Silfit Z 91 in silicone rubber

Alternative to Quartz Flour

Authorship: Nicole Holzmayr
Hubert Oggermüller

VM-0/07.2018/06164980

HOFFMANN MINERAL GmbH • Muenchener Strasse 75 • D-86633 Neuburg (Donau) • Phone +49 (0) 8431 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

Contents

1 Introduction

Some silicone rubber compounds require a filler loading of 25 to 75 phr. In most cases, the meanwhile well-known Aktisil Q from Hoffmann Mineral is the product of choice. Compounds loaded with this surface-treated filler offer extremely low compression set as well as outstanding oil resistance.

For compounds with low requirements, frequently the use of non-surface-treated quartz flour is sufficient, which means from a technical point of view working with Aktisil Q is not necessary.

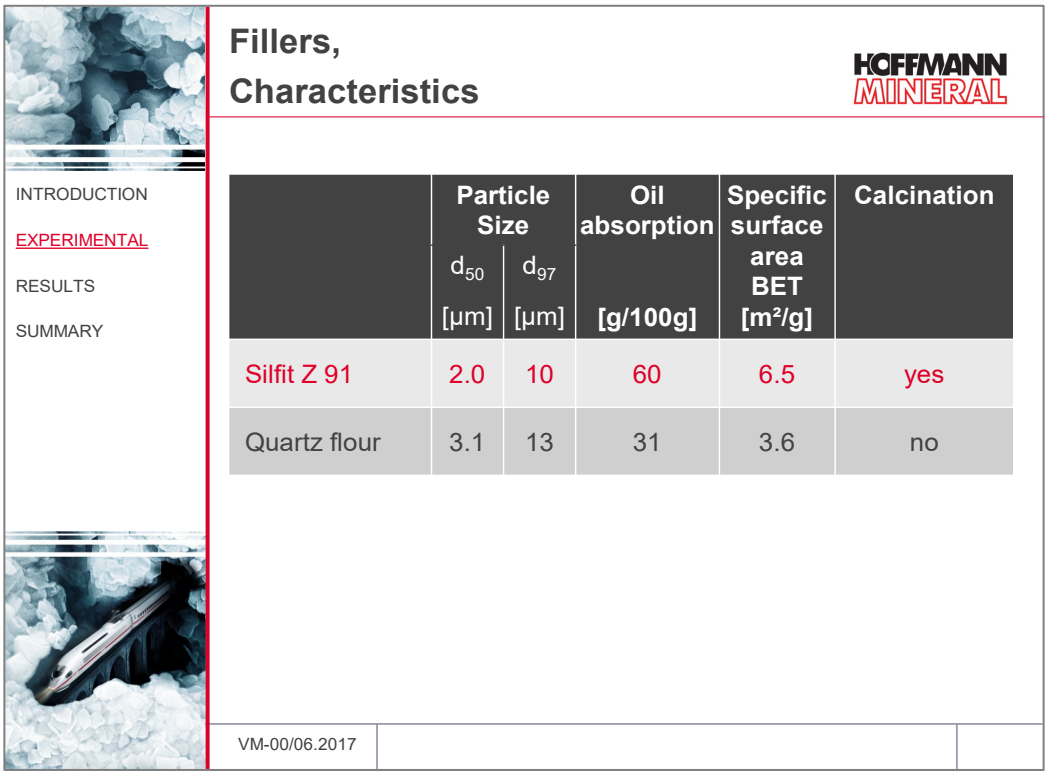
With the Calcined Neuburg Siliceous Earth Silfit Z 91 Hoffmann Mineral is now in a position to suggest an alternative to untreated quartz flour which is more cost effective than Aktisil Q and offers several advantages vs. quartz flour.

The objective of the present study is to demonstrate the benefits of the Calcined Neuburg Siliceous Earth Silfit Z 91 when compared with the traditionally used un-treated quartz flour in silicone rubber with respect to wear and safety & occupational health, mechanical properties, extrusion properties, blooming and color.

Two different peroxides will be used in order to show the property profile of Silfit Z 91 in a compound for molded parts as well as in a formulation for extrusions.

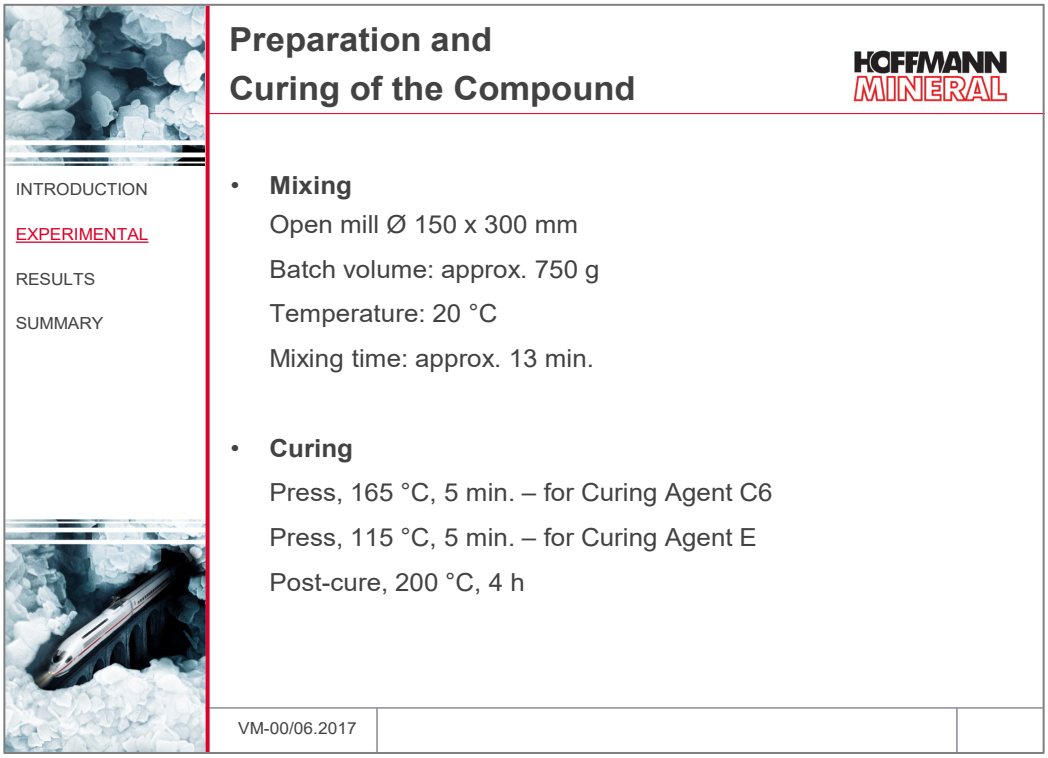
2 Experimental

2.1 Fillers and compound preparation



	Particle Size		Oil absorption	Specific surface area BET	Calcination
	d_{50} [µm]	d_{97} [µm]	[g/100g]	[m²/g]	
Silfit Z 91	2.0	10	60	6.5	yes
Quartz flour	3.1	13	31	3.6	no

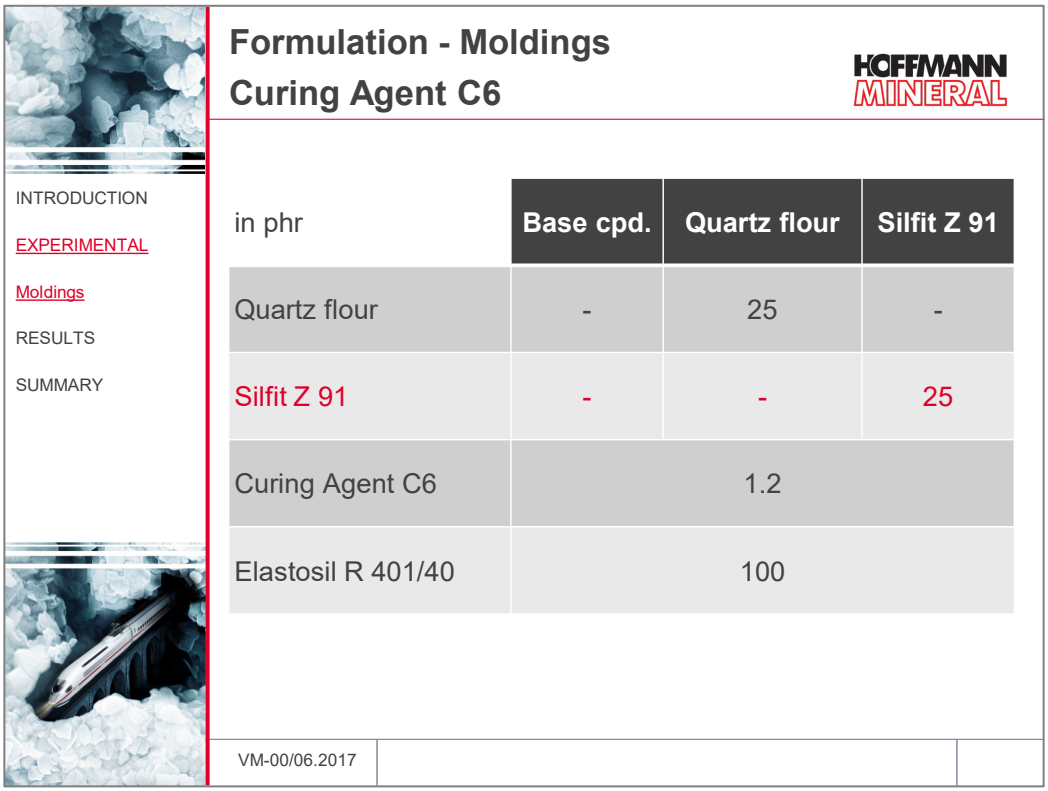
The calcined Silfit Z 91 has a higher fineness than the non calcined quartz flour. The oil absorption number, as well as the BET specific surface area, is about twice as high compared with the quartz flour.



Compounding was done on a laboratory mill (Schwabenthan Polymix 150 L). The rubber was fed to the mill at 20 °C and milled to a homogenous sheet. After the filler was incorporated, the paste-like peroxide was spread onto the sheet with a spatula. A typical mixing cycle time was 13 min. Press-cure was carried out 5 min. at 165 °C with Curing Agent C6 resp. 115 °C with Curing Agent E. Post-curing was done 4 hours at 200 °C.

3 Results – Molding compound

3.1 Formulation



Elastosil R 401/40: silicone rubber, hardness: 40 Shore A

Curing Agent C6: 2,5-Bis-(t-butylperoxy)-2,5-dimethylhexane (45 %)

The polymer chosen was a silicone rubber base compound for an initial hardness of 40 Shore A, which has served already as a starting point for many studies at Hoffmann Mineral.

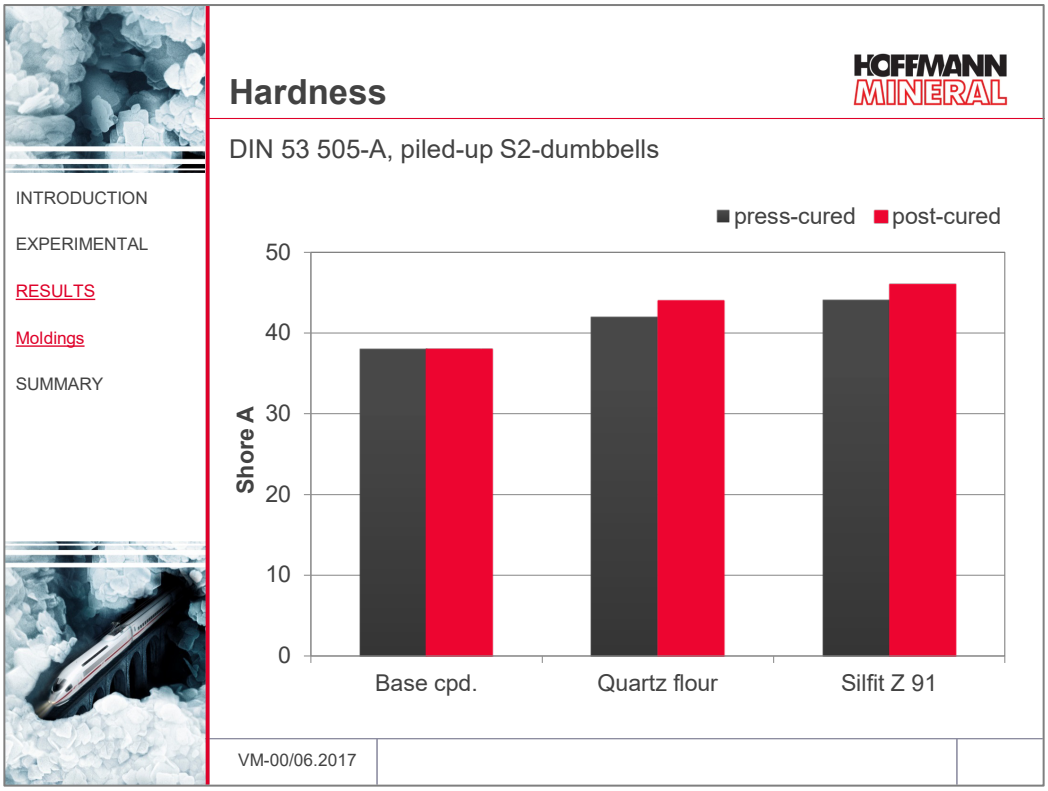
2,5-Bis-(t-butylperoxy)-2,5-dimethylhexane (Curing Agent C6) is typically used in compounds for molded articles.

Frequently, for molded parts only rather low filler loadings of the order of 25 phr are used. For this reason, in the present study, Silfit Z 91 and quartz flour are compared at a level of 25 phr.

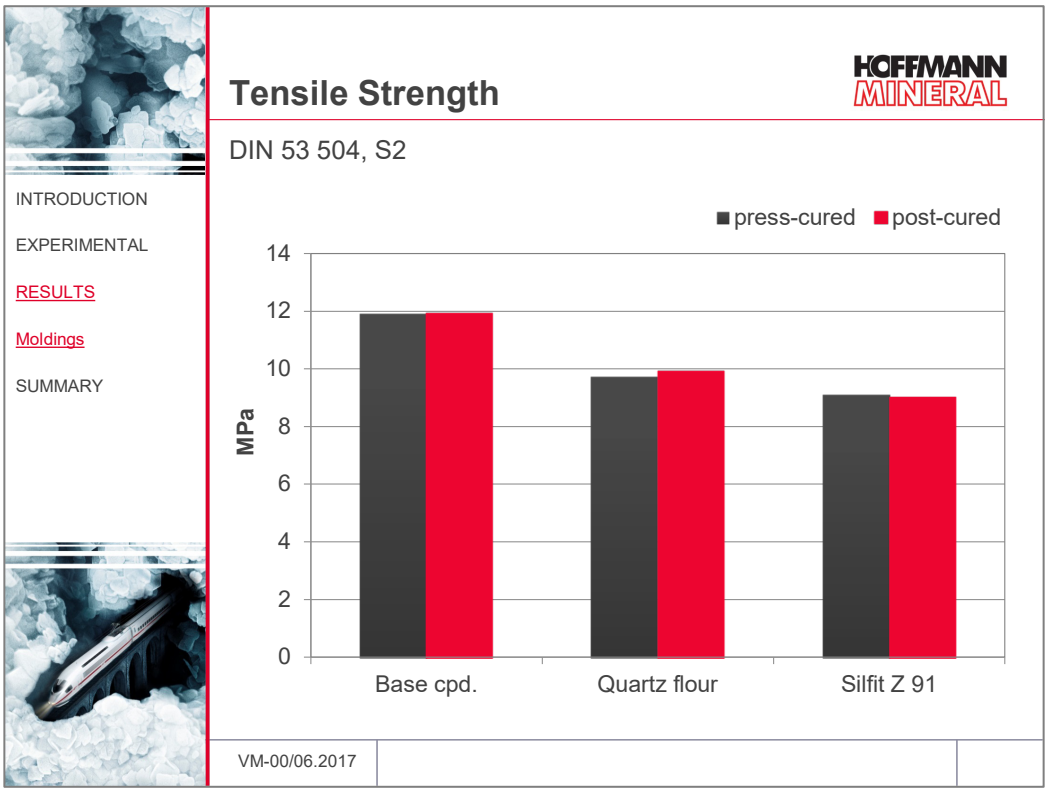
For the sake of completeness, the results of the base compound (without further filler addition) will be also presented here.

As already mentioned, the compounds were press-cured for 5 minutes at 165 °C, post-cure was done 4 hours at 200 °C.

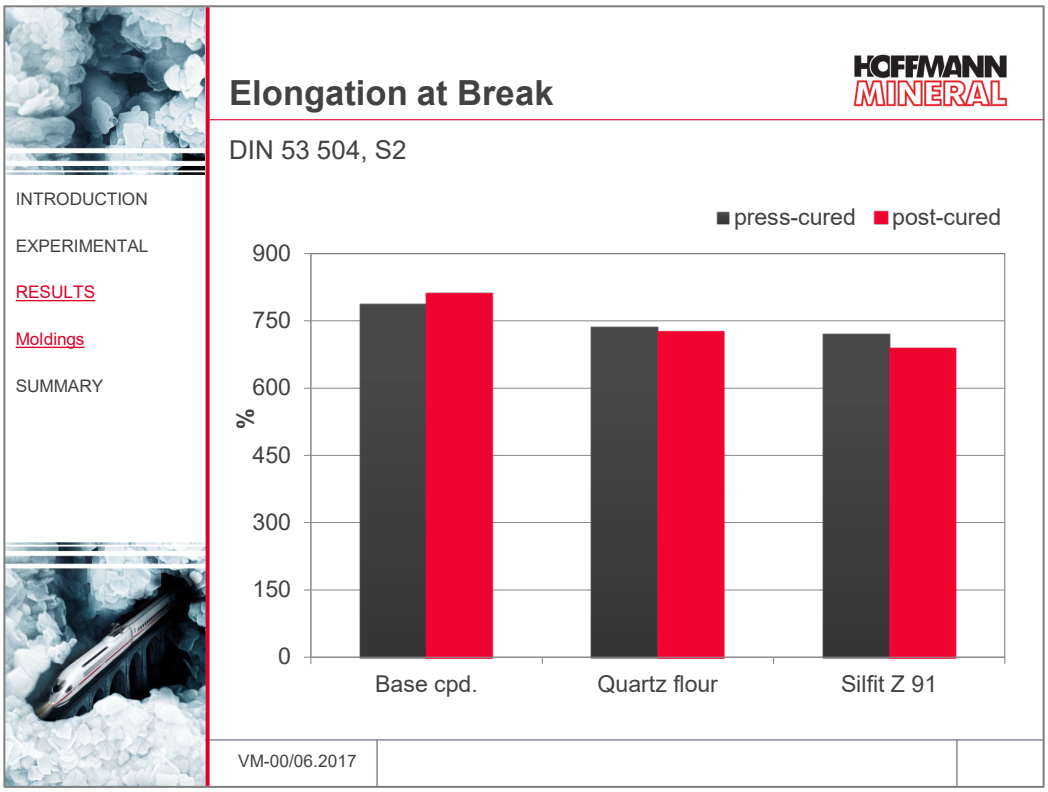
3.2 Mechanical properties



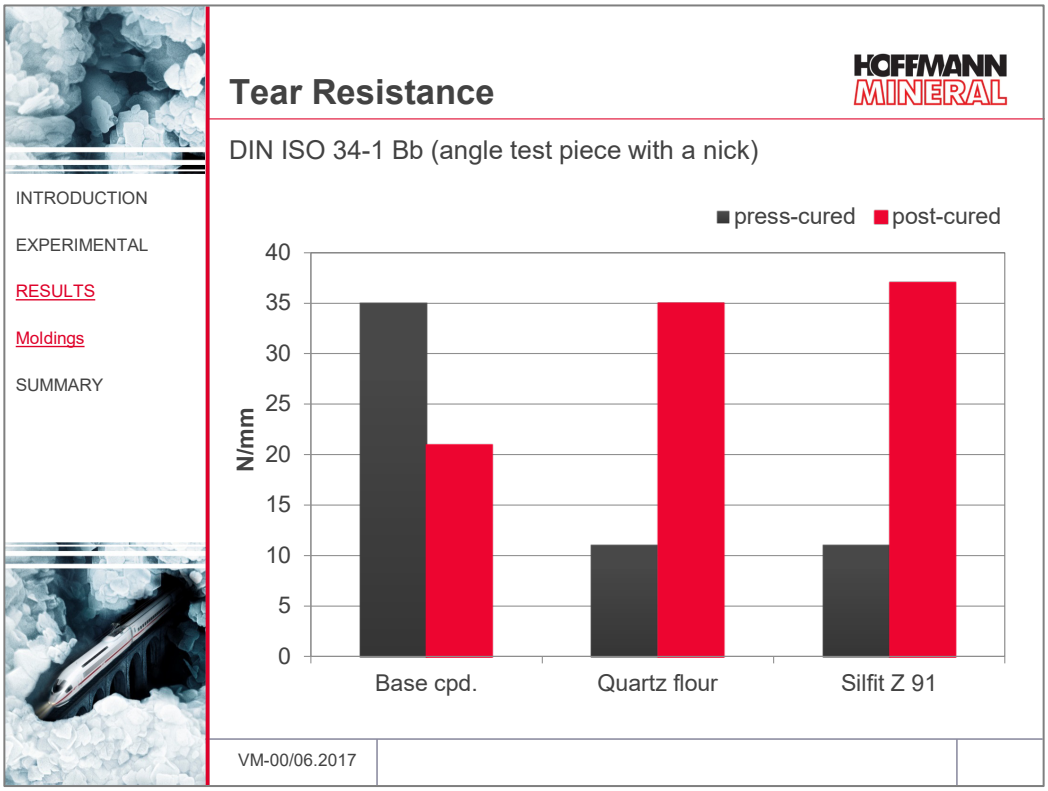
Both fillers, as expected, lead to a slight hardness increase of the base compound, while no significant difference can be detected between Silfit Z 91 and the quartz flour. With both fillers, post-curing further increases the hardness a little.



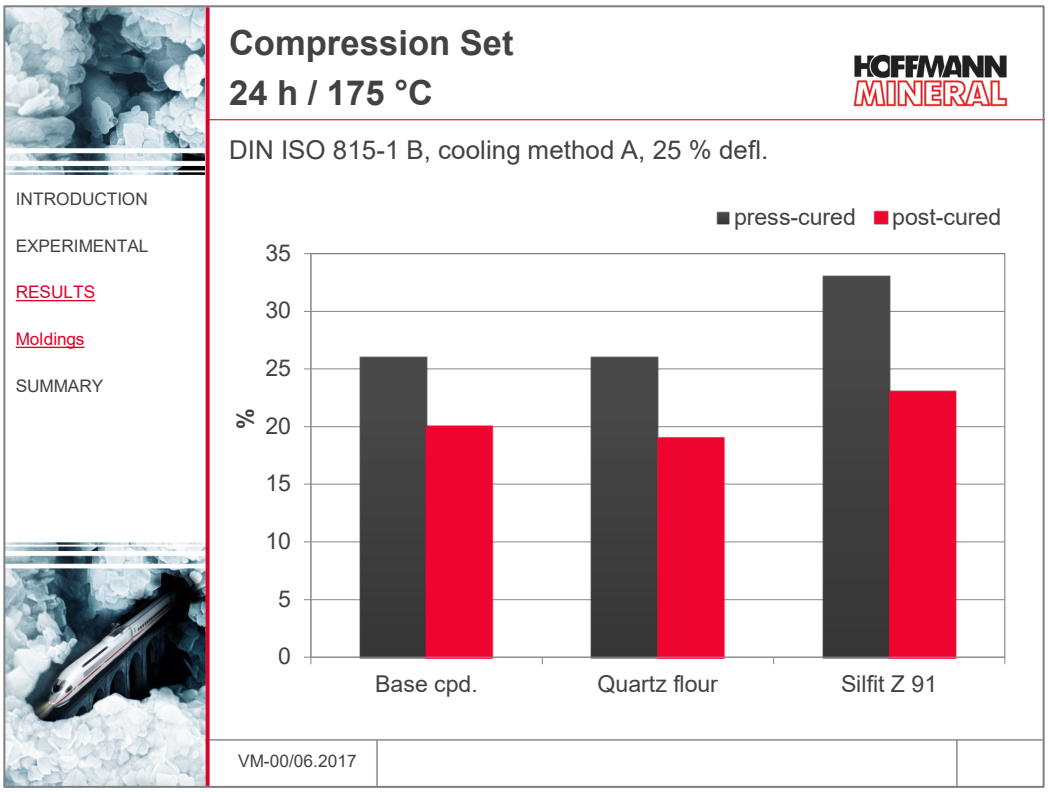
By adding the fillers, the tensile strength of the base compound is somewhat reduced. The compounds filled with Silfit Z 91 give rise to only marginally lower levels than those with quartz flour. Post-curing here shows practically no effect.



The elongation at break with 25 phr filler is only marginally lower compared with the base compound. The choice of the filler has no significant influence on the results, as little as the post-curing step.

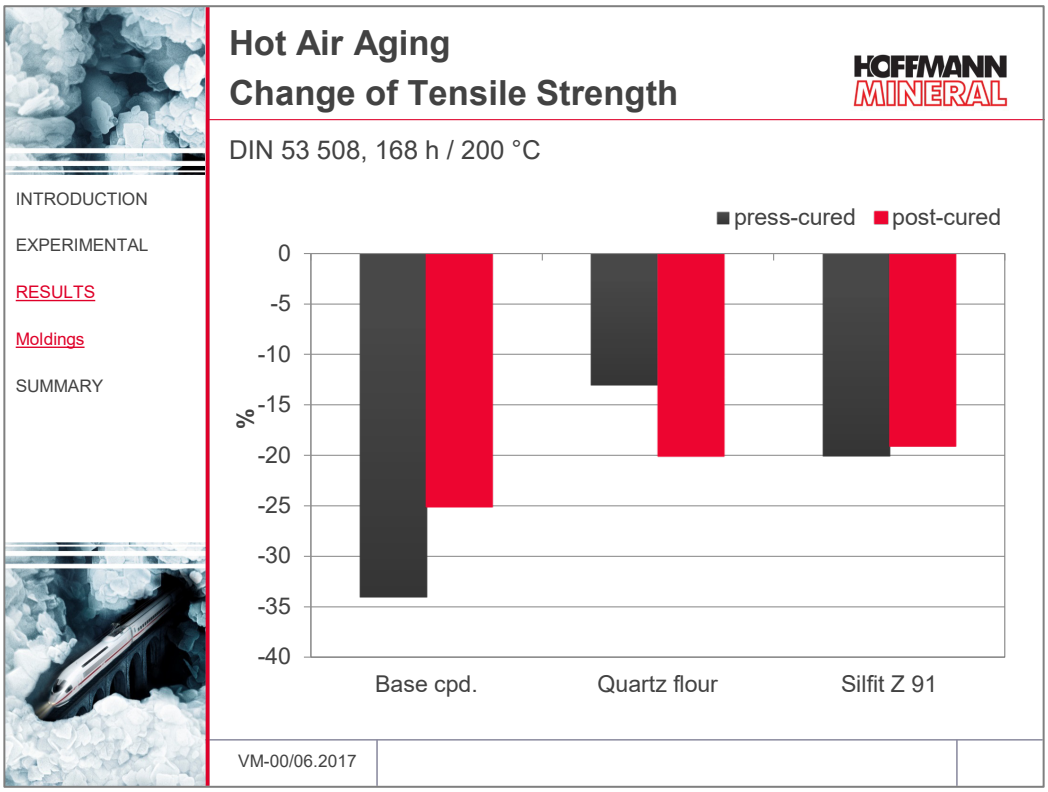


While the tear resistance of the base compound reacts negatively on the post-cure, the results of the compounds with Silfit Z 91 resp. quartz flour come out distinctly higher. A significant difference between the two fillers cannot be detected.

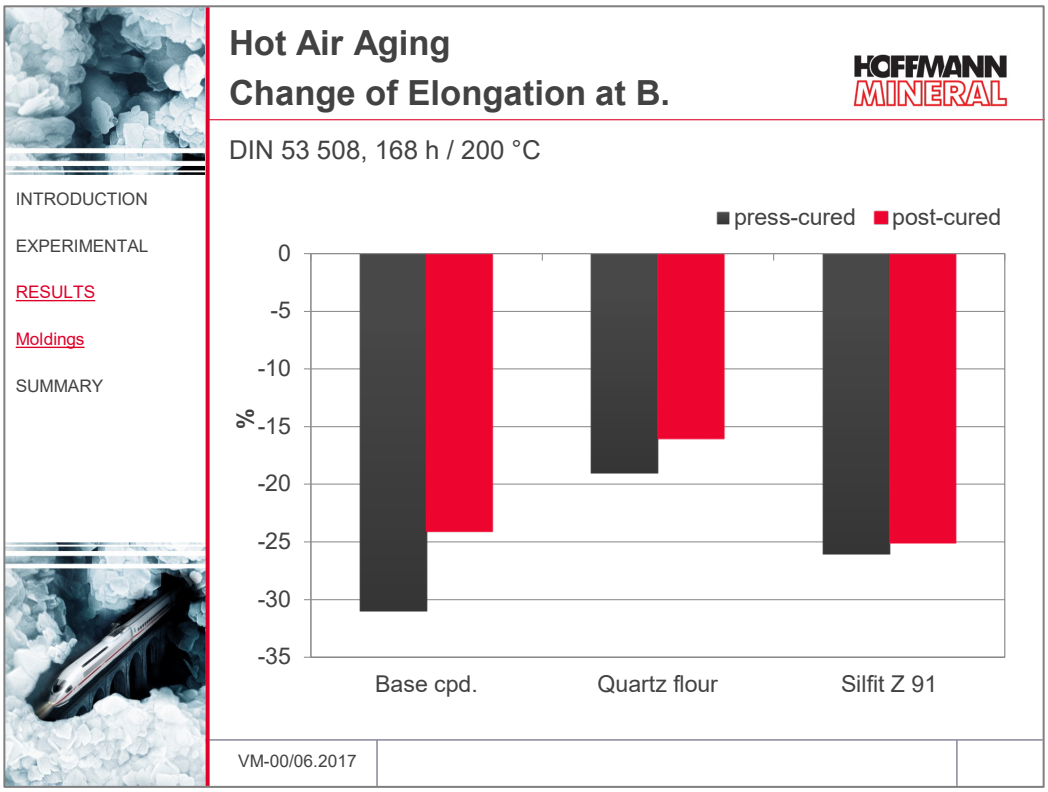


By post-curing, the compression set with Silfit Z 91 can be decreased in a way that the results arrive at a comparable level with the unfilled base compound or the quartz flour.

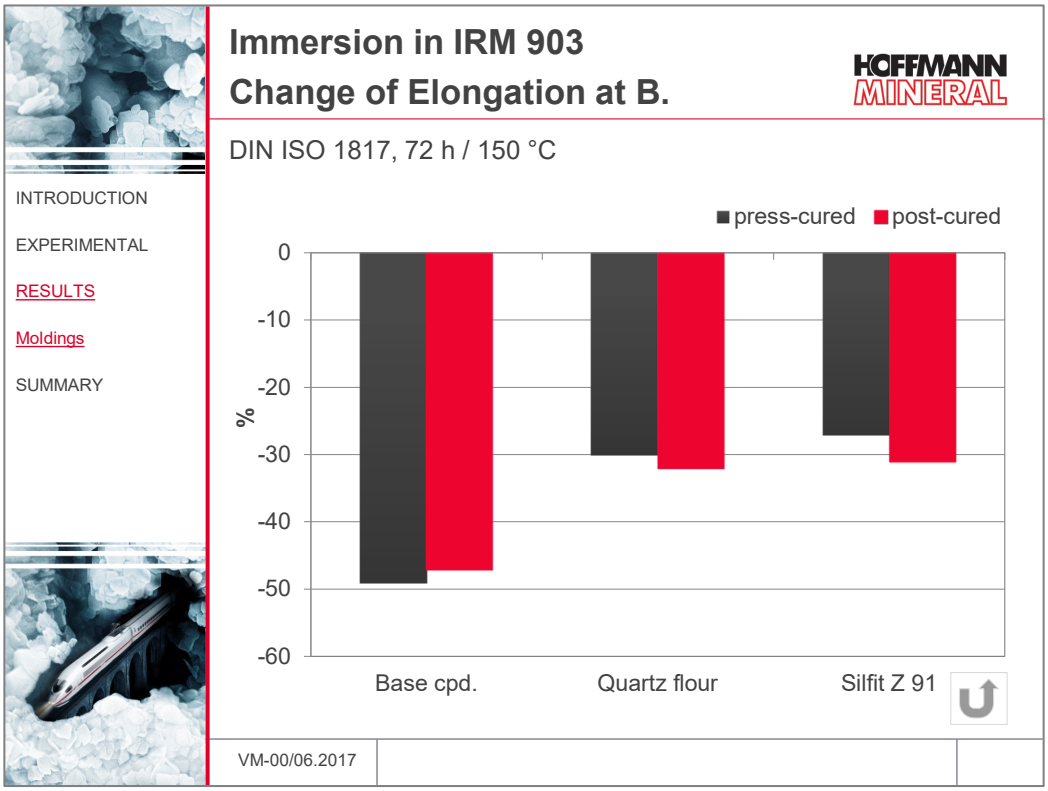
3.3 Resistance properties



The changes of the tensile strength of the press-cured or post-cured compounds by hot air aging (168 h / 200 °C) remain with Silfit Z 91 as well as with quartz flour in an acceptable and comparable range, which represents somewhat an improvement vs. the base compound.



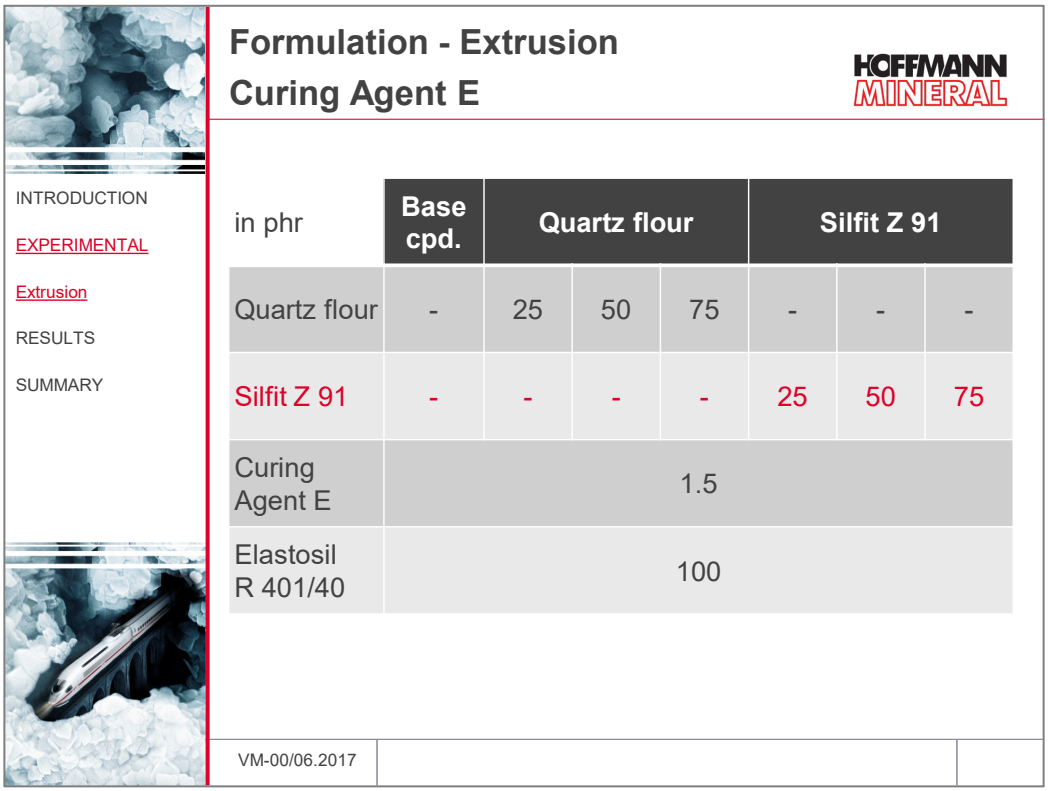
While the quartz flour addition results in a somewhat smaller change of the elongation at break during hot air aging, Silfit Z 91 remains practically on level with the base compound.



In this graph, the change of elongation at break during immersion in reference oil IRM 903 (72 h / 150 °C) demonstrates, to what extent the resistance can be improved by the addition of fillers. Silfit Z 91 and the quartz flour show comparable effects – and this before and after post-curing.

4 Results – Extrusion compound

4.1 Formulation



Elastosil R 401/40: silicone rubber, hardness: 40 Shore A

Curing Agent E: Bis-(2,4-dichlorobenzoyl)-peroxide (50 %)

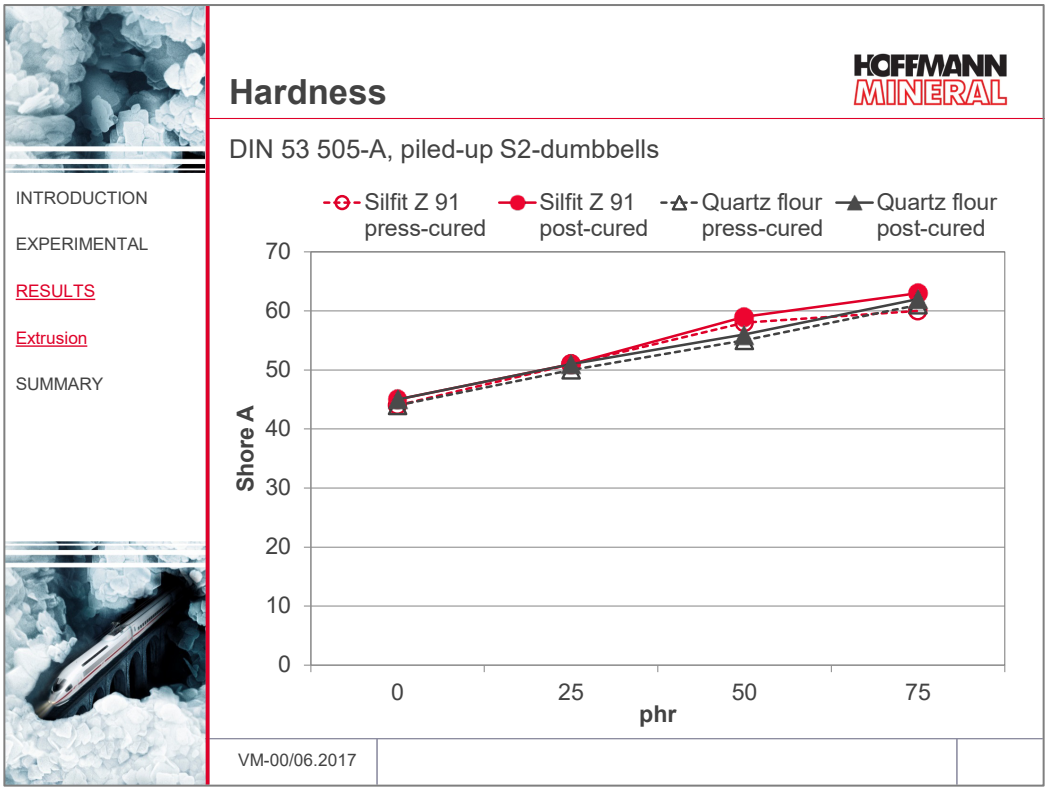
The polymer chosen was a silicone rubber base compound for a hardness 40 Shore A which has served already many times for technical studies at the Hoffmann Mineral laboratories.

The Curing Agent E, Bis-(2,4-dichlorobenzoyl)-peroxide is typically used for extrusion compounds.

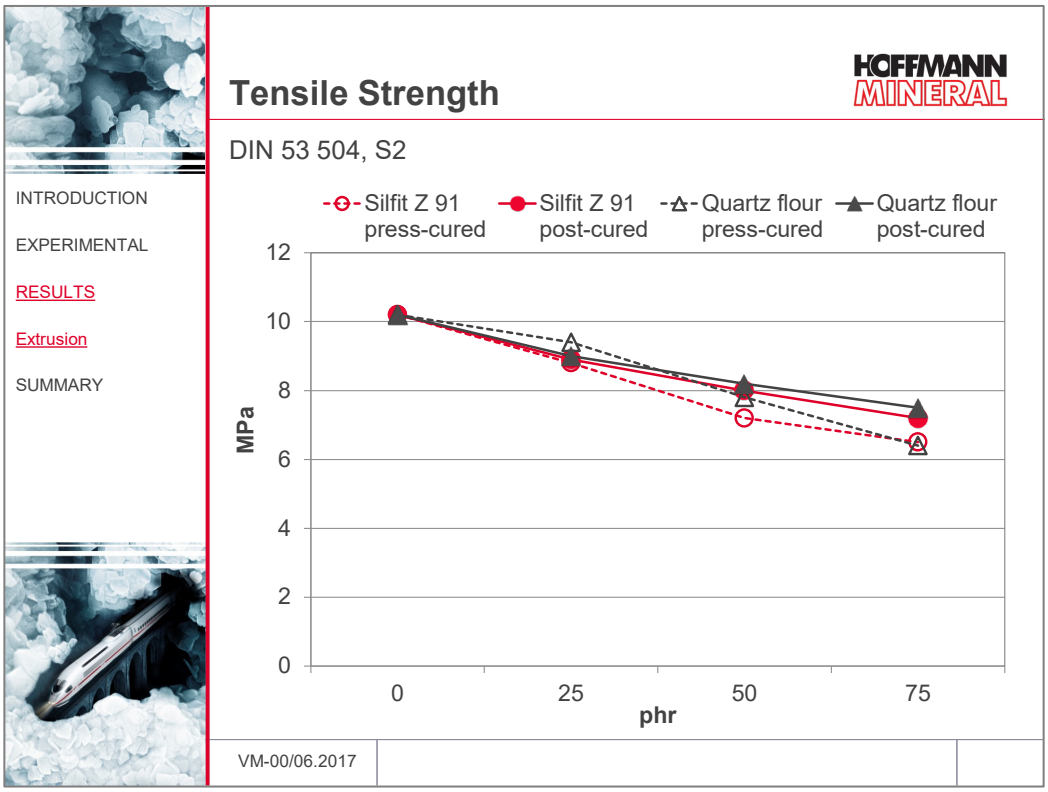
Quartz flour resp. Silfit Z 91 were incorporated into the base compound at levels of 25, 50 and 75 phr and the cured rubber properties were evaluated.

As already explained, the compounds were press-cured for 5 minutes at 115 °C. Post-cure was done for 4 hours at 200 °C.

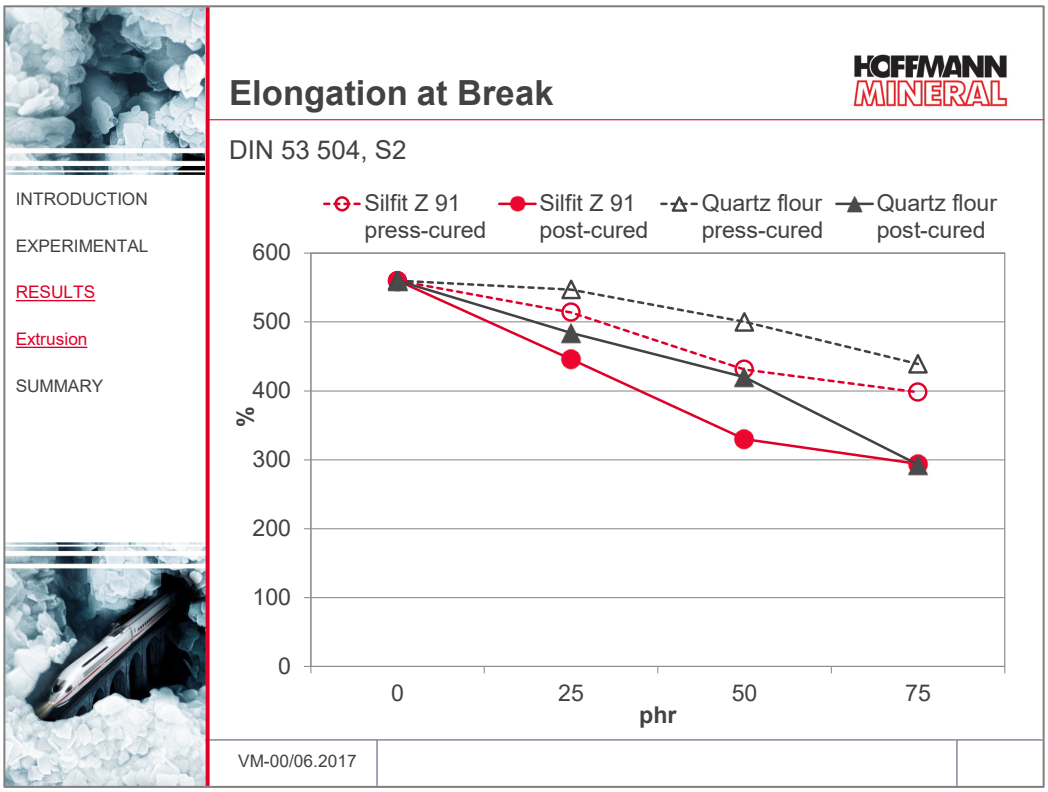
4.2 Mechanical properties



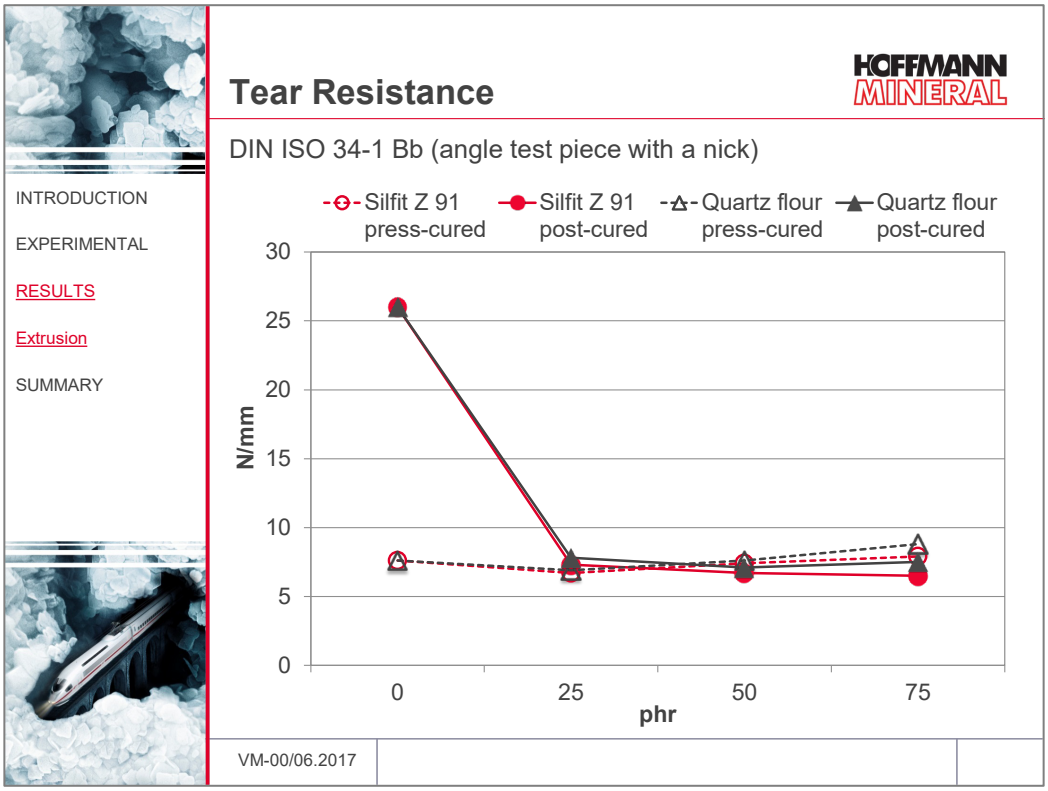
The stepwise increase of the filler loading for Silfit Z 91 and the quartz flour gives rise to comparable increases in hardness.
A post-cure exerts no significant influence, neither with Silfit Z 91 nor with quartz flour.



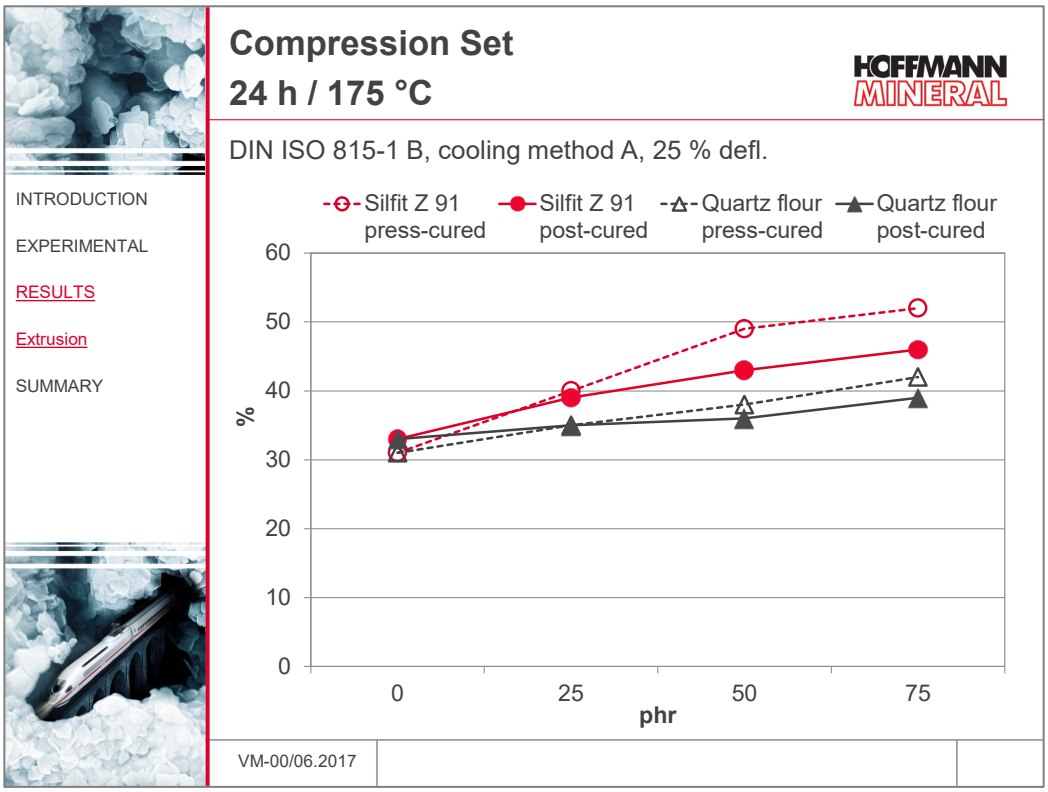
The increasing loading of fillers leads to a decline of the tensile strength of the base compound. Before post-curing, the compounds show small differences only at medium loading, while after post-cure no deviations are observed between Silfit Z 91 and the quartz flour.



The post-cure gives rise to a decline of the elongation at break of the filler loaded compounds by 100 % (in absolute figures). With a loading of 25 resp. 75 phr, the difference between Silfit Z 91 and the quartz flour is not quite as pronounced as with 50 phr.

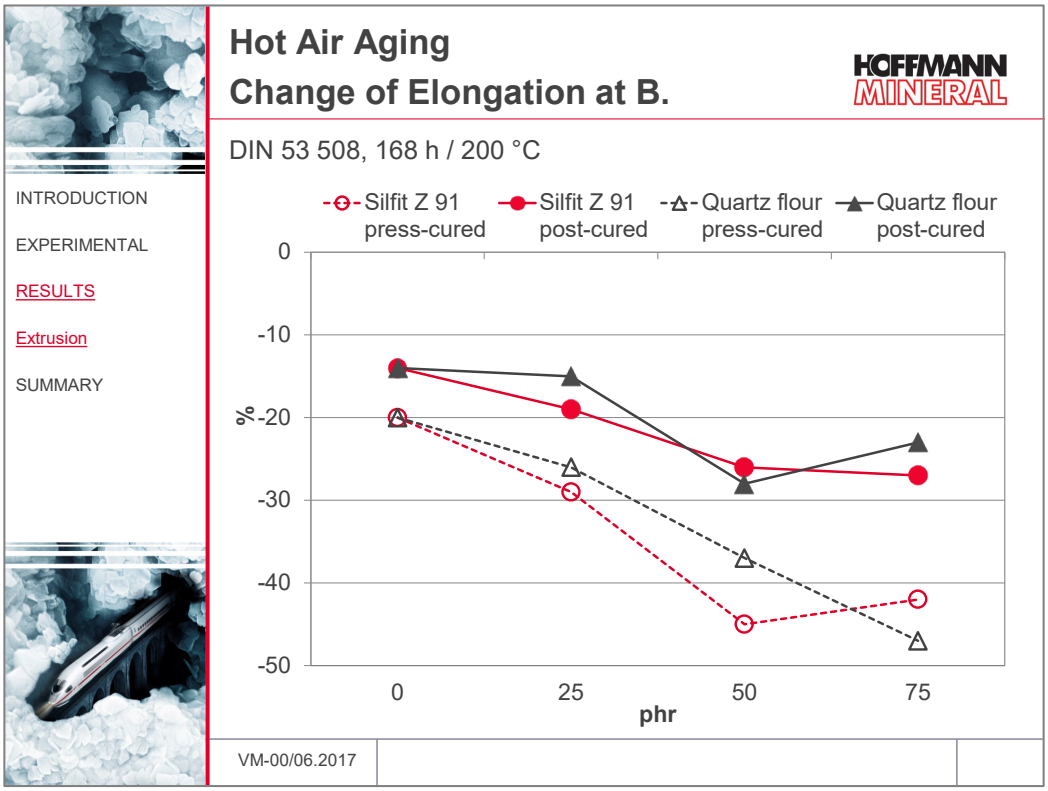


In the post-cured compounds, the addition of 25 phr filler already causes a marked drop of the tear resistance – and this irrespective of the type of filler used. With further increased loadings, no further change in the tear resistance level can be observed and there is no difference either between Silfit Z 91 and the quartz flour.

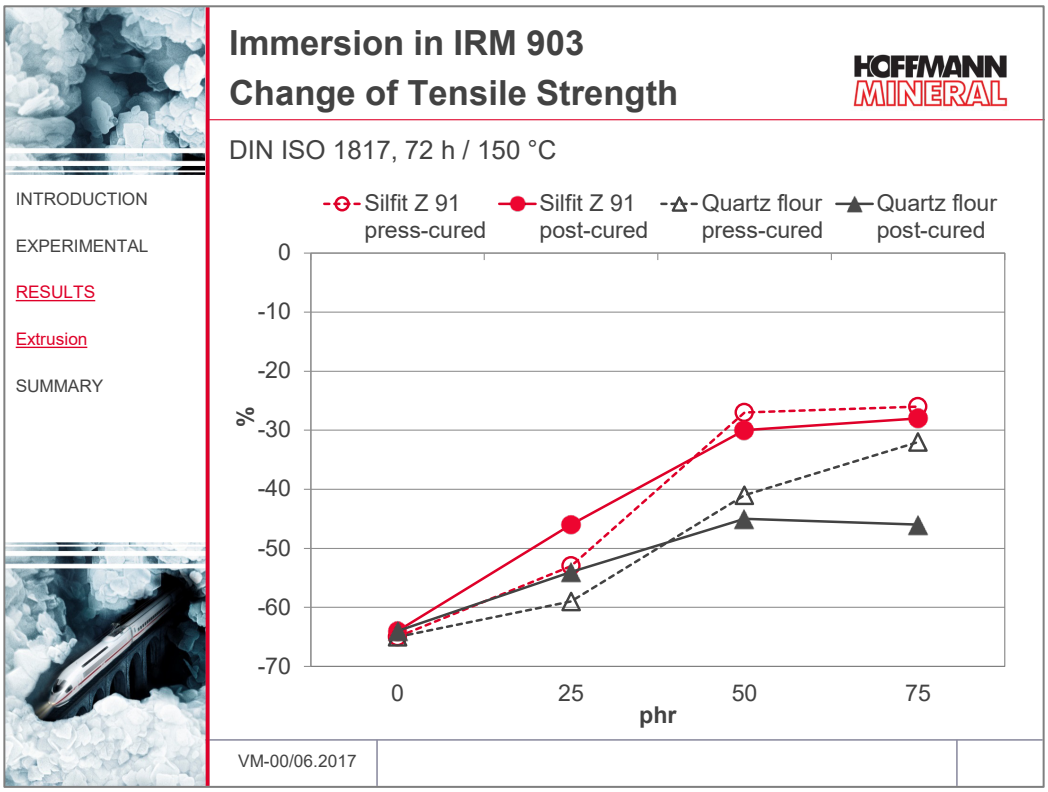


Through post-curing, the compression set of the compounds loaded with Silfit Z 91 can be decreased to a level which comes close to the quartz flour.

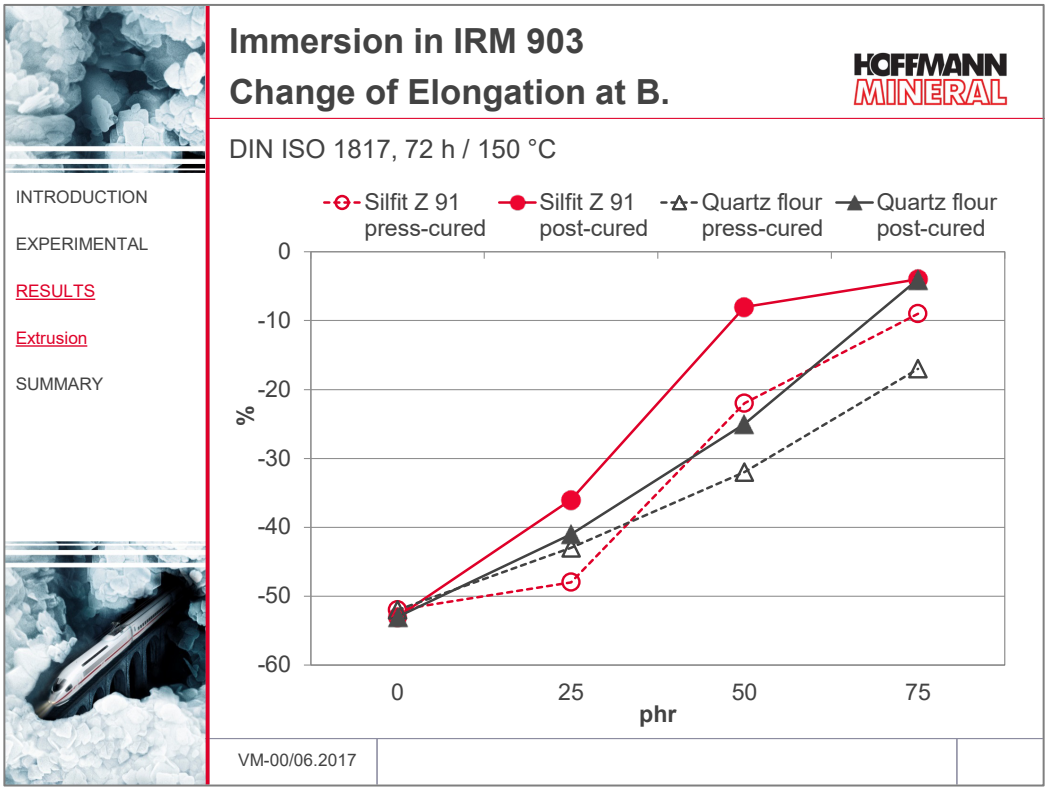
4.3 Resistance properties



Between the two fillers, no significant differences can be found with respect to the aging in hot air (168 h / 200 °C). This is here illustrated by the changes in elongation at break. A post-cure leads to smaller changes in elongation both with Silfit Z 91 and with quartz flour.



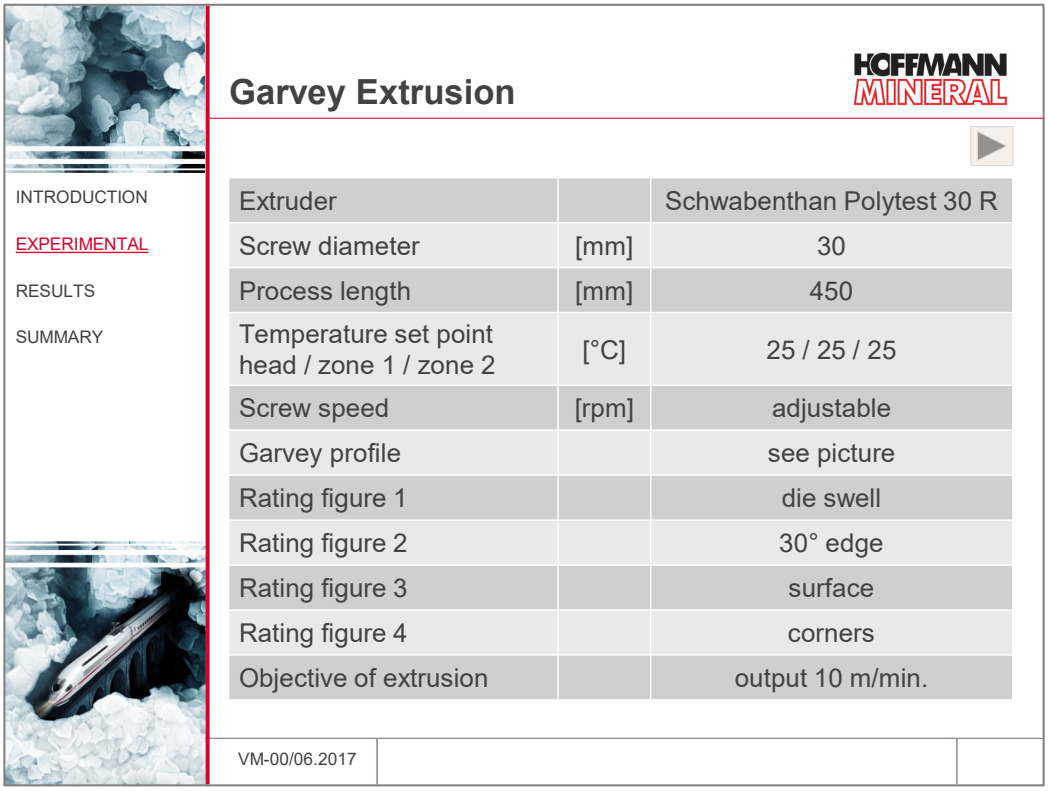
While the volume change upon immersion in reference oil IRM 903 of compounds loaded with Silfit Z 91 does not show any differences vs. those with quartz flour, with respect to changes in tensile strength they give proof of advantages. In fact, the tensile strength results of the press-cured as well as of the post-cured samples with Silfit Z 91 drop less than with quartz flour.



More favorable levels with the post-cured compounds containing Silfit Z 91 also result at loadings of 25 and 50 phr with respect to the elongation at break. In compounds with still higher loadings, no differences can any longer be observed between both fillers.

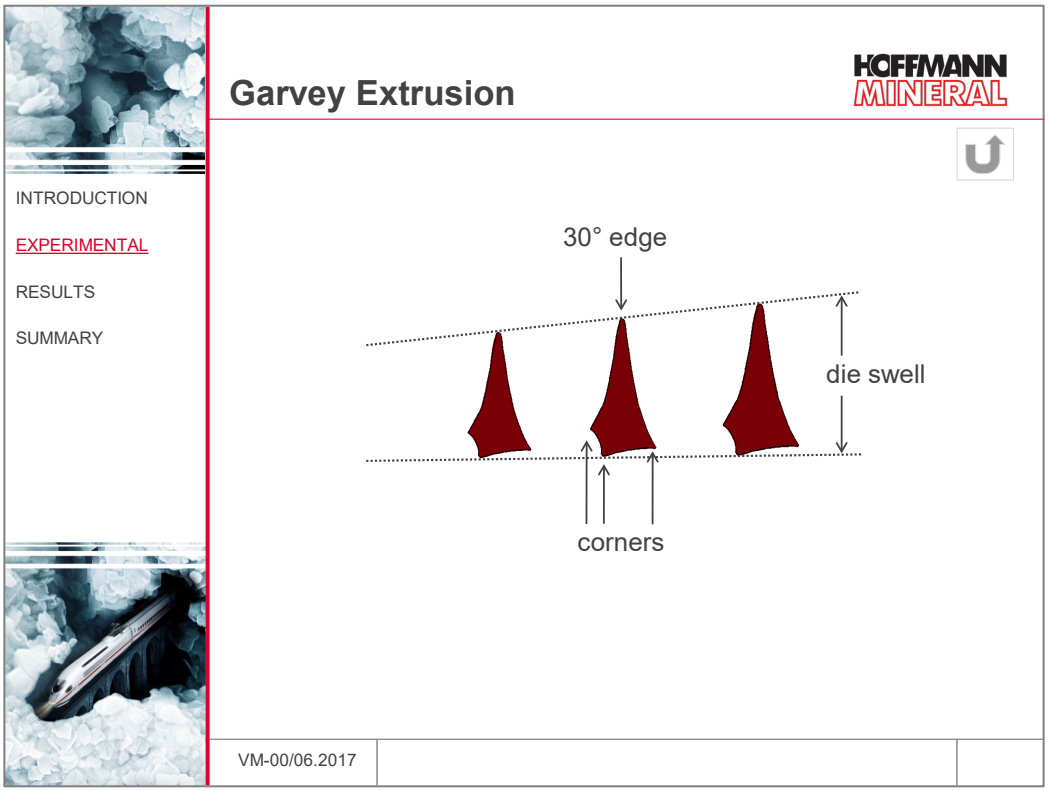
4.4 Extrusion properties

Extrusion was carried out with the following parameters:



Extruder		Schwabenthan Polytest 30 R
Screw diameter	[mm]	30
Process length	[mm]	450
Temperature set point head / zone 1 / zone 2	[°C]	25 / 25 / 25
Screw speed	[rpm]	adjustable
Garvey profile		see picture
Rating figure 1		die swell
Rating figure 2		30° edge
Rating figure 3		surface
Rating figure 4		corners
Objective of extrusion		output 10 m/min.

The Garvey profile looks as this:



This specially developed die geometry allows to evaluate with simple means in relatively short time several compounds with respect to their extrudability and thus to obtain qualitative indications about their extrusion properties.

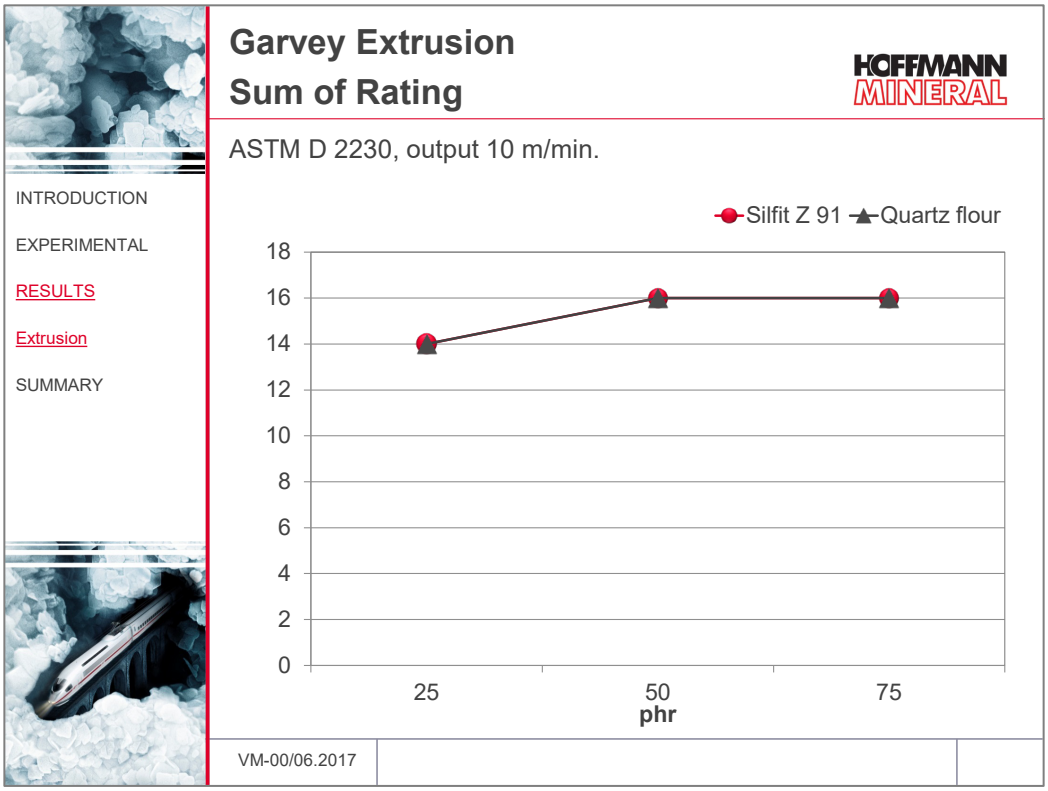
This way, also the compounds with the different loadings if Silfit Z 91 resp. quartz flour were assessed.
As it was possible to extrude all compounds with a rather high rate without losses in extrudate quality, a constant output of 10 m/min was used throughout in the tests.

For a better evaluation of the profiles, they were cured for 7 minutes at 200 °C in an hot air oven.

The assessment of the cured profiles followed ASTM D 2230. This standard assigns points which refer to die swell, the precision of the 30° edge, the surface quality and the corners of the extrudate.

The highest number is 4, the lowest 1. With four assessment criteria, the maximum number of points achievable, therefore, is 16.

Adding the points obtained of the extrudates with Silfit Z 91 resp. quartz flour and plotting them against the filler loading, the following picture comes out:



With a constant output rate of 10 m/min., no differences can be discovered between the extrudates filled with Silfit Z 91 resp. with the quartz flour.

4.5 Blooming

In extrusion compounds, generally Bis-(2,4-dichlorobenzoyl)-peroxide is used as the crosslinking agent. Products cured with this peroxide, however, after some time usually exhibit blooming (insoluble benzoic acid derivatives) on the surface.

As already confirmed in several earlier studies, in compounds filled with Neuburg Siliceous Earth depending on the loading, no such blooming will any longer occur and this irrespective of whether the cured samples have or have not been post-cured.

In order to make such blooming more visible on solid samples, a small part of the raw compounds was colored in black with 4 phr pigment paste (Elastosil PT schwarz 9011).

These cured samples were post-cured and subsequently stored for approx. 7 months at room temperature.

The following figure shows such samples after the 7 months of storage:

It becomes quickly clear that Silfit Z 91 at a loading level of 25 phr already gives rise to a marked reduction of the blooming. From 50 phr upwards, the blooming is completely eliminated.

Rubbers filled with quartz flour will always suffer from blooming – irrespective of the filler loading.

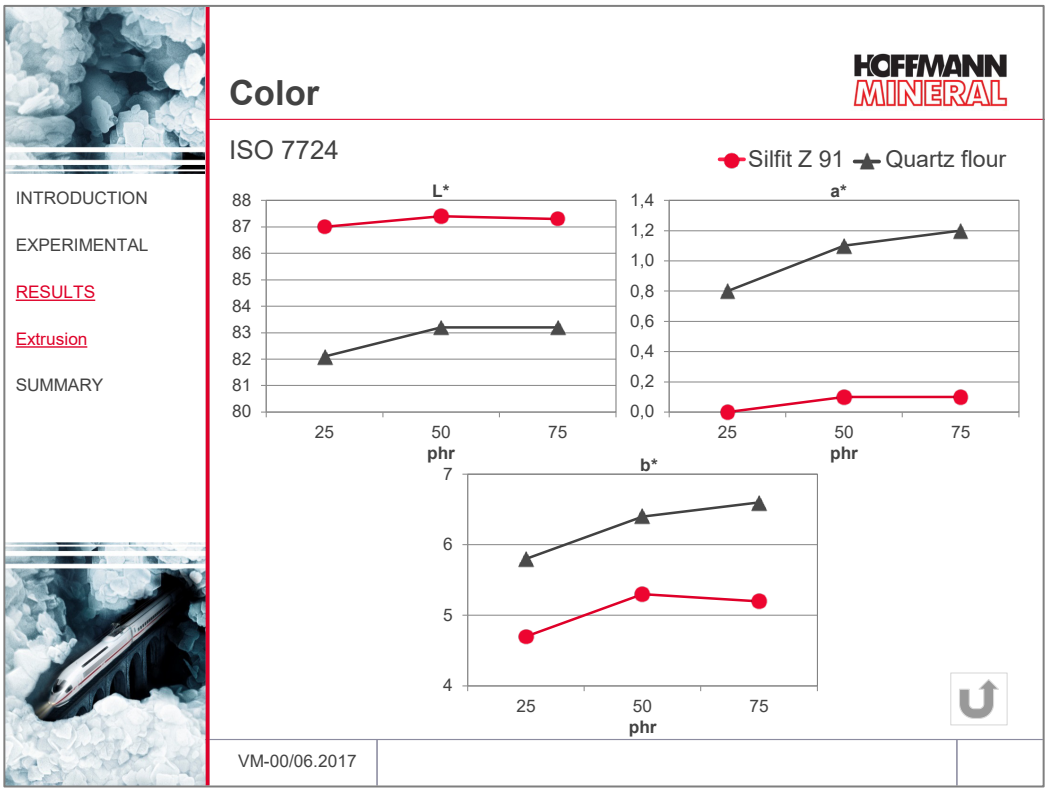
Frequently special additives are added in order to avoid the appearance of blooming. When working with Silfit Z 91, the use of such additives is no longer necessary.

4.6 Color

Neuburg Siliceous Earth – and, therefore, also Aktisil Q which has specifically developed for the use in silicone rubber – typically is characterized by a yellowish tint which is rather objectionable for light-colored or colored compounds.

Through the controlled process conditions of the calcination of Neuburg Siliceous Earth, with Silfit Z 91 a filler is obtained that is brighter than the conventional Hoffmann Mineral products and also is distinguished by a markedly better color neutrality.

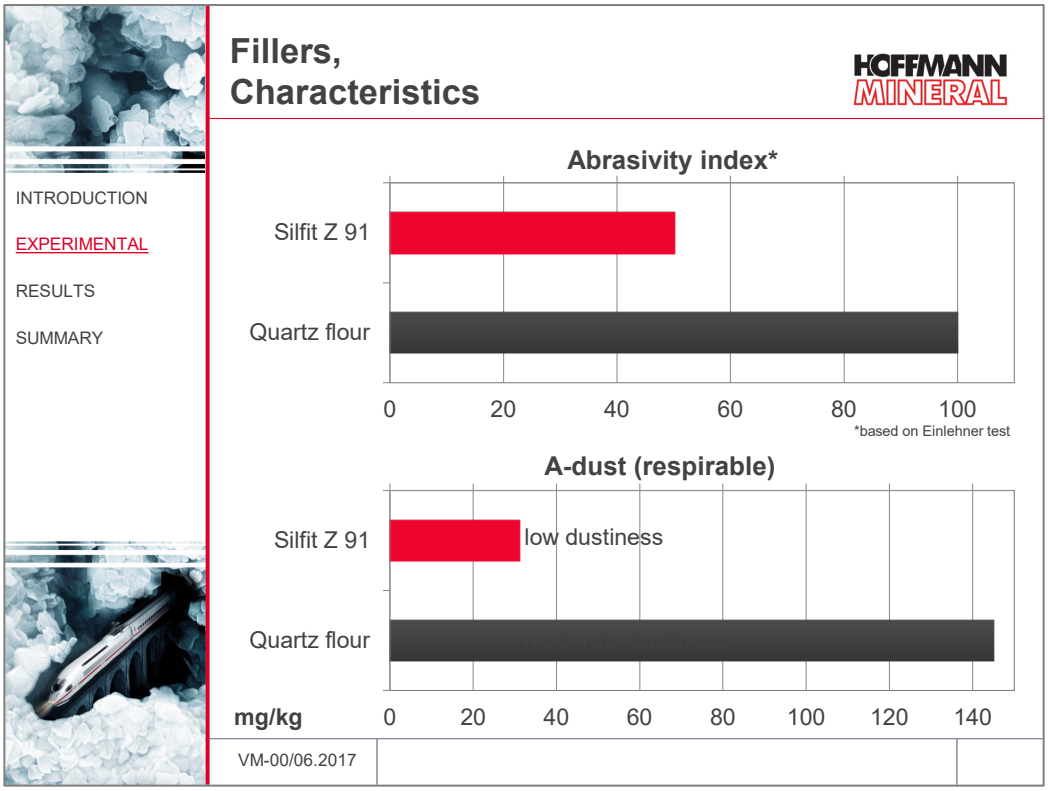
The two product parameters brightness and color neutrality come forward also in comparison with quartz flour, as evident from the color value graph:



Compounds filled with Silfit Z 91 are distinctly brighter compared with quartz flour loading, as confirmed by the L* values in the diagram. While the a* values with Silfit Z 91 doubtless are found in the neutral region, the b* values are clearly oriented towards a shade of blue. The result is a higher color neutrality of the compounds loaded with Silfit Z 91 in comparison with the samples with quartz flour.

The color results are independent on the peroxide used. The compounds with Curing Agent C6 which were discussed earlier in this report lead to identical color values.

5 Wear of machinery and safety & occupational health



With the help of the Einlehner test which allows to assess the wear of processing machines etc., it can be confirmed that Silfit Z 91 offers a marked improvement over the quartz flour with respect to abrasivity.

In addition, the calcined filler generates many times less of respirable A-dust (particle size < 10 µm according to DIN 33897-2) and therefore can get along with less stringent requirements in the realm of health protection compared with the quartz flour.

6 Summary

As the study clearly confirmed, Silfit Z 91 represents an outstanding alternative to untreated quartz flour for use as a filler in silicone rubber.

Silfit Z 91 is less abrasive which should allow a longer service life of the processing machinery.

In addition, with Silfit Z 91 there is less dust formation than with quartz flour which means lower requirements in the realm of occupational health.

Apart from largely comparable mechanical and identical extrusion properties, Silfit Z 91 makes it possible to manufacture highly color-neutral or bright compounds.

Furthermore, the typical blooming when working with Bis-(2,4-dichlorobenzoyl)-peroxide can be minimized or completely avoided.