Investigation of Wall Slippage in Silicone Rubber Compound by means of High-pressure Capillary Rheometer

Introduction
Wall slippage is a significant rheological phenomenon of some materials and is one of the greatest challenges when it comes to the extrusion of rubber, since the effect of wall slipp will reduce the pressurization efficiencies of the extruder by reducing the shear rate near the wall and will also affect the stability of the extrusion process [1]. However, currently in the processing of elastomeric materials, wall adhesion (in which the melt is always sticking to the wall and moves with the same velocity with the wall along the flow-path) is the prevalent approach in extrusion design due to its simplicity. In return, the consideration of wall slippage would lead to a more sophisticated model of flow behavior [2]. Some of the major disadvantages of the assumption of no-slip boundary condition are: the failure of true-shear rate calculation, while if wall slippage appears, the required shear rate in the processing will be reduced [3]; and wall slipp will also reduce the throughput rate of the process [4]. In contrast, wall slip can also lead to an advantage, such as in reducing the energy requirement for the process [5]. Therefore, there is an urgent need to take this phenomenon into consideration, which should not be discounted in the analysis as it usually is.

Given the limitations of the wall adhesion assumption all along the flow path, it is therefore critical to describe the phenomenon of wall slippage. Only by investigating this complex flow anomaly, the rheological behavior of the material will be better analyzed. Consequently, one will be able to determine the suitable parameter for processing. Two models have been developed to illustrate the wall slippage behavior [6, 7]. The first model is Coulomb’s friction model that describes the wall slippage as a function of inadequate adhesion between the wall and the fluid, in which the wall shear stress is a function of pressure. On the other hand, the thin slip layer model from Girard describes the wall slippage as the presence of a thin slip layer between the wall and the fluid, where the wall shear stress is a function of the velocity.

In illustrating the wall slip behavior, the term wall slippage is closely bonded by commonly named critical shear stress as the onset of wall slip. Several researchers have studied this issue and showed that wall slippage is observed in rubber compound after the material exceeds the critical shear stress [4, 9, 10]. On the other hand, contradictory finding has been reported by Geiger [11]. With EPDM as the investigated material, it is claimed that wall slippage is taking place before the critical shear stress, and wall-sticking is arising after the critical shear stress. Therefore, based on these contradictory results, this paper aims to call into question the slip behavior of silicone rubber compounds.

In an attempt to analyze the rheological anomaly and to determine the critical shear stress, one of the methods that is frequently adopted is the use of capillary rheometer. This instrument has been proved its ability to observe the wall slip...
phenomenon in a rubber compound because of its ability to reach high shear rates [12]. The wall slippage can be observed by examining pressure drop inside the capillary, as it has been demonstrated as the indication of the change of condition from wall adhesion to wall slippage behavior [13]. In describing the wall slippage behavior, the Mooney method [14] has been utilized by several researchers [15, 16, 17] and is frequently used in determining the slip velocity, which is the difference between the velocity of the fluid and the velocity of the wall [18].

There is mounting evidence of wall slippage in elastomeric material [11, 12, 19], however, there is still an inconsiderable amount of researches that portray the behavior of silicone rubber compound, compared to the examinations of wall slippage in organic rubber compound. Therefore, this study will enhance the understanding of wall slippage behavior in silicone rubber compound. Silicone rubber is selected to be the investigated material because of its growing importance and position in the industry, considering its excellent flexibility, thermal insulation, high resistance to chemical influence, and stability at high temperature [20]. In order to achieve the desired results, high-pressure capillary rheometer (HCR) will be utilized in investigating the silicone rubber compounds. The system is fully integrated with rectangular slit capillary.

Experimental Section

Materials
Silicone rubber or silicone elastomers (scientific name: Polydimethylsiloxane) are inorganic synthetic elastomers made from cross-linked silicone-based polymers. They are derived from silica or quartz and have an inorganic main chain [21]. Solid silicone rubber is an elastomer with high molecular weight and relatively long polymer chains and referred as high-temperature-vulcanizing silicone rubber [22]. Compared to the organic rubber that has carbon to carbon backbone, silicone rubber offers better resistance to UV and heat because of the absence of carbon to carbon backbone in the main chain of this material. In this study, non-vulcanized solid silicone rubber is investigated and supplied by Wacker-Chemie AG, Burghausen, Germany.

The Mooney viscosity (ML(1+4)) is determined at 25°C by a Mooney Viscometer (MV2000) by Alpha Technologies GmbH, Heilbronn, Germany. The density of the material is determined with a pycnometer (AccuPyc 1330) from Micrometrics GmbH, Aachen, Germany. Further, heat capacity of the material is also determined with DSC Q1000 from TA Instruments Inc, New Castle, USA and is carried out for two repetitions. The materials are prepared with maximum weight of 10 grams at 25°C. The following table summarizes the material data which are obtained from the apparatuses.

<table>
<thead>
<tr>
<th>Material property of silicone rubber compound</th>
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<td>Hardness [Shore A]</td>
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<td>60</td>
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High-pressure capillary rheometer (HCR) test
A high-pressure capillary rheometer (Rheograph 2002), manufactured by Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany, is utilized in the experiments in order to generate a pressure-driven flow. The instrument is mounted with a die with rectangular slit cross section (5 mm²). A piston with a diameter of 15 mm is used to push the test silicone rubber compound through the capillary and to generate different shear rates with various piston velocities. Three pressure transducers are mounted along the slit cross section in order to measure the pressure level in the capillary for determining the viscosity and to observe the wall slippage. The experiments are carried out at temperatures of 25°C and 45°C. The width, height, and length of the rectangular capillary are 10 mm, 0.5 mm, and 100 mm respectively. The material is observed under shear rates ranging from 5 s⁻¹ to 260 s⁻¹. The experiments are repeated three times to ensure the reproducibility of the data obtained and the standard deviation is being monitored. The experimental setup in HCR is illustrated in Figure 1.

Fig. 1: Experimental setup of high-pressure capillary rheometer test

Fig. 2: Apparent flow curve of silicone rubber at 25°C and 45°C
Results and Discussion

Pseudoplastic flow behavior of silicone rubber compound

From the raw data obtained from the high-pressure capillary rheometer, the apparent flow curve can be determined. Apparent flow curve is used to portray the rheological properties of the material and made without any capillary flow correction. With the use of volume flow rate, \( V \), the apparent shear rates can be determined by

\[
\dot{\gamma}_{\text{app}} = \frac{6 \cdot V}{B \cdot H^2} \tag{1}
\]

where \( B \) is the width and \( H \) is the height of the slit capillary. Consequently, from the pressure difference of each pressure transducers (\( \Delta p \)), cross sectional area (\( A \)) and the area of the wall of capillary rheometer (\( A_w \)), the wall shear stress can be determined by

\[
\tau_w = \frac{\Delta p - A}{A_w} \tag{2}
\]

The apparent viscosity is determined based on the pressure drop between the measurement point of pressure transducer 1 and 3. In Figure 2, it is shown that the apparent flow curves at the two different temperatures of the material are both showing a pseudoplastic behavior, where it experiences a lower viscosity with increasing shear rates. Figure 2 also demonstrates that the temperature difference of 20°C has not considerable effect on the flow behavior of the material and the line of some points are in contact with one another, while they still have the identical viscosity value. However, the flow curve of the material observed under 45°C shows that the viscosity at higher temperature is little lower.

From the apparent flow curve, the relationship between viscosity and shear rate, plotted on log-log coordinates, can be estimated with Ostwald de Waele equation and the flow behaviour index (\( n \)) that characterizes the shear-thinning behavior can be calculated. The flow behavior index and the consistency factor (\( K \)) are determined from the point of shear rate, where wall adhesion is expected to occur between the capillary wall and the melt, which is predicted on the points before the critical wall shear stress. It should be noted that the flow behavior index will determine the pseudoplastic behavior under no-slip boundary condition. Table 2 summarizes the data on the flow behavior index at both temperatures. In general, the flow behavior index shows that the lower its value, the higher the shear thinning experiences by the material. The results in Table 2 obtained from the mathematical modeling, with Ostwald de Waele equation written as:

\[
\tau_w = K \cdot \dot{\gamma}^n \tag{3}
\]

and the relationship of the apparent viscosity and shear rate can be written as:

\[
\eta = K \cdot (\dot{\gamma})^{n-1} \tag{4}
\]

Determination of true shear rate of wall-sticking area

The application of Weissenberg-Rabinowitsch correction for non-Newtonian fluid flow must be implemented to portray the true viscosity function of the material at wall-sticking area [11]. This correction should be performed since unlike the flow of Newtonian fluid which has the parabolic velocity profile, non-Newtonian fluid will encounter the non-parabolic velocity profile. Without this correction, error around 10-20% in viscosity will prevail in the calculation of shear rate [23] and shear rate will be underestimated. In determining the correction, a plot of \( \ln \dot{\gamma}_{\text{app}} \) and \( \ln \tau_w \) needed in determining the slope for the correction. This correction is only performed for the points that experience the wall-sticking behavior. Figure 3 shows the true flow curve of wall sticking area. It can be seen that after the correction, the true shear rate that is applied to the material will shift to higher value, compared to apparent shear rate. The equation for this correction is as below [11]:

\[
\dot{\gamma}_{\text{true}} = \left( \frac{2}{3} + \frac{1}{3} \frac{d \ln \dot{\gamma}_{\text{app}}}{d \ln \tau_w} \right)^{1/2} \dot{\gamma}_{\text{app}} \tag{5}
\]

Identification of Wall Slippage

The first step of the identification of wall slip behavior can be performed with the raw data of pressure over measurement time, acquired directly from the high-pressure capillary rheometer, as can be seen from Figure 4. It can be observed that pressure fluctuations is occurring from the start of the measurement, which is from the highest ap-
plied shear rate, until 330 seconds ($\dot{\gamma} = 125$ 1/s). This point might be related to the critical point, where the onset of wall slip happens. This test also reveals that after this critical point the pressure fluctuation is no longer observed, which is in lower shear rate area. This pressure fluctuation might be caused by extrudate distortion [24] and may also become the signal of the onset of wall slip after the point of $\dot{\gamma} = 125$ 1/s, as demonstrated in Figure 5.

Regarding the results in Figure 4, the existence of a critical point can be observed, which might indicate the onset of wall slip. In order to justify this point, the shear stress of the material is plotted as a function of apparent shear rate as presented in Figure 6. It is apparent from Figure 6, that different shear rate measurement points will lead to different flow behavior in high pressure capillary rheometer experiments. It can be examined that the material is always having an increase in shear stress with increasing shear rate only until a certain level of shear stress, and after this peak or critical point the material is not experiencing an increase in shear stress with rising shear rate. At 25°C the critical point lies at 0.13 MPa ($\dot{\gamma} = 125$ 1/s). At 45°C, the critical point lies at 0.11 MPa ($\dot{\gamma} = 150$ 1/s). It is remarkable to observe, after this critical point, anomalies are observed, in which the value of shear stress is keep declining although there is a growing value of shear rate. This anomalous flow behavior may indicate that the material is experiencing the plug flow at high shear rate region and should be associated with an increase in wall slip velocity, where it cannot be neglected anymore. Lately, it is reported that at wall-sticking to wall-slipage change cross section, an increase of shear stress will be observed before the flow undergoes a complete slip condition, as it is the case in Figure 5 [13]. Consequently, if both results of Figure 5 and Figure 6 are analyzed, it can be seen that wall slip phenomenon might be the answer or closely related with melt instability of the material. In addition to illustrate the flow anomaly clearly, the shear stress under the assumption of pseudoplastic behavior of the material (under no-slip boundary condition) is also shown in comparison to the experimental data. The curve of the pseudoplastic behavior was determined based on the power law model, whereby the coefficients $K$ and $n$ were determined from the flow curves of the

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**Fig. 4:** Pressure over time diagram of all pressure transducers, at 25°C

**Fig. 5:** Different behavior of melt instability with increasing shear rate at 25°C

**Fig. 6a:** Wall slip identification by varying shear rate at 25°C

**Fig. 6b:** Wall slip identification by varying shear rate at 45°C
The consistency factor $K$ has been verified by parallel plate rheometer tests. The determined values for $K$ are in the same order of magnitude for both measuring methods.

In Figure 6, the effect of temperature on the critical point can also be noticed. It is shown that with increasing temperature, the value of critical wall shear stress will also shift to lower values. On the other hand, at the point of shear rate where critical shear stress appears, the shear rate will be shifted to higher value. Therefore, the range of wall-sticking area will be broader, as can be seen from Figure 6b. With rising temperature, there will be a reduction in viscosity because the molecules of the material are easier to move because of an increase in thermal energy. The findings from this study suggest that the critical shear stress for this silicone rubber compound with hardness of 60 shore A is around 0.13 MPa at room temperature. In addition, as has been mentioned before, extrudate distortion is one of the substantial indications of the flow transformation from wall adhesion to wall slippage behavior, as can be seen from figure 5. This result also reveals that with rising value of shear rate, the flow instability is becoming more serious. Wall slip is believed as the participant of the melt fracture phenomenon, since it appears at the corresponding value or lower critical shear stress as does the shark-skin melt fracture appear [25].

**Determination of slip velocity and slip ratio of wall-slipping area**

As has been mentioned before, the identification of wall slip is closely related to the identification of wall slip velocity. The higher the value of this velocity means the stronger the wall slippage is. Respectively, if the value of wall slip velocity is zero means wall slip does not exist [12]. The determination of wall slip velocity in silicone rubber compounds should be made. Since the experiment performed in this study reveals that the material experiences wall slippage after critical shear stress. With the help of modified Mooney correction for wall slippage [11, 12, 14, 19], the calculation of the velocity of wall slip will be able to be performed. The determination of wall slip velocity can only be performed after the determination of wall sticking and wall slippage area. The calculation of wall slip velocity is starting from the formula of the total volume flow rate, as shown below:

$$V_{\text{total}} = V_{\text{slip}} + V_{\text{sharur}}.$$  

(6)

The wall slip velocity is derived from the slip volume flow rate, as below:

$$V_{\text{slip}} = B \cdot H \cdot V_{\text{slip}}$$  

(7)

and the shear volume flow rate is calculated from [23,25]:

$$V_{\text{sharur}} = \frac{n \cdot B \cdot H^2}{2 \cdot (1 + 2n)} \left( \frac{\tau}{K} \right)^{1/4}$$  

(8)

From all of the equations above, the slip velocity that is experienced by the material can be determined from:

$$V_{\text{slip}} = \frac{V}{B \cdot H \cdot \left( \frac{n \cdot H}{2 \cdot (1 + 2 \cdot n)} \left( \frac{\tau}{K} \right)^{1/4} \right)}$$  

(9)

It is reported that equation 9 is the value of the minimum slip velocity undergoes by the material, not the absolute wall slip velocity [26]. In Figure 7, the effect of applied shear rate to the wall slip velocity can be pointed out. After the wall slip velocity is established, slip length can also be calculated. Slip length is the amount of the fluid that is slipped and can be calculated with equation 10 [27]. In Figure 8, it is shown that the slip length of the material is ranging around, which is considered as a huge slip [27]. From Figure 7, it can be seen that with increasing shear rate, the slip velocity of the material will also be higher. Consequently, the value of slip length will also be higher. This phenomenon shows that with higher shear rate, the material will experience lower drag flow, when it is compared to the bulk material [28].

$$b = \frac{V \cdot \eta}{\tau_w}$$  

(10)

**Conclusions**

In this study, the rheological behavior of silicone rubber compound as non-Newtonian fluids under wall slippage has been analyzed by means of high-pressure capillary rheometer. The critical shear stress, which is observed for the material is found to be around 0.13 MPa at room temperature, determined by the
sudden onset of pressure drop after this value, which indicates the change in boundary condition from wall-sticking to wall-slipping. With this value the region of wall-sticking and wall-slipping can be classified, where wall-sticking region is below the critical shear stress and wall-slipping region is above this value. Wall slip velocity and slip length has also been estimated, which value are increasing with higher shear rate that is applied to the material. From the value of slip length, it can be concluded that the silicone rubber compound under investigation is experiencing huge slip with the value of slip length ranging from 78-102 μm.

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References