Flexible Foams made of Liquid Silicone Rubber and expandable Microspheres

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Abstract

In this study, the possibility of foaming liquid silicone rubber (LSR) was investigated. The foam was produced by injection molding with two different thermoplastic, expandable microspheres. Different properties were tested using the S2-tensile bar, e.g. density, tensile strength, specific tensile strength, elongation at break, stress at 100 % strain and the hardness. It was found that the two types of microspheres used have similar effects on density, specific tensile strength and elongation at break, but differ in hardness and stress at 100 % strain.

Introduction

Silicone Rubber belongs to the group of high-performance elastomers. It can be used between -50 °C and +200 °C, it is biocompatible and weather-proof and it is a good isolator. These excellent properties have led to a sharp increase in silicone rubber consumption, since 2008 about 4.2 % p.a. and studies continue to predict a continuous increase of 4 % p.a. until 2024 [1]. Common areas of application for silicone rubber are electrical & electronics, automotive, consumer goods and medical technology industries.

Silicone rubber is divided into high temperature curing and room temperature curing. The high temperature curing materials are divided secondary into liquid silicone rubber (LSR) and high-consistency rubber (HCR). Both materials need more than 120 °C for curing. HCR is cured typically by peroxides and it is processed by extrusion. LSR has a lower molecular weight as HCR and it is cured by hydrosilyzation with the aid of platinum catalysts. LSR is usually processed in the injection molding process. [2]

Elastomer foams have been used for different applications for many years. By means of foaming rubber, modifications to the properties can be made. The most important aim is to reduce the density of products, because the price of silicone rubber is much higher compared to that of other elastomers. Property modification can help to enhance the thermal and acoustic insulation properties, improve volume compressibility and damping, as well as a change of the haptics. [3]

There are currently two types of silicone foams that have technical applications. One is extruded HCR foam and the other is foam made of room temperature curing silicone rubber. There isn't currently any technical application with LSR-foams. This depends on the high machine costs involved in physical foaming with injection molding machines and these LSR-foams are very inhomogeneous. [3]

Due to the special temperature conditions in the injection molding process of LSR (extruder and runner cold, mold hot), a simple foaming method is available. The solution is to add fillers which expand at typical mold temperatures of 140°C to 200°C. The investigated fillers are expandable, thermoplastic microspheres.

Goal of this study is to show the potential of the new foaming process of LSR with thermoplastic microspheres focusing on the mechanical properties and the density reduction. These special foaming processes of LSR have not yet been investigated.

Materials

The LSR used was the QP1-30 from Dow Corning. It is a two-part, Pt-catalyzed, heat-cured silicone elastomer designed for the fabrication of medical devices and device components, including those intended for implantation in humans for less than 30 days, and non-implant applications. The elastomer has a Shore A target hardness of 28, a tensile strength of 6.4 MPa and an elongation at break of 680 %. [4]

Two different thermoplastic, expandable micro-spheres were used. Both fillers have an outer shell made of a thermoplastic copolymer which contains acrylonitrile (AN) and Methylmethacrylat (MMA). The shell is filled with hydrocarbon. During heating, the copolymer becomes elastic, and, simultaneously, the hydrocarbon expands. This is shown in figure 1. Once cooled down, the shell becomes solid again. Expandable thermoplastic microspheres are available for various applications in sizes ranging from 6 to 40µm when unexpanded. Different expansion temperatures can be employed and diverse volume increases are possible [5,6]. Both types of microspheres used belong to the low temperature expanding types. The first microspheres used here are sold

by Tramaco and were called UNICELL™ MS 140 DS. The mean particle size is approx. 20 µm and the expansion begins at temperatures approx. 90 °C. Iospentane is used here as the hydrocarbon [7]. The second microspheres were manufactured by Akzonobel under the name Expancel 031 DU 40. The mean particle size is 10-16 µm and the expansion begins at temperatures ranging between 80-95 °C. These shells are filled with isobutene [8].

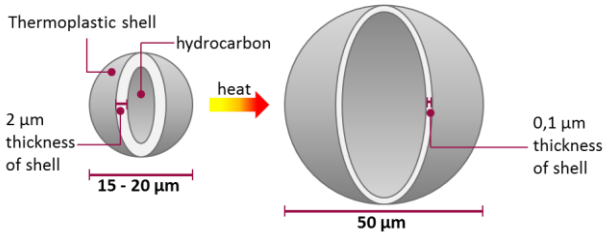

Figure 1. Concept of expansion of thermoplastic microspheres.

Experimental

Production of Tension Bars

For the analysis of the foam properties, S2 tension bars (DIN EN ISO 517-1) were produced in a liquid injection molding process on a Babyplast micro injection molding machine, which is modified for processing LSR. The molding machine has a piston injection unit with a water-cooled shut-off nozzle. The raw material has to be premixed in a 500 ml cartridge, which can be placed in the integrated dosing system. The mold can be heated and the specimen is connected to the injection gate by a film gate. The mold temperature was 160 °C. The heating time was adapted to the amount of microspheres (≤ 2 wt-% – 25 seconds, 3 wt-% – 27.5 seconds). The degree of filling was adjusted for every factor combination by increasing the dosage volume of the injection unit in 0.02 cm³ steps until a complete filling of the mold was achieved.

Experimental Design

The foamed LSR specimens were produced with a different weight in percent of filler in the used silicone rubber. For UNICELL MS 140 DS 0%, 0.5%, 1.0%, 1.5%, 2.0% and 3.0% were investigated and for Expancel 031 DU 40 0%, 1.0%, 2.0% and 3.0%.

Density

The density of the foamed LSR in comparison to unfilled tension bars was identified with an electronic scale and the density determination kit YDK04 of Sartorius. The fluid used was demineralized water.

Hardness

The micro shore A hardness was measured according to DIN ISO 7619 part 1 with an automatic testing machine produced by Bareiss Prüfgeräte GmbH/Germany. Each S2 tension bar was measured on both shoulders because one shoulder is in the near of the injection molding point (position 1 in figure 2) and the other shoulder is away from the injection molding point (position 2 in figure 2).

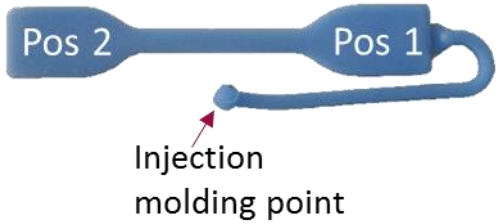

Figure 2. Tensile bar

Tensile Test

The quasi-static tensile test was carried out according to DIN 53504 on a universal testing machine from Hegewald & Peschke Meß- und Prüftechnik GmbH/Germany. The initial force was 0.75 N and was approached at a feed rate of 50 mm/min. The subsequent test speed was 200 mm/min. The extensometer had a distance of 20 mm.

Scanning Electron Microscopy (SEM)

Microscopic analysis was carried out with an scanning electron microscope called CamScan MV 3200 from Electron Optic Services, Inc./Canada. The fracture surfaces of the tensile bars were examined.

Results and Discussion

The results of this study are differentiated according to the type of microsphere. Furthermore, there is a difference between the amount of filler and between the position on the tensile bar of the measured density and micro shore A hardness (figure 2).

Density

Figure 3 shows the density of the LSR-foams for both types of microspheres. The effect of the density reduction is similar. The density decreases with a higher amount of microspheres. This means a higher proportion of blowing agent (microspheres) leads to a better density reduction. The maximal density reduction is 47 % with the

microspheres called Expancel 031 DU 40 and 35 % for the UNICELL MS 140 DS.

Furthermore, the density reduction is higher at position 2 which is away from the injection molding point (see figure 2). This effect depends on the flow front. The microspheres expands better at the beginning of the flow front because there is less back pressure.

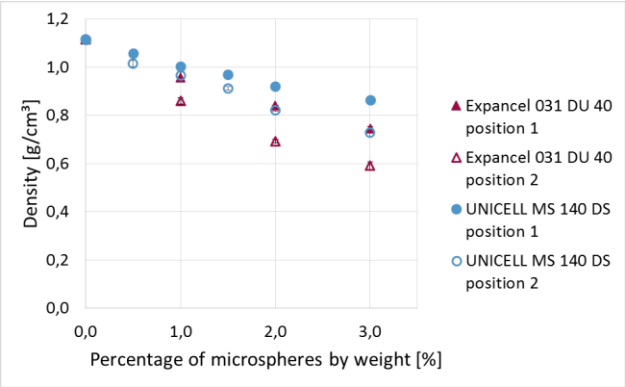

Figure 3. Results of the density as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

Tensile Test

Figure 4 shows the tensile strength as a function of the filler content. The decrease is comparable for both microspheres. While unfoamed QP1-30 has a tensile strength of 8.5 MPa, the foamed QP1-30 reached its minimum at 3.4 MPa with 3 wt-% UNICELL MS 140 DS and 2.8 MPa with 3 wt-% Expancel 031 DU 40. This means a reduction of 60 % respectively 67 %. The specific tensile strength is the tensile strength in relation to the density and is shown in figure 5. It has the same value of 4.2 N·m/g for both types of microspheres at 3 wt-%. This is a reduction of 45 % in correlation to the unfoamed LSR.

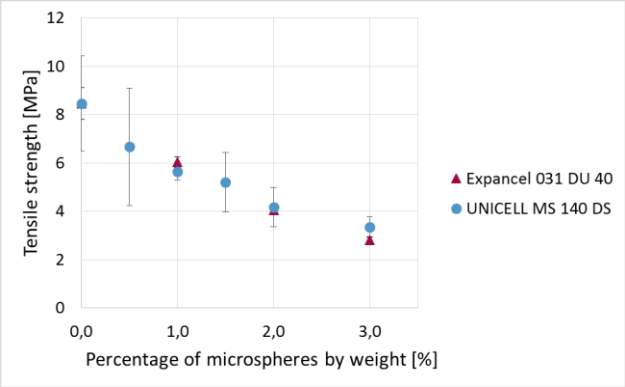

Figure 4. Tensile strength as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

It can be assumed that the interface between the LSR-matrix and the shell of the microsphere hasn't any adhesion and the increase of the interface with higher amount of filler leads to the decrease of the specific tensile strength. Due to the larger interface, the resulting load bearing cross-section is much lower.

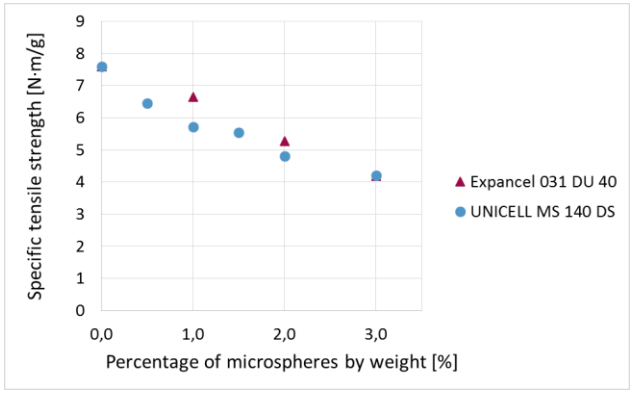

Figure 5. Specific tensile strength as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

The elongation at break decreases, too (see figure 6). There is a reduction of 14.6 % for 3 wt-% UNICELL MS 140 DS (634 %) and 12.4 % for 3 wt-% Expancel 031 DU 40 (650 %) in correlation to the unfoamed LSR (742 %).

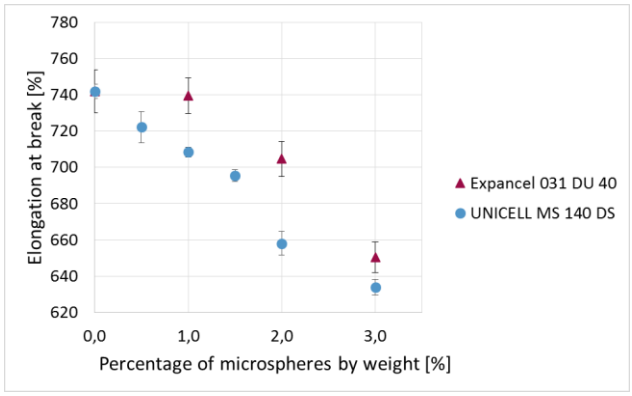

Figure 6. Elongation at break as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

The stress at 100% strain is a value for the elasticity of the silicone rubber. Figure 7 shows this value as a function of the filler content. A higher filler content increases the stress at 100 % strain. This means, that a higher force is necessary for the same deformation. The foamed LSR with Expancel 031 DU 40 show a lower increase as the foamed LSR with UNICELL MS 140 DS. The unfoamed QP1-30 has a stress at 100 % strain of 0.45 MPa, the foam with 3 wt-% Expancel 031 DU 40 has a stress at 100 % strain of 0.55 MPa and the foam with 3 wt-% UNICELL MS 140 DS has a stress at 100 % strain

of 0.69 MPa. This effect depends on the shell of the microspheres. During the tensile test, the LSR-matrix is constricted and exerts pressure on the shell of the microspheres. This causes the microspheres to be elongated. This deformation requires additional force and the stress at 100 % strain increase with a higher amount of microspheres. The UNICELL MS 140 DS have a higher increase, so it can be concluded, that the shell is harder than the Expancel 031 DU 40.

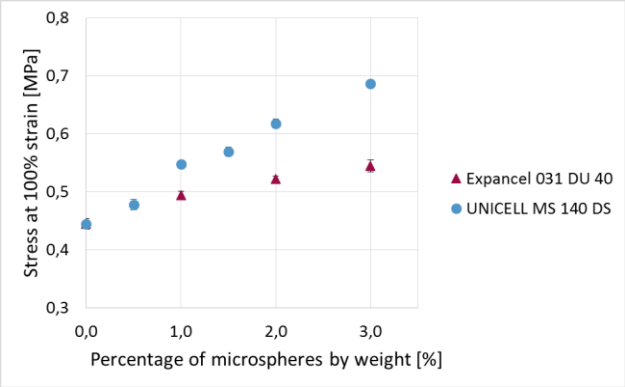

Figure 7. Stress at 100% strain as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

Hardness

Figure 8 shows the micro shore A hardness as a function of the filler content and for both position (see figure 2). The position 2 which is away from the injection molding point (see figure 2) has a lower hardness as the position 1. This effect could be seen at the density, too (see figure 3). The hardness of the Expancel 031 DU 40 decreases with increasing filler content. A higher filler content also means a lower density. From this it can be concluded that the shore hardness depends on the density.

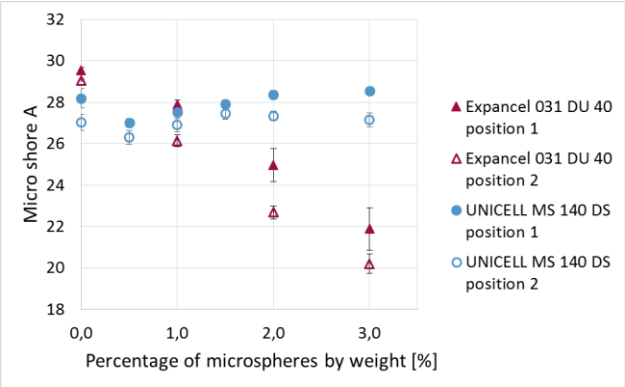

Figure 8. Micro shore A hardness as a function of filler content for Expancel 031 DU 40 and UNICELL MS 140 DS.

The foam with UNICELL MS 140 DS shows another effect. The shore hardness remains at a comparable level. At first there is a small decrease with 0.5 wt-% microspheres and with a rising amount of the filler the hardness increases again. One possible explanation for this is that the shell material from the UNICELL MS 140 DS has a similar or higher hardness than the LSR and that the component becomes harder with increasing filler content. This thesis also agrees with the increase in stress at 100 % strain.

Scanning Electron Microscopy

Figure 9 shows the fracture surface of the tensile bar with 1 wt-% UNICELL MS 140 DS. In the detail view (down) it can be observed that the shell of the damaged microsphere lies in the pore. Figure 10 shows the same for 3 wt-% UNICELL MS 140 DS. Due to the higher density with 1 wt-% of microspheres, it is shown in the detailed view that the amount of LSR is higher for 1 wt-% of microspheres than for 3 wt-% of microspheres. Whether the microspheres were damaged during the tensile test must be determined in further studies. However, the damaged shells do not show any adhesion to the LSR matrix.

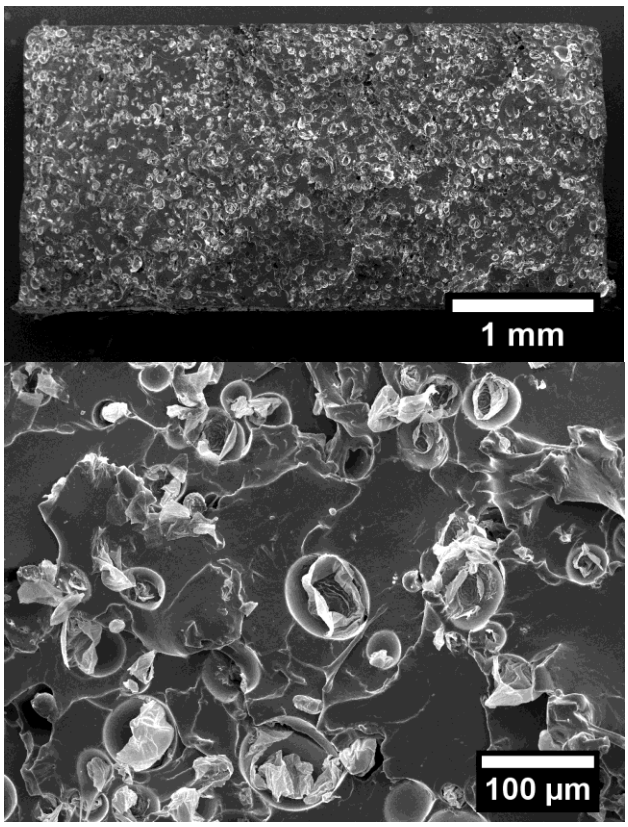

Figure 9. SEM micrograph of the fracture surface of a tensile bar with 1 wt-% UNICELL MS 140 DS, overview (top) and detail view (down)

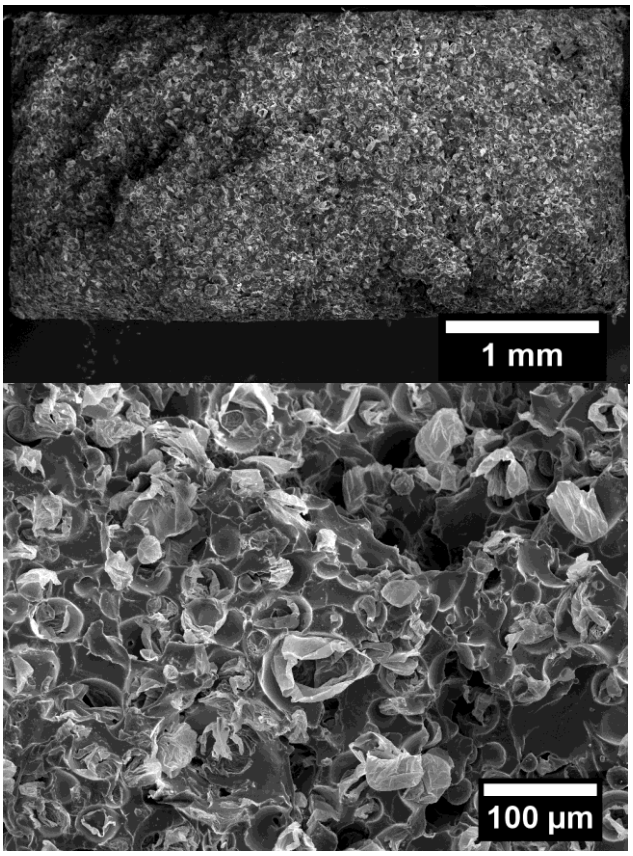

Figure 10. SEM micrograph of the fracture surface of a tensile bar with 3 wt-% UNICELL MS 140 DS, overview (top) and detail view (down)

Conclusions

This study shows that a density reduction up to 50 % is possible with 3 wt-% of expandable, thermoplastic microspheres. But with a high amount of filler the elongation at break and the (specific) tensile strength decrease. This is due to the increasing interface between the LSR-matrix and the microspheres. Because there is no adhesion between the two components, cracks can spread more easily. The shore hardness and the density are lower at the position away from the injection molding point than near the injection molding point, as a result of the pressure drop from the gate to the flow front. The hardness and stress at 100 % strain are significantly influenced by the hardness of the microsphere shell. This can be seen from the different values, although the other properties are similar for both microspheres.

References

1. Ceresana, *GAK - Gummi Fasern Kunststoffe*, **70**, 214 (2017).
2. F. Röthemeyer, F. Sommer, Kautschuktechnologie: Werkstoffe- Verarbeitung- Produkte, *Hanser-Verlag*, Munich, (2013).
3. T. Häuser, Herstellung von physikalisch geschäumten Flüssigsilikonbauteilen im Spritzgießprozess, *Verlagsgruppe Mainz GmbH*, Aachen (2011).
4. Dow Corning, Product Information Healthcare, QP1 Liquid Silicone Rubber Products (2011)
5. Akzo Nobel, Expancel Short introduction, *Akzo Nobel Pulp and Perfomance Chemical AB*, Sundsvall (2011).
6. M. Jonsson, Thermally expandable microspheres prepared via suspension ploymerization - synthesis, characterization and application, *KTH Chemical Science and Engineering*, Stockholm (2010).
7. Tramaco, Produktinformation UNICELL MS 140 DS (2018)
8. Akzo Nobel, Product Specification for Expancel microspheres (2014)

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