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LSR-Foam

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LSR-Foam produced by injection molding

Abstract für Inhaltsverzeichnis (max 450 Zeichen)

This paper illustrates the effect of expandable thermoplastic microspheres as blowing agents in liquid silicone rubber. They can significantly reduce the density of the vulcanizates and thus lead to material savings in the application and positively influence the insulation behaviour against heat and cold as well as the floatability.

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Abstract

Liquid Silicone Rubber (LSR) is mainly processed by injection molding because the material is particularly suitable for this purpose due to its low viscosity during processing. The density of the vulcanizate is about 1.1 g/cm³. With the aid of foamed silicones, density reductions of 0.5 g/cm³ to 1.0 g/cm³ can be achieved. This reduces the material requirement and consequently also the price. In addition, the insulation behavior against heat and cold as well as the floatability can be positively influenced. The floatability is decisive for separation processes in the recycling of materials. In this study, the positive effect of expandable thermoplastic microspheres as blowing agents in LSR will be illustrated.

1 Introduction

In plastics manufacturing, the processing of High Consistency Rubber (HCR) and Liquid Silicone Rubber (LSR) is becoming increasingly important. In medical technology, LSR is given preference over other elastomers because of its good processability and physiological compatibility. In automotive engineering, silicones are often used in the temperature range between -50 °C and +200 °C because of their ideal elastic properties. Another strongly growing market for silicones can be expected in consumer electronics, since they have excellent damping and haptic properties. Silicone rubbers are also popular in sanitary applications (e.g. showers) because they have ideal sealing properties and are easy to remove limescale. Foamed silicone parts are also, or especially, suitable for all the above-mentioned fields of application in order to make components cheaper and lighter. The foam structure also improves compressibility, which can have a particularly positive effect in terms of more uniform surface pressure for sealing applications.

Foamed plastics have been used in many areas for decades. The best known material is foamed polystyrene, also known as Styropor. This is mainly used as insulation and packaging material. Technical plastics, such as polyamide, are also increasingly being foamed and used primarily in automotive engineering. In addition to the weight reduction of the components, the focus here is on a positive effect in injection molding with regard to mold filling and the avoidance of residual stresses. Foamed components for technical applications are mainly produced by injection moulding and extrusion. Examples include instrument panel bases, fan housings, plastic pallets and pipe insulation [1, 2].

Processes for foaming silicone rubbers (here mainly HCR, but also LSR) [3] are the processes of physical and chemical foaming also known from thermoplastics [4]. Chemical foaming requires organic or inorganic compounds that are added to the silicone. Parallel to the vulcanization process, nitrogen or carbon oxides are formed from the additives at higher temperatures, which in turn become free and expand, forming foam structures [5]. A major disadvantage of this method is that degradation during foam production can result in toxic substances that are then released. A difficulty with chemical foaming is the interaction of the vulcanization speed with the expansion behavior of the blowing agent. In physical foaming, gases such as nitrogen or carbon dioxide are added to the thermoplastic melt in the injection moulding unit under high pressure. However, there is also a process in which the granulate is first loaded with gas, usually nitrogen and carbon dioxide, in the autoclave [6]. If the gas-loaded melt is fed into an empty cavity, the pressure drops. The gas expands and forms the pores in the foam. At the beginning of the 2000s, the first experiments with physical foaming processes were also carried out in silicone injection moulding [7]. Negative effects were observed in process control. A reproducible production of components is not yet possible. This resulted in the process not being able to establish itself on the market [8].

The idea of using expandable thermoplastic microspheres to foam silicone rubbers in the injection molding process can help here. The microspheres used consist of a thermoplastic shell filled with a blowing gas (e.g. isopentane). The microspheres are added to the silicone in proportions of up to 5% by weight before processing. When processed in the injection molding process, the microspheres in the mold cavity only expand from approx. 120°C mold temperature onwards. The thermoplastic shell softens and becomes flexible while the gas expands. This creates pores in the silicone elastomer (silicone foam).

2 Experiments

2.1 Production of test specimen

The analysis of the silicone foams is carried out on injection-moulded tensile bars of form S2 according to DIN EN ISO 517-1. A Babypalst injection moulding machine of type 6/10P is used for the production, which is specially adapted to the processing of liquid silicone rubbers and small shot weights. The compact injection moulding machine has a water-tempered injection module with valve gate nozzle and electric mould heating control circuits. The liquid silicone rubber is supplied via a 0.5 I cartridge inserted into the plasticizing module, which contains the basic components A and B of the LSR and the filler, in this case the microspheres, as a mixture. After weighing, the components are mixed using a hand mixer until the microspheres are evenly distributed in the raw material.

The functionality of the dosing and injection process of the injection moulding machine used differs from that of a classic screw injection moulding machine. During dosing, a hydraulic cylinder builds up material pressure in the cartridge. The raw material flows in the direction of the injection piston via a spring-actuated non-return valve and pushes it back to the set dosing position. During the injection process, the LSR is injected at a defined speed and injection pressure via the injection piston into a vacuumed and heated mould cavity, whereby the non-return valve of the dosing unit closes and thus prevents backflow into the cartridge. The cavity of the moulded part is connected to the machine nozzle in the injection mould via a film gate and a runner.

The S2 tension bars are manufactured at a mould temperature of 160 °C and a heating time of 25 s. In order to determine the required dosage volume of the compact component without blowing agent, a filling study was first carried out.

This value represents the reference for the foaming tests. Filling studies are then also carried out for increasing proportions of microspheres in order to achieve the minimum dosing volumes or maximum weight reduction of the foams. To set a defined foam density, the LSR dosing volume for the foamed component is determined as a function of the proportion of microspheres by reducing the reference volume by the proportion of expanded microspheres in the foamed component (in percent). This volume fraction of the pores (expanded microspheres) also represents the weight reduction of the foamed LSR component (**Table 1**). An advantage here is that a defined setting of the foaming degree (ratio of the dosing volumes for the foamed sample to the non-foamed sample) is possible via the dosing volume.

The prerequisite for this is a sufficient proportion of blowing agent so that expansion in the mold leads to complete filling of the molded part cavity, as the expansion capability of the microspheres is limited from a certain point. The foam components were manufactured with different proportions of microspheres in weight percent and different degrees of foaming or dosing volumes, as shown in **Table 1**.

2.2 Analysis of test specimen

To determine the density, the YDK03 density determination kit from Sartorius is used, using demineralized water as the test medium. For samples with a density > 1 g/cm³, the pan hanger assembly is used; for samples with a density < 1 g/cm³, the immersion sieve is used.

The tensile strength is determined in accordance with DIN 53504 on a universal tensile testing machine called Inspekt Table blue from the manufacturer Hegewald & Peschke, Meß- und Prüftechnik GmbH. The machine configuration includes a force transducer for determining the stresses with a maximum force of 500N and a touching long-stroke transducer with the designation MFE 910-SA for determining the strains.

The LFA 467 HyperFlash from Netzsch is used to determine the thermal conductivity. For this purpose, round specimens are punched out of the shoulders of the tensile bar and thinly coated with graphite. The thermal conductivity is measured by heating the underside of the specimen with a light beam and measuring the temperature rise at the top of the specimen with an IR detector. The thermal conductivity is then calculated directly in the software via the thermal conductivity, density and heat capacity.

2.3 Used Materials

The liquid silicone rubber used in this paper is Dow Corning QP1-30 Liquid Silicone Rubber. This is a platinum-catalyzed, two-component, hot-temperature-curing silicone rubber approved for the medical sector. It is characterized by high elongation at break and low Shore hardness.

Tramaco GmbH's expandable thermoplastic microspheres Unicell MS 140 DS were used as blowing agents. These have a low expansion temperature (approx. 90 °C) and a grain size of approx. 20 μ m (unexpanded). Microspheres are hollow spheres whose shells consist of a copolymer of acrylonitrile and methyl methacrylate and are filled with isopentane. In these investigations, percentages between 0.5% and 3.0% by weight of microspheres are used in the non-crosslinked LSR.

3 Results and discussion

The results of this study show the relationships between the set density reduction and the mechanical properties as well as the thermal conductivity. The density of the unfoamed QP1-30 is 1.115 g/cm³ and is reduced by 29 % to 0.796 g/cm³ by using 3 wt.% microspheres (**Fig. 1**). This also corresponds to the degree of foaming.

The expansion of the microspheres reduces the effective cross-sectional area, which also reduces the tensile strength (**Fig. 2**). At a density reduction of 29% (3% by weight microspheres), the tensile strength decreases from 8.5 MPa to 3.4 MPa. This corresponds to a decrease of 60%. If the specific tensile strength (**Fig. 3**), which is calculated from the quotient of the tensile strength and the density, is examined more

closely, a decrease can also be observed. For the foaming degree of 3 wt.% (4.2 N·m/g) the reduction is 45 % compared to the compact LSR (7.6 N·m/g).

The elongation at break also decreases with an increasing proportion of microspheres (**Fig. 4**). This decreases from 742 % for unfoamed QP1-30 to 634 % for 3 % by weight microspheres. This corresponds to a decrease of 15 % and can again be explained by the decrease of the effective interfaces with increasing filler content and the missing adhesion between LSR matrix and microspheres.

The tensile test determines the stress at 100 % elongation. This increases with increasing filler content (**Fig. 5**). Since the shell material of the microspheres has a higher hardness, more force is required to deform the microspheres and to achieve the same elongation.

As shown in **Figure 6**, the thermal conductivity of foamed LSR decreases with increasing proportion of microspheres. The compact material has a thermal conductivity of 0.209 W/m·K. A thermal conductivity of 0.126 W/m·K was determined with 3 wt.% microspheres. This corresponds to a reduction of 40 %.

In the injection molding process, functional components such as plugs can be manufactured continuously. The plugs shown in **Figure 7** is an injection-molded component made of LSR with 2% by weight of microspheres. In the process, the LSR is vulcanized at a low temperature (150 °C), which gives the microspheres a longer time to expand. The density of the produced components is below 1 g/cm³ which makes them floatable. **Figure 7** shows both the plugs and the pore structure in the component.

4 Summary and outlook

The investigations show that lightweight foamed injection moulded parts made of LSR can be produced using the injection moulding process. With the material combination shown here, density reductions of up to 30 % are possible. The mechanical properties such as tensile strength, elongation at break and thermal conductivity decrease as expected. If the characteristic values are considered in relation to density, a decrease can also be seen. The decisive factor for the application is which density reduction is really required. If, for example, a floating component is to be produced, a reduction of approx. 10 % is sufficient and the mechanical characteristic values remain within an acceptable range. Since the price per kg microspheres is similar to the price per kg LSR, material costs can be saved up to 30%.

It will also be shown that functional components such as plugs can be manufactured continuously in the injection moulding process. In the future, dosing capability will be tested via the color line of dosing systems. First tests show a basic practicability. In addition, further products are to be sampled, also for multi-cavity moulds.

5 Literature

[1] Schwachulla, T.: Schäume sind keine Träume, K-Magazin 04 2018.

- [2] Stöcker, M.: Leichte Leere, Scope 07 2012, https://www.scope-online.de/zulieferer/mucell-spritzgussteile/leichte-leere.htm, zuletzt aufgerufen am 4.7.2019
- [3] Häuser, T.: Herstellung von physikalisch geschäumten Flüssigsiliconbauteilen im Spritzgießprozess, Verlagsgruppe Mainz GmbH, Aachen, 2011.
- [4] Gruber, M.: Alt bekannt und doch innovativ, Plastverarbeiter 01 2005.
- [5] Harper, J.R.; Baumann, T.M.; Klempner, D.: Silicone Foams. Handbook of Polymeric Foams and Foam Technology, Hanser-Verlag, München, 1991.
- [6] Gaub, H.: Schäumen mit geringem Faserbruch, Kunststoffe, 02 2016.
- [7] Habibi-Haini, S.; Schlummer, C.; Schmid, R.; Virlogeux, F.: Geschäumtes Flüssigsilicon eröffnet neue Wege, Kunststoffe, 04 2006.
- [8] Sitz, S.: Extrusion physikalisch geschäumter Profile aus Siliconkautschuk, Verlagsgruppe Mainz GmbH, Aachen, 2015.

Tabellen:

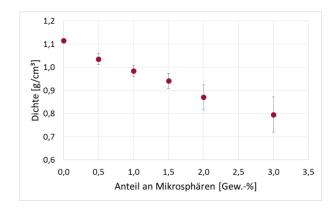
Tab. 1: Degree of foaming investigated as a function of the proportion of microspheres

Proportion of	Dosing volume of LSR	Degree of foamin in %
microspheres wt%	in cm ³	
0	1,67 <mark>(100%)</mark>	0
0,5	1,45 <mark>(87%)</mark>	13
1,0	1,38 <mark>(83%)</mark>	17
1,5	1,32 <mark>(79%)</mark>	21
2,0	1,27	24
3,0	1,19	29

Abbildungen:

Fig. 1: Density as a function of microsphere content.

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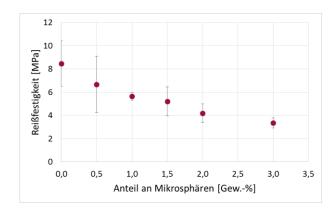


Beschriftung

[g/cm³]: in g/cm³ [Gew.-%]: in Gew.-%

Fig. 2: Tensile strength as a function of microsphere content.

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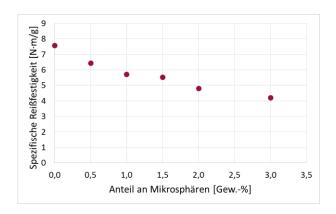


Beschriftung:

[MPa]: in MPa

[Gew.-%]: in Gew.-%

Fig. 3: Specific tensile strength as a function of microsphere content. Aus Datei: mechanische Eigenschaften_GAK.xls

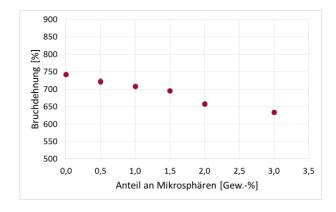


Beschriftung:

[N·m/g]: in N·m/g [Gew.-%]: in Gew.-%

Fig. 4: Elongation at break as a function of microsphere content.

Aus Datei: mechanische Eigenschaften_GAK.xls

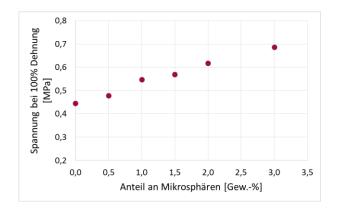


Beschriftung:

[%]: in %

[Gew.-%]: in Gew.-%

Fig. 5: Stress at 100% strain as a function of microsphere content. Aus Datei: mechanische Eigenschaften_GAK.xls

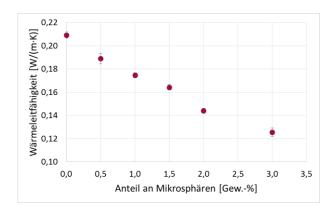


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100%: 100 % [MPa]: in MPa

[Gew.-%]: in Gew.-%

Fig. 6: Thermal conductivity as a function of microsphere content. Aus Datei: Wärmeleitfähigkeit_GAK.xls



Beschriftung:

[W/m·K]: in W/m·K [Gew.-%]: in Gew.-%

Fig. 7: Porestructure of LSR-Foam (left), Plug (right)

Datei: Abbildung7.jpg

