A new and highly efficient method to measure steady shear viscosity and wall slip of rubber compounds. Closed boundary rheometer (RPA)

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ABSTRACT

This instrument has successfully measured steady shear viscosity with high repeatability without correction. The results fit well with other rheometers/viscometers when no-slip conditions are assured. The closed boundary configuration prevents edge fracture as commonly experienced with open boundary rheometers (DMA) on high viscosity, high elasticity materials. The comparison of results using grooved dies (no-slip) and polished dies (slip) readily provides wall slip velocity under constant pressure. The results of wall slip versus shear stress follow a power-law function as per Navier's slip law – $[F_{(V)} = -k(V_r)^e]$.

This method separates shear rate from pressure effects on wall slip. It questions pressure-driven flow instruments which are using pressure measurement for shear stress calculation.

INTRODUCTION

Steady shear viscosity of rubber compounds is commonly measured using a capillary rheometer. This instrument however is requiring numerous tests to achieve the required corrections for true viscosity calculation to be used in modern flow simulation. These corrections are entrance pressure drop (Bagley), non-Newtonian flow (Rabinovitch), and wall slip, making this test highly time-consuming and rather inaccurate.

Steady viscosity measurement is performed in the RPA in a similar manner than standard open boundary DMA in rotational conditions. After the initial transient shear and when steady shear condition is reached, the shear stress is calculated from the torque plateau using Eq. 1.

$$\sigma_{12} = \frac{3M}{2\pi R^3} \quad (1)$$

In the RPA, steady shear test procedures are set using strain (γ_0) and time. Shear rate is therefore calculated using Eq. 2.

$$\dot{\gamma} = \frac{\gamma_0}{t} \quad (2)$$

Viscosity is simply calculated according to Eq. 3.

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (3)$$

In standard operation, the RPA closed boundary test cavity provides an internal pressure of 4 MPa ± 0.3 MPa. This high pressure coupled with grooved dies provides slip-free shear as per a 2008 presentation at the XVth Congress of Rheology[1] and free of edge fracture.

Wall slip is particularly difficult to apprehend essentially due to the complexity of rubber compound formulations and their interaction with the production tool. Wall slip is essentially an interface property. In 1931,

Mooney2 proposed a simple method for wall slip measurement using a capillary rheometer. It was nevertheless targeted to thermoplastic polymers rather than rubber compounds. The method is assuming that the total output (Q_t) of the capillary rheometer is the sum of output in no-slip (Q_{ns}) and slip (Q_s) conditions as per Eq. 4.

$$Q_t = Q_{ns} + Q_s \tag{4}$$

Shear rate is calculated as per Eq. 5 in true shear conditions

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \tag{5}$$

By rearrangement, substitution in Eq. 4 and simplification, it gives Eq. 6.

$$\dot{\gamma}_{app} = \dot{\gamma}_{ns} + \frac{4V_s}{R} \tag{6}$$

By plotting the apparent shear rate ($\dot{\gamma}_{app}$) as a function of 1/R at constant shear stress, the intercept of this linear relationship provides the no-slip shear rate ($\dot{\gamma}_{ns}$). The slope is equal to four times the slip velocity ($4V_s$). This relationship is illustrated in Fig. 1

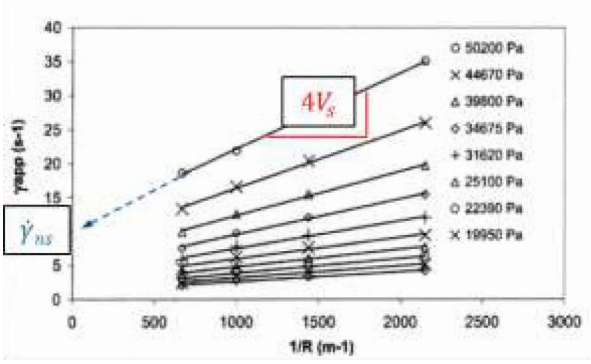

Figure 1: Slip velocity calculation method according to Mooney

Unfortunately, the application of this method on a large number of rubber compounds by several authors[3] returned negative values for the intercept thus a negative no-slip shear rate. This is undoubtfully scientific nonsense and is illustrated in Fig. 2.

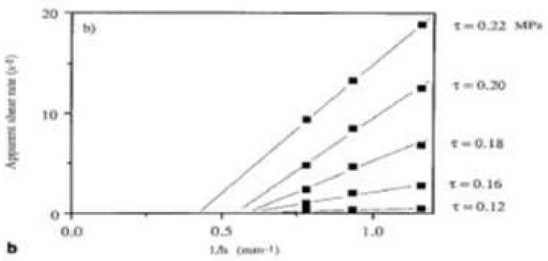

Figure 2: Prediction of negative no slip shear rate according to Mourniac et al

This problem was later addressed, amongst many authors, by Wiegreffe[4] and Geiger[5]. They respectively proposed a linear relationship between shear rate and $1/R^2$ for capillary die and an exponential relationship using slit dies. The different approach between Mooney and Geiger as described by Crié[6] is summarized and illustrated in Fig. 3.

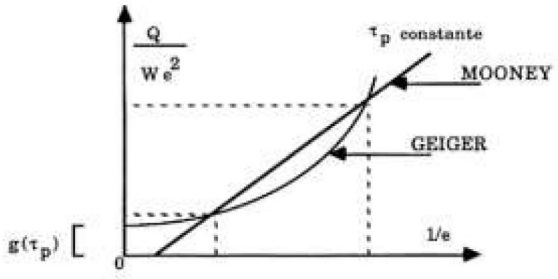

Figure 3: Illustration of Geiger versus Mooney approach for wall slip calculation

A different instrument and method were proposed by Turner and Moore[7] to study wall slip. This instrument (TMS rheometer) was based on the original Mooney viscometer but equipped with a biconical rotor and a variable rotation speed drive. In addition, the material was injected into the instrument cavity via a transfer chamber and a piston. This feature offered the opportunity to study the effect of pressure on viscosity and wall slip.

Wall slip was extensively studied in the mid-eighties using the TMS rheometer by

Basir and Freakley[8] comparing shear stress with grooved and polished rotors.

Following the same method, after testing rubber compounds on an RPA with grooved dies in no-slip conditions, the upper die of the instrument is replaced by a grooveless polished die. The residual surface roughness of this die was not quantified.

An identical shear rate range is applied on the compound of interest with the combination of grooved/polished dies thus providing shear stress and viscosity in slip or partial slip conditions.

The comparison of shear stress versus shear rate under both conditions allows a simple calculation of slip velocity under constant pressure. This calculation method is illustrated for linear shear in Fig. 4

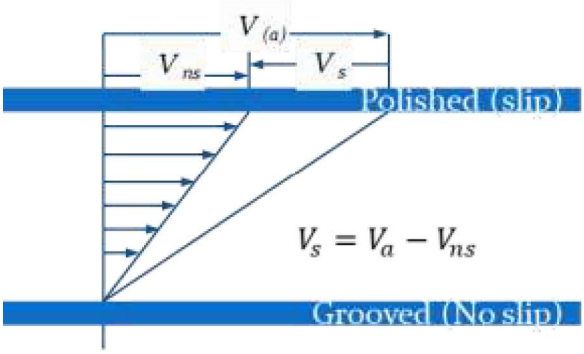

Figure 4: Wall slip measurement principle in linear drag flow

Since we use a rotational rather than linear shear method, we are dealing with angular velocities. So the angular slip velocity is given by Eq. 7.

$$\Omega_s = \Omega_a - \Omega_{ns} \tag{7}$$

In a rotational device, shear rate ($\dot{\gamma}$) is given by Eq. 8.

$$\dot{\gamma} = \frac{\Omega}{\alpha} \tag{8}$$

With α being the cone angle (0.1251 Rad).

By rearrangement and substitution in Eq. 7, we obtain the angular slip velocity as per Eq. 9.

$$\Omega_s = \alpha \cdot (\dot{\gamma}_a - \dot{\gamma}_{ns}) \tag{9}$$

Both apparent and no slip shear rate are given by the graph of shear stress versus shear rate. The difference shall be calculated at constant shear stress as illustrated in Fig. 5.

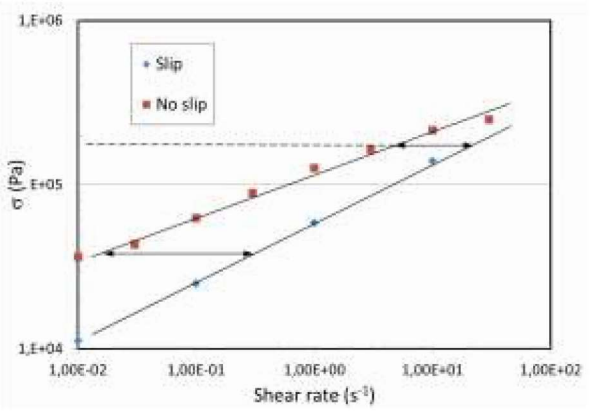

Figure 5: Angular slip velocity calculation based on slip versus no slip shear stress

Angular velocity can subsequently transformed into linear velocity using Eq. 10.

$$\Omega = 2\pi R \text{ at R} \tag{10}$$

EXPERIMENTAL

All measurements were performed using the RPA Elite from TA Instruments, Newcastle, DE, USA.

Four compounds with largely different formulations and properties were used in this study. Except for EPDM/Silica, all others are real production compounds. The precise formulations will not be disclosed although some technical information is listed here below.

1. High slip EPDM with high level of carbon black, process oil and calcium carbonate.
2. Truck tread compound, NR/BR blend.

3. EPDM-Silica (No other additives) very low slip "model" compound.
4. SBR/NBR compound.

The test procedure is identical with both grooved and polished dies. The test temperature was set to 90° C, the shear rate range covers from 10-2 to 30 s-1. The shear rate values were set according to Eq. 2. To eliminate or reduce any thixotropic effect of fillers, the steady shear test was preceded by a preconditioning step under the following dynamic conditions: 80° C, 2 minutes at 100% strain (g0=1), and 1 Hz.

The raw data of torque versus time for the EPDM/Silica compound are illustrated in Fig. 6. This graph confirms that steady shear conditions are reached, enabling the calculation of the corresponding viscosity.

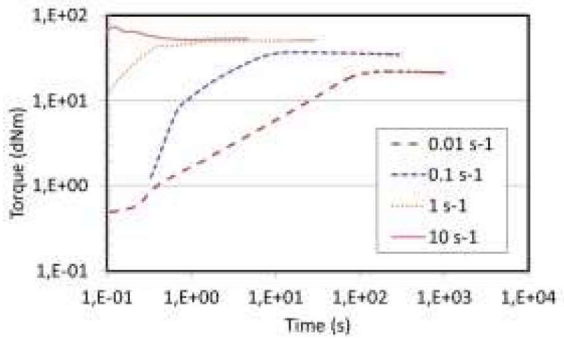

Figure 6: Raw torque data versus time for the EPDM/Silica compound.

For all compounds, the results of shear stress versus shear rate have been treated using the Ostwald/De Wael (power law) model in slip and no slip conditions. The values of both model paramters ("K" and "n") are given in Table 1.

Table 1: Ostwald/De Wael model parameters in slip and no slip conditions

$\sigma = K \cdot \dot{\gamma}^n$	Slip		No slip	
	K	n	K	n
EPDM (high slip)	59106	0,365	116105	0,256
Tread	173744	0,226	186358	0,212
SBR/NBR	42725	0,448	72344	0,298
EPDM/Silica	281707	0,190	314523	0,221

In all cases, the values of the parameter "K" show lower values for slip conditions. The ratio of "K" between slip and no-slip conditions, indicates the "slippery" nature of each compound. The highest ratio (~50%) is observed naturally with the EPDM high slip compound and the lowest with the EPDM/Silica compound (~ 10%). But, except for this EPDM/Silica, the pseudo-plasticity index "n" for all productive compounds is found larger in slip as compared to no-slip conditions. This implies that, for the studied compounds, slip ratio DECREASES with shear rate/stress.

Using the parameters from the Ostwald/De Waele model, the linear slip velocities were calculated for each compound using Eq. 9 and 10. The slip velocity versus shear stress for each compound is illustrated in Fig. 7.

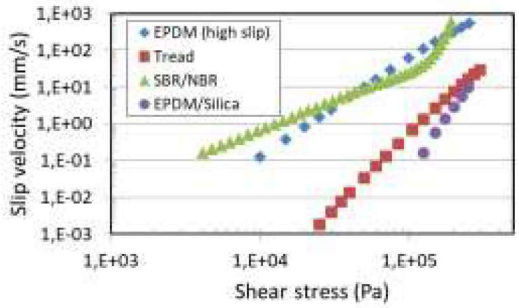

Figure 7: linear slip velocity versus shear stress

These results show that the slip velocity increases with shear stress/rate. It follows as well a power-law versus shear stress as stated

by Navier's slip law. It is although interesting and somehow intriguing to see an abrupt change in slope of the Navier slip law for the SBR/NBR compound. This change occurs around a shear stress value of 135,000 Pa with a sudden increase of slip velocity. No explanation for this abrupt change has been proposed other than the relative incompatibility of the base polymers. The values of the Navier slip law coefficients are listed in Table 2.

Table 2: Power law coefficients for the Navier's slip law.

$V_{(s)} = K \cdot \sigma^n$	K	n
EPDM (high slip)	5.10^{-12}	2.605
Tread	10^{-20}	3.914
SBR/NBR	3.10^{-7} (10^{-35})	1.585 (7.137)
EPDM/Silica	10^{-40}	7.482

The values in parenthesis for the SBR/NBR compound are valid only above the threshold stress value of 135,000 Pa.

If Fig. 7 confirms that the slip velocity increases with shear stress, it is interesting to consider as well the variation of the slip ratio as per Eq. 11.

$$Slip\ ratio = \frac{Slip\ velocity}{Apparent\ velocity} \qquad (11)$$

This ratio indicates how much the material exhibits a plug versus pure shear flow. The values of the respective slip ratio are illustrated in Fig. 8.

Fig. 8 shows that all productive compounds exhibit a decrease of wall slip while increasing shear stress/shear rate. The EPDM high slip compound exhibits an almost pure plug flow between 10 KPa and 100 KPa with a slip ratio close to 1 below a shear stress value of around 30 KPa. To further investigate the behavior of this high slip compound, shear viscosity was plotted as a function of shear stress in slip and no-slip conditions as illustrated in Fig. 9.

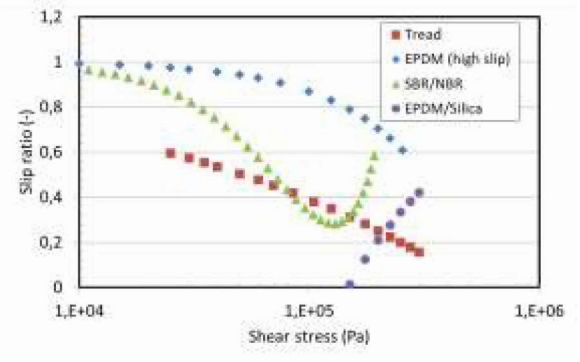

Figure 8: Slip ratio versus shear stress.

This graph clearly shows a yield stress behavior with a critical stress value of 32,000 Pa. According to the Herschel-Bulkley model for high concentration suspension, the viscosity tends to infinity below the yield stress value. Therefore, the material can only move in a pipe as a solid so a pure plug flow. This effect was described by Kalyon[9] in a previous paper for concentrated suspensions. Fig. 9 also shows that this yield stress does not appear in the case of a slip. This finding sheds some light on the controversy on the existence of yield stress for rubber compounds (Barnes[10]) when viscosity measurements are performed under partial or full slip conditions.

As explained earlier, the closed cavity of the instrument provides an internal pressure of around 4 MPa. By reducing the closing force of the instrument main air cylinder, this internal cavity pressure can be varied and measured in the case of a dual transducer (torque and normal force). This feature provides the instrument a unique ability to INDEPENDENTLY vary shear rate and pressure when measuring steady shear viscosity. This is unfortunately impossible on a capillary rheometer.

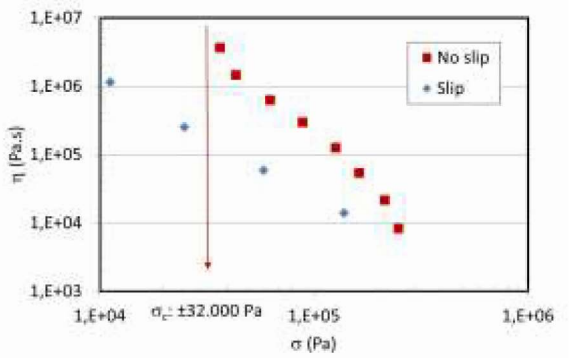

Figure 9: Determination of the EPDM high slip compound yield stress value as per the Herschel-Bulkley model.

The influence of pressure on wall slip has only been measured on the tread compound at one single shear rate of 1 s^{-1}. In this case, the variation of wall slip versus pressure is illustrated in Fig. 10 as a reduction of the measured shear stress. The error bar on the shear stress value in the no-slip condition is set at 95% confidence limits. It indicates excellent repeatability.

The measured shear stress at variable pressure required a correction for the instrument compression compliance. Reducing the instrument cavity pressure also reduces the die gap, thus artificially increasing the measured shear stress. This is highly machine-dependent. A new set of corrections shall be used with an instrument of a different origin/supplier.

Fig. 10 shows that, indeed, wall slip depends upon pressure. As described in some previous publications by Geiger[5], Jepsen[11], and Graf[12], wall slip may depend upon pressure through the effect of the tool residual roughness.

The manufacturing of the instrument dies, conical or flat, with well-defined roughness will provide the adequate tool to further study the pressure effect on wall slip.

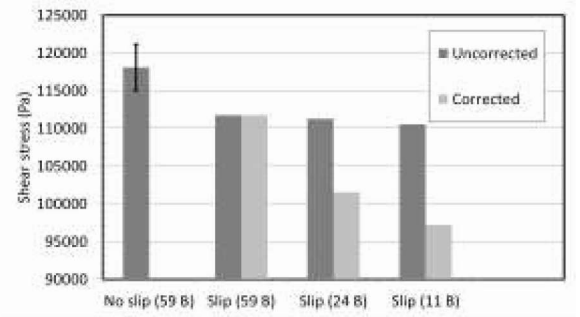

Figure 10: Variation of shear stress values at 1 s-1 on the tread compound under variable pressure.

Finally, the RPA steady shear viscosity measurement was confronted with other steady shear viscosity methods such as biconical rotor variable speed Mooney and capillary rheometer on the SBR/NBR compound. All results are illustrated in Fig. 11.

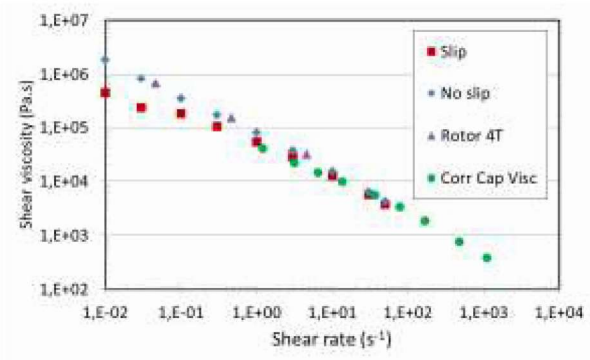

Figure 11: Viscosity versus shear rate on the SBR/NBR compound using various rheometers. RPA slip and no slip, biconical variable speed Mooney and Capillary rheometer.

Fig. 11 clearly shows that the RPA in no-slip conditions provides true viscosity data without the need for time-consuming correction. It confirms as well that capillary rheometer data require not only Bagley and Rabinovitch correction but as well wall slip correction whenever possible. Capillary rheometer data are found to follow the RPA data that include wall slip, especially at a low shear rate.

SUMMARY AND CONCLUSION

The proposed technique using a closed boundary rheometer such as the RPA has been found very efficient to measure the steady shear viscosity of rubber compounds. Testing with grooved dies and polished dies enables as well the precise measurement of wall slip. A full study for true viscosity and wall slip can be performed in only a few hours. As wall slip remains an interface property, one must consider the results only valid for the used combination of compound formulation and tool material (steel, alloy, etc.) and surface roughness. In the case of the RPA, the die material and surface roughness can easily be changed for additional studies.

This study also demonstrated that rubber compounds slip in a different way than regular thermoplastics such as polyolefines. Polyolefines tend to slip more at a high shear rate/shear stress than at a low shear rate[13]. Most of the tested productive rubber compounds behave oppositely. Due to the huge variety of rubber compound formulations, this conclusion will require further investigations for possible generalization.

The used instrument provides a maximum shear rate of 50 s-1 with biconical dies. The replacement of one conical die by a flat one (Cone-plate) increases the maximum achievable rate 100 s-1. The maximum shear rate could be further increased by using parallel plate dies with a reduced die gap. It must be kept in mind that the maximum shear rate available will always be limited by the compound critical shear stress above which appears melt fracture. In the current study, the occurrence of melt fracture appeared around 300,000 Pa at a shear rate between 1 and 10 s1 for the EPDM/Silica compound.

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