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Mechanical Properties of Polydimethylsiloxane as a Function of the Amount and Type of Crosslinking Agent

In this investigation, a high-consistency rubber (HCR) was mixed with five different, typically used crosslinking agents that are based on organic peroxide. Furthermore, the amount of crosslinking agent was varied in order to quantify the effect on the mechanical properties. All materials were processed in a hot pressing process, and, subsequently, post-cured. The properties were characterized by the measurement of the swelling ratio, shore A-hardness, rebound resilience and tensile test. We successfully proved that the swelling ratio is a suitable indicator for the evaluation of the crosslinking density of silicone rubber. The results show that the crosslinking density increases as the amount of crosslinking agent increases. The hardness, rebound resilience, and stress at 100 % elongation increase as the crosslinking agent does. In contrast, the ultimate elongation decreases as the crosslinking density rises. The absolute values depend on the type of crosslinking agent used. The most commonly used crosslinking agent for high-consistency rubber is Di(2.4-dichlorobenzoyl) peroxide. We were able to verify that there are more possible curing agents based on organic peroxides on the market. Depending on the required properties, customized silicone elastomers could be easily produced.

1 Introduction

Silicone rubber has a unique molecular structure, which consists of alternate silicone and oxygen bonds. This special structure creates organic and inorganic properties, and is responsible for the excellent heat resistance, chemical resistance and flexibility properties that can withstand a wide range of temperatures (Heiner et al., 2003; Baquey et al., 2005b; Shit and Shah, 2013; Lopez et al., 2007). This great range of properties makes silicone rubber well-suited for applications in the field of automotive industry, or in the pharmaceutical industry (Shit and Shah, 2013; Lopez et al., 2007; Bayer AG, 1989). Silicone

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elastomers are made of crosslinked polydimethylsiloxane (PDMS). The process of curing transfers the raw PDMS to an elastomeric three dimensional network (Heiner et al., 2003; Lopez et al., 2007).

The types of heat cured silicone rubbers are differentiated into liquid silicone rubber (LSR) and high-consistency rubber (HCR). The biggest difference lies within the length of the molecular chain and the resulting viscosity of the entire material in the one case, and the type of curing reaction in the other (Bayer AG, 1989; Röthemeyer and Sommer, 2013). LSR has shorter molecule chains, and, because of this, displays a significantly lower viscosity, making this material well-suited for injection molding. LSR is a two-component system, and is usually cured in an additional curing process with the help of a platinum complex (Heiner et al.; 2003; Shit and Shah, 2013). In contrast to that, HCR has longer molecule chains and is usually cured using organic peroxides (Heiner et al.; 2003; Noll, 1968). Moreover, HCR is mainly processed during extrusion or pressing. The typical recipe of a heat-cured, high-consistency rubber is 100 phr (parts per hundred rubber) silicone rubber, 20 to 200 phr filler/additives, and 0.5 to 3.0 phr curing agent (Lopez et al., 2007; Röthemeyer and Sommer, 2013; Noll, 1968).

The organic peroxides are classified in vinyl group specific peroxides (I) and vinyl group non-specific peroxides (II) (Baquey et al. 2005a, 2005b). The first class is not able to crosslink PDMS, which has no vinyl groups, while the second one is able to crosslink every type of PDMS (Baquey et al., 2005a, 2005b). The following groups of peroxides are available: diaroylperoxide (I), dialkyl peroxide (II), Diaralkylperoxide (II), Alkylaroyl- (II) and Alkylaylperoxide (II), or mixtures of different groups (Bayer AG, 1989). The most commonly used peroxide is Di(2,4-dichlorobenzoyl) peroxide, which belongs to the group of Diaroylperoxides (Baquey et al., 2005a).

Besides the type of PDMS which could be crosslinked, the main differences between the peroxides are their optimal processing temperatures and their curing rates. Heat causes the peroxide to degrade into free radicals, and, in turn, these radicals eliminate hydrogen atoms from the side groups of the PDMS and form chemical bonds to the backbone of the silicone rubber (Noll, 1968). The mechanism of the radical reaction during curing is shown in (Baquey, 2005b; Lopez et al., 2007). The vulcanisation causes the development of cleavage products, which should be removed before usage by a post-cur-

ing process, e. g. at 200 °C for 4 h (Lopez et al., 2007; Bayer AG, 1989; Wacker Chemie AG, 2015).

It is well known that in addition to the type of crosslinking agent the amount of curing agent has a fundamental influence on the processing conditions and on the properties of the silicone rubber (Noll, 1968). The processing parameters are influenced by the optimal operating temperature of the employed peroxide. Thermal degradation does not occur below this temperature, and, as a result, no crosslinking reaction takes place. The degree of crosslinking is proportional to the concentration of crosslinking agent (Röthemeyer and Sommer, 2013). The crosslinking density increases in correlation with the increasing crosslinking agent concentration (Dunham et al., 1957; Vennemann et al., 2006). The degree of crosslinking affects the hardness, ultimate level of elongation, and other properties, like the tear strength (Röthemeyer and Sommer, 2013; Vennemann et al.; 2006). The level of hardness increases with the rising amount of peroxide (Bayer AG, 1989). Compared to the technical data sheet from Dow Corning (2009), the ultimate level of elongation is determined by the type of crosslinking agent. Camenzind et al. (2010) found out that the swelling ratio of unfilled PDMS in Toluene decreased as the crosslinking agent amount increased.

The influence of a crosslinking agent based on organic peroxide and its influence on the properties of the silicone elastomer has not been analysed in depth yet. Furthermore, a range of amounts is provided in the data of the material producer, but no statement is made about the influence of additional crosslinking agent on the silicone elastomer.

In this investigation, a high-consistency rubber was mixed with five different, typically used crosslinking agents that are based on organic peroxide. Furthermore, the amount of crosslinking agent was varied in order to quantify the effect on the mechanical properties. After mixing, all batches were run through a curing press. Then, after processing, all sheets were post-cured for 4 h at 200 °C to remove the cleavage products which occurred during the radical reaction. Subsequently, the specimens were stamped out. Their properties were characterized by the measurements of the swelling ratio, shore A-hardness, rebound resilience, and tensile test.

The goal of this investigation is to understand and clarify the influence of different crosslinking agents on the chosen properties of the silicone rubber. Furthermore, we aim to show that the amount of crosslinking agent has a significant influence on the crosslinking density, and, accordingly, also on the properties of the silicone elastomer. With this knowledge, producers will be able to select a suitable crosslinking agent and amount to obtain the required properties. These customized products could reduce costs by minimizing the amount of crosslinking agent employed.

2 Experimental

2.1 Materials

In this study, the base polymer is a Xiameter RBB-2100-60 Base from Dow Corning, Wiesbaden, Germany. This translucent polymer has a density of 1.17 g/cm³. The Shore A hardness is approximately 61. The tensile strength amounts to 11 MPa, and the elongation at break is approximately 400 %. The manufacturer recommends application in the field of e. g. extrusion and molding (Dow Corning GmbH, 2009).

Five different types of crosslinking agents were used. All these types were manufactured by the Akzo Nobel GmbH, Amsterdam, The Netherlands), and were used for crosslinking silicone rubber. All crosslinking agents were dispersed in silicone oil and delivered as a paste in order to enable them to be measured out easily (Akzo Nobel, 2015).

The following table summarizes the most important properties of the crosslinking agents.

2.2 Preparation

All materials were mixed using a conical twin mixer from Colmec S.p.A., Busto Arsizio, Italy, after mixing the different batches were press-cured for five minutes (2 mm sheets) and ten minutes (4 mm sheets) at the specific curing temperature (Table 1). After processing, the specimen in form of plates

Crosslinking agent	Chemical formula	Appearance	Curing temperature °C	Molecular weight g/mol	Density g/cm³	Recommended amount phr
Perkadox PD-50S-PS	Di(2,4-dichloro-benzoyl) peroxide	off-white	90	380.0	1.18	1.1 – 2.3
Perkdaox PM-50S-PS	Di(4-methylbenzoyl) peroxide	white-yellow	105	270.3	1.22	1.1 – 2.3
Perkadox L-50S-PS	Dibenzoylperoxide	white	105	242.2	1.12	0.7 – 1.4
Perkadox BC-40S-PS	Dicumyl peroxide	white	175	270.4	no data	no data
Trigonox 101 – 45S-PS	2,5-Dimethyl-2,5-di(tert-butylperoxy)-hexane	transparent	175	290.4	no data	no data

Table 1. Selected properties of the different crosslinking agents (Akzo Nobel, 2015)

$(160 \times 160$ mm) were post-cured at 200 °C for 4 h. Subsequently, they were punched out to form sample specimen: the tension bar S 2 with a thickness of approximately 2 mm according to DIN 53504 and the puck geometry according to DIN 815 part 1 $(29 \times 4$ mm). Figure 1 shows the employed specimens.

Table 2 provides the recipes of the different batches. The amount of crosslinking agent was chosen in a manner that resulted in the same amount of peroxide in each batch. Batch 4 had only 40 % peroxide in the paste, and batch 5 had 45 % peroxide. Owing to this, the entire amount of crosslinking agent was raised to the values shown in Table 2.

2.3 Characterisation

All specimens were characterised in a standard atmosphere (23 °C and 50 % air humidity). The mechanical testing was realised after post-curing at 200 °C for 4 h in an oven (Memmert, Schwabach, Germany), model: UF75plus. Only the specimens for testing the swelling ratio were simply press-cured and not post-cured.

2.3.1 Swelling Ratio

The swelling ratio, which is an indicator used to evaluate the crosslinking level, was measured as is described by Mostafa et al. (2009). The specimens were weighed before and after storage in toluene for 24 h at room temperature (by an analytical scale made by Sartorius, model: A200S and has a standard deviation of ± 0.0001 g). The swelling ratio was defined as:

$$Q_\% = \frac{(M_t - M_0)}{M_0} \times 100, \tag{1}$$

where $Q_\%$ = swelling ratio, M_t = mass after storage, M_0 = mass before storage. After storage in toluene, all specimens were dried for 24 h at 80 °C in an oven (UT 12 P, Heraeus Instruments, Hanau, Germany). They were then weighed again. Two specimens were used per batch in order to characterise the swelling ratio of every batch.

2.3.2 Hardness

The Shore A-hardness was tested with an automatic testing machine produced by Bareiss Prüfgeräte GmbH, Oberdischingen, Germany, according to DIN ISO 716 part 1. Two pucks were stacked in order to achieve the required height. The hardness was measured at five different points of the two puck specimen.
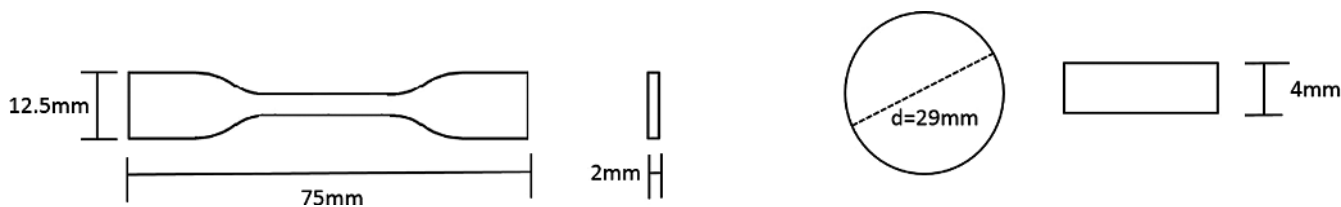

Fig. 1. Geometry of the employed specimen according to DIN 53504 (left – tensile bar S 2) and DIN 815 part 1 (right – puck)

Current number	Base polymer	Crosslinking agent	Base polymer phr	Crosslinking agent phr
1a	Xiameter 2100-60	Perkadox PD-50S-PS	100	0.50
1b	Xiameter 2100-60	Perkadox PD-50S-PS	100	1.00
1c	Xiameter 2100-60	Perkadox PD-50S-PS	100	1.50
2a	Xiameter 2100-60	Perkdaox PM-50S-PS	100	0.50
2b	Xiameter 2100-60	Perkdaox PM-50S-PS	100	1.00
2c	Xiameter 2100-60	Perkdaox PM-50S-PS	100	1.50
3a	Xiameter 2100-60	Perkadox L-50S-PS	100	0.50
3b	Xiameter 2100-60	Perkadox L-50S-PS	100	1.00
3c	Xiameter 2100-60	Perkadox L-50S-PS	100	1.50
4a	Xiameter 2100-60	Perkadox BC-40S-PS	100	0.63
4b	Xiameter 2100-60	Perkadox BC-40S-PS	100	1.25
4c	Xiameter 2100-60	Perkadox BC-40S-PS	100	1.88
5a	Xiameter 2100-60	Trigonox 101-45S-PS	100	0.56
5b	Xiameter 2100-60	Trigonox 101-45S-PS	100	1.11
5c	Xiameter 2100-60	Trigonox 101-45S-PS	100	1.67

Table 2. Recipes of the produced batches

2.3.4 Rebound Resilience

In accordance with DIN 53512, the rebound resilience was measured with an automatic testing machine from Bareiss Prüfgeräte GmbH, Oberdischingen, Germany. Three pucks were stacked in order to achieve the required height of approx. 12 mm. Three specimens were tested for each batch.

2.3.5 Tensile Test

The tensile test carried out according to DIN 53504 employed a universal testing machine from Hegewald & Peschke Meß- und Prüftechnik GmbH, Nossen, Germany. The testing speed was 200 mm/min and used a typical damping distance of 20 mm. Five different specimens were used for every batch.

3 Results and Discussion

3.1 Outward Appearance

All specimens were investigated after processing and post-curing. The colours of all specimens were compared with the data of the material producer. The appearance of the raw crosslinking agent had a significant influence on the later appearance of the specimens. All specimens except batch 3 displayed a very similar colour after processing. Only batch 3 displayed yellow discoloration. Once the post-curing process was completed, all specimens were discoloured. An increase of this effect was observed as the amount of crosslinking agent increased.

3.2 Swelling Ratio

Figure 2 shows the results of the swelling ratio. As the amount of crosslinking agent rises, the swelling ratio decreases to a lower level. This indicates a higher level of crosslinking density compared to Vennemann et al. (2006) and Vieyres et al.
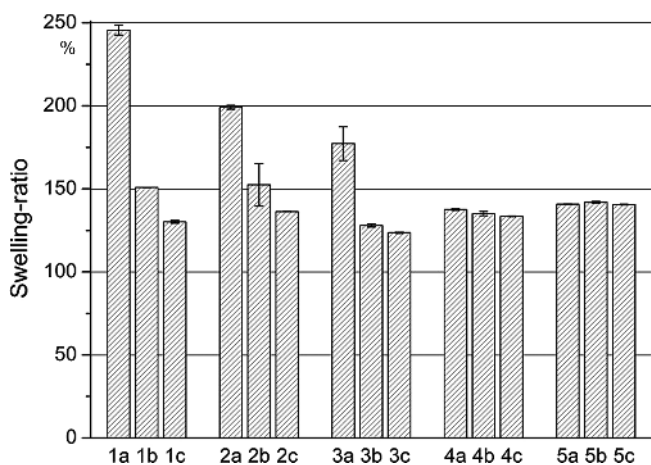
(2013). The results are divided into two groups: batches 1 to 3 and 4 and 5. The first stage (between a and b) is much larger in comparison to b and c for the batches 1 to 3. As a function of the type of crosslinking agent, the swelling ratio decreases from max. 250 % (1a) to 130 % (1c). Batches 4 and 5 show comparable values for the swelling ratio, and only display small differences concerning the differing amounts of crosslinking agent.

Once the storage in toluene was completed, all specimens were dried for 24 h at 80 °C in an oven. All specimens nearly achieved their initial weight. This is an indicator that the silicone rubber had fully cured. Uncured components are flushed out of the specimen, and, in turn, this changes the weight.

The recommended processing parameters in terms of the curing temperature (see Table 1) form with rising curing agent a rising number of crosslinking points and in consequence of that an increasing crosslinking density. The toluene is not able to go through the molecule chains, and cause the material to swell. As a result, a smaller swelling ratio is the outcome for batches 1 to 3. Batches 4 and 5 achieve nearly the same swelling ratio, which indicates a comparable level of crosslinking density.

3.3 Shore A Hardness

Figure 3 shows the results of the hardness measurement. As the amount of crosslinking agent increased, the Shore A-hardness of the batches 1, 2 and 3 increased from 43 Shore A (1a) to 64 Shore A (3c). Batches 4 and 5 showed no significant difference in their Shore A-hardness. All batches except for 1a, 1b, 2a and 3a possessed a similar level of hardness, which equalled approximately 61 Shore A (similar to the base polymer (Dow Corning GmbH, 2009)). Depending on the type and amount of crosslinking agent, the hardness increases by approx. 138 % (1a to 1c).

According to Bayer AG (1989), Röthemeyer and Sommer (2013) and Vennemann et al. (2009), the crosslinking density has an influence on the hardness. Compared to the results of the swelling ratio, batches 4 and 5 show similar results in regards to their hardness. Batch 1a shows the smallest value in
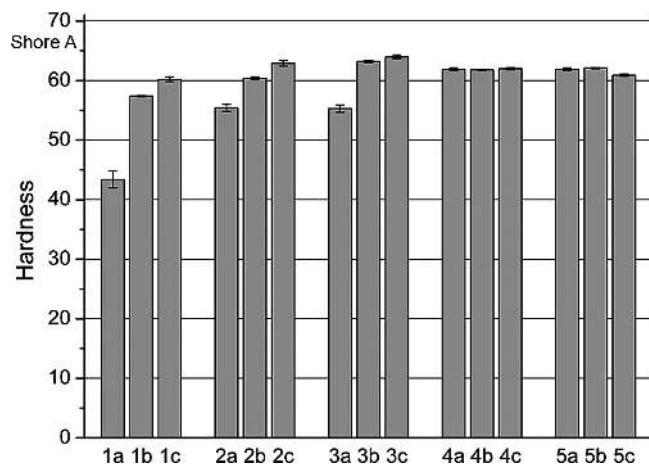

Fig. 2. Swelling ratios of the different batches

Fig. 3. Shore A hardness measured with an automatic testing machine

terms of hardness, and, as a result of that, the highest values in terms of its swelling ratio. The amount of crosslinking agent was smaller in comparison to the recommended amount made by the material producer (Akzo Nobel, 2015). The hardness was directly influenced by the crosslinking density.

3.4 Rebound Resilience

The results of the rebound resilience test showed similar results as the Shore A hardness (Fig. 4). The results were also divided into two groups. Batches 1 to 3 show similar behavior and batches 4 and 5 have similar results. Batches 1 to 3 displayed an increase in the rebound resilience from approx. 32 % to 50 % with the rising amount of crosslinking agent. The lowest values were again achieved by batch 1a. The second group (4 and 5) displayed a slight decrease of the rebound resilience by approx. 1 % as amount of crosslinking agent rose. The standard deviation of all specimens was on a low level (< 1 %).

The results show that the elasticity of the specimens is influenced by the type and the amount of crosslinking agent used. Depending on the crosslinking agent, the elasticity shows an increase in the values. Only Dicumyl peroxide (batch 4) and 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (batch 5) have no significant influence on the rebound resilience.

3.5 Tensile Test

The results of the tensile test were divided into the level of stress at 100 % elongation and the ultimate elongation (Fig. 5). There are no results for the batches 1a and 3a. The added amount of crosslinking agent (0.5 phr) was lower than the amount recommended by the material producer (compared to Akzo Nobel (2014)). According to that, there was no sufficient level of vulcanisation for the plates with a thickness of 2 mm. As a result, the plates could not be demolded and tested.

In the case of batches 1, 2, 3 and 5, the ultimate elongation decreases as the amount of crosslinking agent increases. In contrast to the technical data from the producer, the ultimate elongation is lower (Dow Corning GmbH, 2009). Batch 4 showed an increase between the steps a and b, and, after that, a small decrease. As the crosslinking agent amount increased, so did the number of chemical bonds, and, in turn, the ultimate elongation became smaller (Röthemeyer and Sommer, 2013; Vennemann et al., 2006). All specimens achieved higher values in terms of their ultimate elongation in comparison to the technical data sheet provided by the manufacturer (more than 400 % with Di(2.4-dichlorobenzoyl) peroxide compared to batch 1 and more than 500 % with 2.5-Dimethyl-2.5-di(tert-butylperoxy)hexane compared to batch 5). The standard deviation of 2c was much larger in contrast to all other batches.

The level of stress at 100 % elongation displayed a similar tendency for all batches (Fig. 6). With the rising amount of crosslinking agent, the stress increases similar to Vennemann et al. (2009) and Vieyres et al. (2013). Depending on the type of agent, the increase has different levels. The highest levels of stress are achieved with Dibenzoyl peroxide (batch 2c) and 1.5 phr (2.15 MPa).
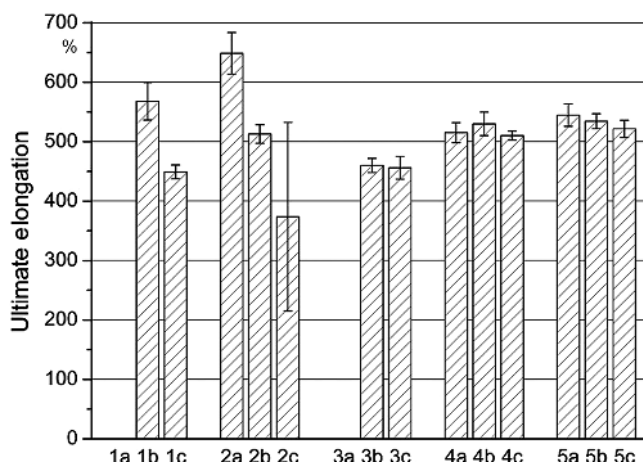

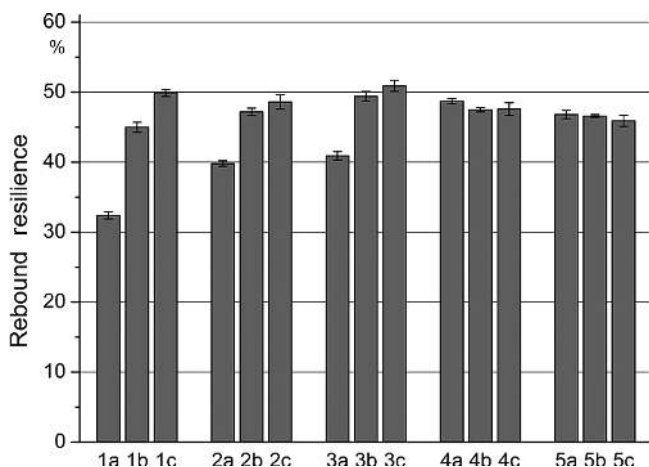Fig. 5. Ultimate Elongation of all batches except for 1a and 3a

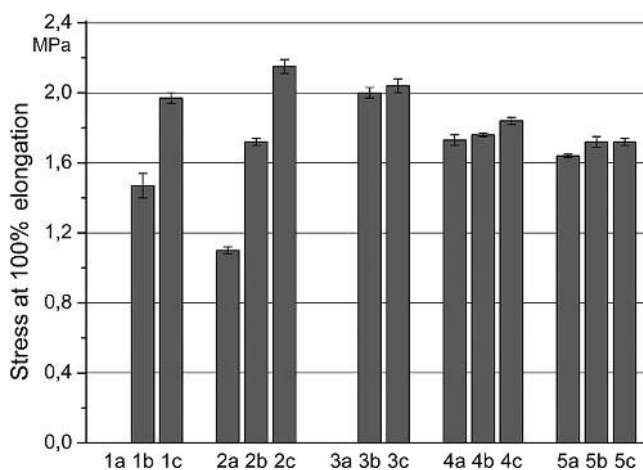Fig. 4. Rebound Resilience of all batches

Fig. 6. Stress at 100 % elongation (except for 1a and 3a)

4 Summary and Conclusion

In this investigation, a high-consistency rubber was mixed with five different types of crosslinking agent. The amount of crosslinking agent was also varied. All specimens were press-cured according to the thickness of the sheets, and post-cured for 4 h at 200 °C.

Their outward appearances were similar to the data from the material producer, except batch 3, which displayed a visible yellow discolouration. The post-curing process magnified the effect of discolouration for every batch.

The swelling ratio, which is an indicator for the crosslinking density, showed the same effect for Di(2.4-dichlorobenzoyl) peroxide, Di(4-methylbenzoyl) peroxide and Dibenzoyl peroxide (batch 1 to 3). As the amount of crosslinking agent increased, the swelling ratio decreased. Batches 4 and 5 (Dicumyl peroxide and 2.5-Dimethyl-2.5-di(tert-butylperoxy)hexane) have the same swelling ratio regardless of the amount of crosslinking agent. The crosslinking density is an indicator of the swelling ratio, and increased with the rising amount of crosslinking agent.

The results for the hardness were comparable to those obtained for the swelling ratio respectively to the crosslinking density. As the crosslinking density increases, the silicone rubber becomes harder. A difference in hardness does not occur if the swelling ratio is on a similar level.

The results of the rebound resilience showed nearly the same tendency: As crosslinking density rose, the batches became more elastic. The rebound resilience increased from 32 % to 50 % (batch 1). Batches 4 and 5, which displayed similar values in terms of their crosslinking density, both had the same rebound resilience of approximately 47 %.

The results of the tensile test showed that the level of stress at 100 % elongation rose in correlation with the rising amount of peroxide. Hence, the ultimate elongation decreased. The absolute values depend on the type of crosslinking agent used.

We were able to show that the amount of crosslinking agent has a significant influence on the mechanical properties depending on the type of crosslinking agent employed. The results obtained for the swelling ratio, hardness and rebound resilience show nearly the same tendency, and confirmed general statements (Bayer AG, 1989; Röthemeyer and Sommer, 2013; Noll, 1968; Dunham et al., 1957; Vennemann et al., 2006) that claimed that the properties would increase in correlation with the rising crosslinking density. Depending on the agent, the absolute values spread.

This study verifies the effect of a curing agent on the mechanical properties of the rubber. High-consistency rubber could be crosslinked with a large number of curing agents based on organic peroxides. Depending on the required properties, customized silicone rubber could be produced.

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