

Elongational viscosity of rubber compounds and improving corresponding models

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ABSTRACT

As good as the topic of elongational viscosity is covered by scientific work on thermoplastics, as little research has been done on rubber compounds. This paper focuses on the elongational properties of an SBR rubber compound using different measurement methods. First measurements were made on a Sentmanat Extensional Rheometer (SER). This method is limited to elongation rates up to 20 s⁻¹. Higher elongation rates (up to 300 s⁻¹) can be covered with a High Pressure Capillary Rheometer (HPCR), where Cogswell's and Binding's models were used. The simplifications of these methods were precisely depicted and their influence on the results was evaluated. For further improvement of Cogswell's method a previously unreleased method by Obendrauf was applied using two different laws for the approximation of shear viscosity which is essential for the calculation of elongational viscosity. The calculated elongational viscosities could be ascertained using an orifice die for the refinement of the inlet pressure measurements. Finally, the elongational viscosity curves from the HPCR were compared with the SER-viscosity data and a good correlation could be found. This suggests that elongational viscosity ascertained from converging flow measurements is comparable to SER measurements, which would be of great practical use hence HPCRs are available at many laboratories.

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1. Introduction

Elongational viscosity or so called uniaxial extensional viscosity is a very broad topic in polymer science and rheology. Since the first reference in scientific literature by Trouton [1], there have been numerous approaches for measuring the extensional behaviour of polymers. Up to now only a few techniques exist which are scientifically established. The first well known rheometer has been developed by Meissner [2], where a rectangular strip sample is extended in the horizontal direction by two rotary clamps in an oil bath. Modified versions are described in more recent works [3, 4]. The extensional rheometer from Münstedt [5] features two grips and a strip sample is stretched in the vertical direction also supported by an oil bath. A more recent development is the Filament stretching rheometer by McKinley and Sridhar [6], where a cylindrical sample is fixed between two plates which apply the stretching force. The change in the geometry of the filament is controlled by laser microscopy. One of the most common tensile rheometers is the Sentmanat Extensional Rheometer (SER) [7]. A rectangular sample cut from a film is fixed on two counter rotating drums enclosed in an air conditioned chamber. The sample

is stretched by the rotation of the drums and the torque is measured. Extensional viscosity can be calculated from the torque considering the changing cross-section of the sample. Alternatively to the rheometers presented above, elongational viscosity (uniaxial extensional viscosity) can also be calculated from inlet pressure losses on a High Pressure Capillary Rheometer (HPCR). Cogswell [8] presented an analytical approach for the determination of the elongational viscosity from converging flows. Some years later Binding [9] published a different approach for the same rheological problem. Both of these analyses have been used and revised in numerous scientific works [10, 11, 12, 13]. The advantage of these methods is that elongational viscosity can be calculated from data that is assessed with a HPCR which is standard rheological equipment. It is available at many research facilities and test laboratories to measure shear viscosity data of polymer melts. Thus additional test equipment or sophisticated machinery is avoided.

In the work of Obendrauf [12] the method of Cogswell was revised and two major sources of error were identified.

- The power law is used for the description of shear viscosity which is not valid for unfilled polymers at low shear rates.
- The elongational viscosity is considered to be constant over the whole inlet area, which is not true due to transient elongational rates.

Obendrauf proposed an improved method and a computer program for the computation of the elongational viscosity of polymer melts.

The main objective of this paper is to measure the elongational viscosity of an SBR rubber compound. The analytical models of Cogswell, Binding and Obendrauf are used for the evaluation of the viscosity data and their suitability for rubber compounds will be assessed by comparison to SER measurements.

2. Theory

2.1 Obendrauf's model

As already mentioned two major sources of error in the original Cogswell's method are eliminated by improvement of the analytical approach (see below). Based on these new assumptions formulas for the elongational viscosity and the elongation rate were derived. The full deductions and all equations can be found in [12]. These can no longer be solved analytically like in [8]. A numerical solution was found and a computer program for the evaluation was developed.

- Implementation of the Carreau-law

Instead of the Power-law in Eq. 1, the Carreau-law in Eq. 2 will be used for the description of the shear viscosity:

$$\eta_s = K\dot{\gamma}^{n-1} \quad (1)$$

where η_s is shear viscosity in Pa·s, K is material parameters (Pa·s), n is material parameter (dimensionless), and $\dot{\gamma}$ = shear rate in s⁻¹.

$$\eta_s = \frac{A}{(1 + B\dot{\gamma})^C} \quad (2)$$

A is material parameter in Pa·s, B is material parameter in s⁻¹, and C is material parameter (dimensionless).

A direct implementation of the Carreau-law into the derivation of Cogswell's method creates complex integrals that could only be solved numerically. It is much easier and has the same effect to vary the coefficient n of the power law by means of the Carreau-law like it is shown in Eq. 3:

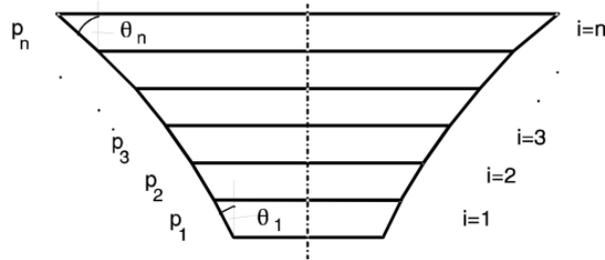


Fig. 1 Discretization of the inlet area into x-segments

$$n = \frac{d(\log \tau)}{d(\log \dot{\gamma})} = \frac{d}{d(\log \dot{\gamma})} [\log A - C \log(1 + B e^{\log \dot{\gamma}}) + \log \dot{\gamma}] = \frac{1 + (1 - C)B\dot{\gamma}}{1 + B\dot{\gamma}} \quad (3)$$

For the description of the converging flow Cogswell used the discretization shown in Fig. 1.

Eq. 4 describes the pressure loss due to shearing in a single conical segment x derived in [8]:

$$p_s = \frac{2\tau}{(3n \tan \theta)} \cdot \left(1 - \frac{r_0^{3n}}{r_1^{3n}}\right) \quad (4)$$

where p_s is pressure loss due to shear in Pa, τ is shear stress in N/m², n is Power law parameter (dimensionless), θ is angle of the conical segment in degrees, r_0 is smaller radius in the segment i in m, and r_1 is bigger radius in the segment i in m.

Eq. 3 is inserted in Eq. 4 and the deduction of the formulas for elongational viscosity and elongation rate is carried out according to [8].

- Implementation of the variable elongational viscosity in the inlet area

The elongational viscosity was considered to be constant over the whole inlet area by Cogswell. This is not true if one wants to ascertain the elongational viscosity dependent on the elongation rate. For the implementation of this dependence a method suggested by Bersted [14] is used. The average elongational viscosity of each segment is varied by means of Eq. 5:

$$\eta_{E,i} = \eta_{E,i-1} \cdot \left(\frac{\dot{\epsilon}_i}{\dot{\epsilon}_{i-1}}\right)^{m_i} \quad (5)$$

where $\eta_{E,i}$ is elongational viscosity in the i^{th} segment in Pa·s; $\dot{\epsilon}_i$ is elongation rate in the i^{th} segment in s⁻¹, and m_i is gradient of the extensional viscosity curve in a double logarithmic scale in the i^{th} segment.

3. Experimental

3.1 Material

The viscosity measurements were carried out on an industrial SBR rubber compound with 52 phr of carbon black, 62 phr of non-carbon filler and other components of unknown quantity. Crosslinking agents were not added to avoid the influence of vulcanization.

3.2 Preparation of samples

The compound was produced in an industrial scale with a GK 190E internal mixer (Harburg Freudenberg Maschinenbau GmbH, Freudenberg, Germany). The mixing process was carried out for five minutes reaching a maximum bulk temperature of 150 °C. First the rubber was inserted into the mixer and second the fillers and the other components were added. Third the compound was formed to a sheet in a roller mill. For the HPCR measurements the sheet was cut into pieces with an approximate length of 40 mm. For the SER measurements the sheets were split into thinner sheets of a thickness less than 1 mm. From these sheets the strip samples were stamped out.

3.3 High pressure capillary rheometer (HPCR)

The viscosity measurements were carried out on a HPCR Type Rheograph 2002 (Goettfert Werkstoff Prüfmaschinen GmbH, Buchen, Germany) with 4 different circular dies (diameter = 1 mm; lengths = 1 mm, 10 mm, 20 mm, 30 mm). The shortest die was used as orifice die for a refinement of the measurements. The pressure loss of this die was used for the correction of shear viscosity and for the calculation of elongational viscosity. The reason for this approach was the strong scattering of the inlet pressure values derived from the Bagley plot. The results of shear viscosity could be measured at shear rates between 9 s^{-1} and $12,000 \text{ s}^{-1}$. Test temperatures were $80 \text{ }^{\circ}\text{C}$, $100 \text{ }^{\circ}\text{C}$, and $120 \text{ }^{\circ}\text{C}$ according to the typical processing parameters of the rubber compound. The elongational viscosities were calculated with 4 different methods. First Coswell's and Binding's analysis were carried out the way they are described in their publications [8, 9]. Obendrauf's method was used like it is described in Paragraph 2.1 with the Carreau-law for the description of the shear viscosity. As alternative it was also carried out with the use of the Power-law. The reason for the Power-law approach is that most of the thermoplastic polymers show a constant shear viscosity at low shear rates (Newtonian plateau), whereas filled rubber compounds tend to have no Newtonian plateau at all [15]. Thus an approximation using the Power-law is usually more appropriate and easier to handle for rubber compounds. Elongational viscosities were measured at strain rates of approximately 1 s^{-1} to 300 s^{-1} at a temperature of $120 \text{ }^{\circ}\text{C}$. This measurement is limited on the one hand by the power and the pressure transducer of the HPCR and on the other hand by the shear and elongational viscosity level of the compounds. Hence, at higher temperatures, higher strain rates are achievable due to lower viscosities.

3.4 Rubber process analyser (RPA)

The viscosity measurements at low shear rates were carried out on a D-RPA 3000 (MonTech Werkstoff Prüfmaschinen GmbH, Buchen, Germany) based on ASTM 6204.

3.5 Sentmanat extensional rheometer (SER)

The SER device was used on a MCR501 rheometer (Anton Paar GmbH, Graz, Austria). The measurements were made at Hencky strain rates (elongation rates) of 0.001 s^{-1} , 0.01 s^{-1} , 0.1 s^{-1} , 1 s^{-1} and 10 s^{-1} . The test temperatures were $80 \text{ }^{\circ}\text{C}$, $100 \text{ }^{\circ}\text{C}$ and $120 \text{ }^{\circ}\text{C}$.

4. Results and discussion

4.1 High pressure capillary rheometer (HPCR)

The results of the HPCR measurements are exemplarily presented in Fig. 2 at $80 \text{ }^{\circ}\text{C}$.

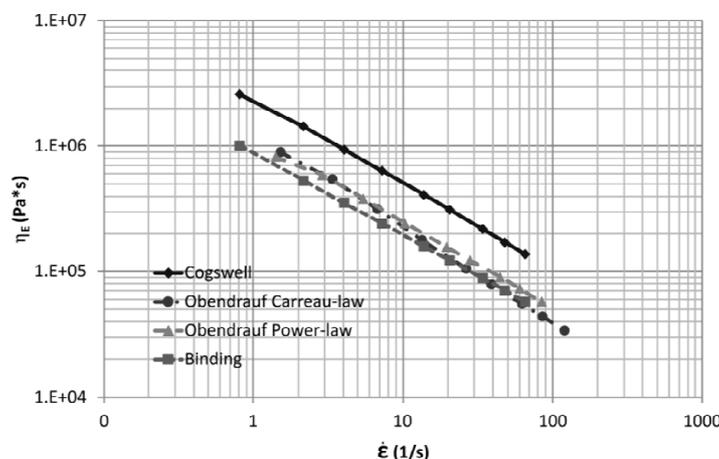


Fig. 2 Elongational viscosity of the SBR-compound at $80 \text{ }^{\circ}\text{C}$ measured on the HPCR evaluated with four different methods; η_E is elongational viscosity in Pa·s, $\dot{\epsilon}$ is elongation rate in s^{-1}

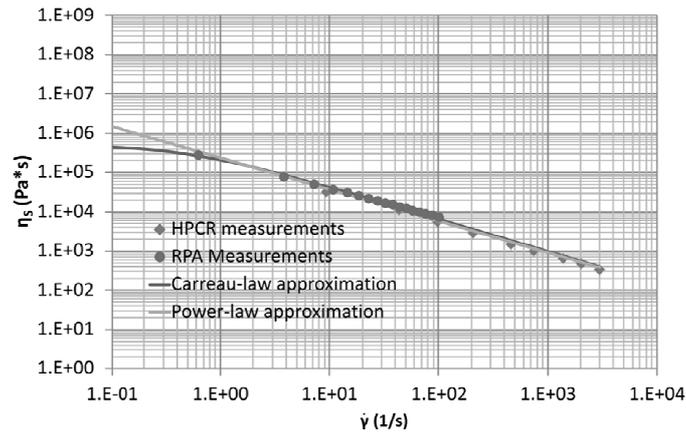


Fig. 3 Approximation of the shear viscosity by Carreau-law and Power-law; dotted values are from HPCR measurements at 80 °C

The highest elongational viscosities are obtained when Cogswell's method is applied, whereas the lowest values are received from Binding's analysis. Similar findings are reported in scientific literature [13]. The deviation can be explained by the different analytical approaches of both methods. Cogswell on the one hand assumes a constant elongational viscosity over the inlet area and calculates the pressure losses due to shear and elongation for small segments of the inlet (see Fig. 1). Binding on the other hand affiliates the complete fields of velocity, shear rate and elongation rate for the inlet area. The corner vortices cannot be taken into account by both methods, but the geometry of the inlet cone is calculated to a minimum pressure loss assumption in Cogswell's analysis and a minimum energy loss assumption in Binding's analysis.

The values calculated with Obendrauf's method lie between the Cogswell and Binding data. The difference to the results from Cogswell's method can be explained by the consideration of the variable elongational viscosity for each segment of the inlet area. The differences between the two curves derived by Obendrauf's analysis can be explained by the differences between the Carreau- and the Power law approximation (Fig. 3).

Fig. 3 shows the shear viscosity to be measurable between 10 s^{-1} and 3000 s^{-1} for the investigated rubber compound at this temperature on the HPCR and between 0.6 s^{-1} and 100 s^{-1} on the RPA.

The approximation was carried out with both the Carreau-law and the Power-law. The parameters were calculated by a least square algorithm. The description of shear viscosity at lower shear rates is an extrapolation for both laws. According to scientific literature [15, 16, 17] a Newtonian plateau is very unlikely to occur at all for a highly filled rubber compound like it is studied in this paper and there are no indications for such a plateau in the measured data. Therefore the Power-law is much more appropriate for the description of the shear behaviour of rubber compounds. The parameters of the Carreau-law could be modified to describe a Newtonian plateau at lower shear rates, but this would still be speculation without having measured values in this shear rate range. Obendrauf's method with the Carreau law is still highly recommended for the measurement of thermoplastics.

From a scientific point of view the curves achieved by Binding's method and Obendrauf's method are the most appropriate, because they do not have the assumption of a steady extensional viscosity in the inlet area and they both use the power law for the description of shear viscosity.

4.2 Sentmanat extensional rheometer (SER)

The results of the SER measurements on the rubber compound the elongational viscosity curves versus the test time are exemplarily illustrated in Figure 4 at a test temperature of 80 °C. For the comparison of the SER method with the HPCR measurements a plot of elongational viscosity versus elongation rate is needed. Thus the range of steady elongation has to be detected in the transient viscosity curves. These values can be found on the envelope of the measured curves before the appearance of strain hardening.

The “evaluated points” in Fig. 4 were used for the generation of the SER curve in Fig. 5. These were maintained by the interception of the tangents of the upper and the lower part of every curve. Fig. 5 displays the comparison between the SER data and the HPCR elongational viscosity by different methods.

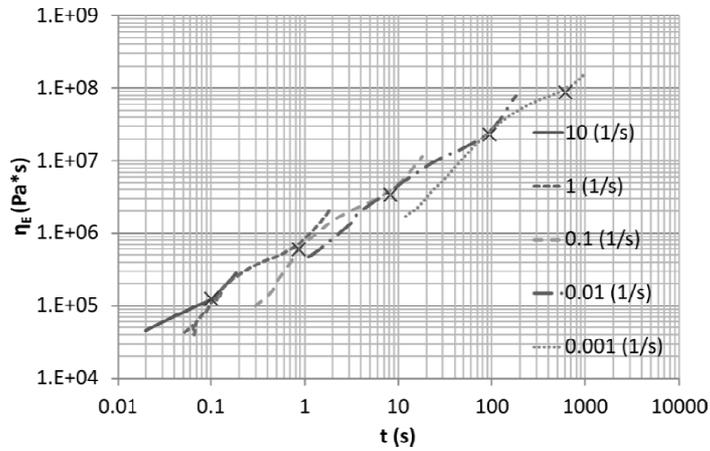


Fig. 4 Elongational viscosity of the SBR-compound at 80 °C measured on the SER; t is testing time in s

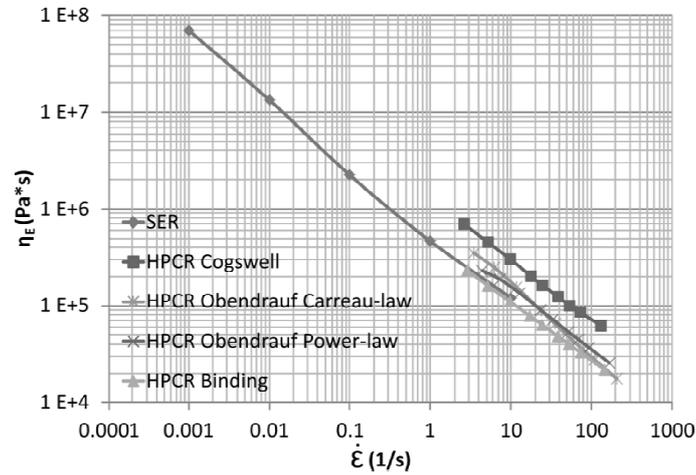


Fig. 5 Elongational viscosity of the SBR-compound at 100 °C; comparison of SER and HPCR data

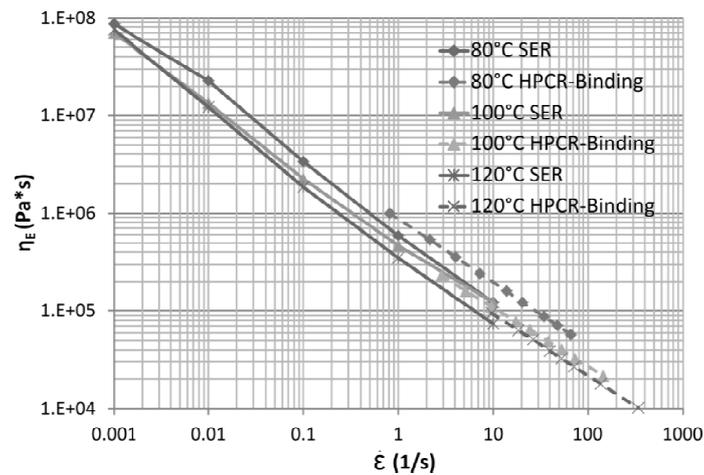


Fig. 6 Elongational viscosity of the SBR-compound at 3 different temperatures measured with the SER and the HPCR evaluated with Binding’s method

The best correlation can be found between the SER data and the data from Binding's method.

In Fig. 6 the viscosity curves from the SER and HPCR (Binding) for all three temperatures are plotted. The correlation of the two methods for 100 °C and 120 °C is quite good whereas the HPCR curve at 80 °C is a bit higher than the SER curve. Note that although the offset of the curves differ, the gradients in a double logarithmic scale are quite the same for the SER and the HPCR curves.

The fundamental difference between the SER and the HPCR measurements is due to the experimental setup and the state of elongation of the material. The SER is a tensile test with a strip-shaped sample that is stretched and torn by rotating drums. On the HPCR a converging flow is created in the inlet area before the capillary rheometer. Then an analytical model of the shear and elongational conditions within the flow is built using different approaches (Cogswell, Binding, Obendrauf). Based on the known shear viscosity and the measured inlet pressure losses the elongational viscosity is ascertained. The second important difference between the two rheometer is the elongation state of the material during the tests. As it can be seen on the SER curves, the elongational viscosity is dependent on the test time which is related to the elongation itself. For the plot of the elongational viscosity only a single point of every curve was taken for a certain extension rate although the material behaviour is much more complex. In the case of the HPCR evaluation the elongational state of the material is completely unknown. It is quite likely that parts of the compound in the flow are already in a state of strain hardening. Despite the fundamental differences between the two elongational viscosity measurement methods the deviations in the viscosity curves were found to be relatively small for the rubber compound used. Furthermore the gradient in a double logarithmic scale is quite the same for all test temperatures. These results are remarkable since huge deviations between the results of extensional viscosity measurement methods [18, 19] were reported in literature.

5. Conclusion

The elongational properties of an SBR rubber compound could be measured successfully on both an SER device and the HPCR. First, a screening of the four different evaluation methods for the calculation of elongational viscosity from inlet pressure losses on the HPCR was made. The deviations in the results could be explained by different analytical approaches and a different approximation of the shear viscosity of the compound. Second, a comparison between the SER and the HPCR was made and a quite good correlation was found despite of the fundamental differences between the two types of measurements. In this work further experience with measurements of elongational viscosities of rubber compounds was gained. The approaches of Cogswell and Binding were revised and partially improved and their applicability was demonstrated. These converging flow methods are still the only way to measure elongational viscosity at high elongation rates. In this work 300 s⁻¹ were reached. For other materials even higher values are possible.

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