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Improvement of an Alternative Method for the Correction of Wall Slip Effects in Rheological Studies of Filled Rubber Compounds

Dennis Kleinschmidt, Jonas Petzke and Florian Brüning

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Improvement of an Alternative Method for the Correction of Wall Slip Effects in Rheological Studies of Filled Rubber Compounds

Dennis Kleinschmidt, Jonas Petzke and Florian Brüning[1]

Abstract: Developing new and improved rubber compounds to meet increasing demands for application specific product properties requires detailed knowledge of material properties to be able to predict the processing behavior. Therefore, rheological material properties, which are traditionally determined using the high-pressure capillary rheometer (HPCR) are of crucial importance. Rubber compounds often exhibit flow anomalies and non-isothermal effects, influenced by the compound ingredients and processing parameters that are generally neglected in rheological studies and simulations. This work presents an improved model for describing wall slip effects based on the Coulomb wall slip model, taking into account dissipative material heating. Rheological studies were performed on a carbon black-filled SBR tire tread compound. Using slit capillaries with different geometric dimensions, the pressure dependence of wall slip effects was confirmed, allowing the separation of the flow curve into wall adherent and wall slip regions.

Keywords: High-Pressure Capillary Rheometry, Rheology, Rubber, Viscosity, Wall Slip

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[1] The authors Dennis Kleinschmidt (dennis.kleinschmidt@ktp.upb.de), Jonas Petzke (jonas.petzke@ktp.upb.de) and Florian Brüning (florian.bruening@ktp.upb.de) are affiliated with the Paderborn University in Germany.

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Introduction

The HPCR is widely used to characterize the flow behavior of thermoplastic melts and rubber compounds, allowing the determination of viscosity over the process-relevant shear rate range. Compared to round hole nozzles, the use of slit capillaries allows the measurement of direct pressure and temperature along the flow direction in the slit capillary, which significantly reduces the measurement effort and allows run-in effects to be neglected [1,2]. During rheological studies, a fully developed, steady flow with Newtonian flow behavior is assumed. Furthermore, dissipative material heating, wall slip, and pressure dependence of viscosity are neglected [2]. These assumptions are not fully valid for different types of complex fluids such as rubber compounds [3]. Accordingly, complex correction procedures are necessary to obtain the true viscosity data. As the shear rate increases, there is an intensification of both shear friction and shear heating. Due to the poor thermal conductivity of rubber compounds, heat accumulation and temperature rise in the material is initiated [4].

Wall slip leads to an incorrect determination of shear stresses and other material properties. When wall slip effects occur during processing, they cannot be minimized or prevented without affecting the process. Therefore, it is necessary to evaluate the wall slip behavior specific to the material and take it into account in modeling and simulation. In the literature, a differentiation is made between the Coulomb wall slip model and the slip film model. The Uhland [6] wall slip model is based on the occurrence of Coulomb friction between the flowing fluid and the flow-limiting wall. In analogy to solid friction, a certain frictional force, which is greater than the static frictional force, must be applied for the slip process. To maintain this condition, only the lower slip friction force must be exceeded. In the slip film model, a low-viscosity layer is assumed to form near the flow-limiting wall, which has a lower viscosity compared to the flowing fluid and thus represents a lubricating film. The fluid then slides on this low-viscosity layer. Therefore, this case of wall slip represents a cohesive failure [5-8].

For the quantification of wall slip velocities in rheological measurements, various approaches exist for different types of rheometers. In particular, the Mooney method [9] as well as the modified Mooney method by Geiger [10] have been used in recent work to determine slip velocities using HPCR. However, the application of the Mooney method to rubber compounds often leads to results that are not physically justifiable [13]. For a review of the main studies on wall slip effects focusing on filled rubber compounds, refer to [14], while Hatzikiriakos [3] provides a comprehensive overview of wall slip mechanisms in complex fluids, more generally.

Brockhaus describes an alternative approach for modeling the wall slip behavior of filled rubber compounds. In this approach, the total volumetric flow is separated into a slip and a shear component. This relation results from the equation of motion in conjunction with the continuity equation, taking into account the boundary condition of a wall slip velocity. It is shown that the velocity profile of the pressure flow in slit capillaries is not influenced by wall slip effects, since the slip velocity v_{slip} occurs as an increase of the total velocity in the form of a plug flow [15]:

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$$v_{slip} = \frac{\dot{V}_{total}}{WH} - \frac{nH}{2(1+2n)} \cdot \left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} \tag{1}$$

v_{slip}	Wall slip velocity	$\dot{V}_{total}$	Total volume flow	W	Width of slit capillary
H	Height of slit capillary	n	Flow exponent	τ_w	Wall shear stress
K	Consistency factor				

This model approach uses the consistency factor K and the flow exponent n to characterize the wall slip velocity in order to consider the shear thinning material behavior. To determine these power law parameters, Brockhaus assumes isothermal conditions and the validity of the Coulomb slip model within the rheological investigations performed, without verifying these assumptions [15]. Since rubber compounds exhibit a shear thinning, non-Newtonian flow behavior, a shear rate correction is also required after the wall slip correction to determine the true viscosity data.

This work examined whether the wall slip behavior of filled rubber compounds depends on the flow channel geometry and can be described by the Coulomb slip model, which is the requirement for applying the wall slip correction method, according to Brockhaus. In addition, dissipative material heating is considered in rheological research in order to verify Brockhaus' assumption of an isothermal flow.

Materials

To demonstrate that the viscosity data for wall adhesion is independent of the flow channel geometry used, preliminary tests were performed on a low-density polyethylene (Lupolen 1840 D) from LyondellBasell used in blown film extrusion. A sulfur crosslinking styrene-butadiene rubber (SBR) tire tread compound was used for the wall slip studies. The base of the compound is a SBR 1502 to which 40 phr of carbon black N 347, 70 phr of silica, and 9.5 phr of processing oils, processing aids, and crosslinking chemicals have been added.

Equipment and Experimental Design

The characterization of the flow behavior was performed on a Rheograph 50 HPCR from Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen (Germany), using four slit capillaries with different cross-sectional area (see Table 1). Three equidistant pressure transducers were used along the length of each slit capillary to determine the normal pressure orthogonal to the flow direction. A shear rate

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range of 0.1 to 1,000 s^{-1} was considered, with measurements taken from high to low shear rates at 200°C for the LDPE and from 80°C to 100°C for the rubber compound.

Table 1. Geometric data of the slit capillaries used.

	Cross-sectional area of the slit capillary (*W* x *H*)			
Dimension	10 mm x 0.5 mm	10 mm x 1 mm	12 mm x 1.2 mm	15 mm x 1.5 mm
Width	10 mm	10 mm	10 mm	10 mm
Height	0.5 mm	1 mm	1.2 mm	1.5 mm
Length	100 mm	100 mm	100 mm	100 mm

Results

To validate the assumption that the viscosity data is independent of the flow channel geometry used under conditions of wall adhesion, rheological tests were performed using an LDPE. The viscosity data obtained were corrected using the Weissenberg-Rabinowitsch method and approximated using the Carreau model [1]:

$$\eta = \frac{A}{(1 + B \cdot \dot{\gamma})^C} \tag{2}$$

η	Viscosity	A	Zero viscosity	B	Transition time
$\dot{\gamma}$	Shear rate	C	Flow exponent		

Table 2 shows that the viscosity data in the considered shear rate range is approximately independent of the geometry and therefore the assumption of wall adhesion is valid.

Table 2. Carreau parameter for the LDPE at 200°C for the slit capillaries used.

Carreau parameter	Cross-sectional area of the slit capillary (*W* x *H*)			
	10 mm x 0.5 mm	10 mm x 1 mm	12 mm x 1.2 mm	15 mm x 1.5 mm
A [Pas]	83,774.6	50,401.6	44,981.8	47,453.1
B [s]	25.31	9.78	8.65	9.41
C [-]	0.59	0.60	0.60	0.60

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Figure 1 shows the apparent viscosity curves for the rubber compound at two different processing temperatures.

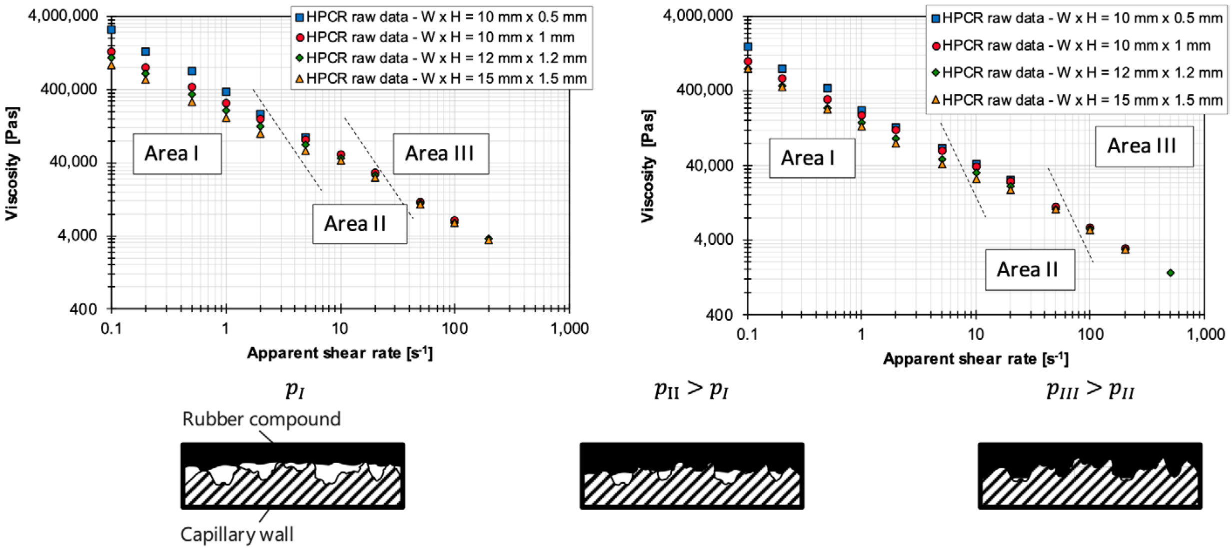

Figure 1. Subdivision of the apparent viscosity curves for 80°C (left) and 100°C (right) taking into account the pressure dependence of the contact area between the flowing rubber compound and the flow-limiting capillary wall.

The comparison clearly shows that there is a significant geometry dependence of the resulting apparent viscosity curve in the low apparent shear rate range. The geometry dependence of the data decreases with increasing apparent shear rate, equivalent to increasing wall shear stress ($\tau_w = \eta \cdot \dot{\gamma}$), until the viscosity data is approximately geometry independent.

The viscosity data available can be divided into three areas with sectionally valid power law functions, as already recognized by Brockhaus [15]:

$$\eta = K \cdot \dot{\gamma}^{n-1} \tag{3}$$

η	Viscosity	K	Consistency factor	$\dot{\gamma}$	Shear rate
n	Flow exponent				

Using power law functions is sufficient for describing the shear thinning flow behavior of rubber compounds, since Leblanc et al. detected neither a yield point or a Newtonian viscosity plateau for highly filled rubber compounds at very low shear rates [16,17]. The determination of the partial

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areas is automated using the method of least squares. The power law parameters of the uncorrected viscosity data obtained for the different areas at 80°C are summarized in Table 3.

Table 3. Power law parameters of the uncorrected viscosity data for the different areas at 80°C.

Power law parameter	Area	Cross-sectional area of the slit capillary (*W* x *H*)			
		10 mm x 0.5 mm	10 mm x 1 mm	12 mm x 1.2 mm	15 mm x 1.5 mm
K [Pas]	I	355,762	262,133	209,013	165,080
	II		259,580	197,236	145,747
	III		428,565	342,317	301,798
n [-]	I	0.14	0.30	0.29	0.28
	II		0.28	0.36	0.43
	III		0.09	0.13	0.15

As the determined power law parameters have a direct influence on the wall slip velocity (see equation 1), the automated determination of the partial areas reduces the error rate compared to the manual and objective determination of Brockhaus. The accuracy of the range subdivision increases as the number of data points in the shear rate range under consideration increases.

For the description of the geometry dependence of the rheological data, the model concept of the pressure dependence of the contact surface between the rubber compound and the flow-limiting wall of the flow channel by Jepsen and Räbinger [18] is used. In rheological studies, an increase in the prevailing pressure with increasing shear rate causes the rubber compound to move into the surface roughness of the flow-limiting wall, thereby increasing the adhesion force (see Figure 1 bottom). At high shear rates, the adhesion force is large enough that any slip motion stops, and no slip motion occurs according to the Coulomb slip model [18]. The results are consistent with observations on wall slip for various materials in literature, where the wall slip effects are greatest when the pressure level reaches a minimum [8]. The nonlinear pressure gradient in the direction of the flow channel also indicates wall slip according to the Coulomb slip model [10]. The Uhland [11] wall slip model is based on the occurrence of Coulomb friction between the melt and the flow-limiting wall. In analogy to solid friction, a certain frictional force, which is greater than the static frictional force, must be applied for the slip process. To maintain this condition, only the lower slip friction force must be exceeded [11,12]. In addition, the experimental investigations yielded homogeneous, smooth extrudate strands throughout, confirming the model concept of Jepsen and Räbinger [18].

An infrared thermal imaging camera was used to determine the outlet temperature of the material strands during the rheological studies. In the shear rate range under consideration, an increase in the shear rate leads to a measurable material heating of up to approximately 15°C on the rubber surface based on the set process temperature. Since an increase in temperature leads to a higher chain mobility and thus to a reduction in viscosity, the shear thinning material behavior of the rubber compound is overestimated, which requires a temperature correction of the viscosity data before the wall slip correction, which is neglected by Brockhaus. In order to have comparable starting points for the wall slip and shear rate correction both for the different apparent shear rates in the slit capillaries and between the slit capillaries, a temperature shift is carried out using the Arrhenius approach [1]:

$$\eta_{corr} = e^{\left(\frac{E_0}{R} \cdot \left(\frac{1}{T_{out}} - \frac{1}{T_{set}}\right)\right)} \cdot \eta \qquad 4)$$

η_{corr}	Temperature-corrected viscosity	E_0	Activation energy	R	Gas constant
T_{out}	Material outlet temperature	T_{set}	Set temperature		

The application of the wall slip correction to the temperature corrected viscosity data shows that an increase in the flow channel cross section leads to higher slip ratios, as the viscosity data is increasingly shifted to lower values (see Figure 2). The use of the Weißenberg-Rabinowitsch correction to take into account the shear thinning flow behavior of filled rubber compounds leads to the true viscosity data under the boundary condition of wall adhesion.

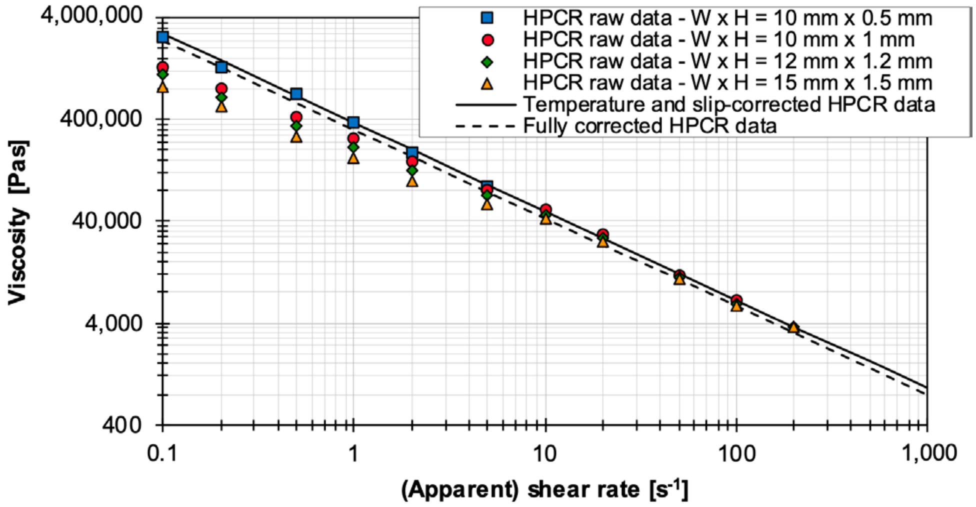

Figure 2. Comparison of viscosity data after different stages of the correction plan.

The distinction between wall slip and wall adhesion is made on the basis of the critical wall shear stress. With respect to the available experimental data, the critical wall shear stress represents the transition wall shear stress between areas II and III. It is found that a temperature invariant critical wall shear stress of approximately 570 kPa is determined for the filled rubber compound (see Figure 1). Unlike the critical wall shear stress, the critical apparent shear rate is temperature dependent. An increase in temperature results in a shift in the critical apparent shear rate to higher values because higher temperature leads to higher chain mobility, which results in a shift in viscosity to lower values. Accordingly, a higher volume flow is required to achieve a comparable wall shear stress.

Conclusion and Outlook

The experimental investigations of the tire tread rubber compound have revealed that the wall slip behavior of filled rubber compounds is significantly influenced by the existing pressure level in the flow channel geometry and thus by the existing wall shear stress. The results show that the existing wall slip effects can be described with the Coulomb slip model, taking into account the model concept of the pressure dependence of the contact surface by Jepsen and Räbinger. This represents the starting point for the use of the wall slip correction method according to Brockhaus, which was extended by an automated partial area determination and the consideration of dissipative material heating. In further investigations, the evaluation routine presented is applied to EPDM rubber compounds used in the field of technical elastomer products.

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