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Liquid Silicone Rubber Foams Made with Water as Blowing Agent

*Svenja Marl, Annette Rüppel, Michael Hartung, Kevin Klier, Ralf-Urs Giesen, and Hans-Peter Heim**

Liquid silicone rubber (LSR) is primarily used in injection molding. Foamed molded parts made of LSR are almost nonexistent because the process reliability of LSR foam injection molding is currently not given. It makes sense to have suitable foaming processes for this material as well, because the density of this elastomer is about 1.15 g cm^{-3}. With the injection molding process presented herein for foaming LSR, density reductions of up to 40% can be achieved. In this process, up to 3% by weight of water is added to the material. In addition, the hardness of the component changes, it becomes softer. Especially in the case of hardness, the process parameter mold temperature has a decisive influence, as it determines the pore size in the component. Herein, the structural properties of the silicone foam are now discussed as a function of the process parameters and additives for foaming. Thus, with the new process, material can be saved, the haptic properties of components can be changed, and a stable processing method for foamed components made of LSR is found.

1. Introduction

Foamed thermoplastics have been used for decades to improve properties such as thermal insulation and weight minimization. Where insulation is required, so-called expandable polystyrene (EPS) is often used. Technical thermoplastics such as polyamide are also foamed and are mainly used in the automotive industry, where they are mainly used to reduce weight. The production of components for technical applications is mostly done by injection molding or extrusion. Further advantages to be mentioned with the physical foaming process in the injection molding process are that components with long flow paths can be produced and that the dimensional stability increases. Products manufactured include engine covers, battery boxes, and dashboards.[1–3]

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In addition to other physical blowing agents such as carbon dioxide or nitrogen, water can also be used as a blowing agent. In general, the advantages of physical blowing agents are that they are toxicologically harmless and also cheaper.[4] In the field of thermoplastic injection molding, there are several publications that show that very good results can be achieved with water as a blowing agent, here, as an example for polycarbonate and polypropylene.[5,6] In the study by Bechmann et al.,[7] the Aquacell process is presented, in which water is added to the polymer via a carrier substance. Elastomers such as TPEs and EPDM can also be foamed with water.[8,9] Experiments with EPDM showed that density reductions of 40–60% could be achieved in the injection molding process with the help of moist silica as an additional filler.[10]

Foamed components made of silicone rubber are only used in very few applications. This is due to the fact that silicone foams made of high-consistency silicone rubber (HCR) can only be produced reliably by extrusion. Foamed molded parts made of silicone rubber, especially liquid silicone rubber (LSR), are very rarely used, as there is still no truly process-reliable injection molding method for foaming with LSR. Possible applications for foamed silicone components made of LSR are, for example, reusable earplugs, as here the foam can have an additional sound-insulating effect and additionally less material is needed, which can reduce the price. As the feel is positively influenced by the foam structure, foamed silicone components can also be used, for example, in breathing masks or diving goggles. In 2016, a patent application was produced for a new process (University of Kassel), in which silicone rubber is foamed using microspheres.[11]

Silicone rubber (especially HCR, but also LSR) can be foamed using the known processes of physical and chemical foaming.[12,13] For chemical foaming, organic or inorganic compounds are added to the silicone rubber. The vulcanization process produces, for example, nitrogen or carbon oxides at high temperatures, which emit and expand in the melt, resulting in foam structures.[14] The disadvantage of this method is that toxic substances can be produced which are then emitted. In physical foaming, nitrogen or carbon dioxide is added to the melt under high pressure in the injection molding unit. When the gas-loaded melt enters an evacuated cavity, there is a pressure drop and the gas expands, forming pores in the rubber. In the beginning of the 2000s, such a process was also tested in LSR injection molding.[15] The process-safe

production of components proved to be complicated. Too low viscosities of the "silicone rubber melt" loaded with gas led to injection flash and heavy stress on the silicone injection molds.[16]

The now patented invention of using water to foam LSR in injection molding is a new available option. Water is added to the LSR by compounding before processing. When this mixture reaches the heated mold by injection, water vapor is produced on the one hand and the silicone rubber is vulcanized on the other. Vulcanization and evaporation take place almost simultaneously, thus creating pores in the LSR. Ideally, mold temperatures of over 140 °C are present for this process, so that rapid vulcanization takes place. A nice advantage of this foam is that the water finally evaporates by the tempering process (4 h, 200 °C) because during production it is not possible for water to escape from the closed mold, and thus a pure silicone elastomer foam is produced. The very good properties of the silicone elastomer, especially from a physiological point of view, are retained.

HCR and LSR are becoming increasingly important in plastics technology. They are relatively easy to process, are physiologically harmless, have very good mechanical properties in the range from −50 to +200 °C, are odorless, and special types have very good optical properties. Due to these advantages over other elastomers, they are increasingly used in the medical and automotive technology, in the field of consumer electronics, as well as in households and the construction industry.

In all these areas, they are also or especially suitable for foamed silicone molded parts to make components cheaper and lighter.

2. Experimental Section

2.1. Materials

For the following tests, an LSR (Elastosil LR 3003/50) with a Shore A hardness of 50 from the company Wacker Chemie AG was used. The material was suitable for various applications in the automotive and household sectors and for use in contact with the food industry. As foaming agent for weight reduction, on the one hand, pure water was mixed into the LSR (1, 2, and 3 phr). On the other hand, fumed silica (mixing ratio: 1:8; 1 part silica and 8 parts water, further called soaked silica), also in the proportions of 1, 2, and 3 phr, was formed. **Table 1** shows the material selection.

2.2. Production of Test Specimen

The analysis of silicone foams was conducted on injection-molded tensile bars, form S2, according to DIN EN ISO 517-1. A Babyplast injection molding machine 6/10P was used for production. The compact piston injection molding machine was specially adapted to small shot weights and the processing of LSR. This required contrary temperature control compared with thermoplastic injection molding. The injection module with a needle valve nozzle was kept at a constant temperature of 20 °C by means of fluid temperature control, and the injection molds were heated by means of electric mold heating control circuits. The LSR was supplied via a 0.5 l disposable cartridge inserted into the plastification module, which contained the base components A and B of the LSR and the blowing agents. After weighing, the components were mixed together with a hand mixer.

Table 1. Material selection.

Material	Designation	Material producer
LSR	Elastosil LR 3003/50	Wacker Chemie AG
Hydrophilic fumed silica (silicon dioxide, SiO2)	Aerosil 200	Evonik Industries
Water		

The operation of the metering and injection process differed from that of a classic screw injection molding machine. During metering, a hydraulic cylinder built up material pressure in the cartridge. Via a spring-actuated check valve, the raw material flowed in the direction of the injection piston and pushed it back to the set stroke. During the injection process, the LSR was injected into a vacuumed and heated mold cavity via the injection plunger at a defined speed and injection pressure. In parallel, the metering check valve was closed to prevent it from flowing back into the cartridge. In the used mold, the cavity of the molded part was connected to the machine nozzle via a film gate.

The S2 tensile bars were produced at mold temperatures of 140 and 180 °C. The vulcanization time was 25 s. To determine the required metering volume of the compact component without the blowing agent, a filling study was first conducted. This value provided the reference for the foaming tests. To set the maximum foam density, starting from the determined reference value of the unfoamed component, the injection volume was gradually reduced until, on the one hand, complete mold filling was achieved at maximum foam density. A further reduction in the metering volume led to incomplete mold filling as the missing volume could not be compensated by foaming. Hence, a specific limit value was set for each combination of mold temperature and water content.

2.3. Test Methods

To determine the influence of the water content, the following test methods were selected.

2.3.1. Scanning Electron Microscopy (SEM) for the Examination of the Pore Distribution

To investigate the foam structure or the distribution of the pores, morphological examinations were conducted on a scanning electron microscope (CAMSCAN MV2300 LV). The sample preparation was conducted in three positions of the test bars (see **Figure 1**) with subsequent fixation on a specimen holder. To generate a high-secondary electrode current, which provides a better image quality with higher contrast, the specimens were exposed with gold before measurement. One specimen was examined per batch.

2.3.2. Investigation of Weight Loss by Means of Sample Weighing

The change in weight of all material batches was investigated by weighing. For this purpose, the test specimens were weighed without damaging them before and after postcuring and the weight was noted. Accordingly, the weight loss after the addition

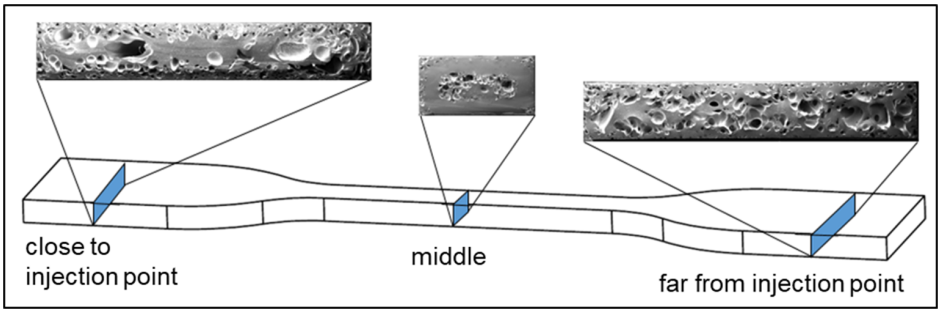

Figure 1. Sampling points for the SEM images using the example of 3 phr water, 140 °C, untempered.

of 1 and 3 phr water/hydrophilic fumed silica was determined and the results compared. Five test specimens per batch were examined.

2.3.3. Determination of Micro Shore A Hardness According to DIN EN ISO 868

To detect changes in material hardness, Micro Shore A hardness measurements were carried out using a Bareiss Digitest 2 measuring device. The measurement was carried out on the shoulder, which was near the injection point. A total of five test specimens were measured in each case and the mean value was calculated.

3. Results and Discussion

3.1. SEM for the Examination of Pore Distribution

SEM images show that increasing the mold temperature from 140 to 180 °C leads to a finer distribution of the pores in the edge region (from **Figure 2–7**). This effect can be observed independently of the blowing agent and its proportion. By increasing the proportion of blowing agents, an increase in pores can also be observed.

No difference could be observed between the tempered and the untempered samples as the tempering step takes place only after molding. For this reason, the pictures of the tempered specimens are not included for the sake of clarity.

For the specimens produced at 140 °C, a difference can be observed between the areas close to the injection point (see Figure 2 and 5) and those far from the injection point (cf. Figure 4 and 7). The shoulder far from the injection point shows a finer distribution of pores compared with the area near the injection point. This can be explained by the longer flow front and the lower backpressure/ambient pressure in the mold. Also, the material remains longer in the hot mold and is thus heated more strongly, which leads to better foaming results. At 180 °C, this effect can also be observed, but it is less pronounced.

Figure 3 and 6 show the foam structure in the webs of the tensile test bars. As these are narrower at the same height, they

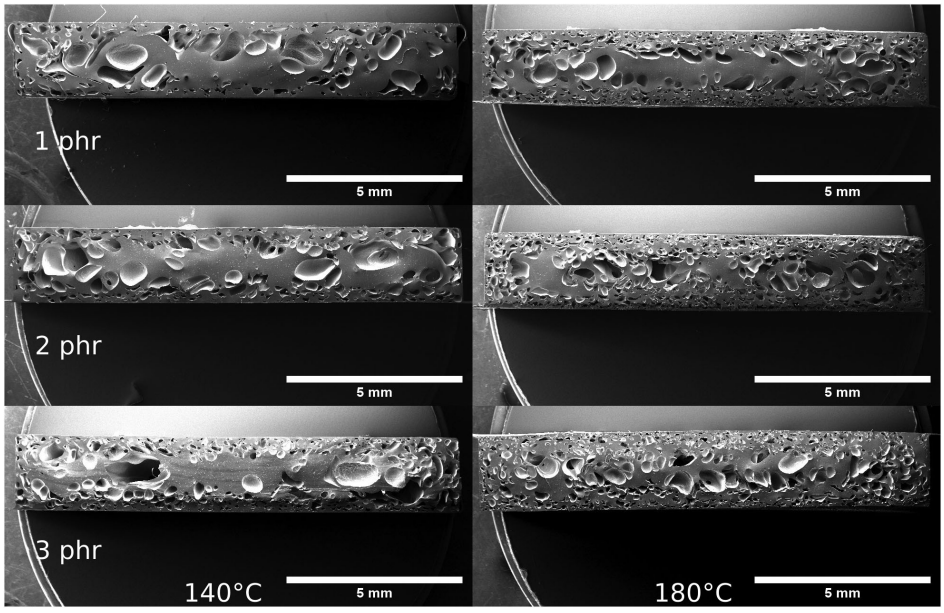

Figure 2. SEM images for water as blowing agent near the injection point as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

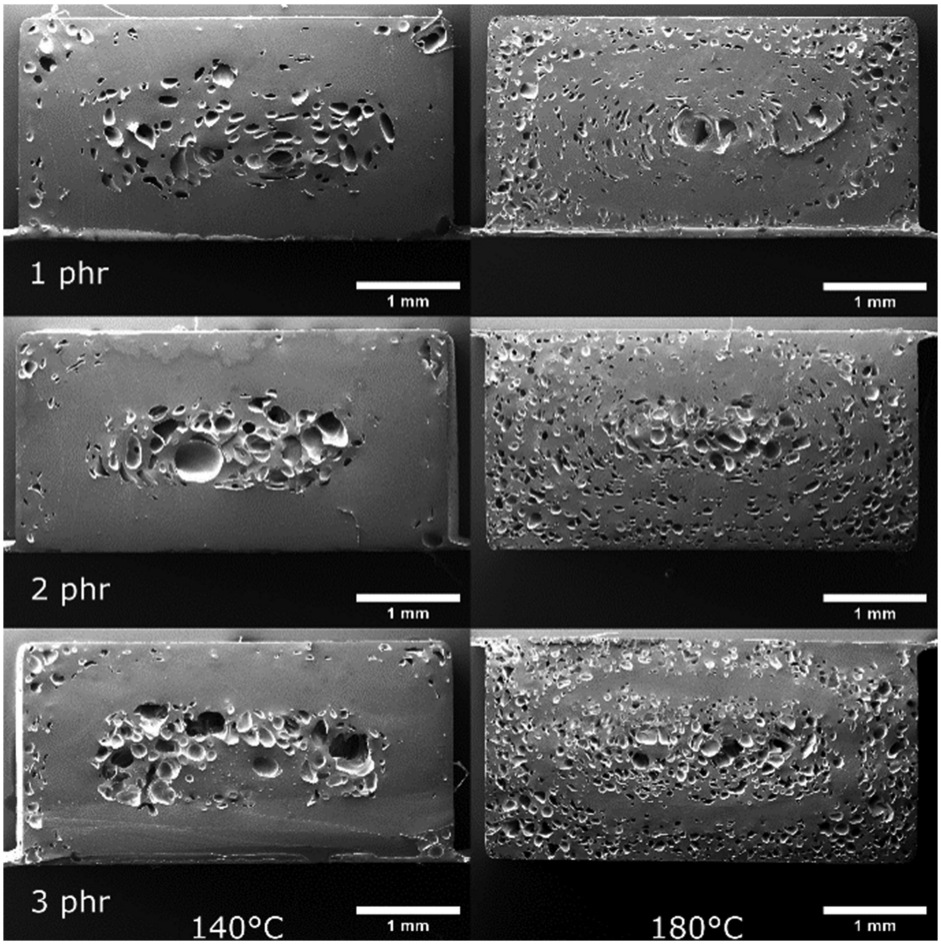

Figure 3. SEM images for water as blowing agent in the middle of the tensile bar as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

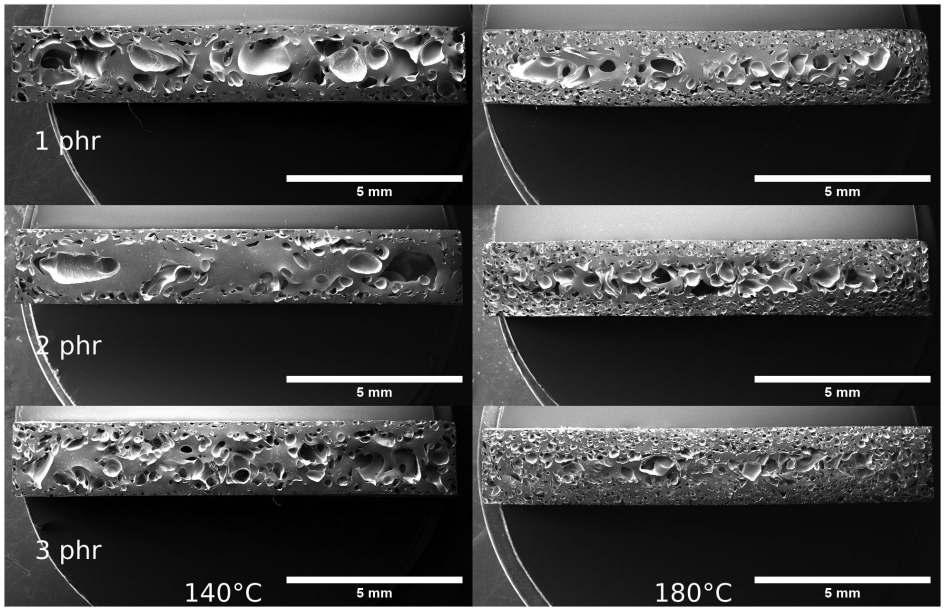

Figure 4. SEM images for water as blowing agent far from the injection point as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

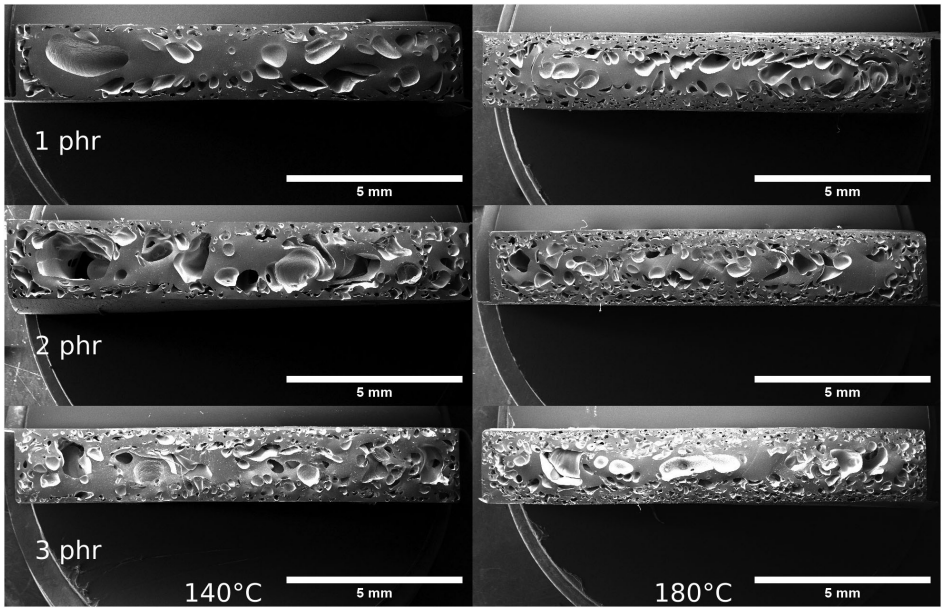

Figure 5. SEM images for soaked silica as blowing agent near the injection point as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

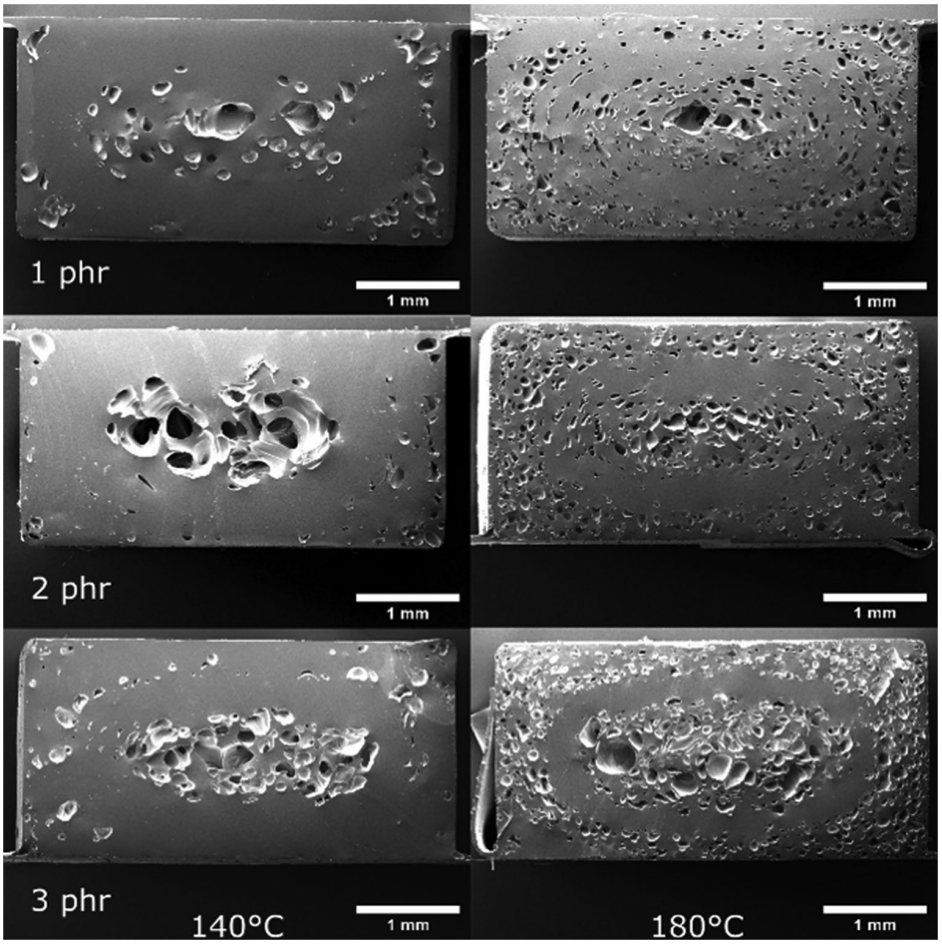

Figure 6. SEM images for soaked silica as blowing agent in the middle of the tensile bar as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

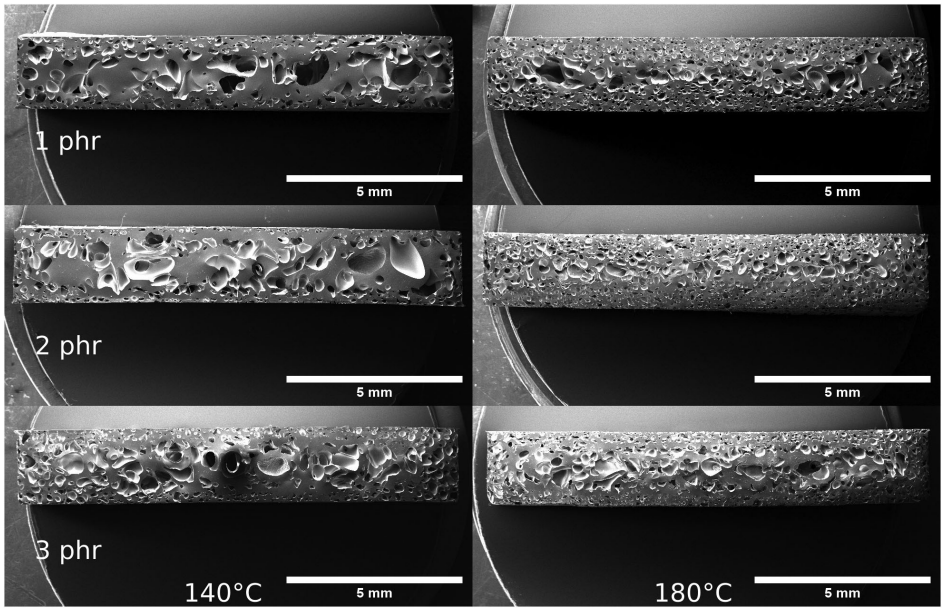

Figure 7. SEM images for soaked silica as blowing agent far from the injection point as a function of the proportion (top: 1 phr; center: 2 phr; bottom: 3 phr) and the mold temperature (left: 140 °C; right: 180 °C), untempered.

have a different height-to-width ratio. This may be one reason why at 140 °C, unlike in the shoulders, an unfoamed edge layer forms and a foamed core is present. At 180 °C, this effect can no longer be observed.

Using the example of the soaked silica, the cell density in the inner region as well as in the outer edge region was investigated in more detail. It was found that the cell density in the outer area increases strongly due to the increase in mold temperature. At 140 °C, ≈7% of the surface area are pores, and at 180 °C, the proportion of pores to surface area in the outer area is between 23% and 27% (see **Table 2**).

In the inside, the area of the pores changes only slightly as a result of an increase in mold temperature. An exception here is the very large area fraction with 52% at 140 °C and 2 phr, as here several pores have grown together to form one large one (see Table 2 and Figure 6). To obtain a more precise and better evaluation of the cell density, X-ray microtomography (μCT) images are planned in the future.

The number of cells increases significantly by increasing the mold temperature, with the size distribution shifting toward smaller cells at higher temperatures (see **Figure 8** and **9**).

Table 2. Cell density in the middle of the tensile bars (see Figure 1) for soaked silica (see Figure 6)

	Cell density: soaked silica			
	140 °C		180 °C	
	Inside	Outside	Inside	Outside
1 phr	20%	8%	25%	23%
2 phr	52%	6%	21%	26%
3 phr	39%	7%	38%	27%

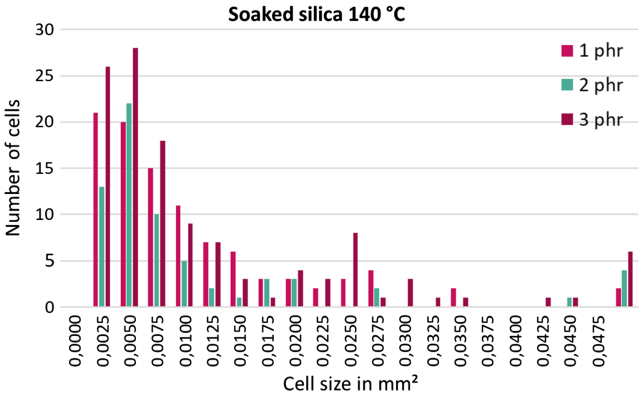

Figure 8. Cell size distribution of the soaked silica at a mold temperature of 140 °C for 1, 2, and 3 phr of soaked silica.

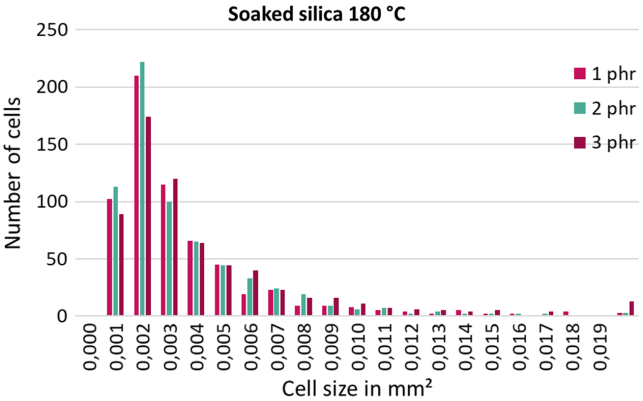

Figure 9. Cell size distribution of the soaked silica at a mold temperature of 180 °C for 1, 2, and 3 phr of soaked silica.

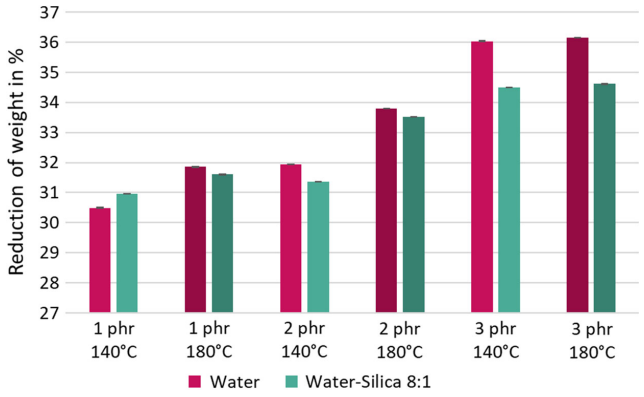

Figure 10. Reduction of weight, tempered.

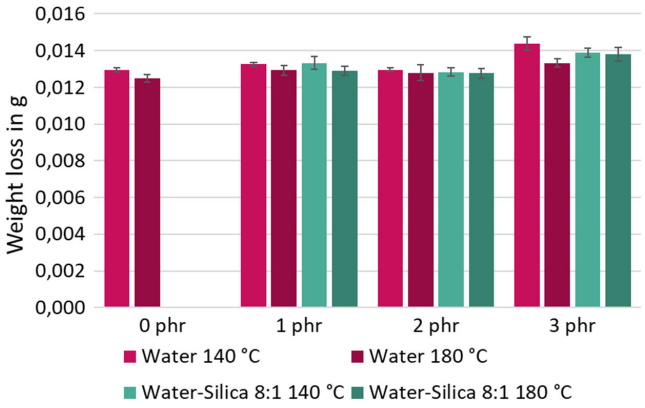

Figure 11. Weight loss after tempering.

At 140 °C, most cells are between 0.0025 and 0.0075 mm^2 in size, regardless of the proportion of blowing agent. However, at 180 °C, most cells are significantly smaller, ranging from 0.001 to 0.003 mm^2, regardless of the amount of blowing agent.

3.2. Reduction of Weight

The factors investigated here that influence weight reduction are the amount of blowing agent and the mold temperature. It was determined that a higher proportion of blowing agents leads to a lower component weight. The weight reduction is 30.5% with 1 phr water and 36.2% with 3 phr water compared with the compact specimen (see **Figure 10**).

For the mixture of silica and water (1:8), except for 1 phr at 140 °C, a somewhat lower reduction could be determined than for pure water. Possible reasons for this are that, on the one hand, 1, 2, and 3 phr, respectively, of the soaked silica were mixed in during blending and that this corresponds to a water content of 0.9, 1.8, and 2.7 phr, respectively. Thus, there is effectively less blowing agent present. Another explanation is the binding of water to the silica. This has silanol groups on the surface, which can form hydrogen bonds with water. Typical energies for these secondary valence bonds are between 4 and 40 kJ mol^{-1} and must be broken before evaporation. Thus, slightly more energy is required for the water to evaporate compared with pure water.[17]

The investigation of the mold temperature on the foaming behavior shows that at a higher mold temperature the water evaporates faster and thus a higher degree of foaming can be achieved. This effect is strongly pronounced at 1 and 2 phr blowing agent and, on the other hand, can no longer be observed at 3 phr. This leads to the conclusion that saturation occurs between 2 and 3 phr, which suppresses further foaming.

There are two reasons for conducting tempering. First, low-molecular-weight components are removed and second, complete crosslinking occurs due to post-crosslinking of the LSR. In this case, the thermal treatment at 200 °C for 4 h is also intended to remove excess water. The reduction in weight due to tempering is between 0.012 and 0.015 g (see **Figure 11**). Depending on the degree of foaming, the tensile test bars weigh between 0.85 g (3 phr water, 180 °C, untempered) and 1.38 g (reference). As the reduction with the reference is similarly high as with 1 and 2 phr blowing agent, it can be assumed in this case that hardly any residual water is present. The situation is different with 3 phr blowing agents. Here, the weight loss is higher, which indicates incomplete evaporation of the water and again points to saturation. As no water can escape during the production of the tensile bars in the closed injection mold, it can be assumed that at 1 and 2 phr of the blowing agent, the water passes completely into the gas phase and thus the foam is produced. At 3 phr, on the other hand, the vapor pressure is not sufficient for all the water to pass into the gaseous phase, so a small proportion remains and evaporates during subsequent annealing in a separate oven, leading to a higher weight reduction.

3.3. Shore A Hardness

The foam structure has a significant influence on the Shore A hardness as the addition of blowing agent creates pores in the silicone rubber, which are easier to compress than the matrix material. The reduction of the Shore A hardness (cf. **Figure 12** and **13**) by adding 1 phr blowing agent is the greatest and ranges between 29% (soaked silica, 140 °C) and 42% (water, 180 °C) for the untempered samples. By increasing the amount of blowing agent to 2 phr, a further but significantly lower

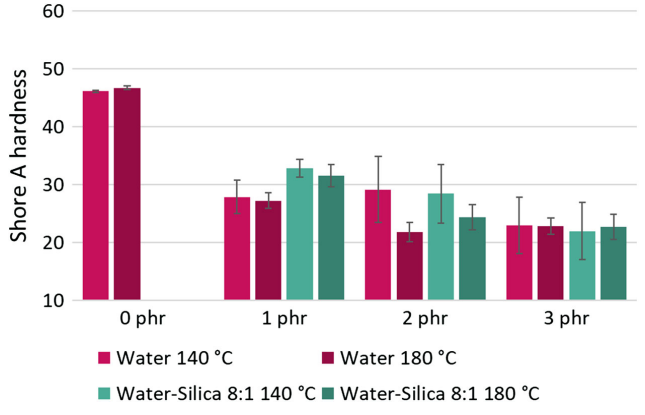

Figure 12. Shore A hardness untempered.

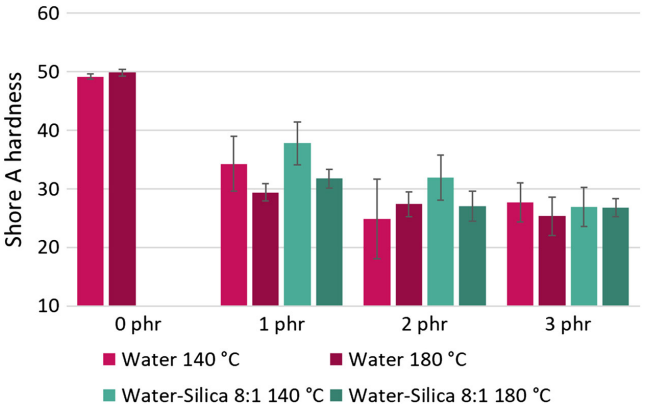

Figure 13. Shore A hardness tempered.

reduction can be observed, especially at 140 °C mold temperature. Between 2 and 3 phr blowing agents, no significant difference can be determined anymore. The maximum reduction compared with the compact part is 53% (2 phr water, 180 °C, untempered). At 3 phr, the reduction is constant for all untempered samples between 50 and 52%. The tempered samples exhibit comparable behavior, although here the reduction is weaker due to post-crosslinking (1 phr: from 23 to 41%; 3 phr: from 44 to 49%). Due to the comparable reduction at 2 and 3 phr blowing agents, it can be concluded that there is no linear relationship between the weight reduction and the Shore A hardness.

Irrespective of the reduction in Shore A hardness, the post-cured samples generally exhibit a higher Shore A hardness than the untempered samples due to post-crosslinking. An exception is the hardness at 2 phr water and a mold temperature of 140 °C, where the high standard deviation indicates an outlier, which can explain the lower value of the tempered samples.

In the comparison between the Shore A hardness and the foam structure, the higher hardness of the tempered samples at 1 phr blowing agent and 140 °C mold temperature compared with 180 °C can be explained by the unfoamed cores (see Figure 2 and 5). These can be compressed less than the pores at 180 °C, resulting in higher Shore A hardness. In the case of the untempered samples, this effect is much weaker or, due to standard deviation, not significantly pronounced.

At 2 phr, the effect is significantly more pronounced for the untempered samples, as the unfoamed core is strongly pronounced at 140 °C and, in contrast, hardly observable at 180 °C.

At 1 and 2 phr, the samples foamed with soaked silica exhibit on average a higher Shore A hardness than those foamed with pure water. This may be due to the slightly lower water content, as already mentioned for the weight reduction and the associated lower pore formation with the soaked silica. At 3 phr, the Shore A hardness is comparable between the two blowing agents, although again silica has lower weight reductions. This can be explained by the very similar pore size in the edge region.

Another striking feature is the larger standard deviation for samples that were produced at 140 °C. This shows that the pore size has a decisive influence on the measurement of hardness for foamed components.

4. Conclusion

The process developed by the University of Kassel expands the field of application of silicone rubbers. This study shows that a density reduction of maximum 36.2% can be achieved with the used blowing agents. Thus, the material costs for components made of LSR can be significantly reduced without adding hazardous foreign substances to the product. The SEM images clearly show that the foam structure can be significantly influenced by the mold temperature. Depending on the geometry of the component, the blowing agent, and the blowing agent content, areas with different foam structures can be generated by a targeted temperature distribution in the mold. These different foam structures significantly influence the Shore A hardness. Components with little-to-no foam structure in the core have a higher Shore A hardness than those with a high foamed core. In further investigations, the compression set and rebound resilience of the foamed LSR components will be investigated. It is also planned to transfer the results obtained to solid silicone extrusion.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

injection molding, liquid silicone rubber, silica, silicone foam, water

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