads to a good agreement for the obtained viscosity curves.

The comparison with the results of the correction methods shows that on the one hand the variation of the power law constants of different capillaries are much smaller and on the other hand the obtained average velocities fulfil the continuity condition of the flow through the capillary. Whether the obtained results lead to better numerical simulations of injection heads for the extrusion of rubber profiles will be the next step of the actual research project.

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9. List of symbols

L	[mm]	length of the capillary
D	[mm]	diameter of the capillary
D_K	[mm]	diameter of the reservoir
T	[°C]	melt temperature
i	[]	duty point
j	[]	number of duty points for one capillary experiment
ν	[mm/s]	stamp velocities for one capillary experiment
p	[bar]	melt pressures for one capillary experiment
d	[mm]	strand diameter after exit of capillary
χ	[]	measured swell values
η	[Pas]	dynamic viscosity
p_E	[bar]	pressure loss
τ	[Pa]	shear stress at the wall of the capillary
$\dot{\gamma}$	[s ⁻¹]	shear strain rate at the wall of the capillary
ν_G	[mm/s]	wall slippage velocity
$\bar{\nu}_Z$	[mm/s]	average velocity in the capillary
k	[Pas ⁿ]	consistency factor
n	[]	viscosity exponent
q	[]	pressure factor for GLEISSLE correction
κ	[]	shift factor
α	[]	constant concerning pressure loss
E_0	[J/mol]	activation energy
R	[J/mol.K]	gas constant
C_1	[]	first material parameter for the WLF equation
C_2	[]	second material parameter for the WLF equation
δ	[]	swell parameter for relationship of TANNER