Viscosity Measurement of filled Rubber Compounds - New insight for Error free Measurements

Introduction
Steady shear viscosity is one of the key properties to be measured for understanding uncured rubber compound process. It is essential for predicting output and pressure in extrusion as well as injection time and length in injection molding for of these commonly used processing techniques.

Measuring steady shear viscosity of rubber compounds is commonly performed using two well-known and defined instruments such as Mooney viscometer and capillary rheometer.

If initially, Mooney viscometer could measure viscosity at one single shear rate, modern instruments with variable speed allow for shear rate dependency of viscosity. This ability allows interpolating or extrapolating viscosity at whatever shear rate which may occur at all stages of industrial processing using properly selected flow models. Unfortunately, while testing at a high rotation speed, the Mooney viscometer closed test chamber does not allow the dissipation of shear-induced heat thus preventing strict isothermal conditions. Also, the test chamber/rotor combination is not well defined so it prevents the calculation of absolute viscosity.

The second instrument for measuring viscosity and viscosity dependence on the shear rate is the capillary rheometer. A capillary rheometer is a pressure-driven flow technique that is conveniently used to investigate the high shear flow region of materials and the only one that provides information about the processing behavior of polymer materials. The test technique is however tedious since a series of cylindrical dies with variable dimensions must be used to assess the various corrections needed to derive true viscosity function. With this instrument, important assumptions are: fully developed, steady, isothermal, laminar flow, no-slip at the wall and viscosity independent of pressure [1]. Unfortunately, these two last conditions are rarely met when testing rubber compounds. Due to their complex formulation using polymers as the base ingredient, rubber compounds can exhibit notorious wall slip and significant compressibility effect due to polymer inherent free volume.

The current paper aims to explore an alternative technique based on cone/cone geometry but performed under pressure in a closed instrument chamber. In normal testing conditions, both cones are grooved to prevent slippage.

Steady shear viscosity measurement.
Polymer material viscosity can be measured using essentially three instruments, Cone/plate rheometer, Mooney viscometer, and capillary rheometer.

1. Cone/plate open boundary rheometer
When considering rubber compound, cone/plate rheometer has been found irrelevant essentially due to an open boundary, thus an unpressurized test cavity. So if they were successfully used on pure polymer melt such as common thermoplastics, this characteristic is prohibitive for testing complex material such as rubber compounds. These materials are so stiff and so elastic that they can hardly be tested in this geometry. In this instrument, it is almost impossible to place the rubber sample in a reproducible manner without generating quasi-permanent stresses in the material. Also, it is generally accepted that rubber compounds require testing in pressurized conditions to achieve reproducible rheological data (e.g. Mooney viscometer, Oscillating Disc Rheometer, Moving Die Rheometer) or submitted to pressure-driven flow (e.g. Cone/plate rheometer).

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Capillary rheometer, instrumented extruder) [2].
This is particularly obvious in Fig. 1. This viscosity curve versus shear rate was performed on a cone/plate rheometer (TA Instruments - DHR1) on silica filled silicone compound. The response is showing a Newtonian or quasi Newtonian viscosity response at a low shear rate which is impossible in filled rubber compounds within the used shear rate range. Previous publication at shear rates as low as 10^{-5} s^{-1} has proved an absence of Newtonian viscosity plateau [3]. Furthermore, the second inflection point may reveal the onset of melt fracture or severe wall slip. So data generated in these instruments are useless to be used in flow simulation software as they do not represent genuine material properties.

2. Mooney viscometer
Mooney viscometers have long been used to measure rubber compound viscosity. Strictly speaking, Mooney viscometers do not measure viscosity but rather “consistency”. This value, which is expressed in Mooney units, is a torque value. Based on calibrated dead weight, Mooney units can easily be converted into SI units (Nm). The conversion factor is 0.083 Nm for 1 MU. Besides, a cylindrical rotor provides neither a simple shape factor nor a homogenous shear rate. Mooney viscometer cavity and rotor can be considered as an addition of a simple Couette and double parallel plate. Using stress calculation equations of these two techniques, we can calculate stress from torque (Nm) using the following equation:

\[
\frac{\tau}{\gamma} = \frac{\sigma}{\gamma} = \frac{\Delta P}{L} \left( \frac{R}{2} + \frac{h}{2} \right) \left( \frac{1}{n+1} \right) \frac{n}{2n} \]

Where \( \tau \) is the ratio of rotor radius, \( R \) and cavity radius, \( h \) the rotor height, \( n \) the pseudo plasticity index of the material (Shear rate dependency of shear stress) and \( T_s \) the Mooney result expressed in Nm [4].

The Mooney test cavity as standardized in ISO 289-1 provides a type of shear in the cavity corner which is not simple thus difficult if not impossible to solve. Nevertheless, the error due to this effect is rather small and has been found less than 10% of true viscosity values as measured on pure elastomers [5].

The calculation of shear stress (Q), shear rate (\( \dot{\gamma} \)) and shear viscosity (\( \eta \)) is based on Poiseuille flow in a capillary using the following equations.

\[
\sigma (w) = \frac{R^2 \cdot \Delta P}{L} \]

\[
\dot{\gamma} = \frac{4Q}{\pi R^2} \]

Where \( \sigma (w) \) is wall shear stress, \( R \) the capillary radius, \( \Delta P \) the pressure drop in the capillary, \( L \) the capillary length, \( Q \) the material output and \( \dot{\gamma} \) the apparent wall shear rate.

3. Capillary rheometer.
A capillary rheometer is by far the most used instrument for steady shear viscosity measurements of rubber compounds. It is used for most of the publications on this subject nowadays. Its main interest may be considered rather trivial. It is the most resembling technique to rubber compound extrusion and is often considered as process simulator. But most researchers may forget that shear history may be different between capillary rheometer and extruder. The first one is using a piston to push the material through the die while the second is using a rotating screw. The strong thixotropic nature of rubber compound due to filler type may result in largely different viscosity between both techniques.

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These equations are only valid for Newtonian fluids and therefore require correction for non-Newtonian materials such as molten polymers and uncured rubber compounds. They require as well pressure correction to deal with die entrance effects. These corrections are well known and are respectively Rabino-witsch and Bagley corrections. Bagley correction requires at least 3 tests using different L/R dies. Since either correction is essential to extract true or corrected viscosity, this technique is rather inefficient.

Furthermore to both corrections, the technique is based on several assumptions which are:

a. Fully developed, steady, laminar flow
b. No velocity in the r and Θ direction
c. No slip at the walls, Ux = 0 at R
d. The fluid is incompressible with viscosity independent of pressure.

If the first two assumptions are indeed correct for rubber compound in fully developed flow, the last two are in most cases incorrect. Polymers and rubber compounds contain free volume which makes their viscosity more or less dependent upon pressure especially at a high shear rate which may produce pressure over 300 to 500 Bar. In the capillary rheometer, pressure measurements are the base of shear stress calculation thus viscosity calculation. This effect makes viscosity calculation dubious at a high shear rate so high pressure. Under these conditions, the effect of pressure on viscosity will inevitably overestimate reading. This overestimation can easily be traced to the upward curvature of the Bagley plot. This effect is illustrated in Fig. 2. Leblanc was successfully using the nonlinear response in the Bagley plot to calculate a compressibility factor of polymers and compounds [6]. The use of a second-order polynomial regression instead of linear regression to extract entrance pressure drop (Pe = P for L/R=0) provides, with the quadratic coefficient, an estimate of the material viscosity dependency to pressure. Table 1 lists the quadratic equation coefficients for all used shear rate.

The increase of the quadratic coefficient at increasing shear rates (Higher P) can easily be observed. Only the highest shear rate coefficient is out of line. This is due to the onset of melt fracture for the 100 s⁻¹ with the longest L/R die (highest pressure).

This onset of melt distortion highlights another limit of a capillary rheometer. According to C. W. Macosko [3], measurements in instable flow conditions shall not be used for viscosity calculation as “the onset of melt distortion means the end of rheological data”. All polymer materials will exhibit critical stress above which melt instabilities will inevitably appear so limiting the maximum achievable shear rate.

Wall slip is the last assumption to be found frequently untrue for rubber compounds. This parameter had been studied since long for pure polymer by amongst others, Mooney in 1931 [7] and Laun & Hirsch in 1989 [8]. Mooney proposed the following method to get an estimation of slip velocity.

\[ \dot{\gamma}_a = \dot{\gamma}_{a,0} + \frac{4 U_s}{R} \]  

(5)

Where R is the die radius and Uₜ is slip velocity and the \( \dot{\gamma}_a \) apparent wall shear rate.

Apparent wall shear rates measured at constant extrusion pressure (cst. \( \dot{\gamma}_{a,0} \)) for a constant L/R are plotted against 1/R. The slope of this function is equal to 4 times the slip velocity and the intercept is the slip corrected apparent wall shear rate as illustrated in Fig. 3.

This technique has been used on rubber compounds by Karam [9]. In some experimental conditions, he found a negative intercept for the slip corrected apparent wall shear rate, which is a physical nonsense. These results are illustrated in Fig. 4. So when considering all required corrections for true viscosity measurements and shortcoming in some of them (slippage), it is surprising to see many researchers using capillary rheometer so extensively. But capillary rheometer remains extremely useful as it is the only available technique for high shear rate experiments such as fast extrusion and injection molding processes. An alternative method for measuring the viscosity of rubber compounds is therefore highly

Table 1: Quadratic equation coefficients for all used shear rate on a tire tread compound.

<table>
<thead>
<tr>
<th>Shear rate (s⁻¹)</th>
<th>X²</th>
<th>X</th>
<th>(Pₑ)</th>
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</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0766</td>
<td>3.7937</td>
<td>4.85</td>
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<tr>
<td>2.0</td>
<td>0.1146</td>
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<td>0.3422</td>
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</tr>
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<td>50.0</td>
<td>0.40</td>
<td>9.25</td>
<td>43.6</td>
</tr>
<tr>
<td>100.0</td>
<td>0.1786</td>
<td>15.981</td>
<td>37.167</td>
</tr>
</tbody>
</table>
welcome provided it is insensitive to most of the capillary rheometer flaws and free of unnecessary corrections.

4. Cone/Cone closed boundary rheometer

In 1992, Monsanto Rubber Instrument and Equipment Company commercialized a closed boundary oscillatory rheometer (RPA2000). It has been found very useful and is still extensively used for elastomer and rubber compound characterization [10]. The RPA was originally designed for oscillatory measurements, which apart of stress relaxation remains its main application. Due to the success of this instrument, many additional competitors commercialized their copy. The term “RPA” is now generally accepted as a generic name. Amongst these competitors, TA Instruments RPA (RPA Elite) is additionally able to program a ramp test at a programmed rotation speed. This device can therefore measure both transient and stationary viscosity in addition to usual dynamic viscosity. The test is programmed as illustrated in Fig. 5. Because of the high-pressure cavity (40 to 65 bars) and grooved die surface, the instrument is free of wall slip effect on polymer materials as demonstrated in Large Amplitude Oscillatory shear conditions [11].

Experimental

Four materials were selected for trial using this technique.

1. Commercially available EPDM polymer (ML(1+4) @125° C = 65MU)
2. Silica/silica compound for architect silicone tests
3. Truck tire tread compound (A)
4. Truck tire tread compound (B)

None of the three compound formulations can be disclosed. Only broad information is given hereafter.

- Hot cure silicone/silica compound
- Compound A: NR/BR blend, N234 carbon black and 10 PHR of process oil.
- Compound B: NR/BR blend.

For the EPDM polymer, two shear rates were selected, 0.3 and 3 s⁻¹ (Cₚ = 10 for 33.3s and 3.33s respectively). Shear stress versus time is illustrated in Fig. 6. The material response is divided into two sections. The initial part is the transient response while the second corresponds to stationary viscosity conditions. By taking the ratio of plateau stress value and shear rate, one can easily calculate viscosity. The plot of calculated viscosities on the graph of DYNAMIC viscosity versus frequency (Fig. 7) shows an excellent correlation and repeatability with an extremely tight 95% confidence limit for the 3 s⁻¹ test and CV (Coefficient of Variation) less than 0.5 %.

Both shear stress (τ) and steady shear viscosity (η) are illustrated in Fig. 8. From this figure, it is obvious that there is no Newtonian plateau as shown with open boundary rotational test. Furthermore, the shear stress curve clearly shows the onset of yield stress. This behavior is well in line with common knowledge of rubber compound heavily loaded with active fillers and confirms claims as per Leblanc’s finding [3].

A proprietary confidential formulation of truck tread compound (Compound A) was tested under the same test type (ramp) and variable shear rates. Test conditions were 90° C, Cₚ = 10 and 0.01-0.1-1.0-10 s⁻¹ of shear rate. Shear stress and stationary shear viscosity were calculated as for the silicone/silica compound here above. The same compound was subsequently tested on a capillary rheometer (RheoArt - http://www.rheoart.com/en/) at 90° C using L/D dies of 4, 8 and 16.

The results of the capillary rheometer (τcorr and ηcorr) and RPA steady shear tests are illustrated in Fig. 9. Corrected viscosity refers to Bagley and Rabinowitsch’s corrected viscosity data. Steady shear RPA viscosity correlates extremely well with apparent capillary viscosity but less with corrected viscosity. This may look strange considering that RPA stationary viscosity is considered as true viscosity measurement unless some slippage occurred during the capillary rheometer test. More investigation on wall slip will be required to fully understand this discrepancy.
A second tire tread compound (compound B) was tested under identical conditions for RPA steady shear viscosity. Five repeat testing was performed at 1 s⁻¹ of shear rate to assess instrument repeatability. The results of shear viscosity versus shear rate, at 1 s⁻¹, 95% confidence limits are illustrated in Fig. 10. Repeatability appears excellent with CV around 1%, far better than the repeatability experienced in capillary rheometer testing. Cox-Merz relation for rubber compounds.

The validity of the Cox-Merz relation is generally accepted for moderately elastic raw elastomer such as EPDM as seen in Fig. 7. The evaluation of this relation for highly elastic material such as natural rubber (NR) and SBR is more difficult. This is essentially due to the difficulty to run valid capillary rheometer tests on these materials.

For rubber compounds, it is generally accepted that the Cox-Merz relation is invalid. It is although somehow difficult to attribute this failure to a distinct instrument error. It is nevertheless true that the measurement of dynamic viscosities (η* and ω') with traditional open cavity DMA are rather difficult if not impossible on rubber compounds. Open cavity DMA suffers from catastrophic slippage even at ultra-low strain (|ε|<0.001) and low frequency. In a traditional DMA, almost one decade of viscosity difference is found when testing glued sample/fixture (No-slip condition) and unglued (slip condition). Besides, gluing the sample jeopardizes the instrument repeatability resulting in broader confidence limits.

To strictly follow linear viscoelasticity theory, dynamic testing has to be performed in a strain domain where strain does not affect modulus so viscosity calculation. For polymer, this domain extends to somehow 20% to 30% (|ε| = 0.2 to 0.3) depending upon polymer characteristics and frequency. For filler loaded compounds the domain of linear viscoelasticity is limited to 0.1% to 0.3% (|ε| = 0.001 to 0.003). Any test performed above this strain value will inevitably reduce modulus as reported by Payne [12] and therefore viscosity. By increasing strain, viscosity values slide toward RPA steady shear viscosity. For Compound A, a good match is obtained for Real dynamic viscosity (η*) at |ε|=0.07 as illustrated in Fig. 11. This strain will depend upon type and loading of filler.

Using strain largely above the limit of the linear viscoelastic domain remains questionable. Under these conditions, stress
is not any longer linearly proportional to strain as demanded by the linear viscoelasticity theory. Under purely sinusoidal strain input, the stress signal appears strongly distorted probably making these measurements irrelevant as illustrated in Fig. 12.

Summary and conclusion
In the current paper, we have outlined the possibility of measuring steady shear viscosity with a closed boundary cone/cone rheometer (RPA). This kind of test requires the instrument to be able to run a "ramp" test at a programmed strain ($\dot{\varepsilon}_0$) at a set time thus programming defined constant shear rate. This technique enables the study of very low shear rate, unreachable by ordinary capillary rheometer. Higher shear rate, with a maximum value of 30 s⁻¹, requires at least a programmable $\dot{\varepsilon}_0>30$.

For higher shear rate, the use of a capillary rheometer may still be required but always limited by the occurrence of distorted flow, “sharkskin” and melt fracture. The RPA ramp test provides true, flawless viscosity data. It can, therefore, be used to realign capillary viscosity data in a common flow model if required.

As this technique does not require lengthy correction, tedious sample preparation, it offers much higher test productivity than capillary rheometer. Finally, this additional test gives the RPA the ability to test both dynamic viscosity and steady shear viscosity data on a single instrument.

The dual-mode of testing (dynamic and steady shear) offered as well a unique possibility to verify Cox-Merz relationship on filler loaded compounds. For all tested compounds, this well-known relationship does not hold when testing dynamic viscosities ($\eta^*$ and $\omega$) in the linear viscoelasticity domain ($\dot{\varepsilon}_0<0.001$). It is nevertheless possible to achieve a fair match between steady shear viscosity and dynamic viscosity when testing at higher strain but with strong distortion of the stress periodic signal so in conditions largely out of the fundamental rule of viscoelasticity.

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REFERENCES