

# Influence of the crosslinking speed and crosslinking type on the foam properties of water-based high consistency silicone rubber foam

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## Abstract

High-consistency rubber is typically processed by extrusion. Due to its excellent properties in terms of flexibility down to low temperatures and wide operating temperature range (-50°C up to 250°C), there are a large number of applications for silicone rubber. Due to the high material costs, foaming HCR makes sense for a large number of applications, such as gaskets, dampers, insulation or similar. In this study high-consistency silicone rubber and the water-based blowing agent were mixed with different crosslinkers in a conical twin-screw mixer and then extruded in order to work out the advantages and disadvantages of different crosslinking systems. In addition to the influence of the blowing agent on the crosslinking behavior, a clear influence of the crosslinker type and quantity on the foam structure was identified.

## Introduction

Products made of silicone rubber have high temperature stability and good chemical resistance. This property is due to the molecular structure of the silicone, which consists of alternating silicon and oxygen bonds, resulting in special organic and inorganic properties. [1, 2]

Silicone rubber is typically processed by compression moulding, injection moulding or extrusion. In the field of high-consistency silicone rubber, the usual processing method is the extrusion process. [3] Peroxides such as (di-(4-methylbenzoyl) peroxides (DMP) or di-(2,4-dichlorobenzoyl) peroxides (DCIBP) are usually used to crosslink the extrudate, which vulcanize without external pressure, as shown in Fig. 1. [4]

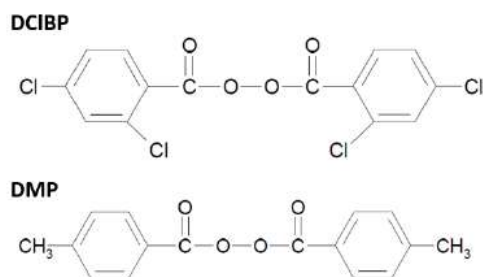


Figure 1: Chemical structure of DCIBP and DMP. [4]

As with other plastics, it is possible to save costs in the area of silicone rubbers by foaming the material. In the field

of high consistency silicone rubbers, both chemical blowing agents (AJBN, ADCA) [5] and physical blowing agents (thermoplastic microspheres, water) [6] can be used.

The problem here is that when chemical blowing agents such as azodicarbonamide (ADCA) are used, carbon monoxide and nitrogen as well as hydrazodicarbonamide and cyanic acid are formed during the decomposition reaction due to the addition of heat [7]. However, these products are problematic when used with addition-crosslinking systems, as they are susceptible to catalyst poisons such as sulphur and nitrogen compounds [8].

In addition to this problem, it is known from the field of natural rubbers that the addition of chemical blowing agents influences the measured shear force when analyzing the crosslinking properties. The reason for this is that the degradation of the blowing agent and the formation of the blowing gases lead to the formation of microcavities, which reduce the shear force compared to a measurement without blowing agent. [9, 10]

## Materials

The high-consistency silicone rubber (HCR) used was Elastosil R 401-40 S and Elastosil R plus 4305/40 from Wacker Chemie AG, which were crosslinked with the crosslinkers or catalysts in table 1. For the peroxide crosslinking 401-40, the peroxides Peroxan PMB (di-(4-methylbenzoyl)peroxide) Di-(2,4-dichlorobenzoyl)-peroxide from Pergan Hilfsstoffe für industrielle Prozesse GmbH and DCLBP-50-PSI Di-(2,4-dichlorobenzoyl)-peroxide from United Initiators were used. Elastosil AUX BATCH PT1 from Wacker Chemie AG was used as a catalyst for the addition-curing rubber 4305/40.

Table 1: Used materials.

Base rubber	Crosslinking type	Amount of crosslinker or catalysator
401-40	peroxide	1 phr PMB
401-40	peroxide	1,5 phr PMB
401-40	peroxide	2 phr PMB
401-40	peroxide	1 phr DCLBP-50-PSI
401-40	peroxide	1,5 phr DCLBP-50-PSI
401-40	peroxide	2 phr DCLBP-50-PSI
4305/40	addition	1,5 phr PT1
4305/40	addition	2 phr PT1

The Elastosil R plus 4305/40 is an addition curing silicone rubber exhibiting good mechanical properties. The Elastosil R 401-40 S has good flexibility and mechanical properties and is suitable for vibration damping, for example. The HCR type is a variant that is preferably crosslinked with peroxide. A water/silica mixture in a ratio of 2:1 served as physical blowing agents. Therefore, a fumed hydrophile silica Aerosil 200 from Evonik Industries AG (Essen, Germany) with a specific surface area of 200 m<sup>2</sup>/g was used.

## Experimental

### Production of stripes

For the compounding of the HCR, a twin-screw internal mixer (CTM-25) from COLMEC SPA was used, which can mix 1.5 kg per batch. The batch consists of three components: rubber, a crosslinker, and the blowing agent. The mixing time for each was 30 min; see Figure 2. The mixing process is divided into three stages. First, the rubber is masticated, which aims to homogenize the material thermally and mechanically. In the second step, the blowing agent is incorporated into the rubber during filler incorporation. After the mixing process, the material was discharged in strips for further processing on the extruder.

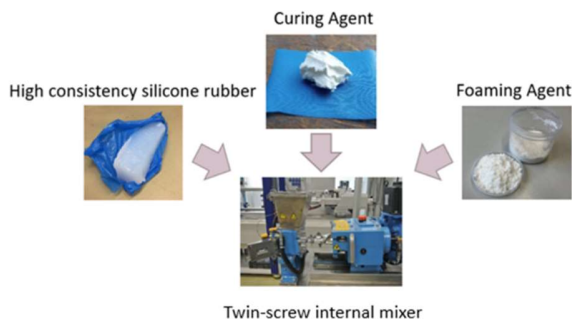


Figure 2. Compounding of HCR in a twin-screw internal mixer with a curing agent, foaming agent, and high-consistency silicone rubber.

In the next step after the compounding the material was extruded into stripes with a length of 40 mm and a thickness of 2 mm. For this a silicone extruder from Rubicon Gummitechnik und Maschinenbau GmbH was used with an infrared unit for the vulcanization. The temperature of the extrudate at the end of the infrared tunnel was set to a temperature of 180±5°C for this purpose. The thermal energy required for vulcanization was generated by the absorbed IR radiation, which excites the polar molecules to vibrate and thus generates heat. [11]

### Characterization of the compounds

The first step was to investigate the properties of the rubbers and compounds used. For this purpose, the crosslinking behavior of the compounds was examined in order to assess the influence of the blowing agent on the type and quantity of crosslinker. A Rubber Process Analyzer (RPA) from Montech was used to determine the vulcanization properties at 180°C for 3 min with an angle of 1° and a frequency of 1.67 Hz.

### Density

The density of the foamed HCR was determined using an electronic balance and the YDK04 density determination set from Sartorius. The liquid used was demineralized water.

### Hardness

The micro Shore A hardness was measured using an automatic testing machine from Bareiss Prüfgeräte GmbH/Germany.

### Scanning Electron Microscopy (SEM)

The microscopic analysis of the pore structure of the foam was carried out using the CamScan MV 3200 scanning electron microscope from Electron Optic Services, Inc./Canada.

## Results and Discussion

In the following the results of the vulcanization measurement, the mechanical and physical parameters, and the foam morphology are presented and discussed.

### Characterization of the compounds

When investigating the crosslinking behavior, an increase in the determined torque with increasing peroxide content was observed for both peroxides tested, as shown in Figure 3 as an example for the peroxide PMB. It was also observed that the addition of the blowing agent leads to an increase in the determined torque and slightly increases the crosslinking speed. Similar to Najib's [10] investigations into chemical blowing agents, this is caused by the formation of microcavities, as the gases produced by both blowing agents cause the rubbers to foam.

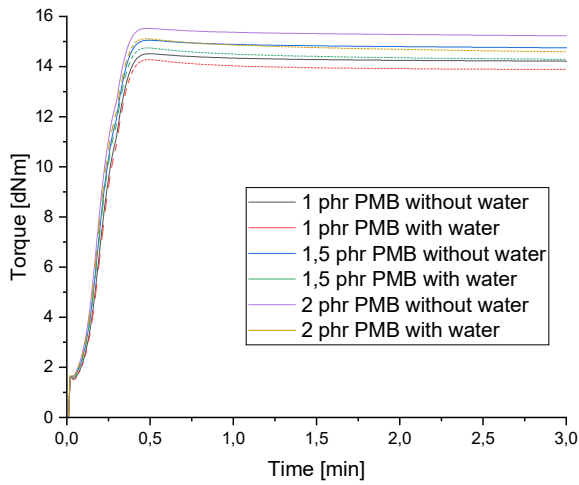


Figure 3: Influence of the foaming agent on the vulcanization properties of PMB.

Another aspect that becomes clear when analyzing the crosslinking, as can be seen in Figure 4, is that the type of crosslinking (peroxide or addition crosslinking) has a significant influence on the crosslinking. When comparing peroxide crosslinking and addition crosslinking, it becomes clear that the addition of the blowing agent influences the torque or the formation of pores to different degrees. With the same crosslinking speed, there is a significantly greater reduction in torque with addition crosslinking, as shown in Figure 4. Furthermore, the peroxide DCLBP crosslinks faster than PMB, as can be seen in the graph.

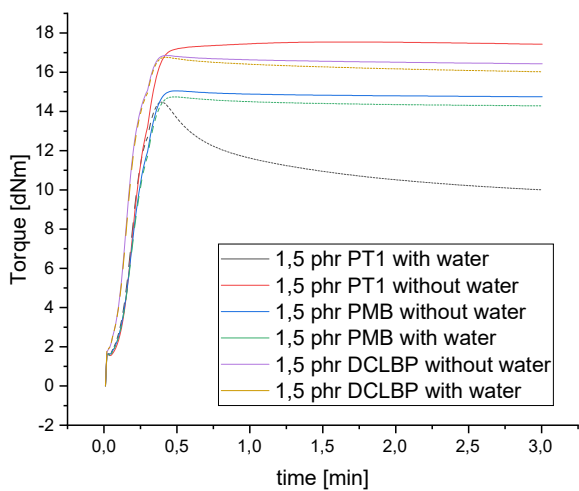


Figure 4: Influence of the foaming agent by different crosslinking systems.

### Density

When evaluating the density, it can be seen that the slower cross-linking of the PMB peroxide produces a lower density than the DCLBP at the same quantity. For both peroxides, an increase in the peroxide content and the associated faster reaction, as determined in the RPA measurements, leads to a decrease in the density produced. Compared to the peroxides, addition crosslinking results in a significantly lower density at the same crosslinking speed. In addition, an increase in the crosslinking speed leads to a higher density.

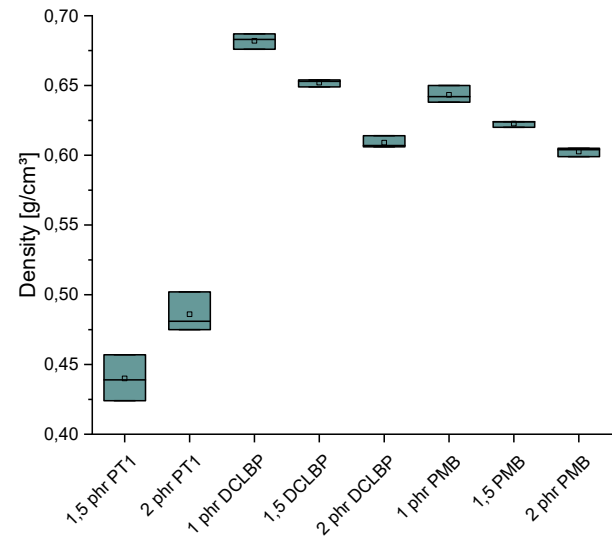


Figure 5: Comparison of the density of the different crosslinkers.

### Hardness

As shown in Figure 6, there is an increase in the hardness of the peroxides as the proportion increases, although there is a decrease in the determined density as described above. However, since an increase in the torque was also determined in the RPA measurements, only the cross-linking density may have increased and thus ultimately lead to an increase in hardness. In the addition-curing systems, an increase in the catalyst also leads to an increase in hardness. However, the overall hardness values are below or at the lower limit compared to the peroxides.

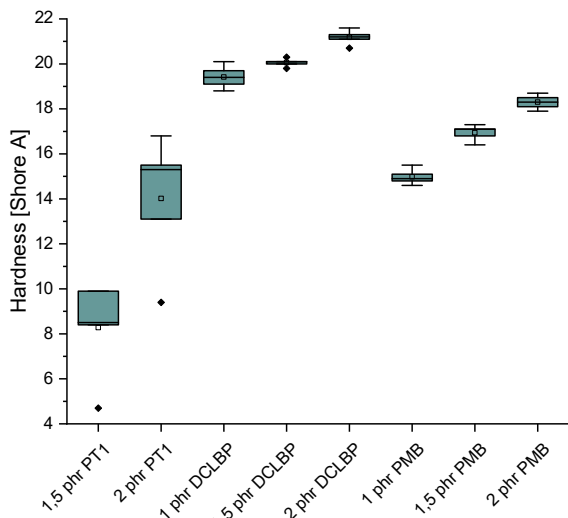


Figure 6: Comparison of the shore A hardness of the different crosslinker.

#### Scanning Electron Microscopy (SEM)

The evaluation of the SEM confirms the previous findings from the preceding analysis methods. As shown in Figure 7, the faster reaction of the DCLBP results in finer pores than the slower crosslinking with PMB as shown in Figure 8. The faster crosslinking associated with increasing peroxide content also leads to additional formation of smaller pores, which explains the decrease in density with increasing peroxide content.

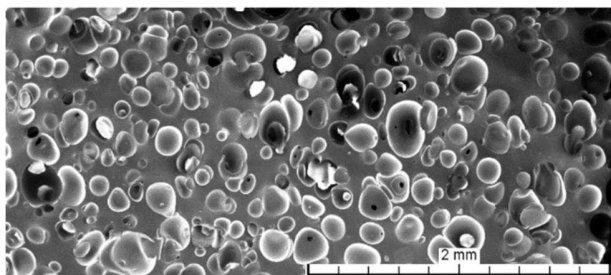


Figure 7: SEM picture of 2 phr DCLBP crosslinker.

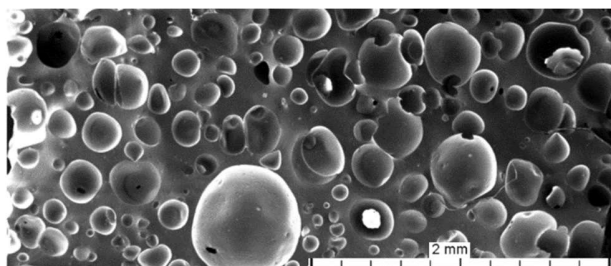


Figure 8: SEM picture of 2 phr PMB crosslinker.

Compared to peroxide crosslinking, addition crosslinking produces significantly larger pores, as shown in Figure 9,

which explains why it results in a significantly lower density.

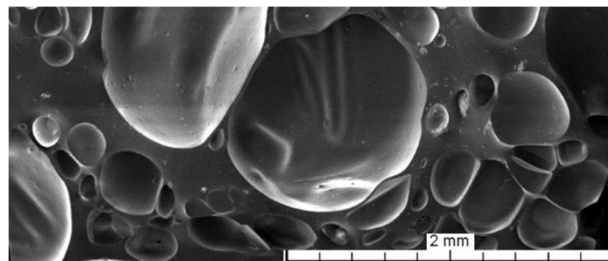


Figure 9: SEM picture of 1,5 phr PT1.

#### Conclusion

In summary, it was found that the amount and type of crosslinking system has a significant influence on the resulting mechanical properties and foam morphology and that the water/silica mixture used leads to a change in the maximum torque in the RPA. The slower peroxide crosslinker PMB leads to larger pores and lower density compared to DCLBP. An increase in the peroxide content, on the other hand, causes the formation of additional smaller pores, which leads to a reduction in density. A comparison of the two crosslinking systems also shows that addition crosslinking produces larger pores and lower density and hardness at the same crosslinking speed than peroxide crosslinking.

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