Neuburg Siliceous Earth

in combination with ATH

flame retardancy of Silicone Rubber

Author: Nicole Holzmayr
Hubert Oggermüller

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1 Introduction

Classic Neuburg Siliceous Earth is a natural combination of corpuscular Neuburg silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods.

Aktisil Q is a grade of Neuburg Siliceous Earth that has been treated with a methacryl functional group and is optimally suited for the use in silicone rubber. The resulting vulcanizates are characterized by extreme low compression set and an outstanding oil resistance. Extrusions offer markedly improved dimensional stability and do not show any tendency towards sticking. Without any problems, all usual peroxide types can be used. Another advantage of Aktisil Q is the fact that the blooming which is typically caused by the curing agent bis-(2,4-dichlorobenzoyl)-peroxide, with this filler, depending on the loading, can be minimized or completely avoided.

The calcined grade Silfit Z 91 is manufactured by thermal treatment of Neuburg Siliceous Earth. When used in silicone rubber, Silfit Z 91 already at low additions apart from cost benefits offers an increased color neutrality which is in contrast to e.g. Aktisil Q, as the optimized manufacturing process succeeds in eliminating the yellowish tint typical for Neuburg Siliceous Earth.

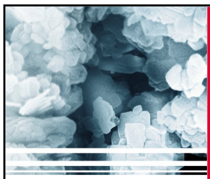
Aluminum hydroxide, also called aluminum trihydrate – abbreviated ATH – often is used as flame retarding filler because its thermal decomposition generates Al_2O_3 and water. This endothermic reaction consumes heat, the water cools the surface and dilutes flammable gases. The Al_2O_3 layer adsorbs sooty particles. In addition, it acts as a protective layer hindering low molecular flammable decomposition products to escape and acts as a heat shield which protects undamaged elastomer.

Neuburg Siliceous Earth at increased loadings only contributes to diluting the fire gases by reducing the polymer portion and therefore does not actively take part in the fire protection.

The objective of the present study is to show synergies which arise from the combination of Neuburg Siliceous Earth with ATH in silicone rubber with respect to flame retardancy as well as rheological and mechanical properties.

2 Experimental

2.1 Formulation



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Formulation

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in phr	ATH	ATH silanized	ATH Aktisil Q	ATH Silfit Z 91
ATH	100	-	70	70
ATH silanized	-	100	-	-
Aktisil Q	-	-	30	-
Silfit Z 91	-	-	-	30
Elastosil AUX Curing Agent E	1.5			
Elastosil R 401/40	100			

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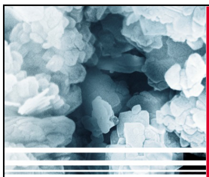
Elastosil AUX Curing Agent E:	bis-(2,4-dichlorobenzoyl)-peroxide
Elastosil R 401/40:	silicone rubber, hardness: 40 Shore A
Filler:	see 2.2 "Fillers and compound preparation"

The untreated ATH was used straight as well as in 70/30 blend with Aktisil Q resp. Silfit Z 91. In addition, a silanized version of ATH was also included.

The polymer used was a silicone rubber with a hardness of 40 Shore A, which has already been used numerous times in studies carried out by Hoffmann Mineral.

The peroxide used, Elastosil AUX Curing Agent E, was bis-(2,4-dichlorobenzoyl)-peroxide which is a preferred grade for extruded articles.

2.2 Fillers and compound preparation



Fillers, Characteristics

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		Benchmark		Neuburg Siliceous Earth	
		ATH	ATH silanized	Silfit Z 91	Aktisil Q
Particle size d_{50}	[µm]	1.7(1)	1.4(1)	2.0	4.9(1)
Particle size d_{97}	[µm]	6.1(1)	3.7(1)	9.7	18(1)
Oil absorption	[g/100g]	29	33	59	40
Specific surface area BET	[m²/g]	3.5(2)	3.5(2)	7.0	6.5
Functionalization		-	vinyl	-	methacryl
Calcination		-	-	yes	-

(1)determined in isopropanol (2)as specified by the manufacturer

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The Neuburg Siliceous Earth grades have a coarser particle size compared with ATH, above all Aktisil Q which is based on the large-grain V fraction. The specific surface areas of the Neuburg Siliceous Earth grades are about twice as high which is also reflected in the oil absorption numbers.

The silanized ATH has been treated with vinyl silane. Aktisil Q carries a methacryl functional group on the surface and Silfit Z 91 has undergone a calcination process.

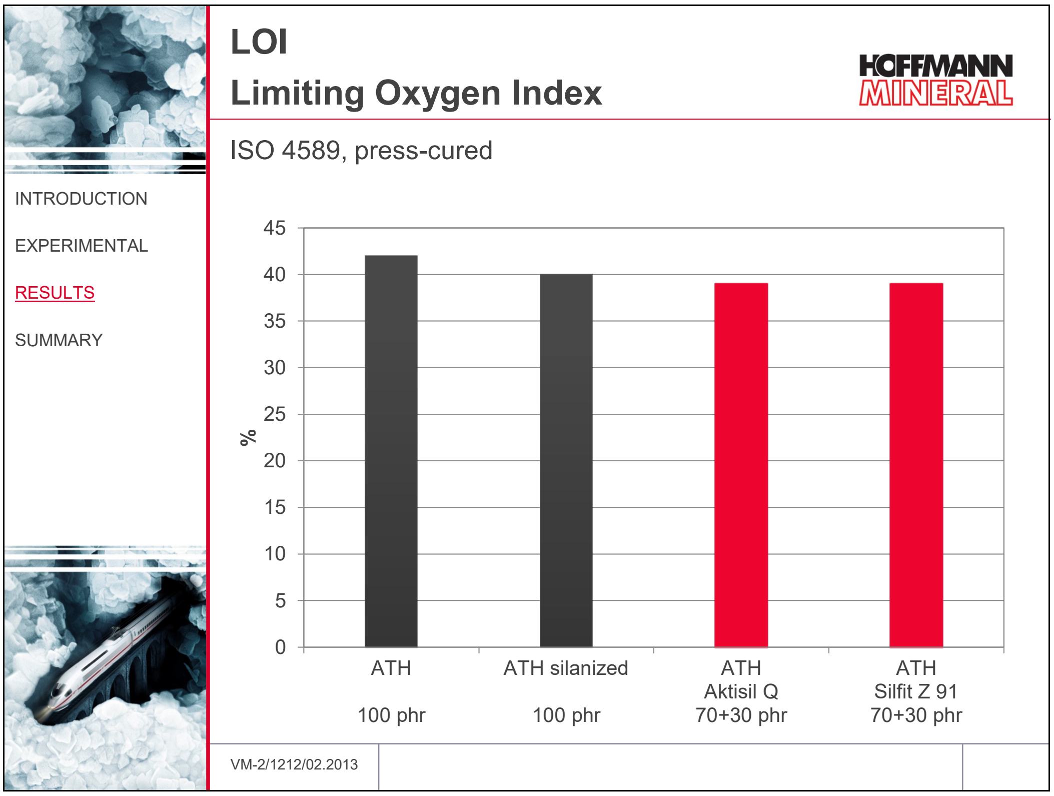
Compound mixing was done on a laboratory open mill (Schwabenthan Polymix 150 L). The rubber was put on the mill at 20 °C and milled to a homogenous sheet. Then the filler was incorporated. The paste-like peroxide was spread onto the compound sheet with a spatula.
The typical mixing time was 10 minutes.
Curing was done in a press for 5 minutes at 115 °C.
The compounds were then post-cured for 4 hours at 200 °C.

During mixing it became evident that ATH was difficult to incorporate into the polymer matrix. The vinyl silane treatment rendered the incorporation somewhat less difficult. In addition, the compounds with only ATH as filler tended to heavily stick on the mill surface, in the curemeter and in the press. The combination with Silfit Z 91 or Aktisil Q was able to resolve these processing problems.

3 Results

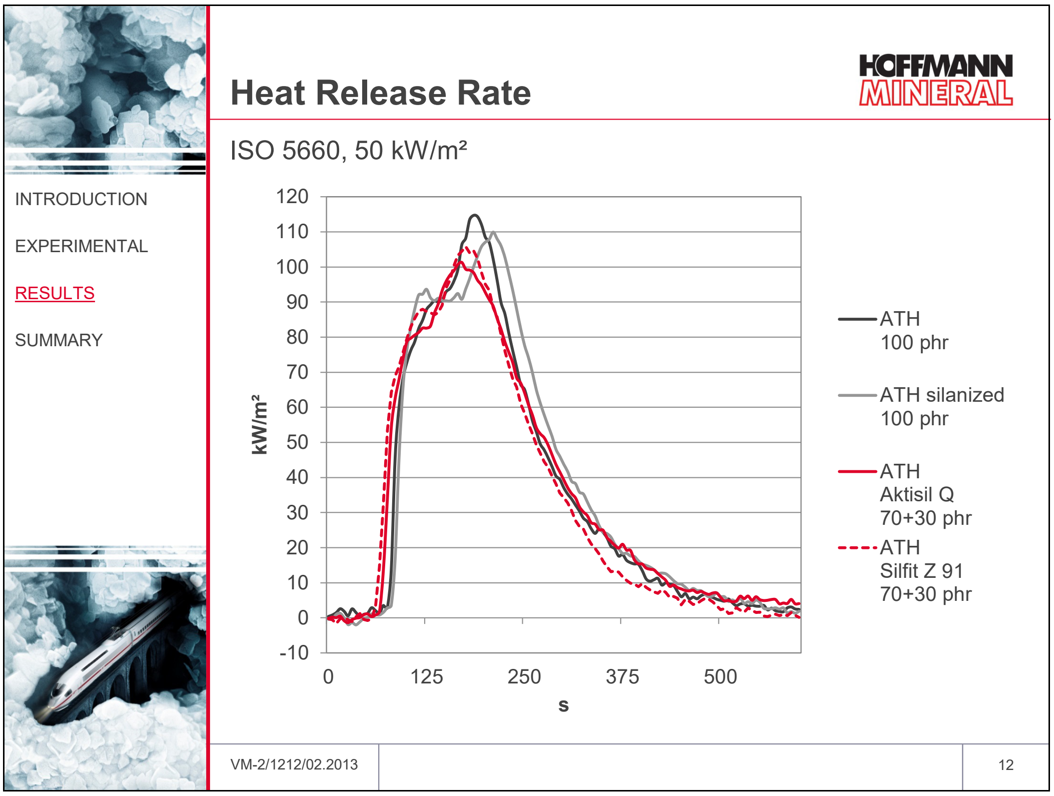
3.1 Fire behavior

The tests were run in cooperation with Nabaltec AG at Schwandorf, the company which also took over the testing of the fire behavior.



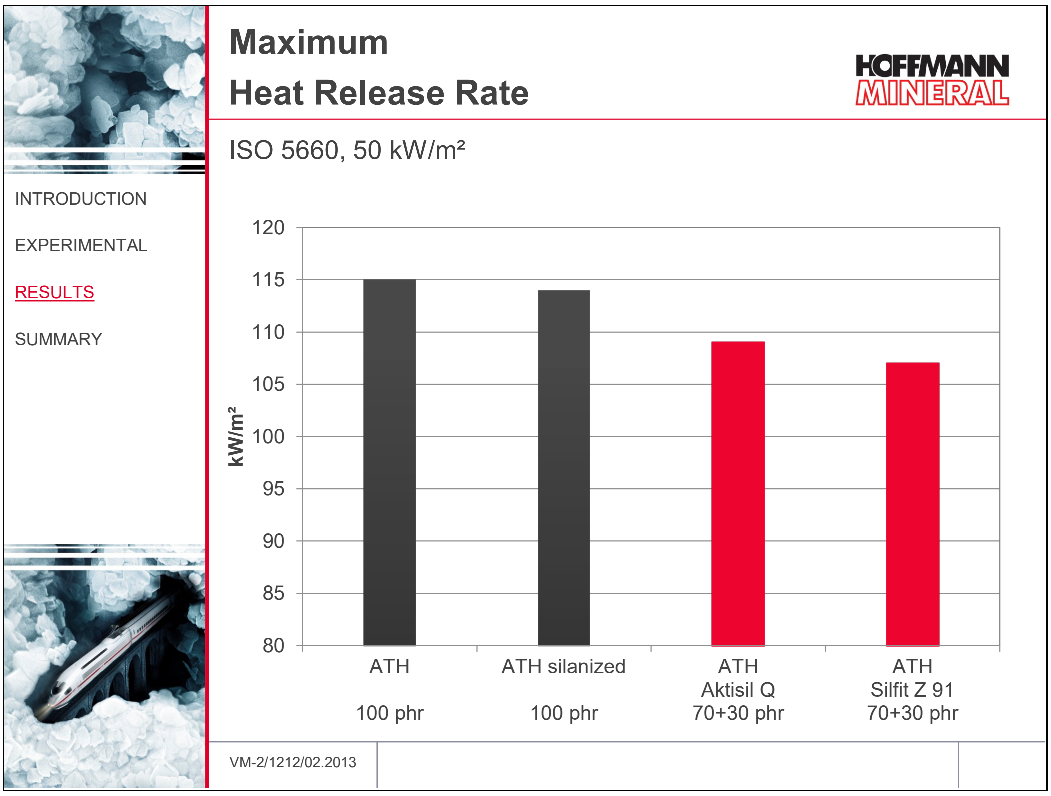
The "Limiting Oxygen Index" (LOI) indicates the oxygen concentration that is required to ignite a sample which is exposed to a defined flame. In order to arrive at a flame retardance, the LOI should be higher than 21 % (the oxygen concentration in air) but is preferred to arrive at values above 30 % (source: Nabaltec AG).

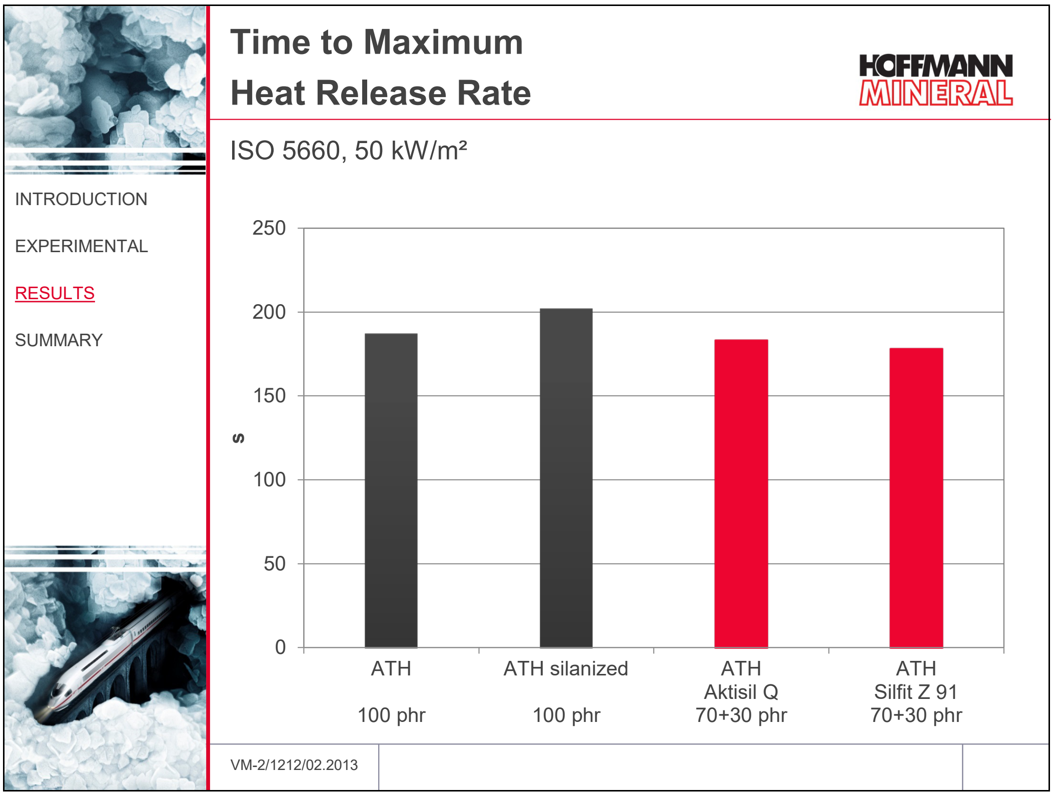
As the graph shows, the LOI of all tested compounds come out largely above 30 %.
The results for the blends of Aktisil Q or Silfit Z 91 are only marginally lower than for the compounds with straight ATH.



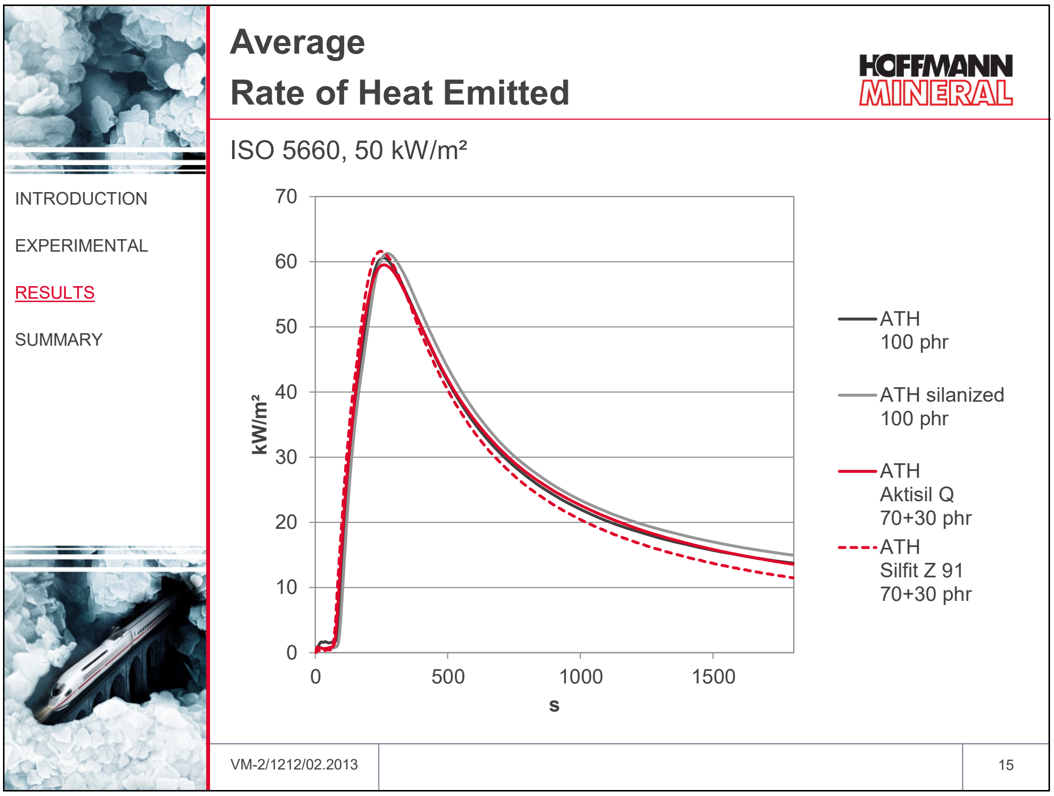
The upper graph shows the heat release versus time at a heat input of 50 kW/m² in the cone calorimeter.

The blends of Aktisil Q or Silfit Z 91 with ATH start with the heat development somewhat earlier than the straight ATHs, the maximum values, however, come out on a comparable or slightly lower level. This situation is also evident from the following diagram which illustrates the individual maxima observed.





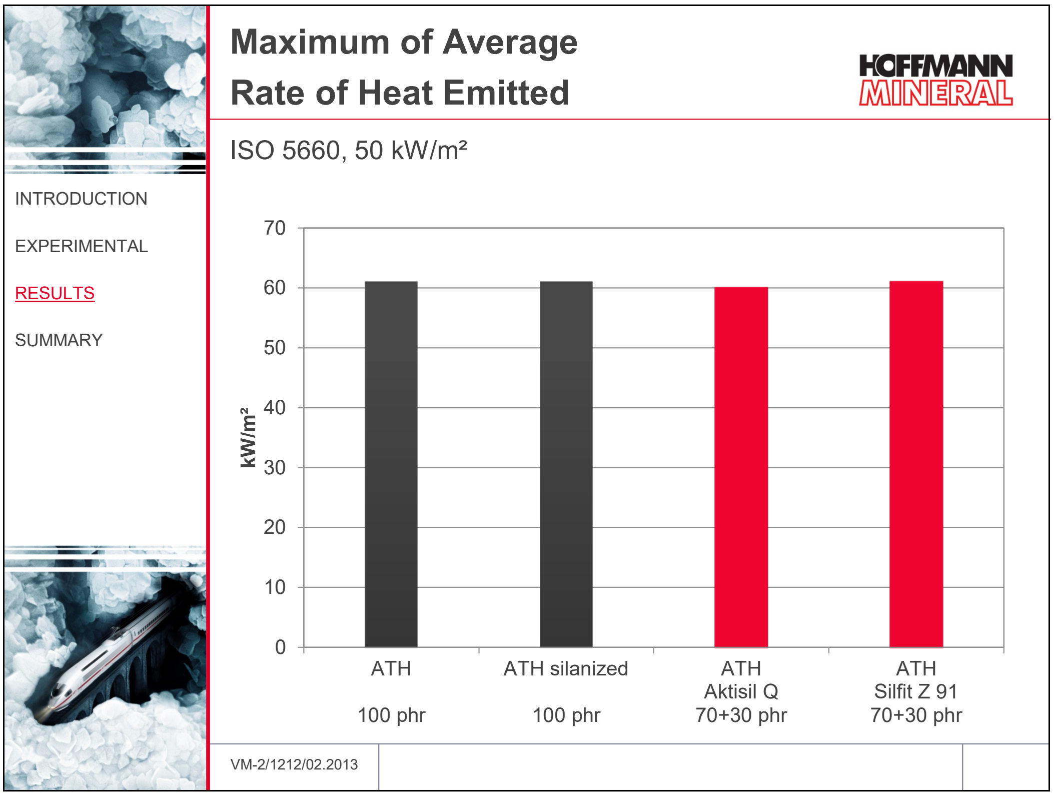
Furthermore, the testing of the fire behavior in the cone calorimeter shows that the partial replacement of ATH by Aktisil Q or Silfit Z 91 does not negatively affect the time to maximum heat release.

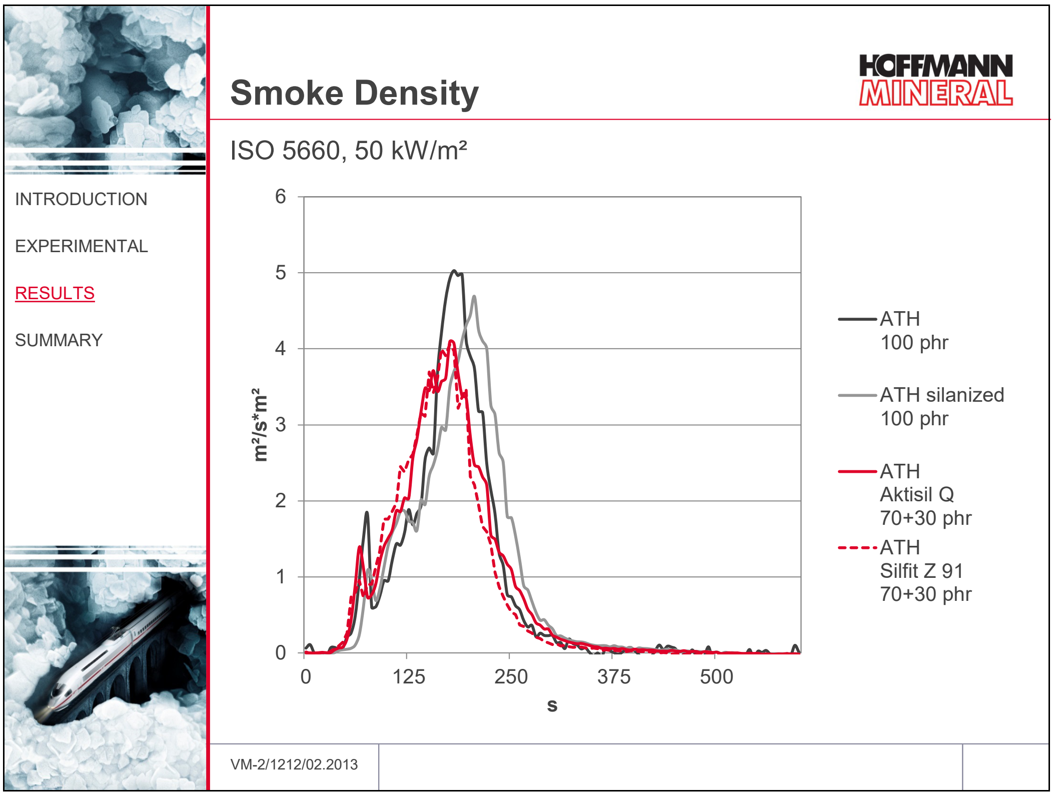


The upper graph illustrates a further possibility to look at the heat release rate. Here, the heat release over time is averaged, which avoids an overestimation of extreme figures which only come up during very short times.

As already evident from the direct results, these calculated diagrams make it clear that the combinations of Aktisil Q or Silfit Z 91 with ATH do not give rise to an increase in the heat release rate.

This also comes out when comparing the maximum values of the average heat release rates.



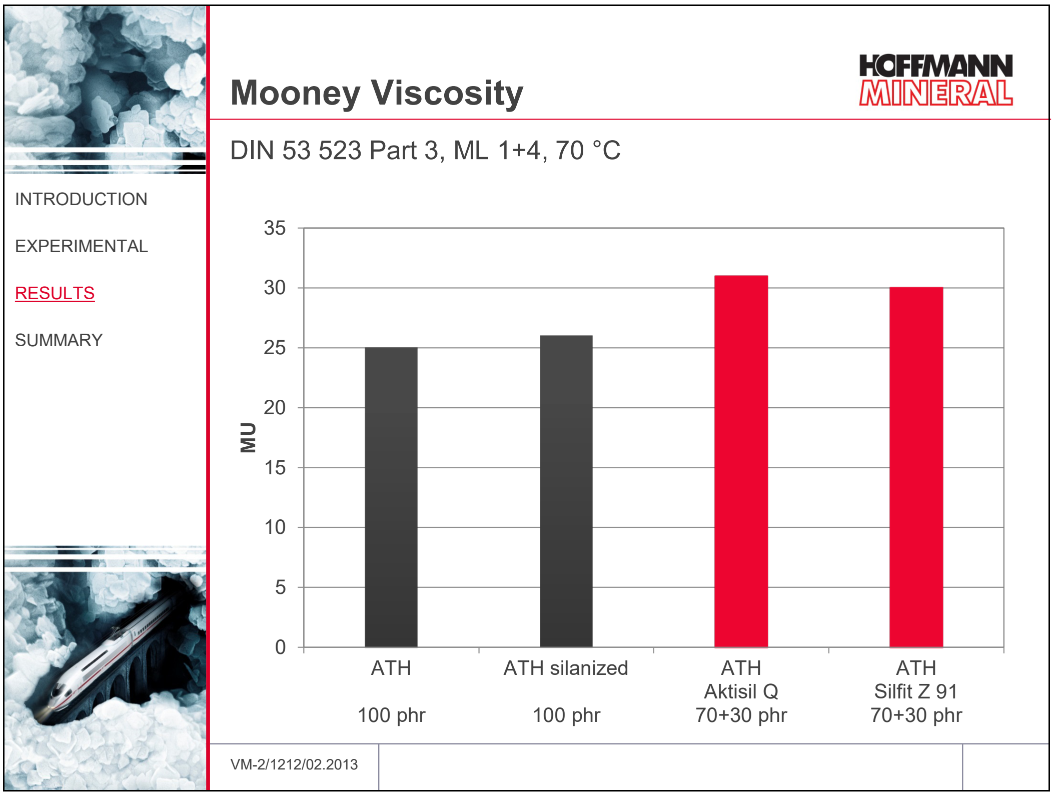


The illustration of the smoke density indicates that a partial replacement of ATH with Aktisil Q or Silfit Z 91 is possible without an increase of the smoke density results. The blends of Neuburg Siliceous Earth with ATH, compared to straight ATH, even allow to arrive at a somewhat reduced smoke density level.

Such results can be of importance for meeting the future standard of EN 45545 (Railway Applications, Fire protection of railway vehicles – EN 45545-2 Part 2: Requirements for fire behavior of materials and components)

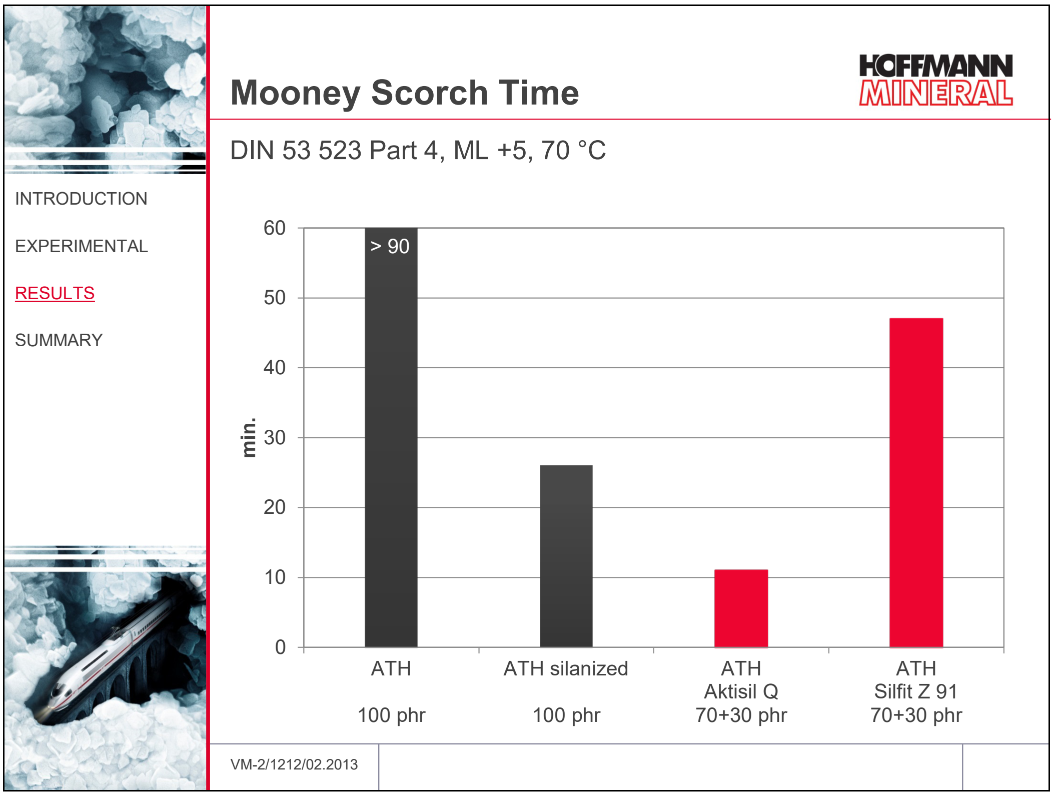
3.2 Viscosity, scorch and cure characteristics

The Mooney viscosity was determined at a temperature of 70 °C since the bis-(2,4-dichlorobenzoyl)-peroxide decomposes at relatively low temperatures and this way gives rise to onset of cure, so that it is almost impossible to measure the viscosity at 100 °C or 120 °C.



The blends of Aktisil Q resp. Silfit Z 91 give somewhat higher Mooney viscosities which leads to assume better extrusion properties compared with straight ATH, as an improved dimensional stability of the extrudates can be expected.

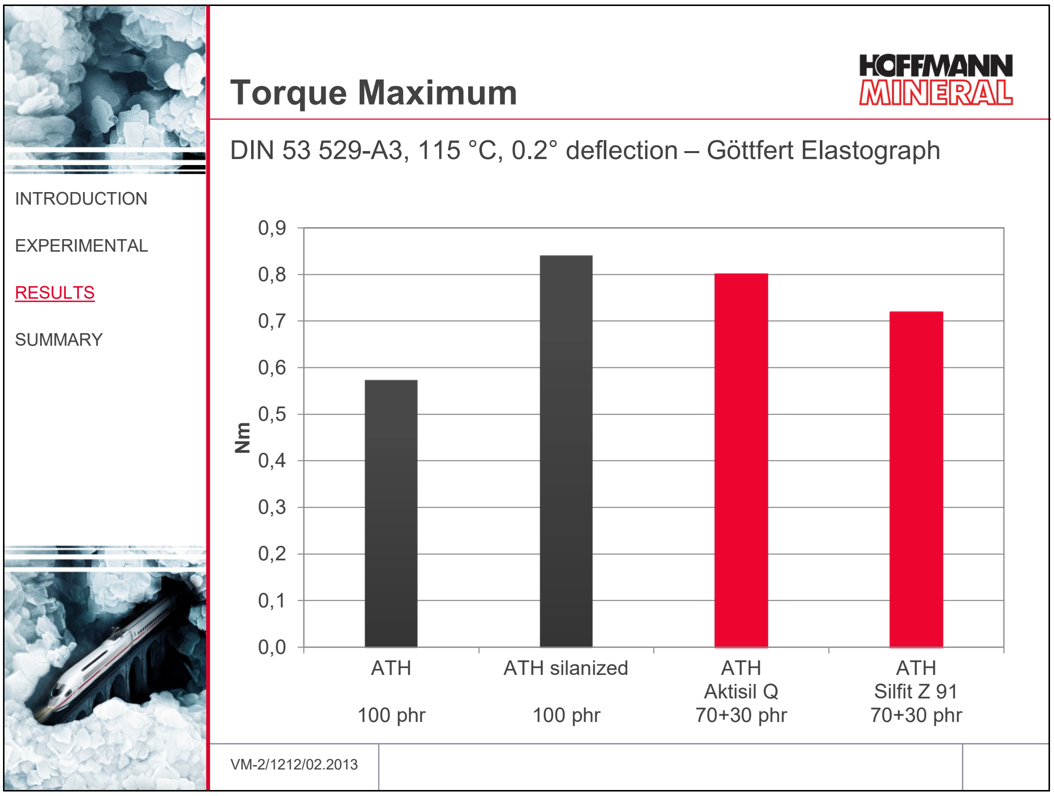
This is also indicated by the scorch times in the following graph:



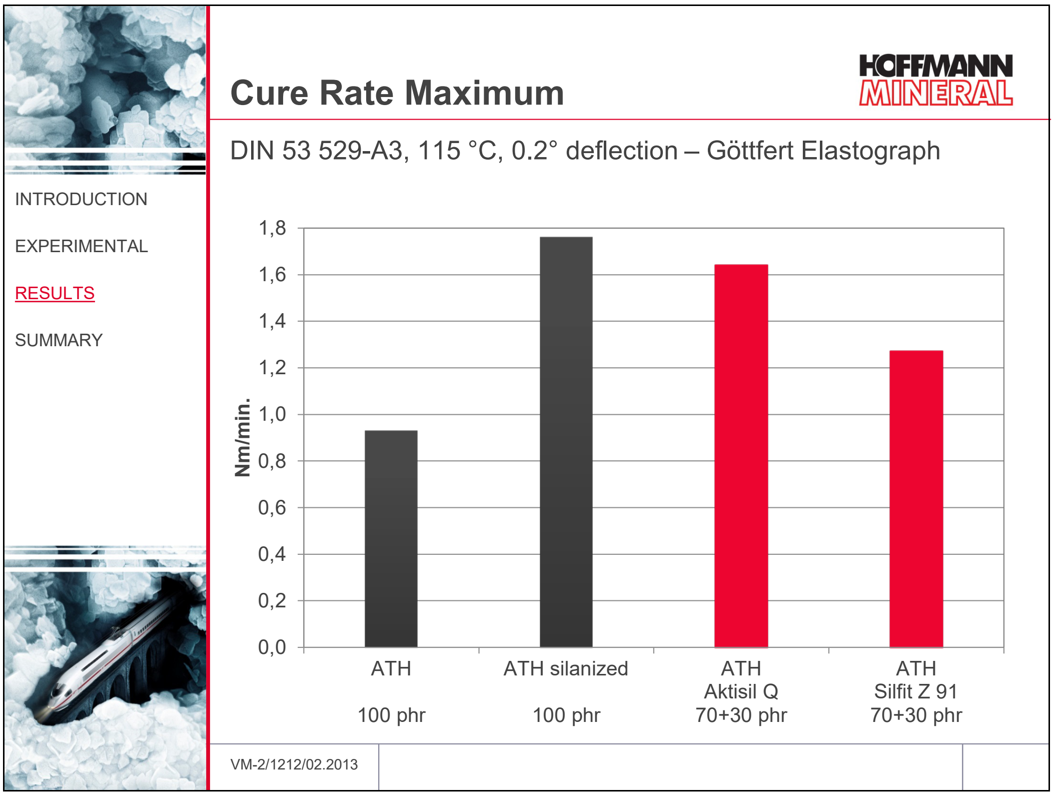
The partial replacement of untreated ATH with Silfit Z 91 leads to a markedly shorter scorch time compared with the straight ATH compound. The silanized ATH gives rise to an even shorter scorch time than the blend of Silfit Z 91 with ATH but is still not as low as the much reduced level imparted by the blend of Aktisil Q and ATH.

While all scorch times come out more or less long, it can be presupposed that along with the higher Mooney viscosities the blends of Neuburg Siliceous Earth grades and ATH will give extrudates with a higher dimensional stability.

The curing properties were determined in a Göttfert Elastograph at a deflection angle of 0.2° and a temperature of 115 °C.

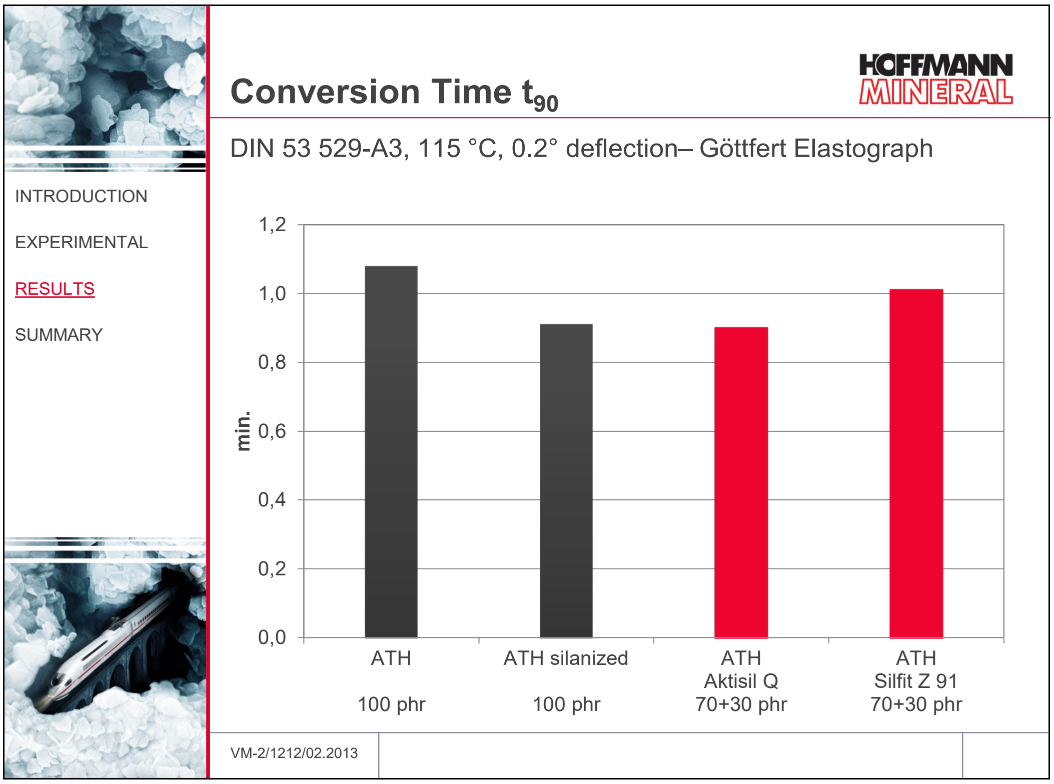


The torque maximum as obtained with untreated ATH can be increased by blending with Silfit Z 91. Aktisil Q blended with ATH comes out even higher and almost equals the level with straight silanized ATH.

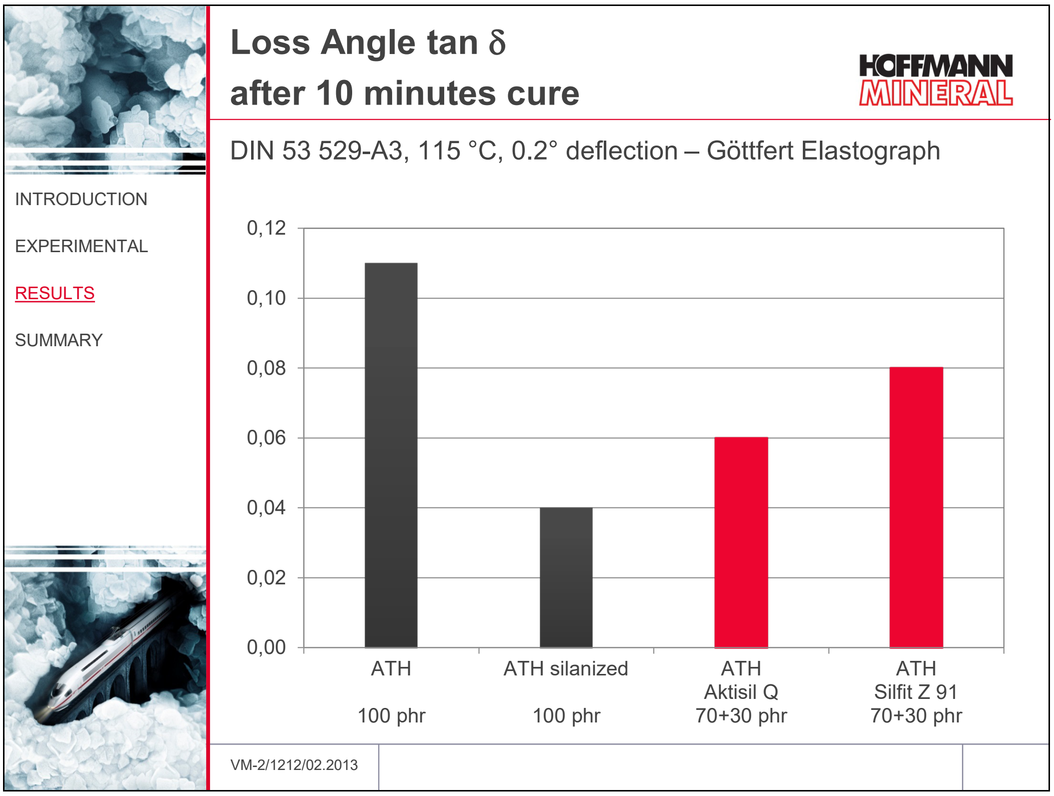


The cure rates present themselves in a similar way.
The Neuburg Siliceous Earth grades in the blends lead to higher cure rates compared with straight ATH, and this with Aktisil Q to a more pronounced extent than with Silfit Z 91, so that again the level of the silanized ATH is almost reached.

The conversion times come out correspondingly:



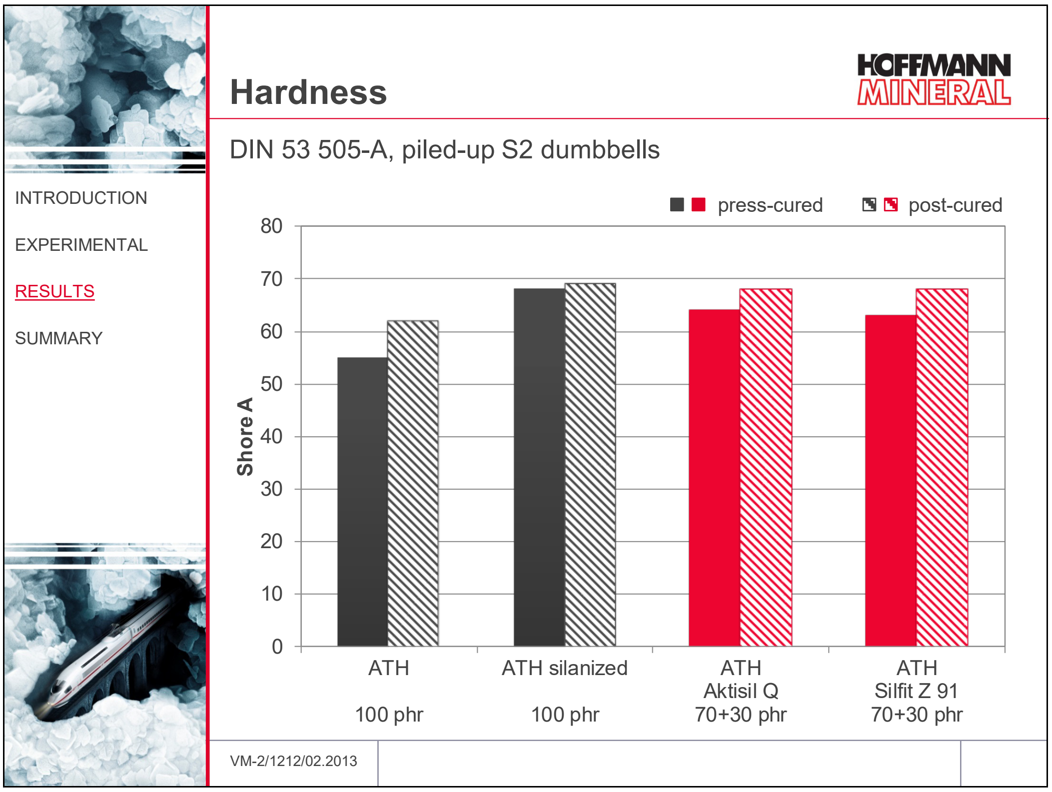
With Silfit Z 91 in the blend with untreated ATH t_{90} can be somewhat reduced. Aktisil Q gives rise to a markedly faster cure (shorter t_{90}), comparable with the straight vinyl silane treated ATH.



After about 10 minutes of testing in the curemeter, untreated ATH leads to a high loss angle which can be much reduced by blending with Silfit Z 91. A more pronounced decrease of the viscous portion can be achieved via the blend with Aktisil Q, which almost arrives at the low level obtained with silanized ATH.

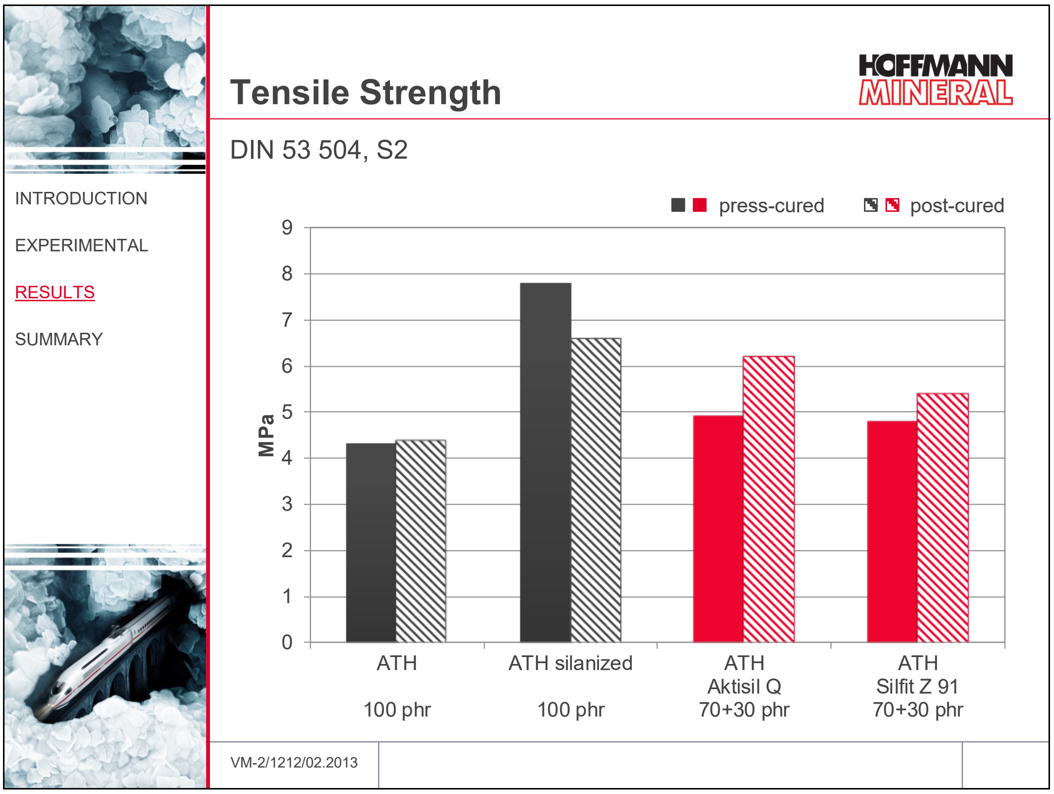
3.3 Mechanical properties

The mechanical properties were determined on press-cured as well as on post-cured samples after a cure of 5 minutes at 115 °C. Post-cure was carried out 4 hours at 200 °C.

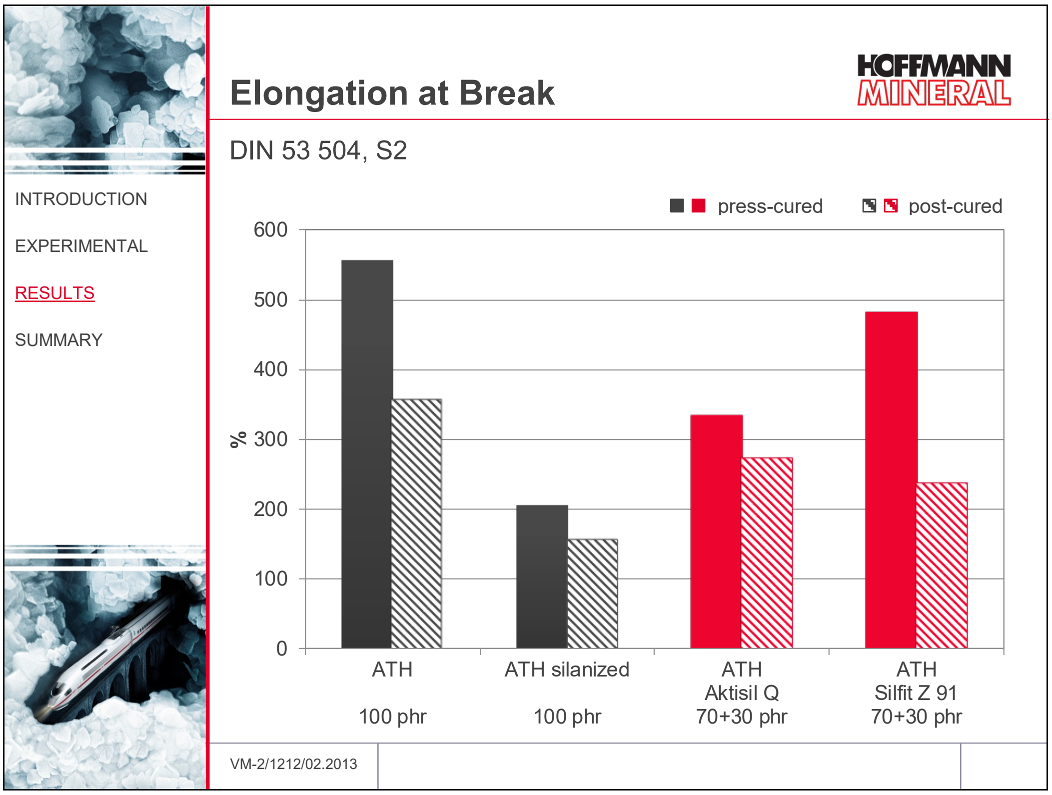


The partial replacement of ATH with Aktisil Q or Silfit Z 91 gives rise to a hardness increase vs. straight untreated ATH.

Press-cured, the hardness levels with the blends position themselves between the untreated and the vinyl silane treated ATH. After post-cure, they are on level with the silanized ATH variant.

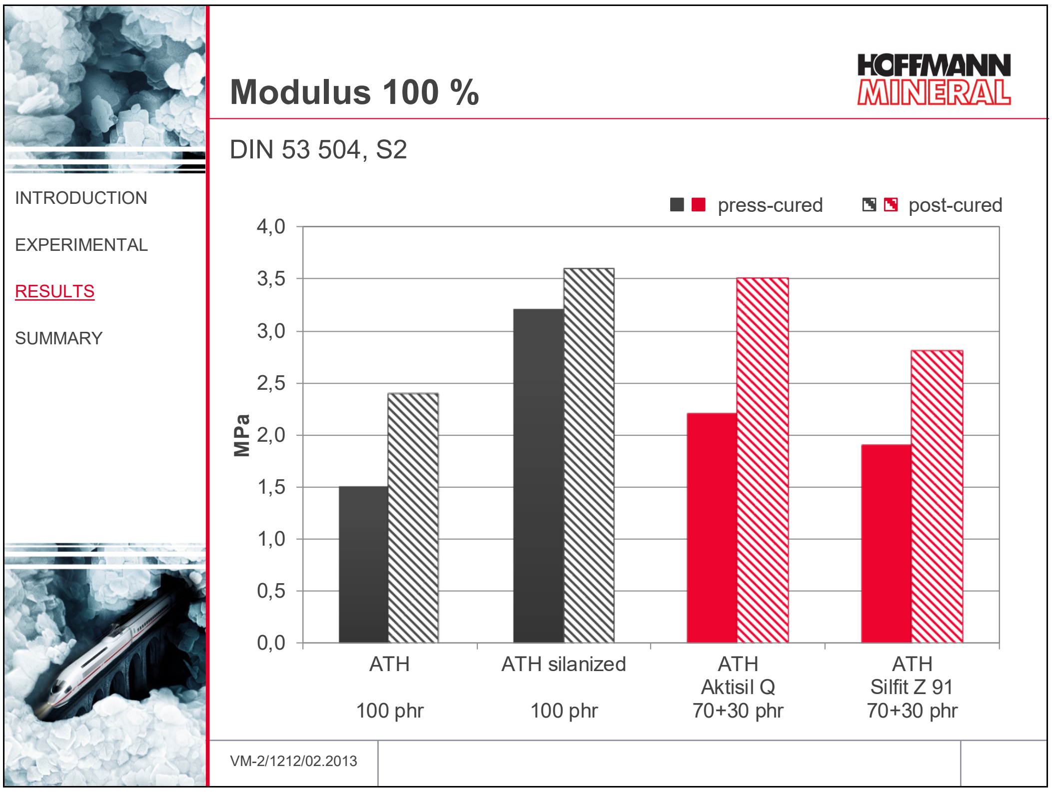


The low tensile strength level of untreated ATH, which even cannot be improved by post-curing, will be raised by blending with Silfit Z 91. Press-cured, the blends with Silfit Z 91 resp. Aktisil Q give practical identical results. After post-cure, the latter, in combination with the untreated ATH, reaches the high level of the silanized ATH grade.

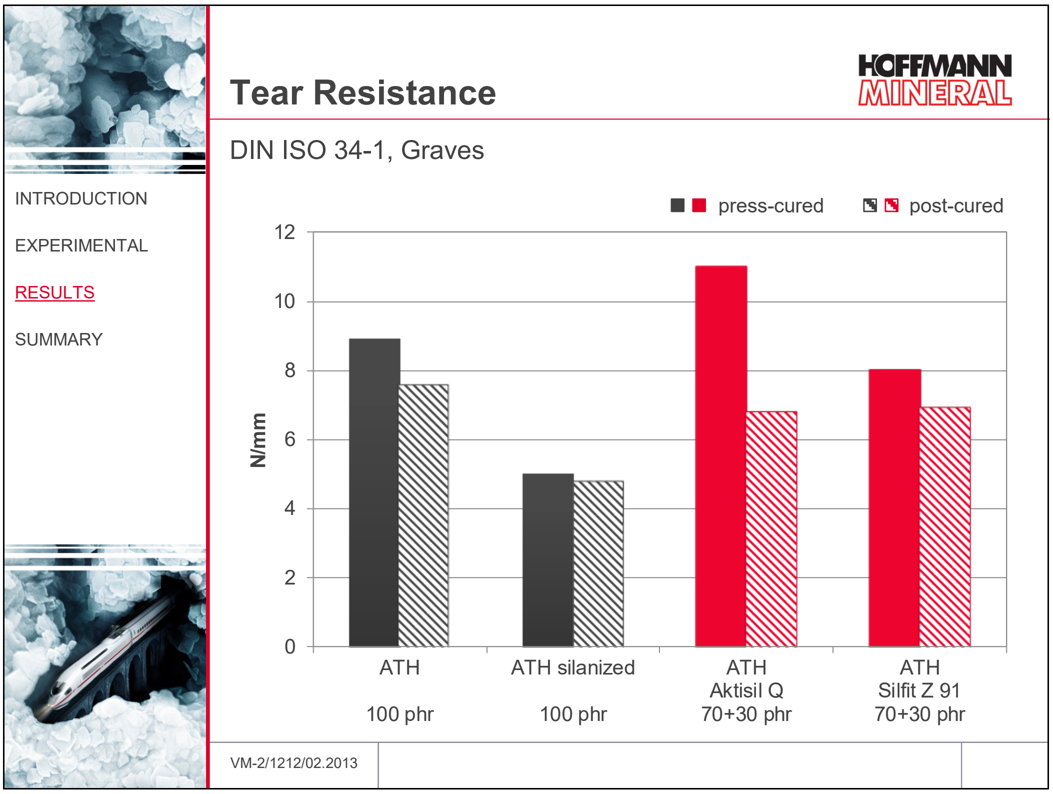


This graph shows the reduction of the elongation at break through post-cure. The compounds with the untreated fillers seem to react more strongly than the silanized grades.

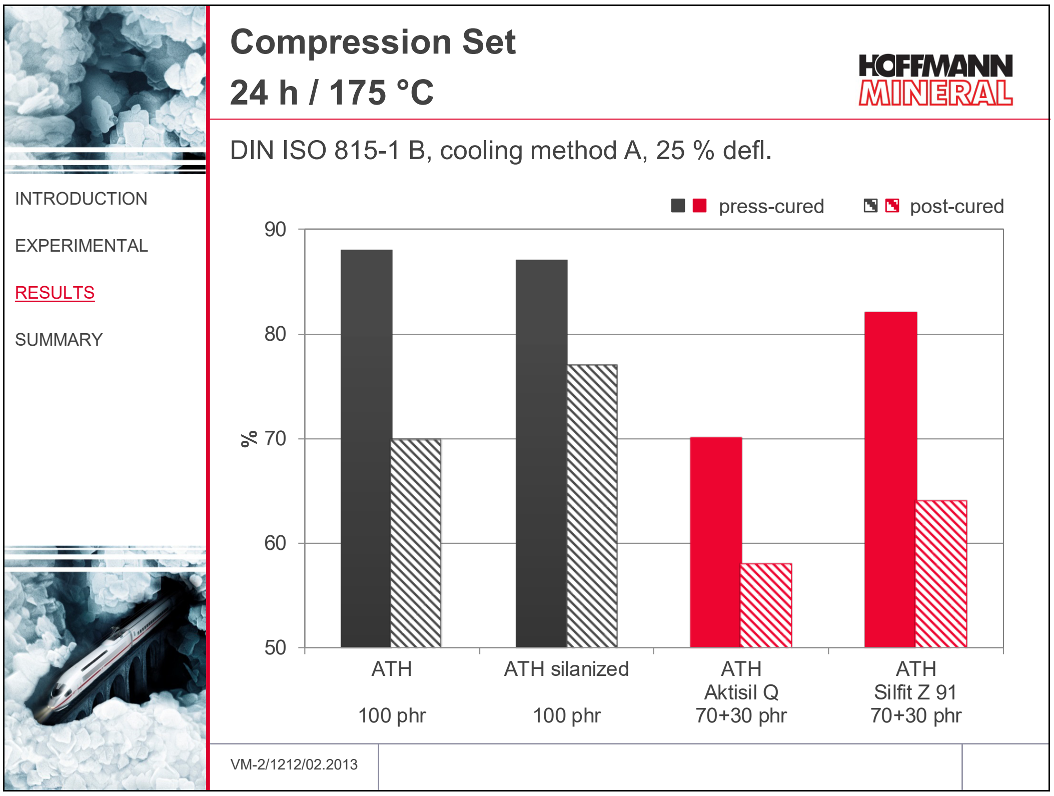
Without surface treatment, ATH also after post-cure is still able to reach a very high level compared with the surface treated grade. The partial replacement of ATH with Aktisil Q or Silfit Z 91 leads to lower elongations, but these still come out distinctly above the level of the silanized ATH. Along with the high tensile strength of the blends of ATH with Aktisil Q or Silfit Z 91, this results in a marked advantage vs. the silanized ATH grade.



The 100 % modulus results show a similar picture as the tensile strength.
By blending with Neuburg Siliceous Earth the results for straight ATH can be increased, which especially in the case of Aktisil Q after post-cure leads to a level comparable with silanized ATH.



This graph points to another advantage of the combination of ATH with Neuburg Siliceous Earth. Due to the surface treatment, the silanized ATH with relation to tear resistance loses against untreated ATH. The partial replacement of ATH with Silfit Z 91 or with the surface treated Aktisil Q allows to arrive at only slightly lower figures after post-cure, which means higher results than with the silanized ATH can be realized here. Along with comparable tensile strengths and higher elongations at break, the blends with Neuburg Siliceous Earth overall yield improved tensile properties.

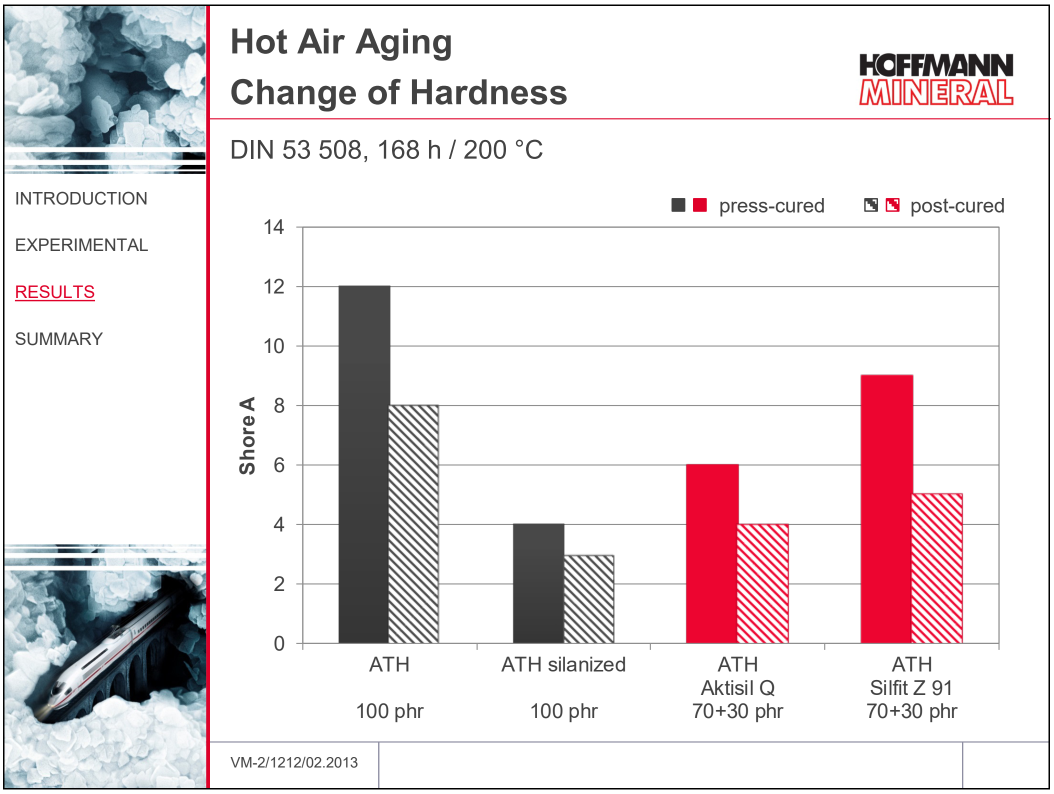


With respect to compression set, the importance of post-curing becomes evident. The high set values of the press-cured samples can be heavily reduced by this step.

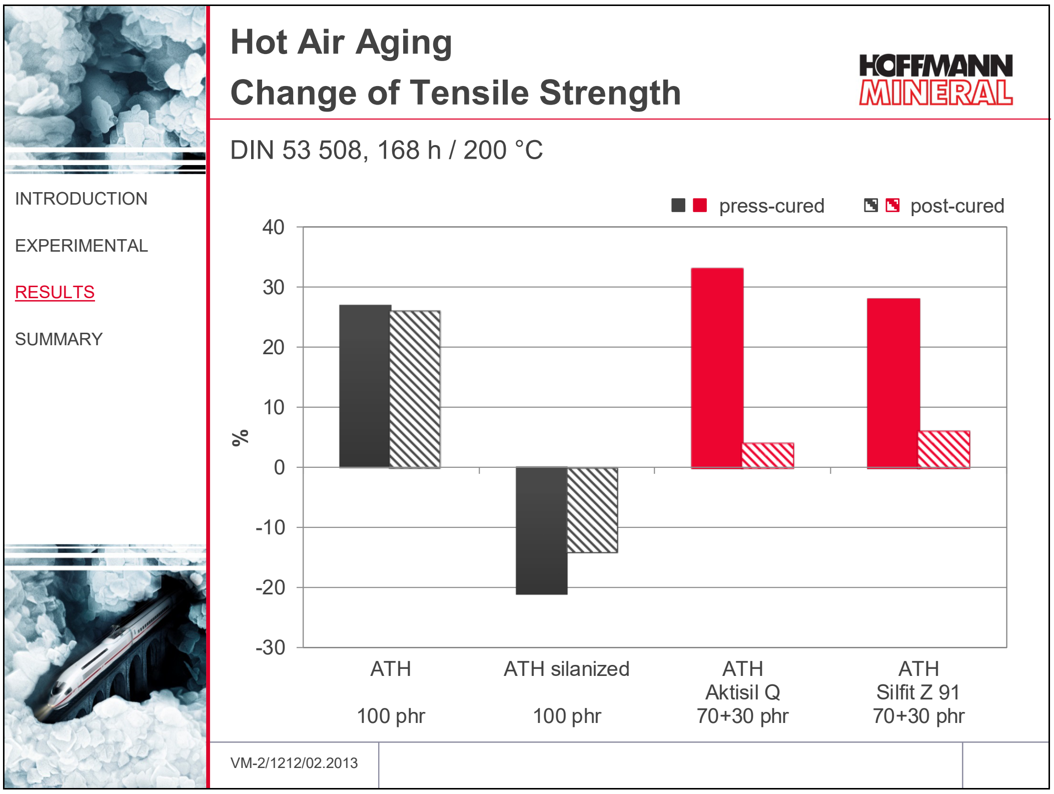
The silanized version of ATH all the same remains at a very high level, with the untreated ATH somewhat lower. The blend with Silfit Z 91 leads to a further decrease of the compression set. As already found in earlier studies, Aktisil Q gives rise to the lowest results – also in combination with ATH.

3.4 Hot air aging

Hot air aging of press-cured and post-cured samples was carried out for 168 hours at 200 °C.

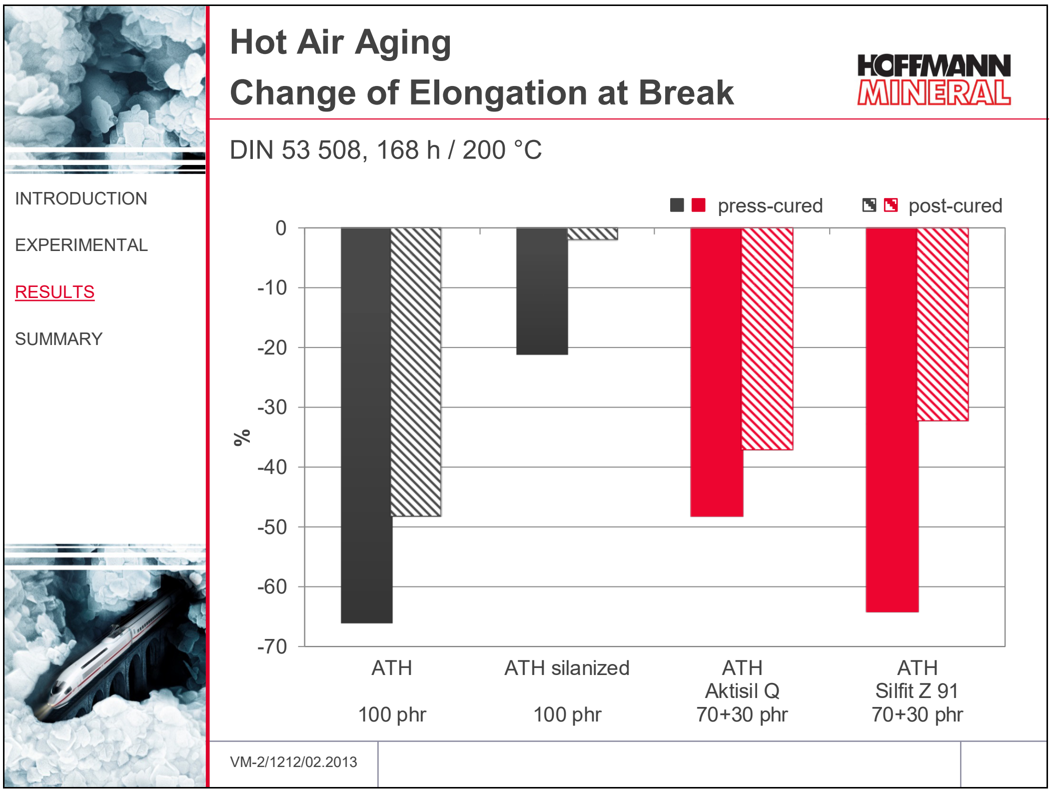


The hardness increase as measured after hot air aging can be minimized by post-curing. All the same, for the compound with the untreated ATH there is still a distinct increase which comes out less significant for the blend with Silfit Z 91. The blend with Aktisil Q too indicates a tendency towards lower change of hardness, in fact close to that of silanized ATH.



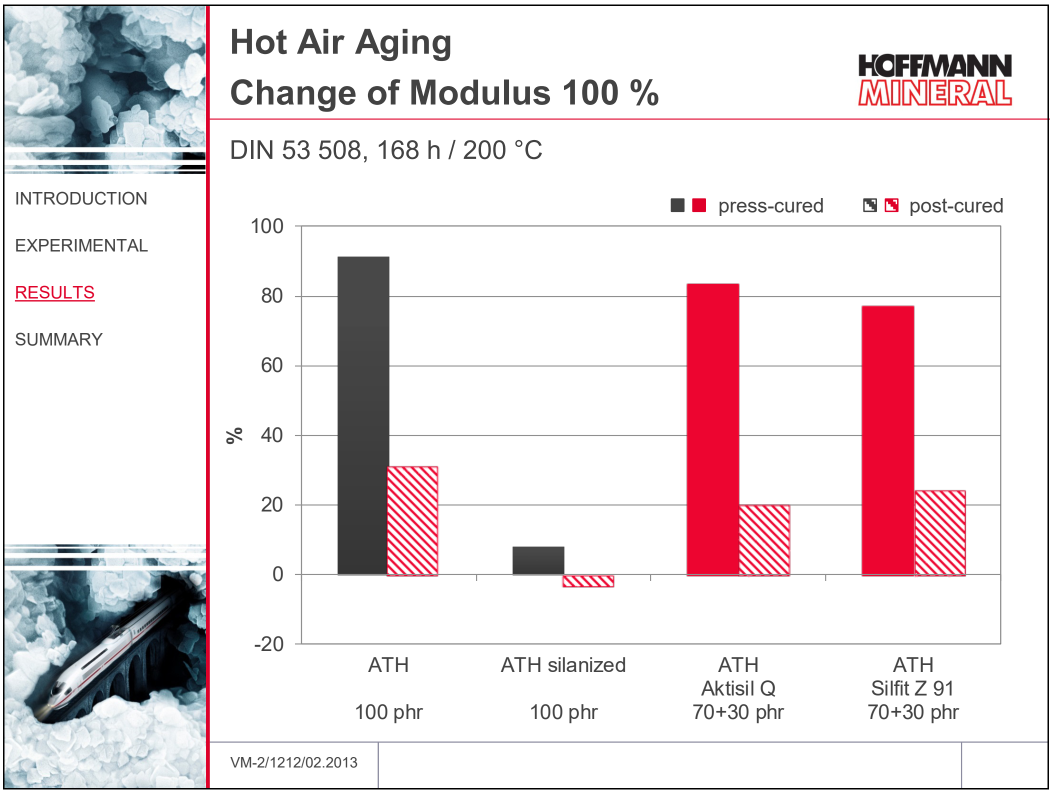
Above all, the blends of ATH with Neuburg Siliceous Earth grades react positively to post-curing, with the result that the high changes of the tensile strength during aging of the press-cured samples are strongly reduced.

This way, the high change of the compound with untreated ATH will be reduced to a minimum, as also is shown by the results for the blends of Aktisil Q and Silfit Z 91. The combination of ATH with Neuburg Siliceous Earth grades comes out favorably also when compared with silanized ATH, as the filler additions lead to a decreased tensile strength change during aging.



Post-curing has also favorable effects on the change of the elongation at break during aging.

Aktisil Q and Silfit Z 91 in blends with ATH give rise to a decreased change in the elongation at break vs. the compound with straight ATH. The silanized ATH after post-cure of the sample practically comes out unchanged after aging in hot air.



The 100 % modulus does practically not change for the silanized ATH during aging and post-curing does not have a noticeable effect. The untreated ATH by contrast, causes a distinct modulus increase, which can be minimized by post-curing the samples. Neuburg Siliceous Earth grades in blends with ATH are able to somewhat further diminish the modulus increase.

4 Summary

The partial replacement of ATH with Neuburg Siliceous Earth does not have any negative effect on the flame retarding properties of the evaluated silicone rubber compound. This was confirmed by the LOI results which are in agreement with straight ATH and the comparable results concerning heat release and smoke density.

The blend of ATH and Silfit Z 91 offers a rheology favorable for extrusions, in particular in comparison with straight untreated ATH. In this comparison, the blend also comes out more favorably in relation to the changes during hot air aging. The mechanical properties were found between the untreated and the silanized ATH along with a decrease of the compression set.

Aktisil Q blended with untreated ATH leads to the same benefits as Silfit Z 91 with respect to rheology and aging resistance. As to the mechanical properties, Aktisil Q is able to further improve the good performance of Silfit Z 91. The compression set will be reduced even more and at the same time the advantages of untreated and silanized ATH are combined. Elongation at break and tear resistance in the blend of ATH and Aktisil Q come out at a similar level to straight untreated ATH while the tensile strength offers a comparable level with silanized ATH.

In summary, the study underlines that a partial replacement of ATH with Neuburg Siliceous Earth grades is possible without losses in flame retardance but at the same time with easier processing and improved rheological and mechanical properties along with compound cost savings.

A special thanks goes to the company Nabaltec AG at Schwandorf for carrying out the fire tests as well as for the friendly and competent support.