Neuburg Siliceous Earth

in MS-polymer based sealants

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1 Introduction

MS polymers are part of reactive one-component systems. The polymers were developed in Japan in the mid-70s. Since then, they have been used for formulating elastic sealants, where they offer the following benefits:

- very low emissions
- absence of isocyanates, solvents, silicone and PVC
- environmental friendliness and no odor
- rapid curing at ambient temperature without formation of blisters
- neutral pH
- outstanding low-temperature elasticity
- inherently good adhesion on various substrates
- good paintability

The objective of the present study is to introduce Neuburg Siliceous Earth in appropriate formulations as a partial or complete replacement for the conventional fillers. In so doing, the usual methods of preparation and application were maintained, and the batches were subjected to pertinent tests.

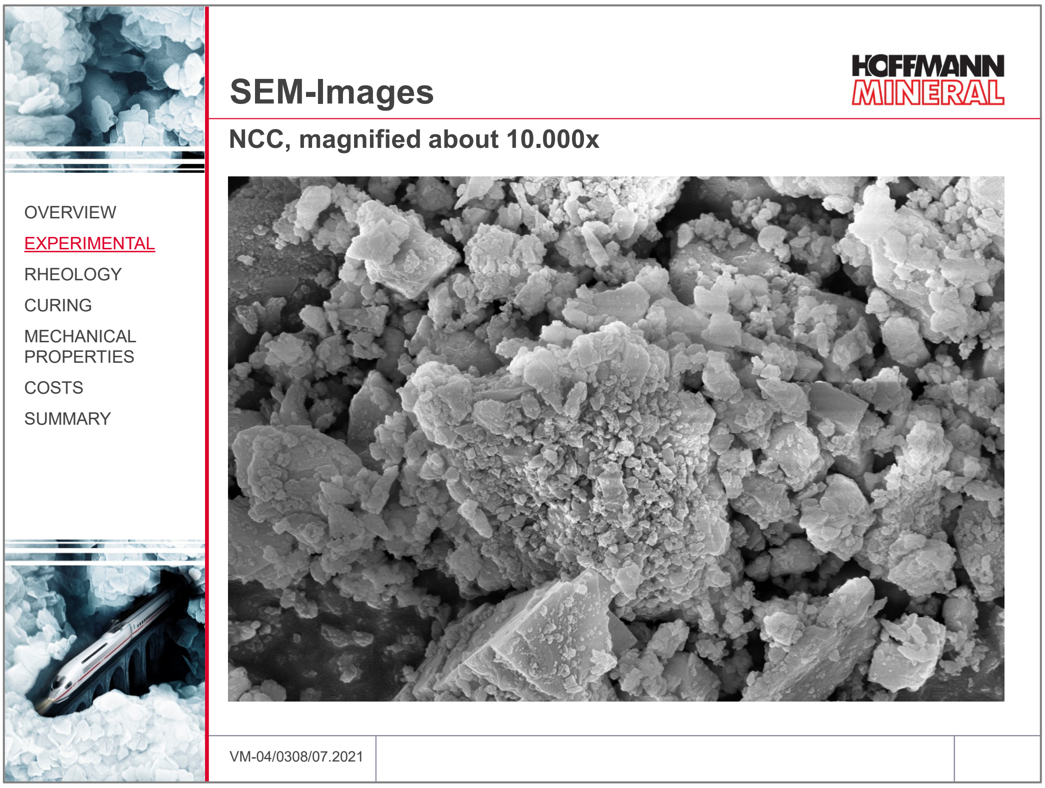
Note:
This study is intended to show the basic effects of the various Neuburg Siliceous Earth grades, although the formulation and raw materials used are in some cases no longer state of the art or are subject to other restrictions.

2 Experimental

2.1 Filler morphology and characteristic properties

Natural calcium carbonate (NCC)

The natural calcium carbonate used was a modification of limestone surface treated with stearate, presenting a compact shape, low oil number and low specific surface area.



Neuburg Siliceous Earth

The Neuburg Siliceous Earth, extracted in the surrounding of Neuburg (Danube), is a natural combination of corpuscular Neuburg silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods. As a result of natural aging, the silica portion exhibits a round grain shape and consists of aggregated cryptocrystalline primary particles of about 200 nm diameter. Such a structure is responsible for a relatively high specific surface area and oil absorption, which result, besides rheological activity, also in a whole range of application properties.

The morphology of the Neuburg Siliceous Earth is illustrated in the following picture:

OVERVIEW
EXPERIMENTAL
RHEOLOGY
CURING
MECHANICAL PROPERTIES
COSTS
SUMMARY

SEM-Images

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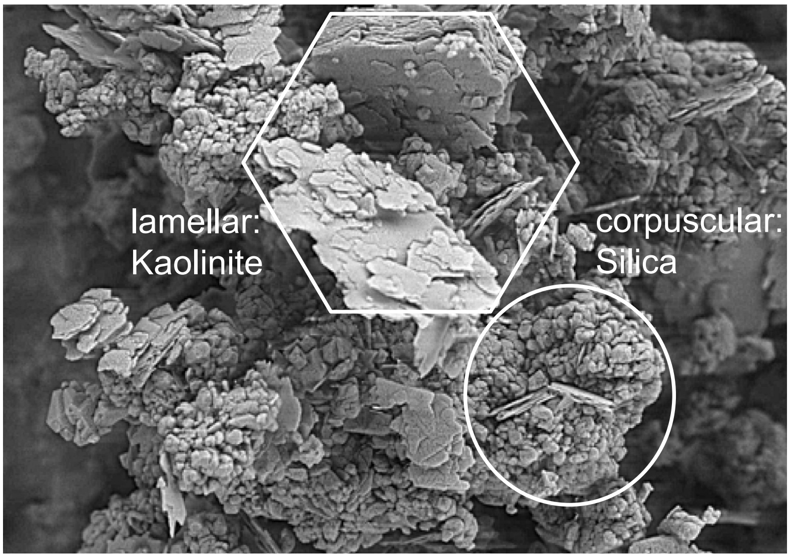
Neuburg Siliceous Earth, magnified about 10.000x



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The table summarizes the characteristic properties of the functional fillers used:

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Filler characteristics

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	Reference Calcium Carbonate natural	Neuburg Siliceous Earth (NSE)	
	NCC	Sillitin Z 86 Sillitin Z 86 puriss	Aktisil PF 777
Particle size d50 [µm]	1.3	1.9	2.2
Particle size d97 [µm]	13	8	10
Oil absorption [g/100g]	20	55	35
Surface area [m²/g]	approx. 8	11	8
Functionalisation	stearate	none	alkyl

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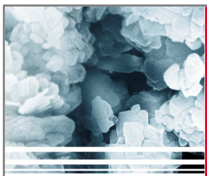
2.2 Formulation



Formulation

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- OVERVIEW
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- SUMMARY

	NCC		NSE
MS Polymer (high modulus)	100	100	100
Plasticizer (DIUP)	55	100	100
Titanium dioxide	20	20	20
Rheological additive (RA) Crayvallac SLX (micronized amide wax)	5	5	5
Light stabilizer / UV-Absorber	2	2	2
NCC	180	180	---
NSE	---	---	180
Drying agent	2	2	2
Adhesion promoter (AS) 3-amino propyl triethoxy silane)	3.5	3.5	5
Catalyst	2	2	2
Total (parts by weight)	**369.5**	**414.5**	**416**

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Starting from the base formulation with 180 parts by weight (pbw) of natural calcium carbonate and 55 pbw plasticizer, the loading of Neuburg Siliceous Earth and plasticizer was to be adjusted in a way to arrive at comparable tensile moduli in the tensile test. For Neuburg Siliceous Earth, this could be achieved with 100 pbw of plasticizer along with 180 pbw of filler.

Apart from Sillitin Z 86, from the range of Neuburg Siliceous Earth grades also the physically aftertreated Sillitin Z 86 puriss and the chemically (alkyl functionalized) surface treated Aktisil PF 777 were included in the study.

In the batches with Neuburg Siliceous Earth, the aminosilane based adhesion promoter will partly be adsorbed at the siliceous filler surface and, therefore, immobilized, resulting in a reduced contribution towards improved adhesion. For this reason, the amount of bonding agent was increased here from 3.5 to 5 pbw. [1)]

The other ingredients were kept constant in all formulations.

[1)] The original base recipe contained as adhesion promoter 3 pbw DAMO (diaminosilane with primary and secondary amino groups).Increasing the amount of this product in the NSE batches would have necessitated a labelling of the formulations as Xi = irritating (DAMO has to be labelled at concentrations >1 %).
Alternatively, A 1100 (a primary aminosilane which does not require an obligation for labelling even at higher concentrations)was used, and the amount in the calcium carbonate batches slightly increased to 3.5 parts, in order to keep the properties at the level of the original base formulation.
A further way to avoid the labelling obligation due to the increase of bonding agent is the use of the surface treated NSE grade Aktisil AM along with an unchanged DAMO concentration. The results with such an approach were comparable with the Sillitin Z 86 batches with 5 pbw A 1100.

2.3 Preparation of batches

The fillers were pre-dried along with the titanium dioxide. [2)]

Binder, plasticizer, rheological additive and light stabilizer were added first

Fillers and titanium dioxide were then added and dispersed for 45 min under vacuum. During this time, the temperature of the batch was kept for 30 min between 60 and 90 °C in order to sufficiently activate the rheological additive.

After cooling down to 50 °C, at intervals of 5 min the drying agent, the bonding agent and the catalyst were added and stirred in.

After short deaeration, the compound was filled into a cartridge.

[2)] *Tests were also carried out without pre-drying the fillers and otherwise unchanged processing conditions. Neither the NSE nor the calcium carbonate batch showed any differences with respect to storage stability vs. the formulations with pre-dried fillers. Obviously, the vinylsilane drying agent in the formulation is sufficiently active to bind the moisture present in the fillers. It was only with a reduced concentration of drying agent that the batches began to harden in the cartridges.*

3 Results

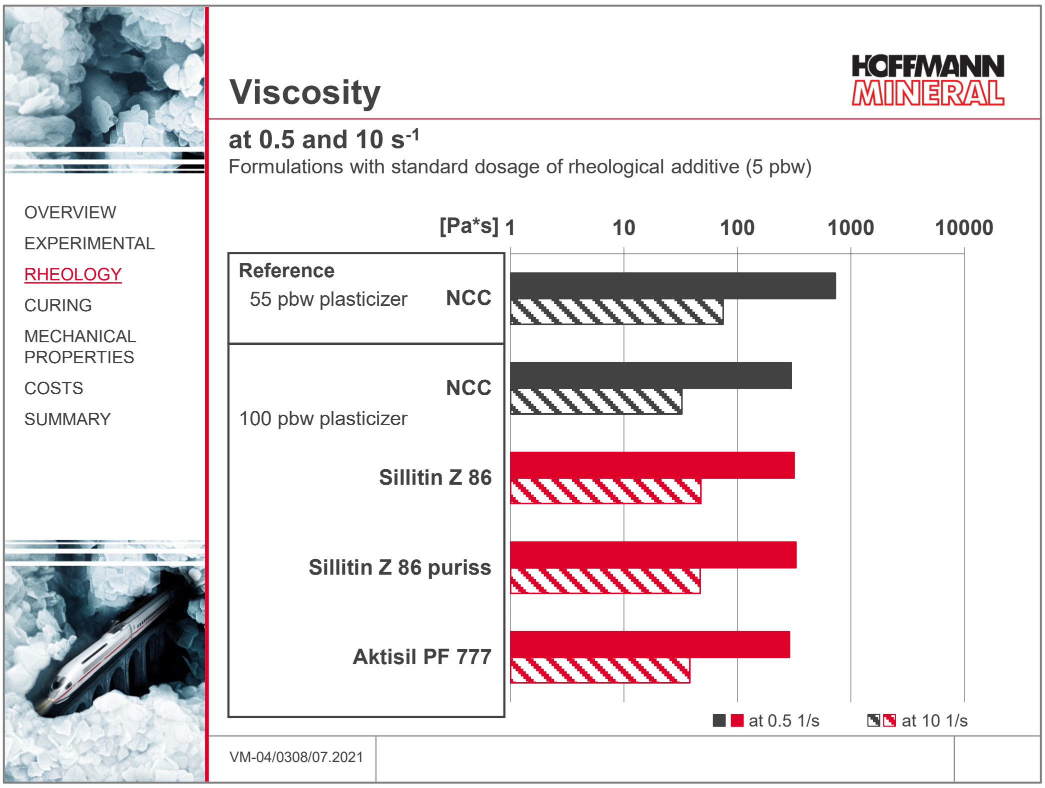
3.1 Rheology

The rheological tests were carried out with a plate/plate instrument (diameter 25 mm, gap 1 mm). For each determination, the system was filled anew. The tests were run under rotation.

Viscosity

The viscosity results were interpolated for the shear rate levels indicated, from a shear rate controlled flow diagram (logarithmic increase from 0.1 to 100 s^{-1}). In particular, comparisons were made between the viscosities of the batches at 0.5 and 10 s^{-1}.

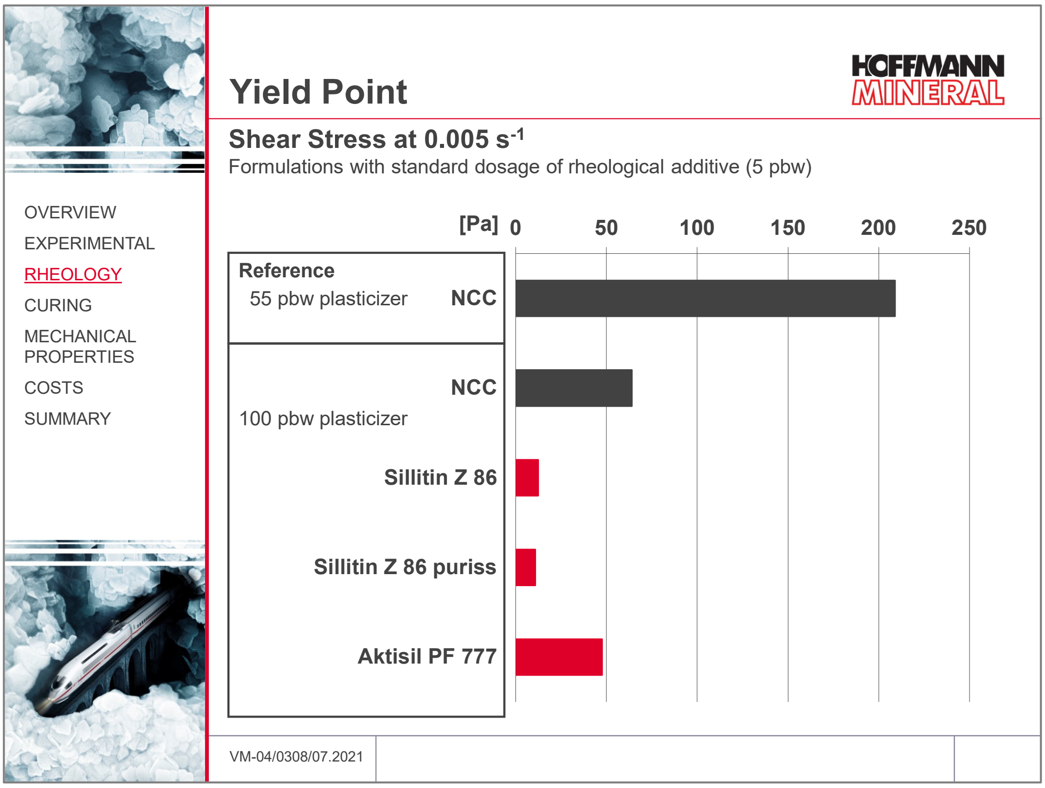
In comparison with the base formulation, all the test batches, as a result of the higher plasticizer content, present a lower viscosity. The individual results of the formulations come out in relation with the oil number of the fillers used: the natural calcium carbonate (oil no. 20 g/100 g) imparts the lowest viscosity, Neuburg Siliceous Earth without surface treatment (oil no. 55 g/100 g) is positioned at a somewhat higher level.



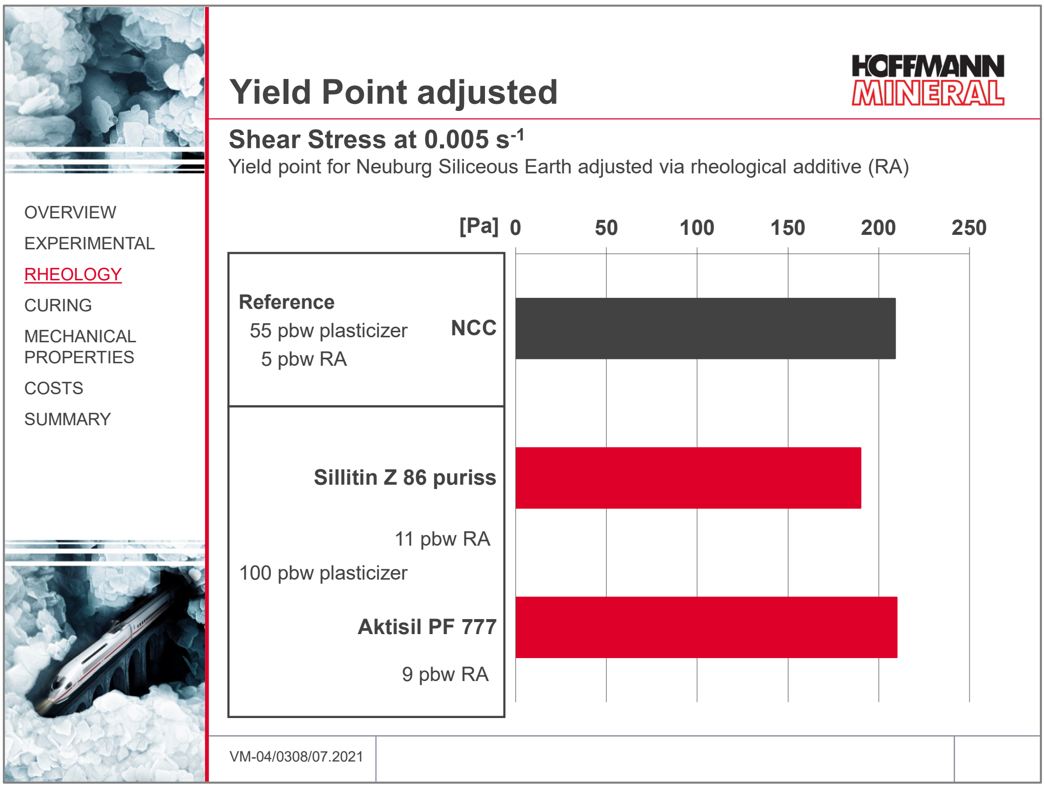
Yield point

The yield point was determined by linearly increasing the shear stress from 2.5 to 1000 Pa with a rate of 2.5 Pa/s. The result was expressed as the shear stress at a shear rate of 0.005 s^{-1}.

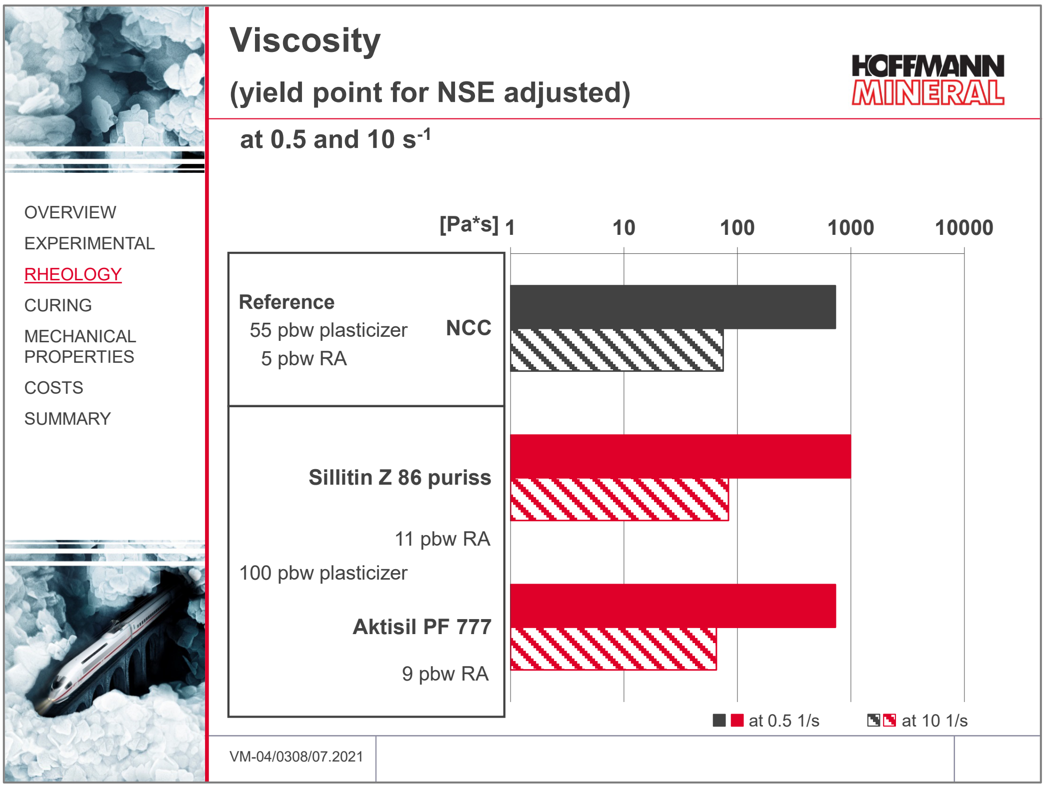
In all test formulations, the higher plasticizer content gives rise to a marked decrease of the yield point. While the with an alkyl funcionalized group modified Aktisil PF 777 comes out similar to the natural calcium carbonate, the yield point with Sillitin Z 86 and Sillitin Z 86 puriss, both without surface treatment, turns out distinctly lower.



If the yield point is to bring back to the level of the reference formulation (with 55 pbw plasticizer), when working with Sillitin – as illustrated in the figure for Sillitin Z 86 puriss – about 11 pbw rheological additive are required, and with the hydrophobically treated grade Aktisil PF 777 about 9 pbw.



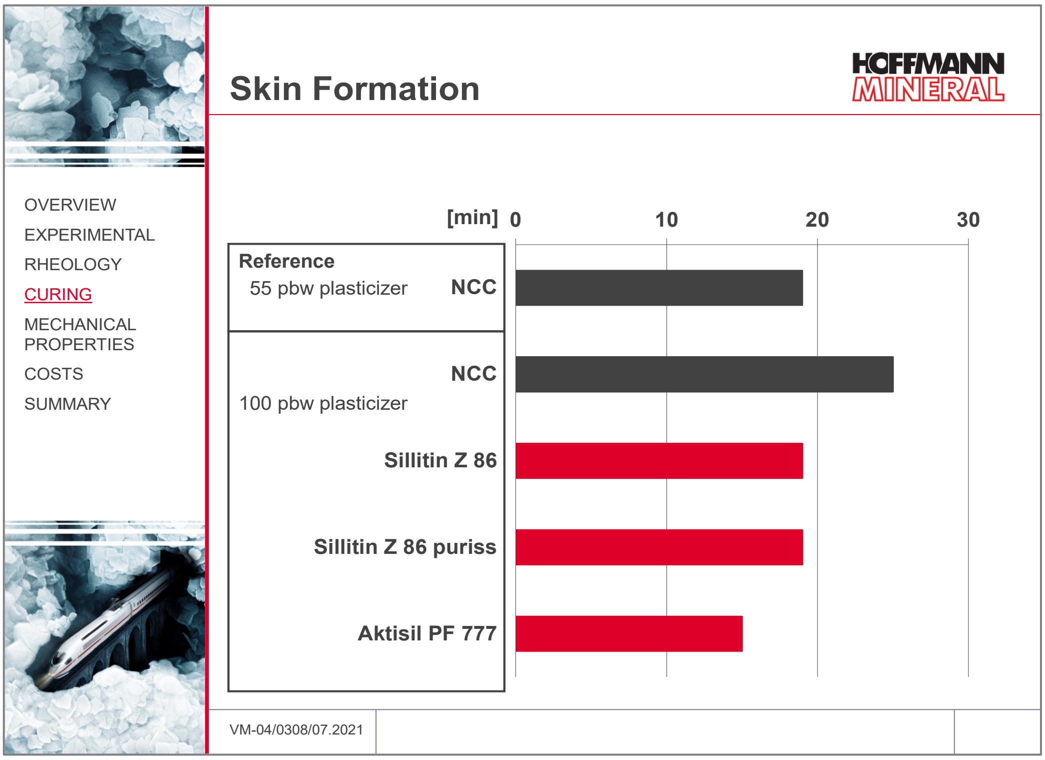
Upon adjustment of the yield point, Sillitin Z 86 tends towards somewhat higher viscosity, while Aktisil PF 777 stays close to the reference.



3.2 Curing

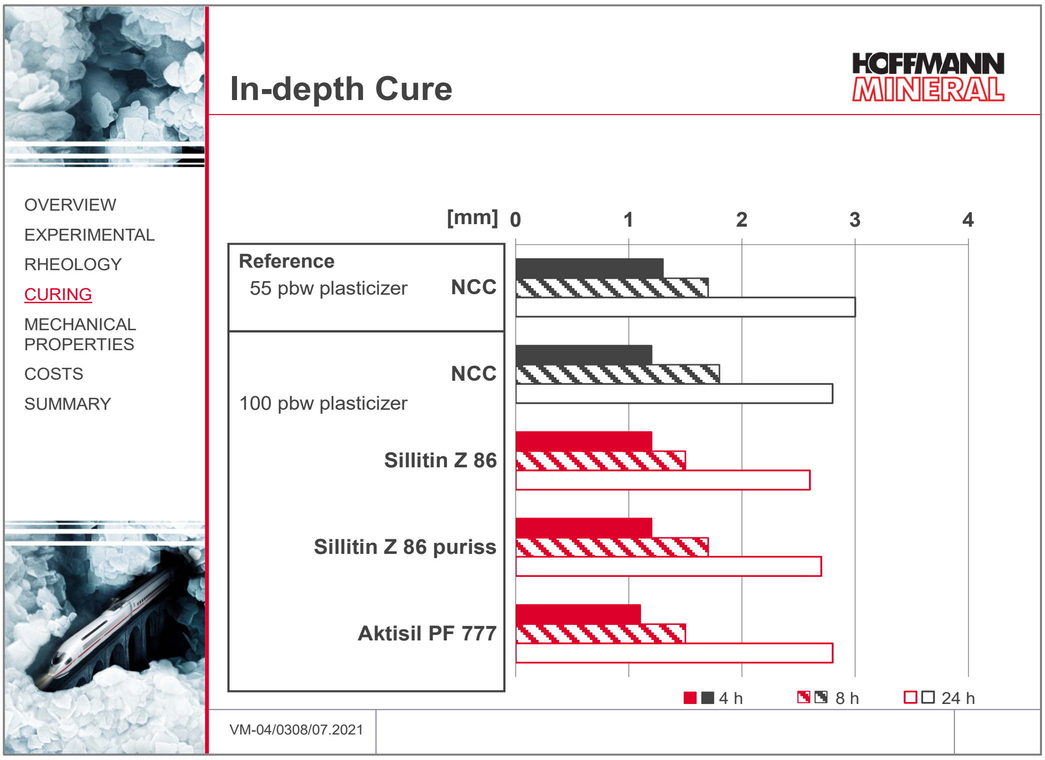
For testing the curing speed, the compound was squeezed out of the cartridge. The test was carried out at normal climate conditions (23 °C, 50 % relative humidity). Skin formation was defined as the time to touch the surface of the extrudate without rests of the compound sticking to the fingers.

Different from natural calcium carbonate, untreated Neuburg Siliceous Earth with increased plasticizer addition does not lead to retarded skin formation. Aktisil PF 777 even gives a faster onset of the reaction.



For the assessment of full cure, the extrudate was cut open after different periods of time, and the thickness of the cured layer was determined with the aid of a caliper rule.

Substantial differences could not be observed.



3.3 Mechanical properties

Varying the amount of rheological additive does hardly at all influence the mechanical and adhesion properties. Therefore, in the following only the results with the standard loading of rheological additive will be presented.

Preparation of test samples

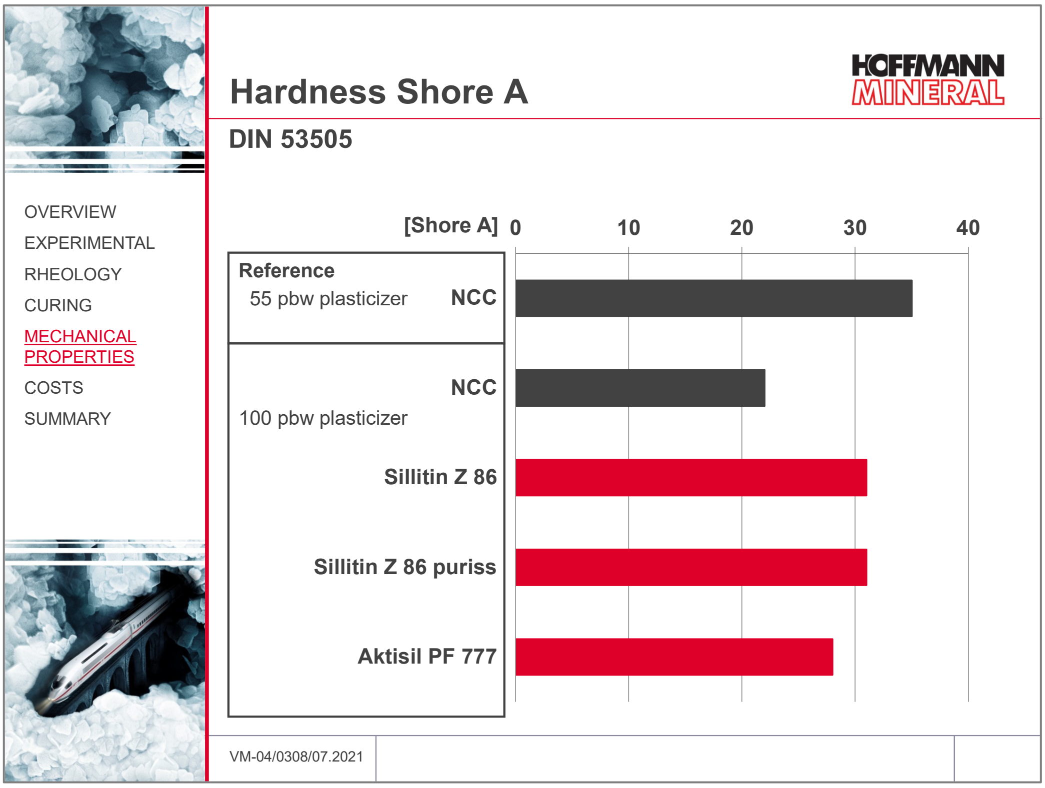
For tensile and hardness tests, sheets with a thickness of about 2 mm were prepared. After curing the sample sheets for 14 days at standard conditions (23 °C, 50 % relative humidity), dumbbell samples S2 according to DIN 53504 were died out and tested.

For the lap shear test, samples of pure aluminum parts were prepared where the overlapping joint surface area was 12.5 x 25 mm with an adhesive thickness of 2 mm. The tests were run after curing for 14 days at standard climate conditions.

Hardness (DIN 53505)

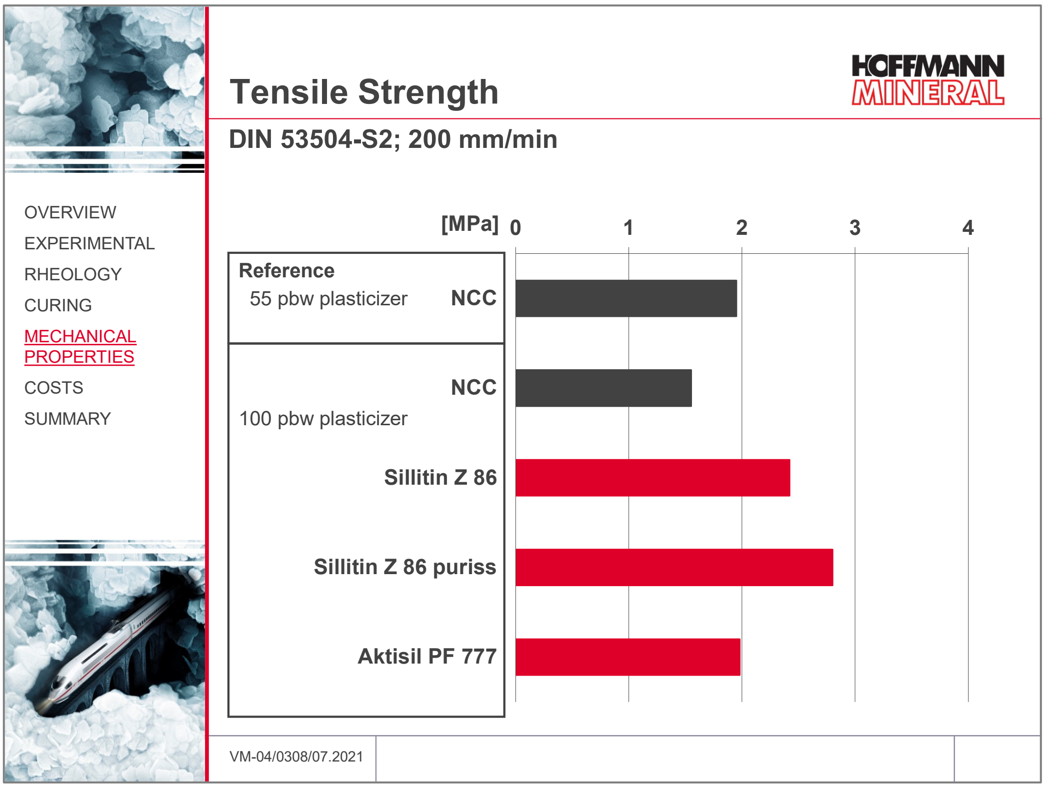
Hardness was determined on piled-up sections of the sample sheets to a height of 6 mm according to DIN 53505.

Contrary to the formulation with natural calcium carbonate, the hardness decrease caused by increased plasticizer addition came out markedly less pronounced when working with Neuburg Siliceous Earth.

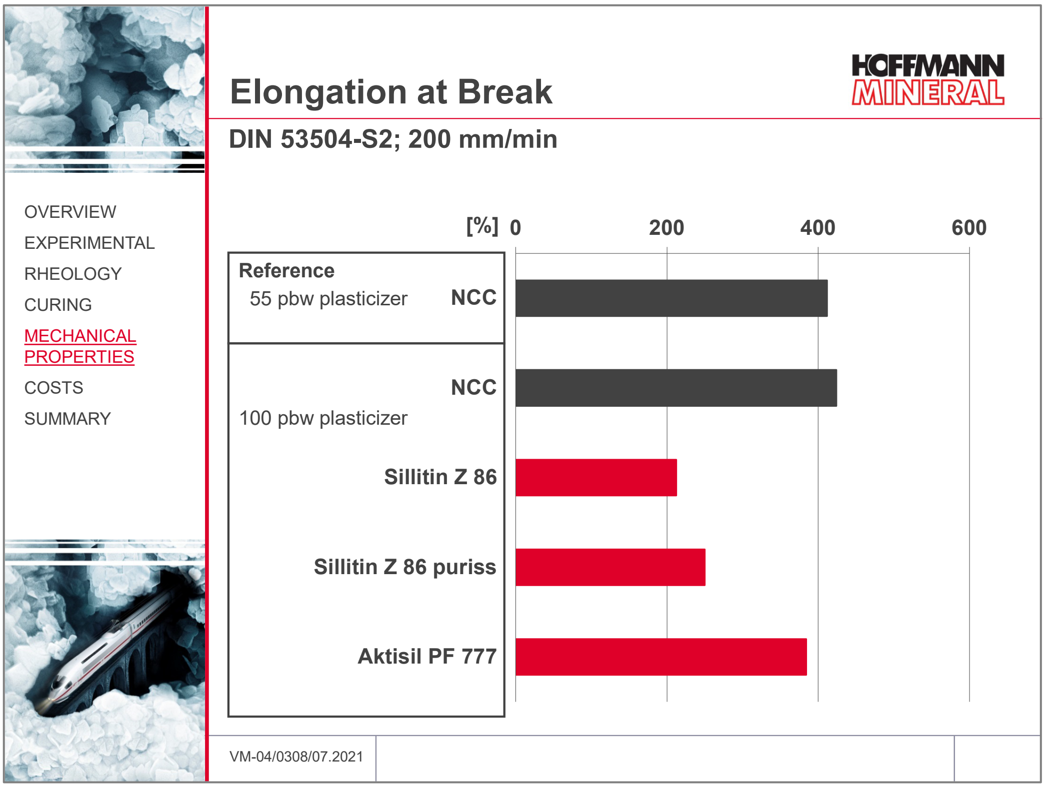


Tensile test (DIN 53504)

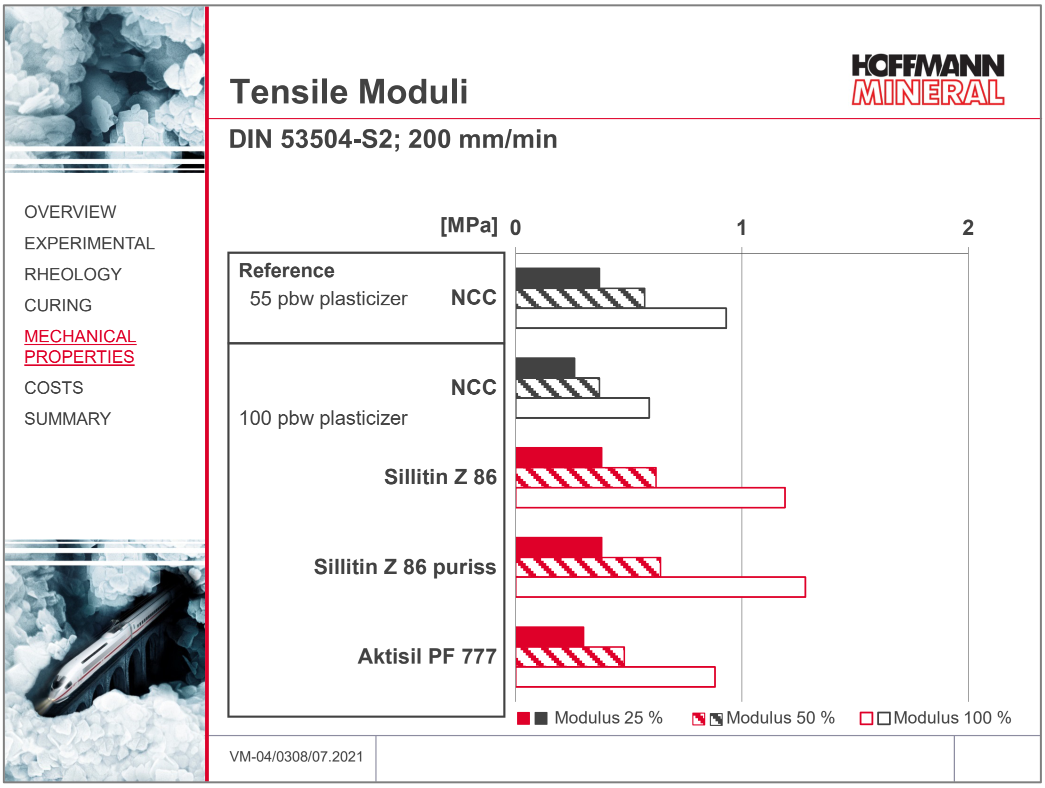
Neuburg Siliceous Earth, and in particular the physically aftertreated puriss grade with improved dispersion properties, gives rise to a markedly increased tensile strength compared with calcium carbonates. The hydrophobic grade Aktisil PF 777 remains at the level of the reference formulation.



Also elongation at break with Aktisil PF 777 is similar to the reference, while the two untreated siliceous earth grades Sillitin Z 86 and Sillitin Z 86 puriss come out markedly lower.



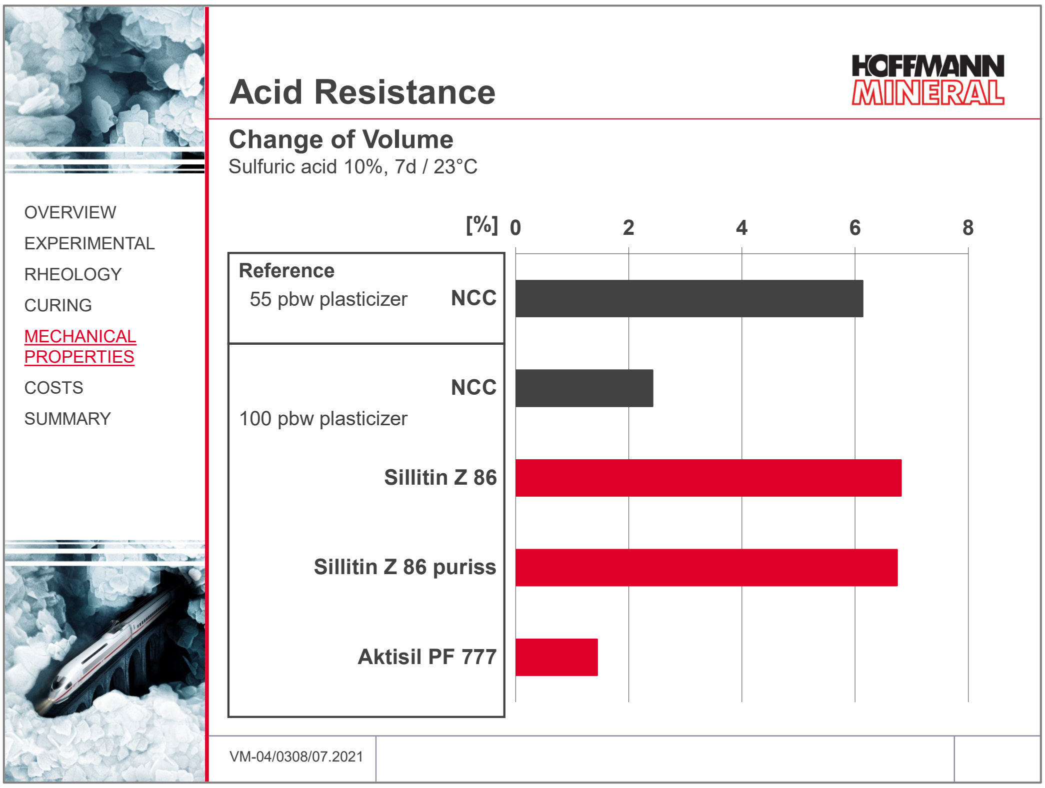
Up to 50 % elongation, also Neuburg Siliceous Earth gives low tensile moduli, while with Aktisil PF 777 the stress/strain ratio at 100 % elongation remains comparable.



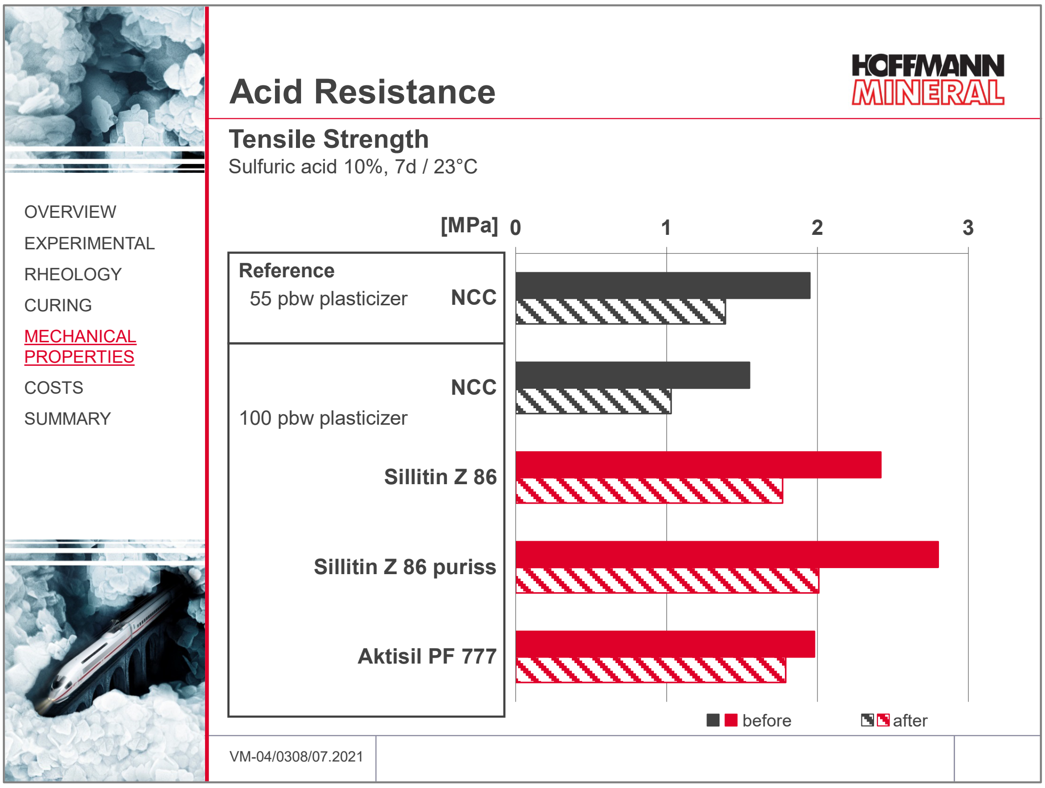
Acid resistance

S 2 dumbbells were died out from the sample sheets and immersed for 7 days in 10 % sulfuric acid at 23 °C. Swelling behavior and tensile properties were tested immediately after taking out of the acid bath.

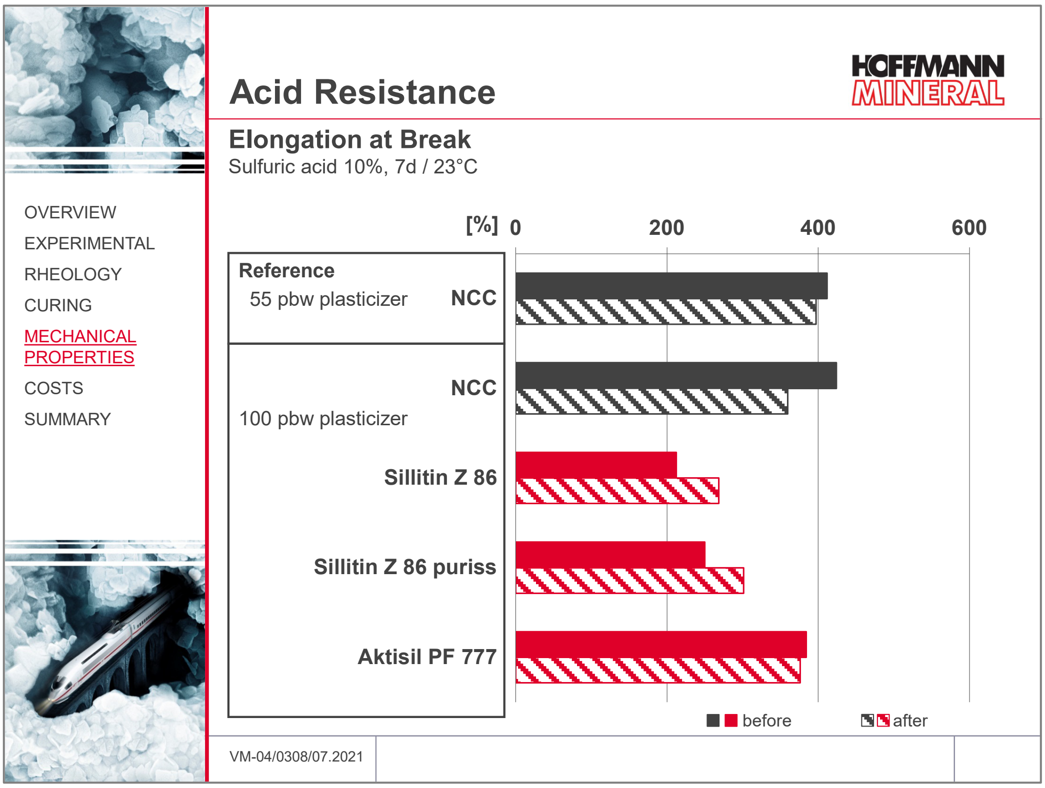
The volume increase of the samples with Sillitin Z 86 and Sillitin Z 86 puriss was practically equal to the reference formulation. Aktisil PF 777 and the natural calcium carbo-nate with increased plasticizer addition gave rise to a markedly lower volume swell.



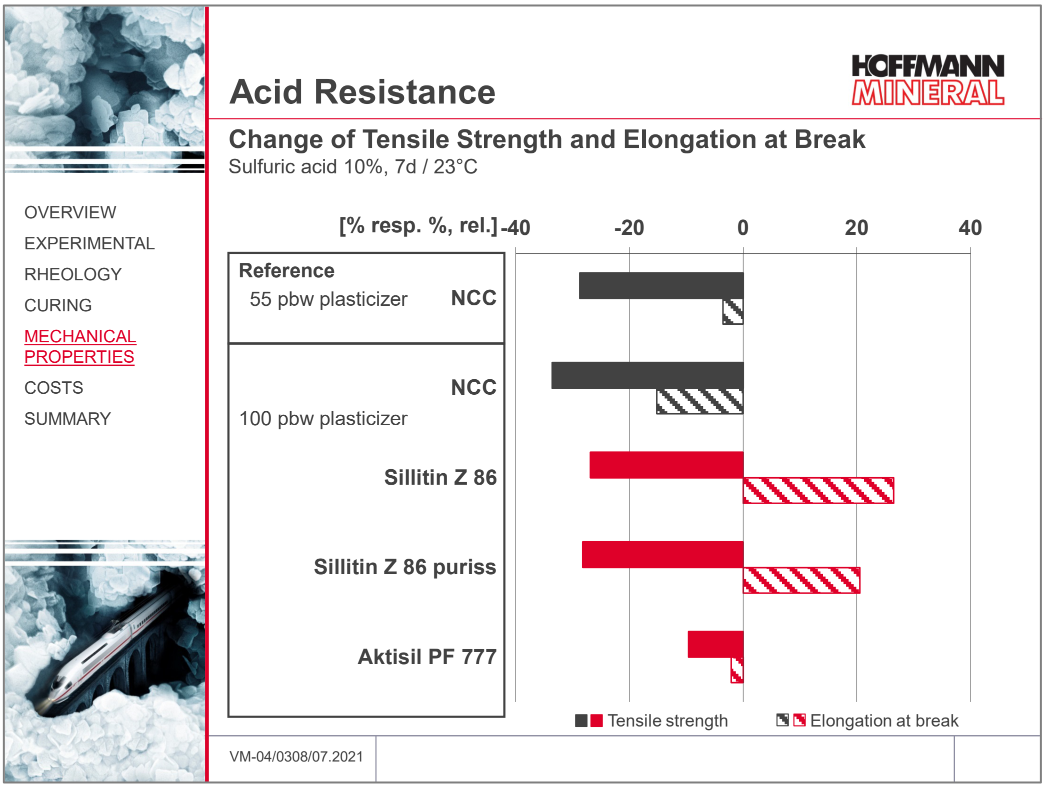
In the tensile test, all formulations showed a decreased tensile strength, with Aktisil PF 777 offering the lowest loss.



Elongation at break with calcium carbonate is reduced by the acid exposure, Sillitin Z 86 and Sillitin Z 86 puriss show a certain increase, and Aktisil PF 777 remains at the original level.

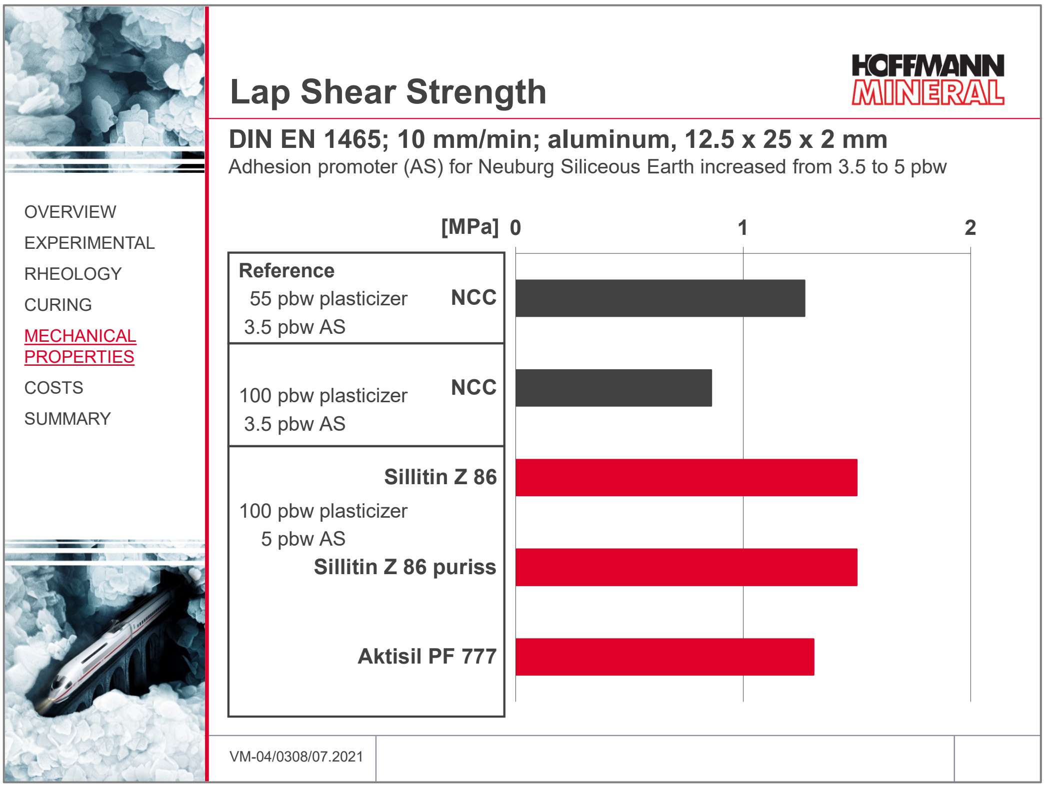


These effects come out particularly distinctly when comparing the percentage changes: the acid exposure of the untreated siliceous earth grades Sillitin Z 86 and Sillitin Z 86 puriss causes a similar loss of the tensile strength as with the calcium carbonate formulation, but elongation at break increases with the siliceous earth filler. Aktisil PF 777 with respect to tensile strength and elongation remains much more resistant than the other fillers.



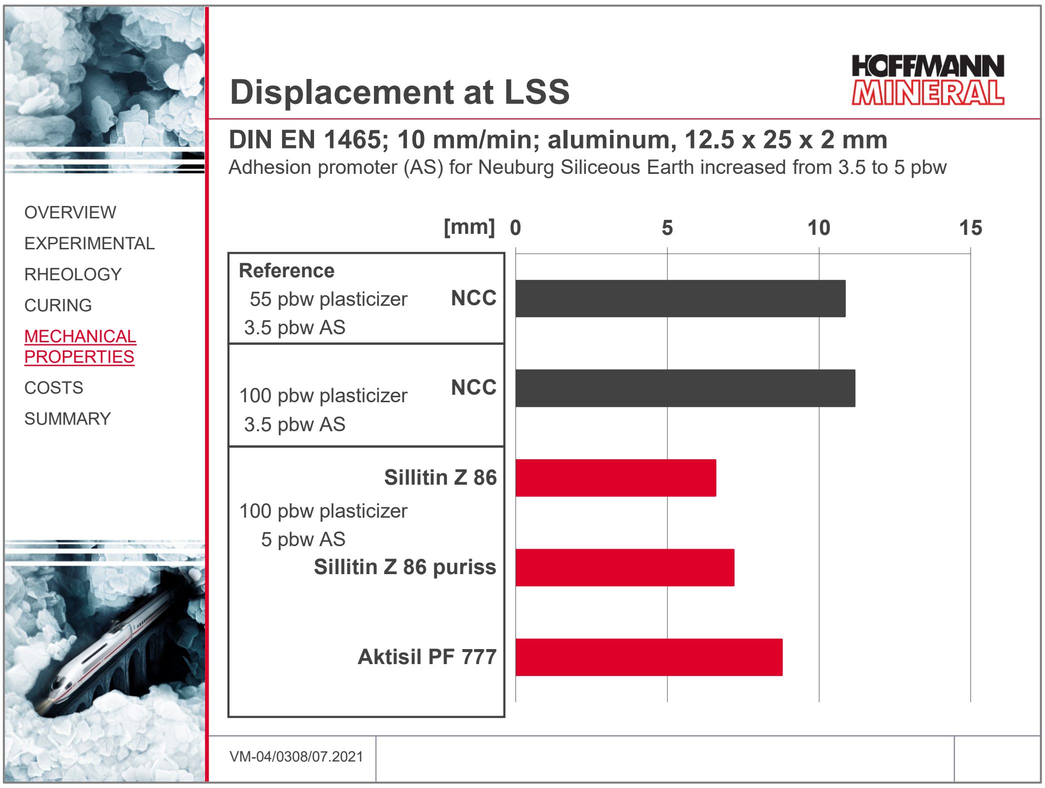
Lap shear test (DIN EN 1465)

Increased plasticizer content leads to a marked decrease of lap shear strength with the natural calcium carbonate. Untreated Neuburg Siliceous Earth gives rather increased results, Aktisil PF 777 remains on the level of the reference.



In order to assess the deformability of the adhesive joint, the shift distance was measured in the lap shear test. Neuburg Siliceous Earth here gives rise to a distinctly different stress/strain curve with a markedly reduced shift distance.

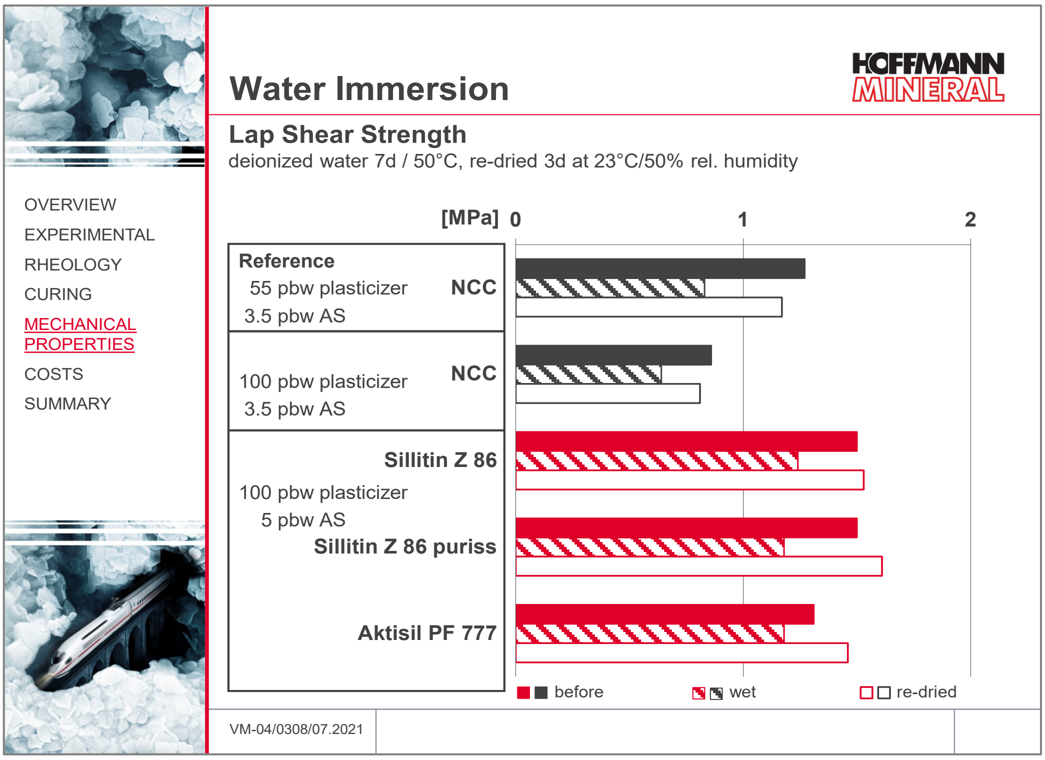
However, the measured shift distance of 6-8 mm at an adhesive joint thickness of 2 mm still corresponds to a potential deformability of 300 to 400 %.



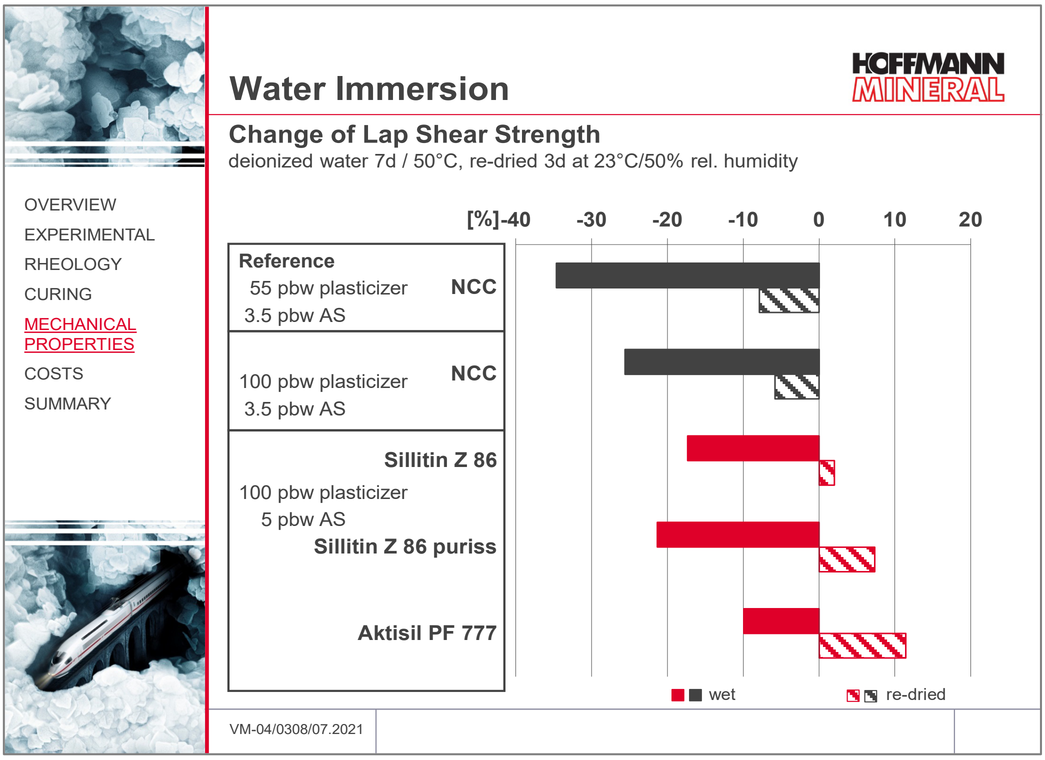
Warm water resistance

The warm water resistance was assessed via the lap shear test. After curing for 14 days, samples were immersed in water for 7 days at 50 °C. Tests were conducted immediately after taking the samples out of the water bath, as well as after 3 days of re-drying at normal climate conditions.

All formulations show a decrease of the lap shear strength in the wet state. After drying, the batches with calcium carbonate did no longer present the original level, while the formulations with Neuburg Siliceous Earth even offered higher results than before the water immersion.

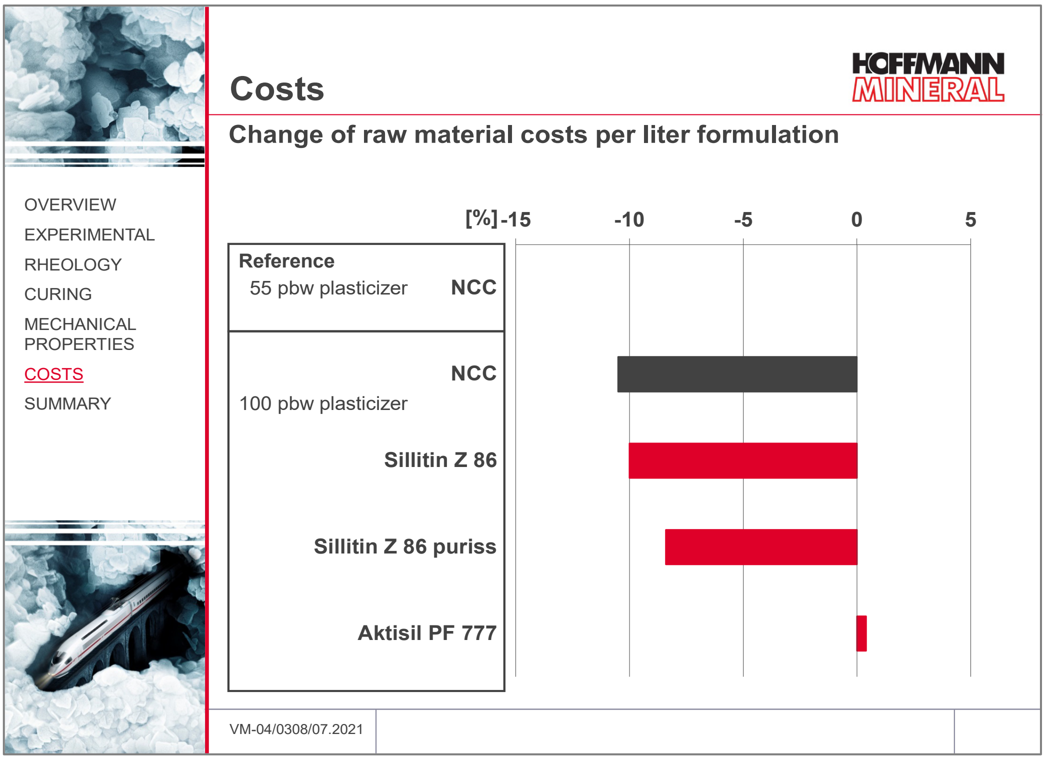


Here too, the comparison of percentage changes underlines the favorable resistance properties of Neuburg Siliceous Earth, in particular Aktisil PF 777.

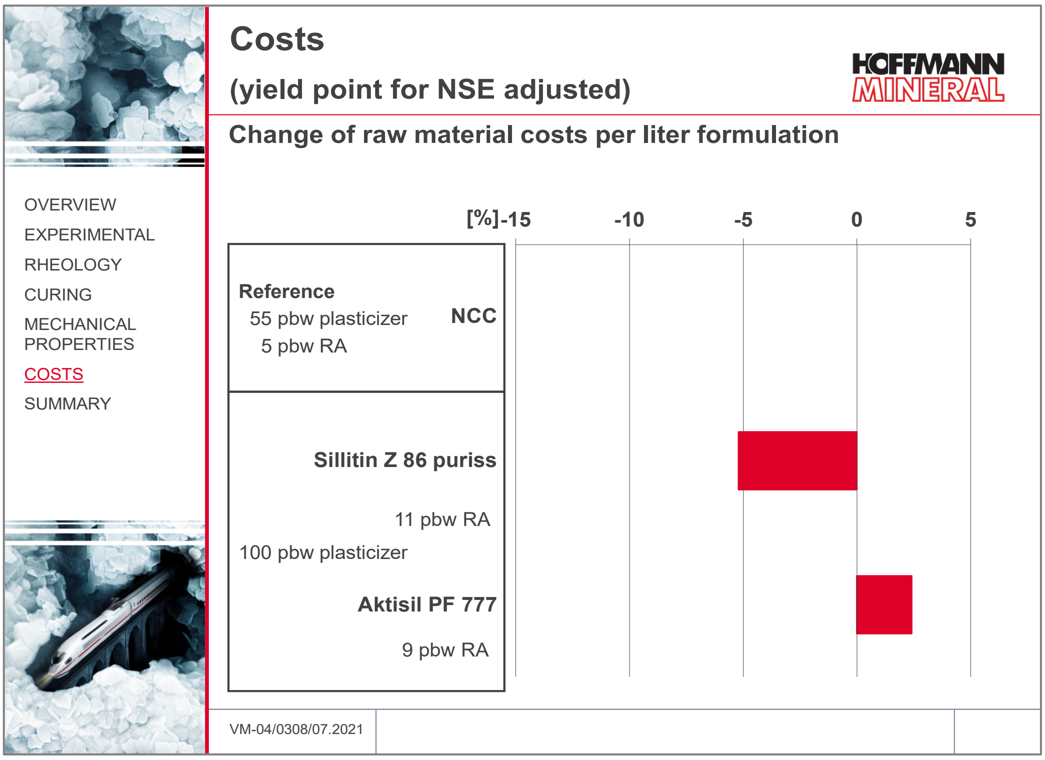


4 Costs

The diagram shows the raw material costs per liter of formulation in comparison with the reference formulation containing natural calcium carbonate and 55 pbw plasticizer. [3] The higher plasticizer addition generally allows a marked reduction of material costs. Only Aktisil PF 777, in view of the additional processing step of its surface treatment, gives rise to a higher raw material cost, and therefore in the formulation remains close to the reference.



Even with an adjusted yield point and therefore higher raw material costs for the rheological additive, the costs per formulation with Sillitin remain below the level of the reference. Aktisil PF 777 gives rise to a slight cost increase.



[3] Cost base: Germany

5 Summary

In comparison with natural calcium carbonate, Neuburg Siliceous Earth, despite the higher required plasticizer addition, offers the following benefits:

- bright color formulations when working with Sillitin Z 89 or Sillitin V 88
- unchanged storage stability (6 months at ambient temperature)
- yield point to be adjusted via dosing of rheological additive
- improved tensile strength but lower elongation at break with Sillitin, Aktisil PF 777 remaining at the level of the reference with calcium carbonate
- comparable low tensile moduli up to 50 % elongation with Sillitin, to 100 % with Aktisil PF 777
- **higher lap shear strength, Aktisil PF 777 comparable to reference**
- **improved resistance to warm water and sulfuric acid, especially with Aktisil PF 777**
- **potential cost advantages**

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