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Characterizing the Rheological Behavior of Liquid Silicone Rubber Using a High Pressure Capillary Rheometer

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Abstract

The injection molding process of liquid silicone rubber (LSR) imposes high demands on the injection molding machines and the tools due to the low viscosity of silicone rubber. There is very little data which describes the rheological behavior of LSR and its influencing factors across a range of shear rates.

In this study, the rheological behaviors of different types of LSR were characterized using a high pressure capillary rheometer with an apparent shear rate that ranged from 350 to 4000 1/s. In order to identify the temperature-dependent behavior, the test temperatures were varied between 27 and 42 °C. The behavior of the material at a high pressure was evaluated by analyzing the pressure profile of each measurement.

All types of LSR displays a low level of viscosity from approx. 150 to 30 Pa s. As the shear rate and temperature rise, the viscosity of LSR decreases by at least 25 %. Additionally, we discover that the viscosity of LSR-materials with the same shore hardness differ strongly depending on which producers had made the materials. It was able to be shown that LSR displays homogenous material behavior across a wide range of shear rates.

The low viscosity of LSR makes it well-suited for applications with complex structures, which require long flow paths in the injection molding process. If the viscosity sinks too low, the requirements for the tool construction increase, and, consequently, also the costs.

Introduction

Polydimethylsiloxanes (=PDMS) are widely used for different kinds of applications in the electronics, medical, and automotive fields. The exceptional properties these materials display when processed using a wide range of temperatures (-40 to 250 °C) make this group of materials interesting for many applications with complex requirements. [1,2].

Liquid silicone rubber (=LSR), which is one material from the group of PDMS, is a silicone elastomer that vulcanizes at a high temperature, and which is normally processed in a liquid injection molding process with shear rates of approximately 5000 1/s. The two-component material is mixed using a ratio of 1:1 before processing, and is cured in an additional reaction. Component A contains the catalyst and component B the cross-linking agent and inhibitor. After processing, the parts are normally post-cured (4 h at 200 °C) to achieve complete vulcanization, and to remove all volatile ingredients [3, 4]

In order to prohibit an early onset of vulcanization in the screw, the material is cooled to a temperature of about 23 °C until it enters the heated cavity that is set at a temperature between 140 – 220 °C [3]. This is needed to predict the processing behavior of LSR, and in order to investigate its rheological behavior across a wide range of shear rates, which, ultimately, could lead to various properties.

In literature, there is some information about the rheology of polymer melts, but there is only a small amount of data about PDMS, especially LSR. Gerhardt et al. [5] used a capillary rheometer to determine that the viscosity of the material decreases to a lower level in comparison to pure PDMS as the amount of CO_2 rises in PDMS. In connection to the rising temperature, the viscosity also decreases to a lower level. Haberstroh et al. [6] analyzed the viscosity of LSR with a capillary rheometer to obtain basic information for the simulation of the injection molding process. They showed that the viscosity of both single components could be negligible. Their measurements also showed that LSR displays a significant thinning of the material when subject to shearing, and also possesses a strong temperature dependency.

Objectives

The processing of liquid silicone rubber requires profound knowledge in regards to the rheological performance of the used materials. The objective of this study is to characterize the rheological behavior of different liquid silicone rubbers using a capillary rheometer. In contrast to other rheometers, a capillary rheometer achieves high shear rates which are close to realistic parameters in the injection molding process. The apparent shear rate was chosen from a range of 350 to 4000 1/s. This wide range permitted a good overview of the material behavior during mixing and processing. Furthermore, in order to identify the temperature dependency of the material, the test temperature was varied from 27 to 42 °C. It was impertinent to ensure that the material did not vulcanize until it escaped from the die of the capillary rheometer. Liquid silicone rubber normally displays a thinning of the material when subject to shearing [6]. Owing to this, it was possible to expect that the viscosity would decrease as the shear rate increased [3,6]. The same effect was expected to occur if the test temperature was increased. Materials with same shore hardness may have a comparable level of viscosity.

Experimental

The following chapter deals with the employed materials and the testing performed using the capillary rheometer.

Materials

Six different types of commercially available liquid silicone rubber were used in this study. QP1-40 and QP1-60 from Dow Corning GmbH, Silopren LSR 2040 and Silopren LSR 2060 from Momentive Performance Inc. and Silpuran 6610/40 and Silpuran 6610/60 from Wacker Chemie AG.
There are three types from different material producers with a Shore A hardness of 40 and three types with a Shore A hardness of 60. All these two-component types of LSR could potentially be used in medical applications. Table 1 shows the selected properties of the employed materials.

Table 1. Selected properties of the employed materials

material	Shore A [-]	density $[\frac{g}{cm^3}]$
QP1-40	42	1.14
QP1-60	59	1.14
Silopren LSR 2040	40	1.12
Silopren LSR 2060	60	1.13
Silpuran 6610/40	40	1.21
Silpuran 6610/60	60	1.23

Characterization

The two components of all materials were hand-mixed using a ratio of 1:1 [3]. After mixing, all uncured samples were filled into the capillary that had a diameter of 12 mm. In this study, the capillary rheometer Rheograph 25 from the company Goettfert Werkstoff-Prüfmaschinen GmbH was used to carry out all measurements (see Figure 1).

Figure 1. Rheograph 25 from Goettfert GmbH.

After filling, the LSR was stored in the capillary for 15 minutes in order to relax the material, and to attain a steady temperature set-point. After this waiting time, the samples were tested with different apparent shear rates that ranged from 4000 to 350 1/s (within seven steps). Table 2 shows the piston speed and the selected apparent shear stress.

Table 2. Piston speed and apparent shear viscosity.

Steps [-]	Piston speed $[\frac{mm}{s}]$	Apparent shear rate $[\frac{1}{s}]$
1	3.47	4000
2	2.31	2667
3	1.54	1780
4	1.03	1190
5	0.69	790
6	0.46	527
7	0.31	351

Two different, full circle capillaries were needed for each measurement of a sample. The first measurement was carried out with a die with a length/diameter-ratio of 20/1. The second one was performed with a 0/1 die. After the measurements were completed, the data was rectified with the Bagley-correction in order to take the inlet pressure drop at the entrance of the capillary into account. Subsequently, the Weißenberg-Rabinowitsch (see Formula 1) correction was applied to obtain the true shear rates at the walls of the capillary (for non-Newtonian behavior). [7,8,9,10]

$$\dot{\gamma} = \frac{3}{4} * \dot{\gamma_{ap}} + \frac{1}{4} * \tau * \frac{d * \dot{\gamma_{ap}}}{d\tau} \quad (1)$$

Results and Discussion

The following chapter shows the results of the different viscosity measurements of the uncured LSR.

Characterizing the Rheological Performance

The following results show the true shear viscosity at a constant test temperature of 30 °C. The decrease in the viscosity of liquid silicone rubber as the shear rate rises is an indication of the thinning of the material that occurs when it is exposed to shearing.
In Figure 2, the various materials show the same tendency (decrease by approximately 27 % from 400 – 5000 1/s), but differing levels of viscosity. The viscosities of the materials range between 70 to 140 Pa*s. In comparison to 6610/40, the viscosity of LSR 2040 is nearly twice as high.

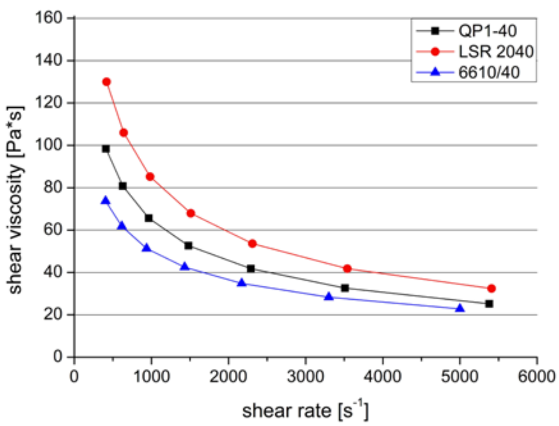

Figure 2. Shear viscosity of samples with 40 Shore A

The materials with a shore A hardness of 60 (see Figure 3) display nearly the same tendencies. As the shear rate increases, the viscosity decreases by about 30 %. QP1-60 and 6610/60 show nearly the same viscosity across this range of shear rates.

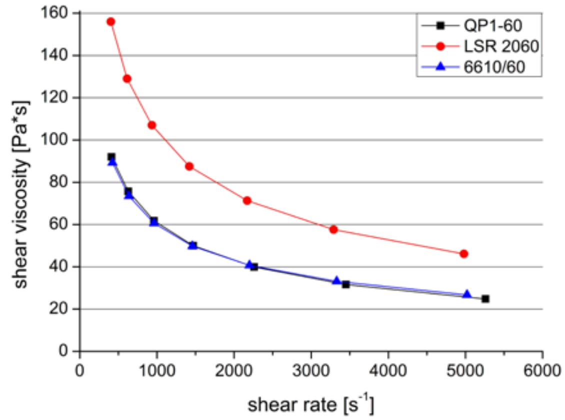

Figure 3. Shear viscosity of samples with 60 Shore A

In the case of a rising shore hardness, the viscosity at lower shear rates is higher for the materials produced by Momentive and Wacker. The materials provided by Dow Corning have similar viscosities irrespective of the shore hardness. At higher shear rates (> 5000 1/s), the viscosity of all materials nearly reaches the same level.

The Viscosity of the Components

Figures 4 and 5 show the results of the viscosity measurements of the single components in comparison to those carried out for the mixed materials at a test temperature of 30 °C. For the most part, LSR 2040 and its components A and B achieve the same viscosity (see Figure 4). LSR 2060, which has a higher shore hardness, displays different behavior. The viscosity of the mixed material is higher in contrast to that of the single components. The material from Wacker AG also performs differently.

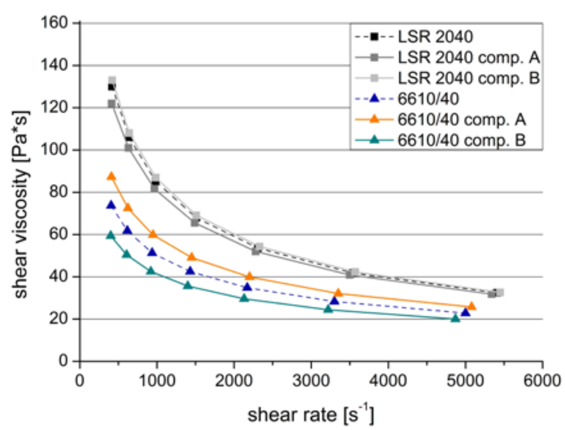

Figure 4. Shear viscosity of the single components with 40 Shore A

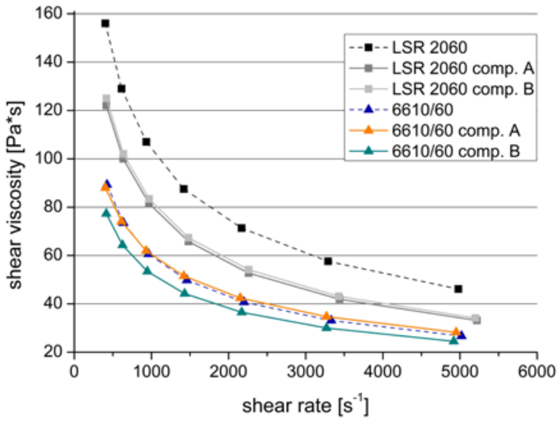

Figure 5. Shear viscosity of the single components with 60 Shore A

In contrast to [6], the viscosity of the single components is not completely negligible. The single components show differing performances in terms of their viscosity. It is obvious that the material behavior differs due to varying material producers and differing levels of shore hardness.

Temperature Dependency

Additional measurements were carried out in order to identify the influence of different test temperatures on the results of the viscosity. Due to the high level of effort such tests require, only select materials were tested (QP1-40 and QP1-60).
As the temperature rose, the viscosity of QP1-40 decreased, as was expected. The lower the level of the shear rate, the higher the influence of the temperature (approximately 20 1/s). The higher the shear rate level (5000 1/s), the more the influence of the temperature decreases toward 30 1/s (see Figures 6 and 7). The influence of the shear rate is nearly the same in all samples, and the viscosity decreases by about 28 % (from 400 to 5000 1/s).

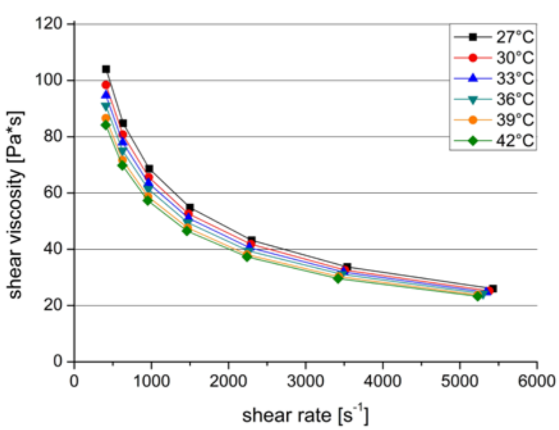

Figure 6. Shear viscosity of samples with 40 Shore A with different test temperatures

Figure 7 (for QP1-60) shows exactly the same tendency as the material with the lower level of shore hardness.

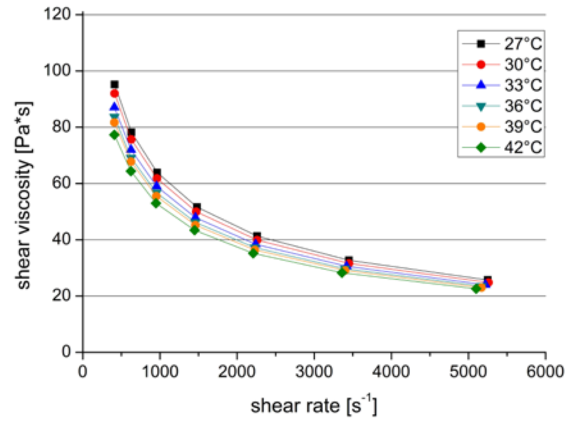

Figure 7. Shear viscosity of samples with 60 Shore A with different test temperatures

It was able to be shown that lower shear rates (< 1000 1/s) can be used to influence the viscosity across a broad range (approximately 20 1/s) by diversifying the temperature in a range of 15 °C. The shore hardness has no influence on the material behavior.

Homogeneity of the Material Behavior

The pressure profile provides an indication of the homogeneity of the material behavior as a function of the pressure. Figure 8 shows the pressure profile of some chosen samples as a function of time at the same test temperature of 30 °C. The different shear rate affects different levels of pressure depending on the selected apparent shear rate. The highest apparent shear rate (4000 1/s) leads to a high pressure level that ranged from 90 to 150 bar. The lowest apparent shear rate results in a pressure level of 25 to 50 bar. Materials with lower level of shore hardness also displays a lower level of resulting pressure. Solely the materials produced by Wacker (6610/40 and 6610/60) achieves exactly the same level of pressure although they have different levels of shore hardness. None of the materials displays any drops in pressure during the test, which indicates that they were processed homogeneously. [11,12]

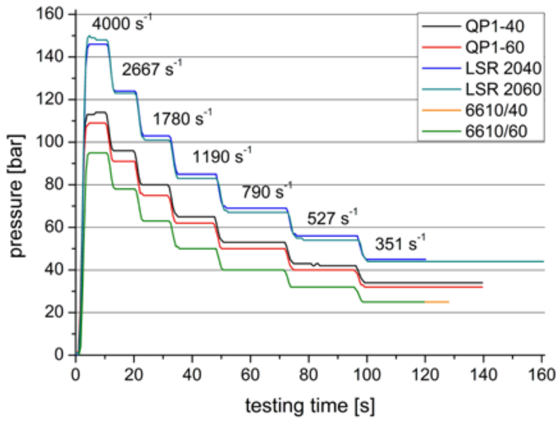

Figure 8. Pressure profile of all tested materials at a test temperature of 30 °C

Conclusions

In this study, the rheological behavior of six different LSRs from three different material producers were characterized using a capillary rheometer.

We found out that the viscosity of a material with the same shore hardness as another material can differ strongly depending on who produced the material. Furthermore, there is no significant correlation between the shore hardness and the viscosity of the uncured material. As the shear rate rises, the effects on the viscosity between the different materials become increasingly smaller. The measurements of the single components produces differing results. Different viscosities were measured for the various materials, and these differences were dependent upon which producer had made the materials and which shore hardness the materials had.

The results of the evaluation of the pressure profile shows that liquid silicone rubber remains homogenous across a wide range of shear rates. The viscosities and the resulting level of pressures of all materials are low (max. 150 bar), making them well-suited for applications in the injection molding process.

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