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Neuburg Siliceous Earth
in MS-Polymer based
Elastic Adhesives

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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, and initially were used predominantly in elastic sealants. Since several years, MS polymers find also application in formulations for adhesives, 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

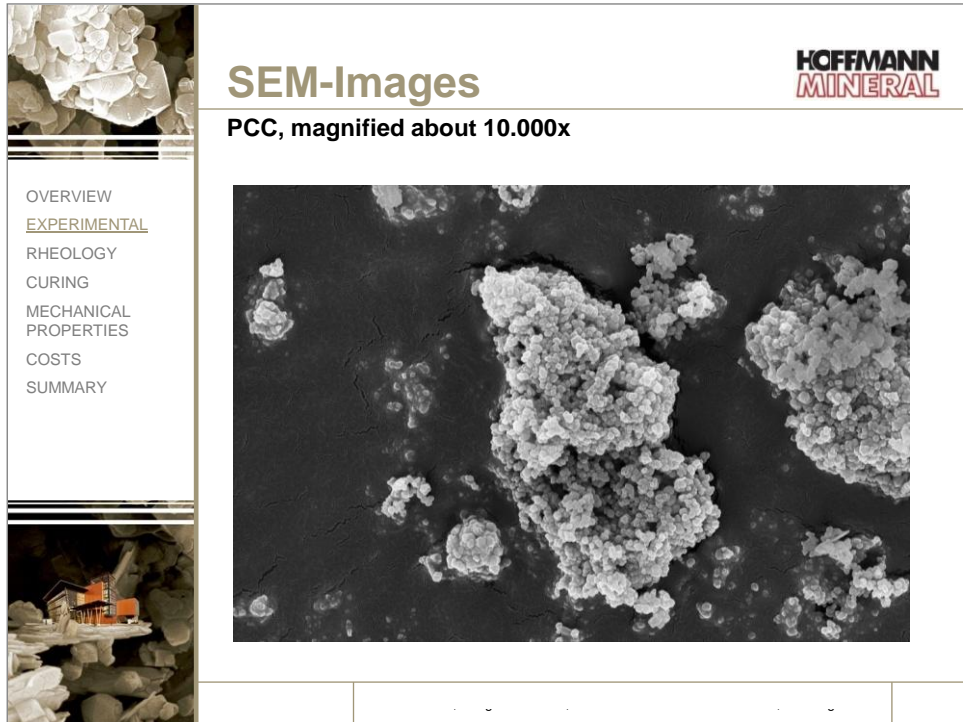
The objective of the present study was to demonstrate the results with Neuburg Siliceous Earth in such formulations as a partial or full replacement of conventional fillers. In so doing, the usual methods of preparation and application were maintained, and the batches were subjected to pertinent tests.

2 Experimental

2.1 Filler morphology and characteristic properties

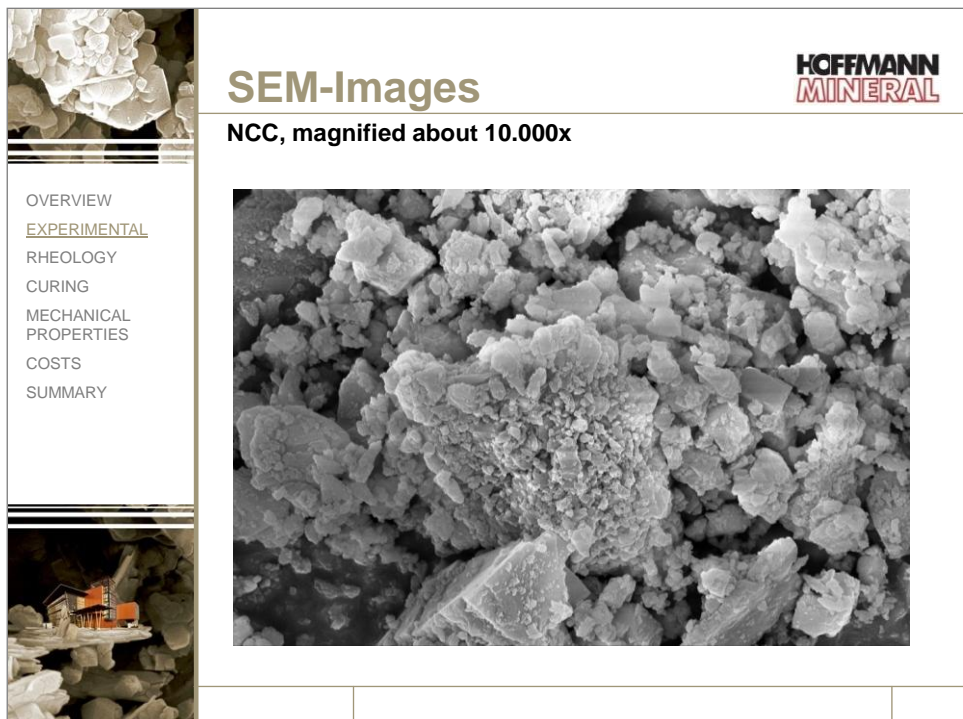
Precipitated calcium carbonate (PCC)

The stearate treated precipitated calcium carbonate was an ultrafine grade with a high specific surface area.



Natural calcium carbonate (NCC)

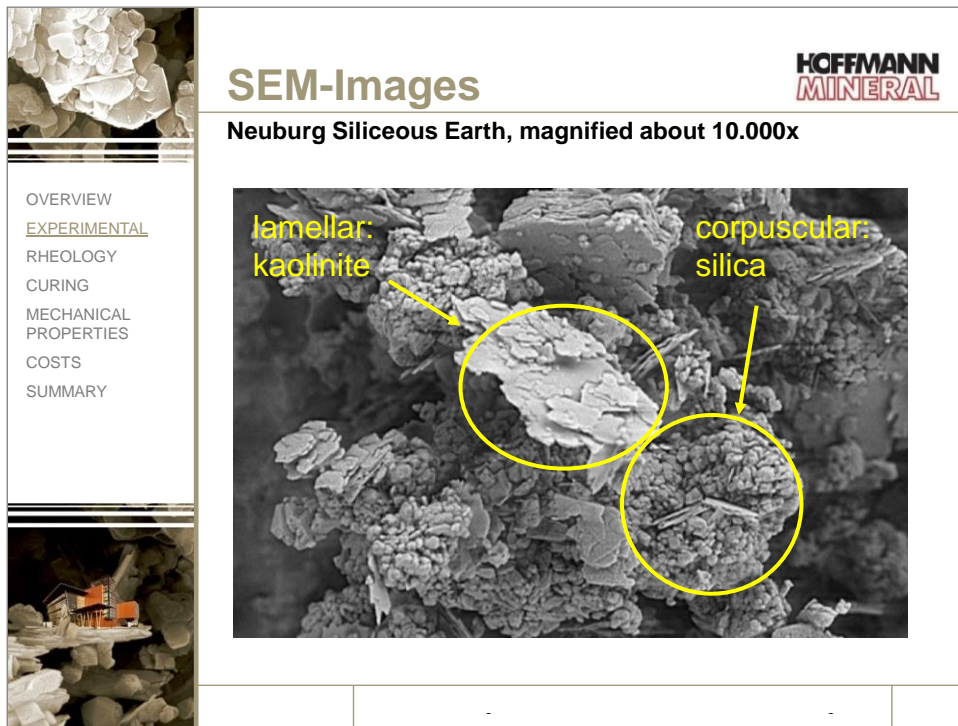
The natural calcium carbonate used was a modification of limestone surface treated with stearate, presenting a compact shape, low oil number and low specific surface area.



Neuburg Siliceous Earth

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

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



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

2.2



Filler characteristics
HOFFMANN MINERAL

Designation	Reference Calcium Carbonate		Neuburg Siliceous Earth (NSE)	
	precipitated	natural	Sillitin Z 86 Sillitin Z 86 puriss	Aktisil PF 777
Particle size d50 [µm]	0.07 *	1.3	1.9	2.2
Particle size d97 [µm]	-	13	8	10
Oil absorption [g/100g]	39	20	55	35
Surface area [m²/g]	20	approx. 8	11	8
Surface treatment	stearate	stearate	none	alkyl silane

* manufacturer information

OVERVIEW
EXPERIMENTAL
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SUMMARY

Formulation

		PCC		NCC	NSE
 OVERVIEW <u>EXPERIMENTAL</u> RHEOLOGY CURING MECHANICAL PROPERTIES COSTS SUMMARY 	HOFFMANN MINERAL				
	MS Polymer (high modulus)	100	100	100	100
	Plasticizer (DIUP)	55	55	55	55
	Titanium dioxide	20	20	20	20
	Rheological additive (RA) Crayvallac SLX (micronised amide wax)	2	2	5	5
	Light stabiliser / UV-Absorber	2	2	2	2
	PCC	120	180		
	NCC			180	
	NSE				180
	Drying agent	2	2	2	2
	Bonding agent (AS) (3-amino propyl triethoxy silane)	3.5	3.5	3.5	5
	Catalyst	2	2	2	2
	Total (parts by weight)	306.5	366.5	369.5	371

Starting from the reference formulation with 120 parts by weight (pbw) of precipitated calcium carbonate, the loading of Neuburg Siliceous Earth was adjusted to arrive at a comparable viscosity level. Preliminary tests herefore indicated an amount of 180 pbw, which then was kept constant also for the comparison with natural calcium carbonate.

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 silane) 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⁾

With the aim to increase the dimensional stability, the dosage of the rheological additive was increased to 5 pbw both for the natural calcium carbonate and for Neuburg Siliceous Earth.

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



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- EXPERIMENTAL
- RHEOLOGY
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- MECHANICAL PROPERTIES
- COSTS
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Preparing of Compounds



The compounds were prepared in a planetary mixer equipped with dissolver disc, kneading tool and scraper.

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.

With the formulation loaded with 180 pbw precipitated calcium carbonate, the filler could only be incorporated very slowly in small portions. The batch was also very difficult to squeeze out of the cartridge.

As already in the laboratory the preparation of this compound was problematic (and will probably be close to impossible under production conditions), this formulation was no longer included in the further testing program.

²⁾ Tests were also carried out without pre-drying the fillers and otherwise unchanged processing conditions. Neither the NSE nor the calcium carbonate batches 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

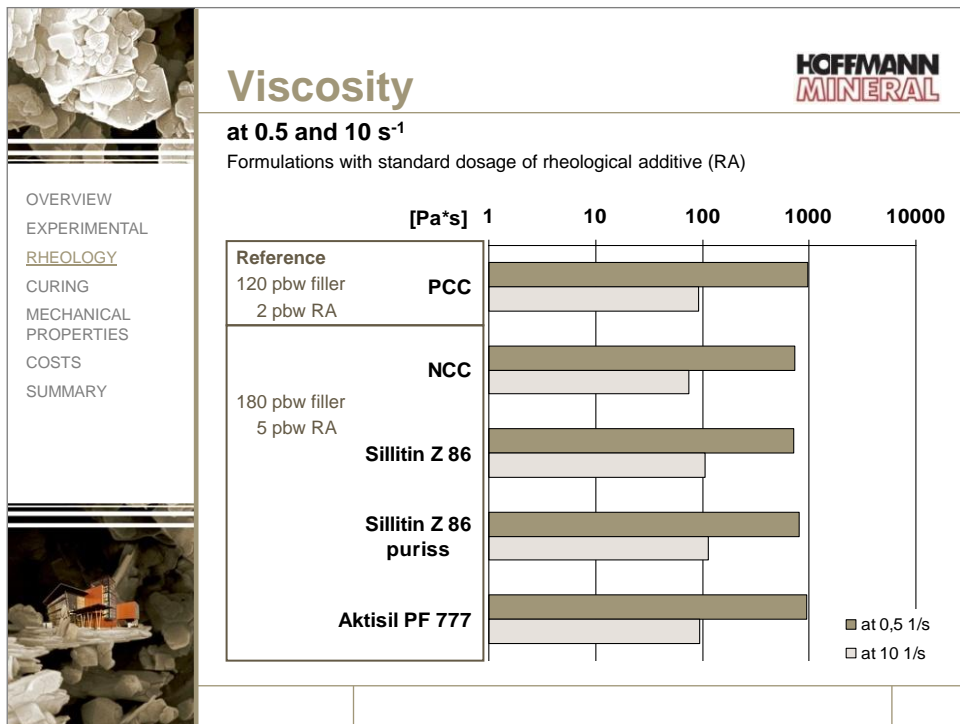
3.1 Rheology

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.

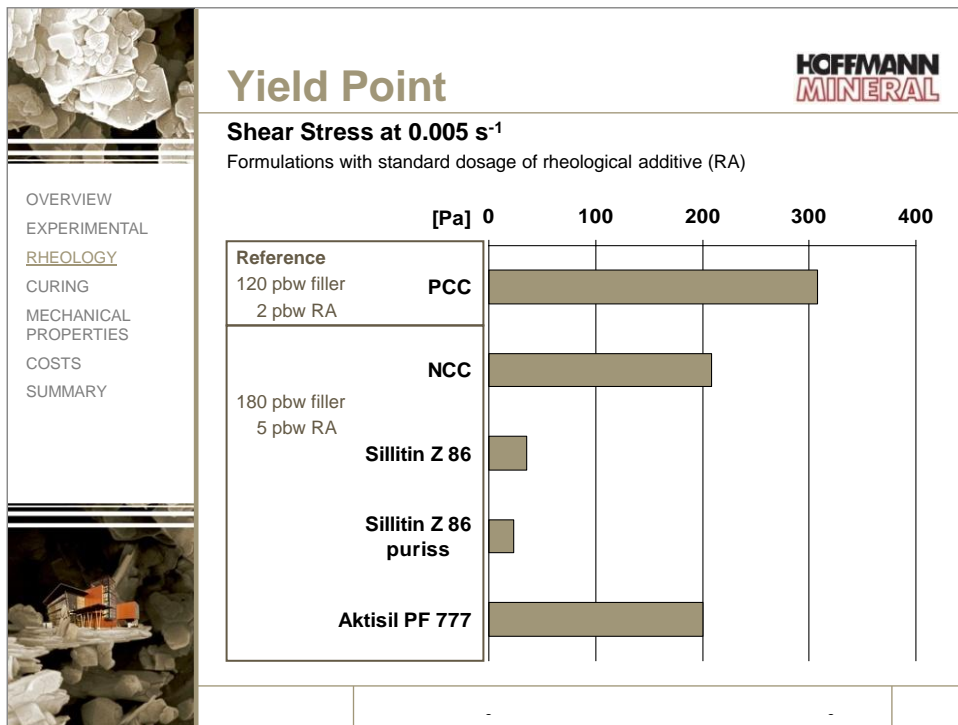
As desired, the viscosity with 180 pbw Neuburg Siliceous Earth or natural calcium carbonate comes out at a similar level as the reference formulation with 120 pbw precipitated calcium carbonate.



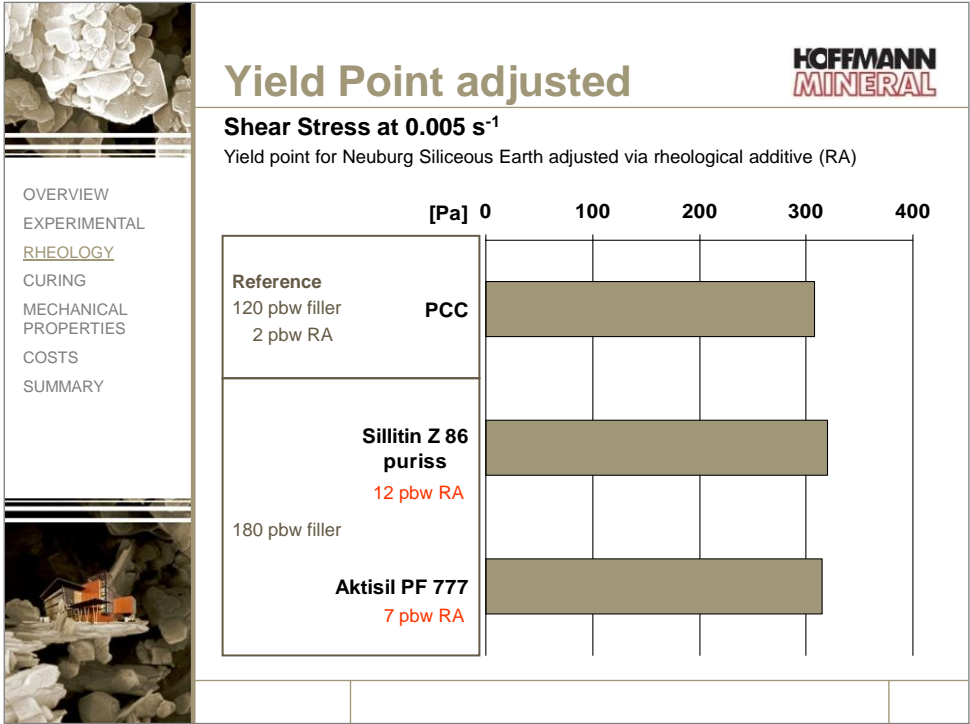
Yield point

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} .

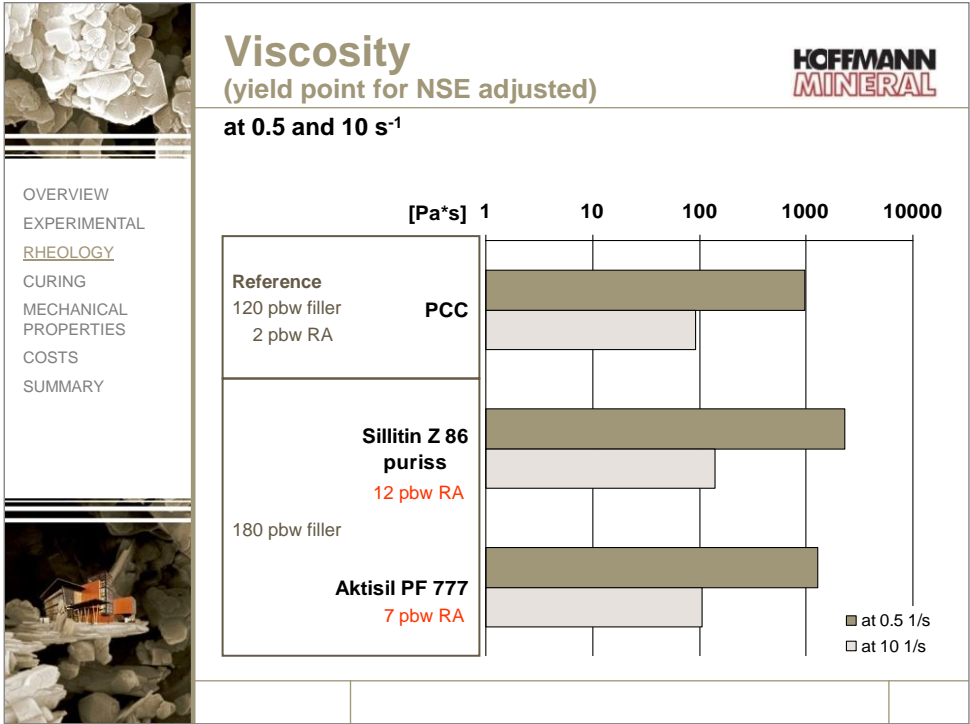
With Sillitin Z 86 and Sillitin Z 86 puriss, two Neuburg Siliceous Earth grades without surface treatment, the yield point of the compounds is markedly lower despite the higher rheological additive dosing of 5 pbw. By contrast, the alkylsilane modified Aktisil PF 777 gives results similar to the natural calcium carbonate.



In order to adjust the yield point to the level of the reference formulation (precipitated calcium carbonate + 2 pbw rheological additive), working with Sillitin – here illustrated on the example of Sillitin Z 86 puriss – requires a dosing of 12 phr rheological additive. The hydrophobic grade Aktisil PF 777 needs approx. 7 pbw.



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

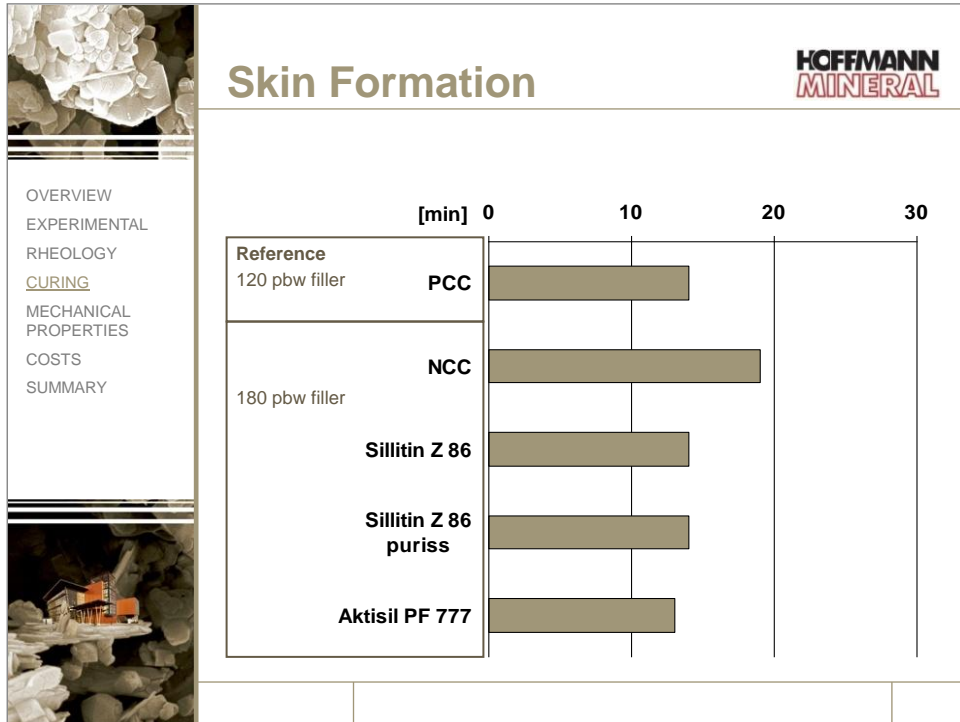


3.2 Curing

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).

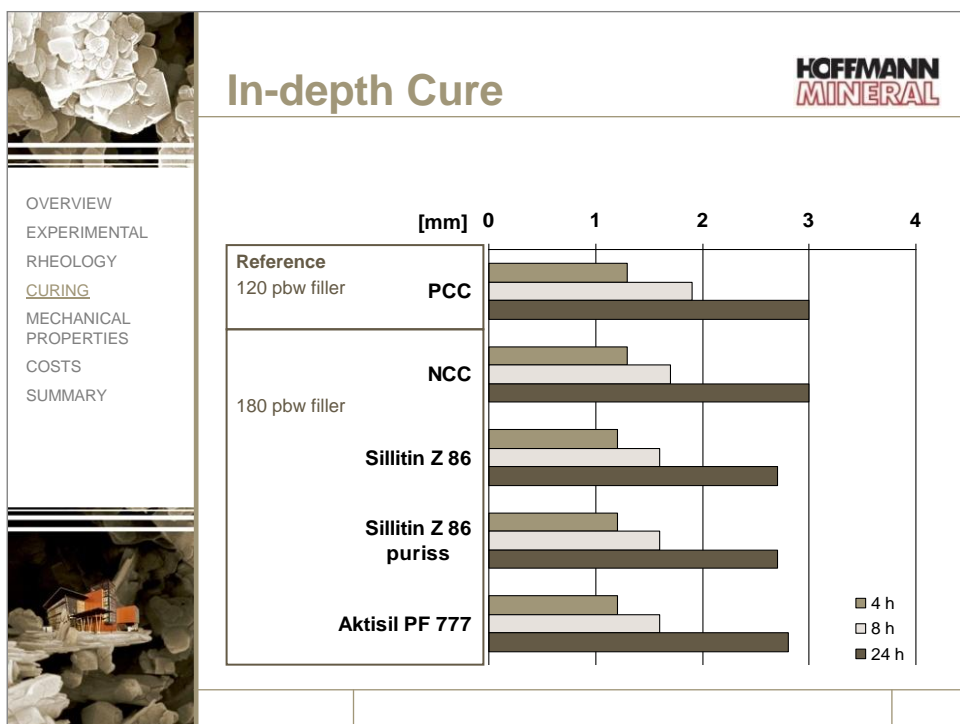
Skin formation was defined as the time to touch the surface of the extrudate without rests of the compound sticking to the fingers.

Neuburg Siliceous Earth does hardly give rise to a change in skin formation time; the natural calcium carbonate shows a somewhat slower set-off.



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

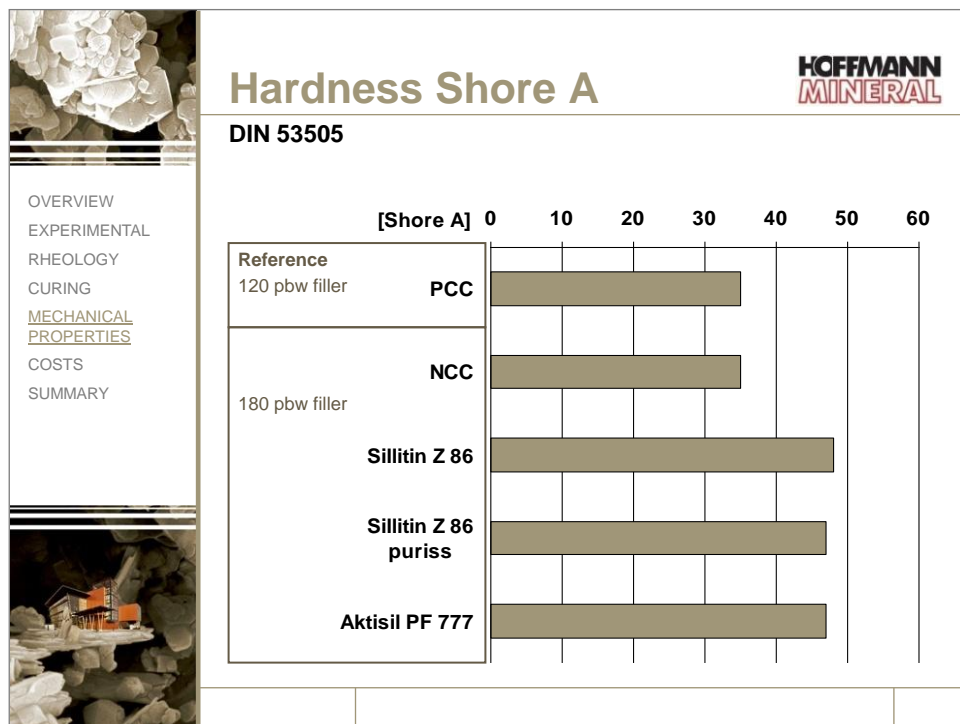
For tensile and hardness tests, sheets with a thickness of about 2 mm were prepared. After curing the sample sheets for 14 days at standard conditions (23 °C, 50 % relative humidity), dumbbell samples S2 according to DIN 53504 were died out and tested.

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)

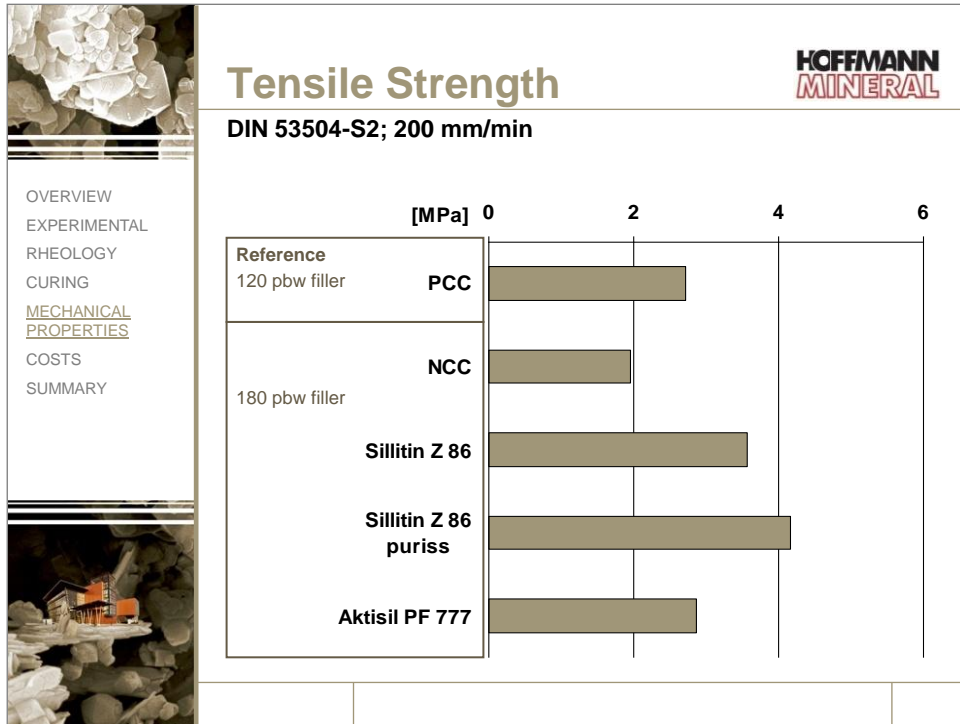
Hardness was determined on piled-up sections of the sample sheets to a height of 6 mm according to DIN 53505.

Neuburg Siliceous Earth leads to a significantly higher Shore A hardness compared with the calcium carbonates used.

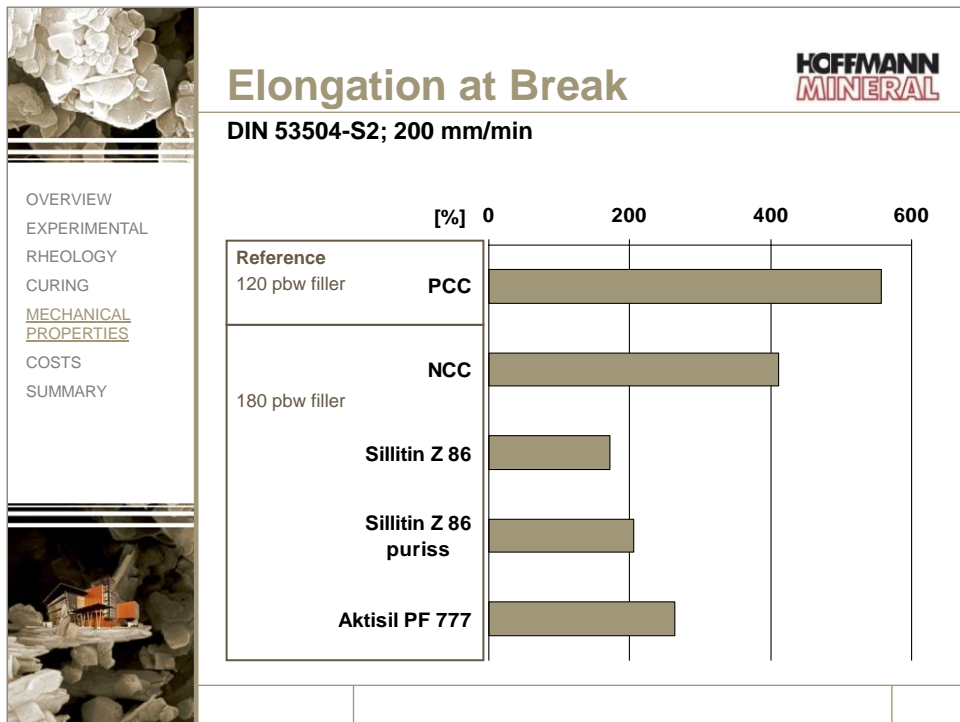


Tensile test (DIN 53504)

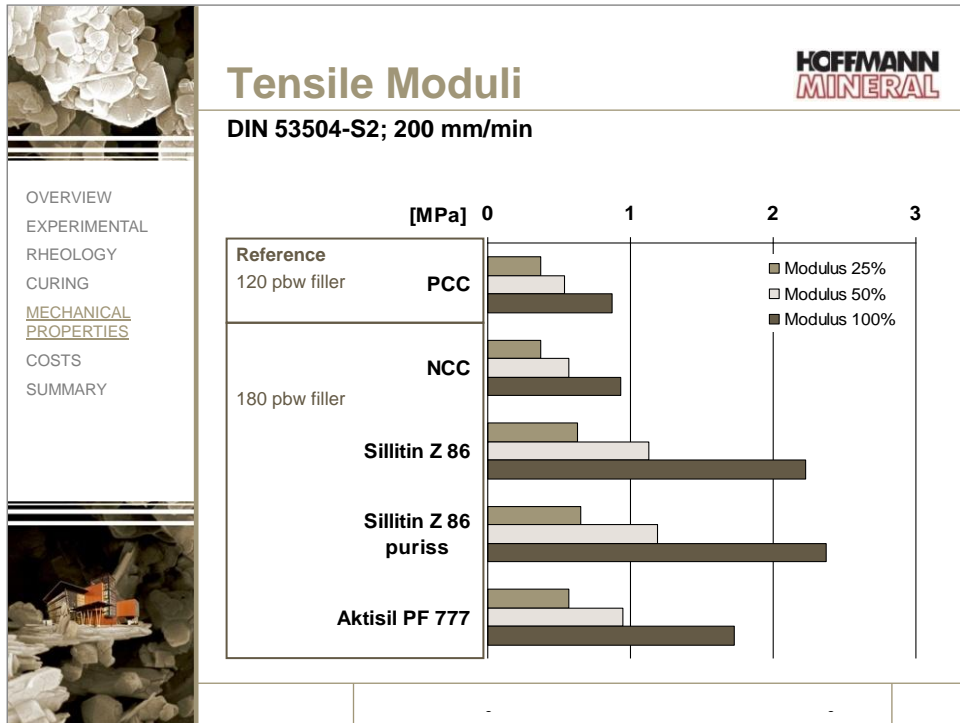
Neuburg Siliceous Earth, and in particular the physically aftertreated puriss grade with improved dispersion properties, shows a distinct improvement of the tensile strength compared with the two calcium carbonates. The hydrophobic grade Aktisil PF 777 remains at the level of the reference formulation.



The high elongation at break with the calcium carbonates, however, cannot be attained with the Neuburg Siliceous Earth fillers. Within those grades, Aktisil PF 777 tends to offer higher elongation levels.

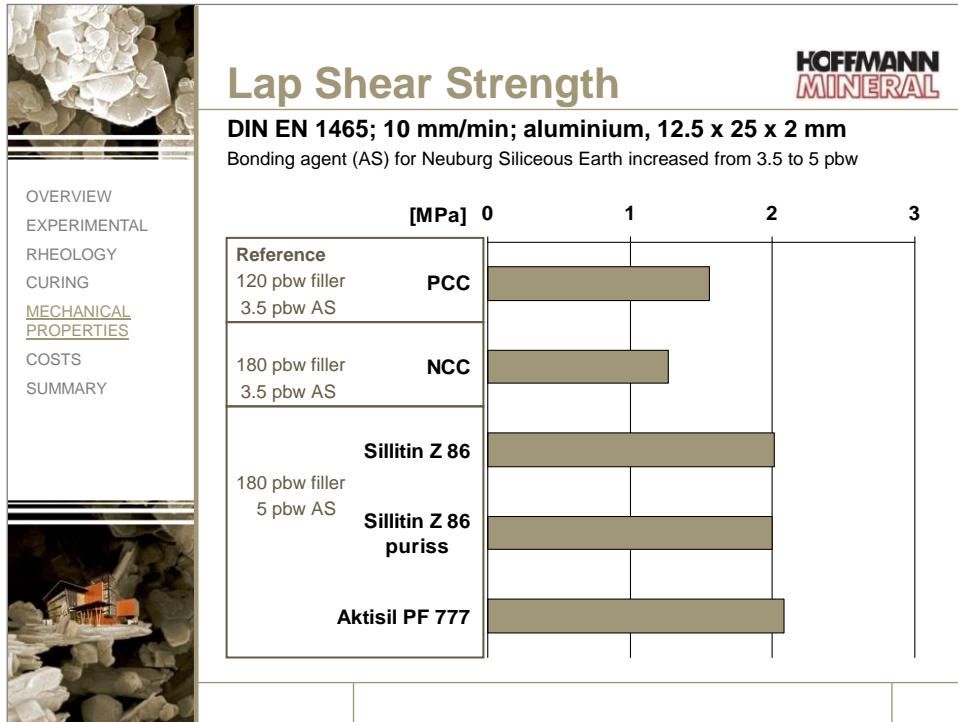


Typically, rather high tensile moduli are obtained with Neuburg Siliceous Earth. For example, Sillitin Z 86 and Sillitin Z 86 puriss lead to twice as high tensile moduli compared with the calcium carbonates; Aktisil PF 777 comes out not quite as high.



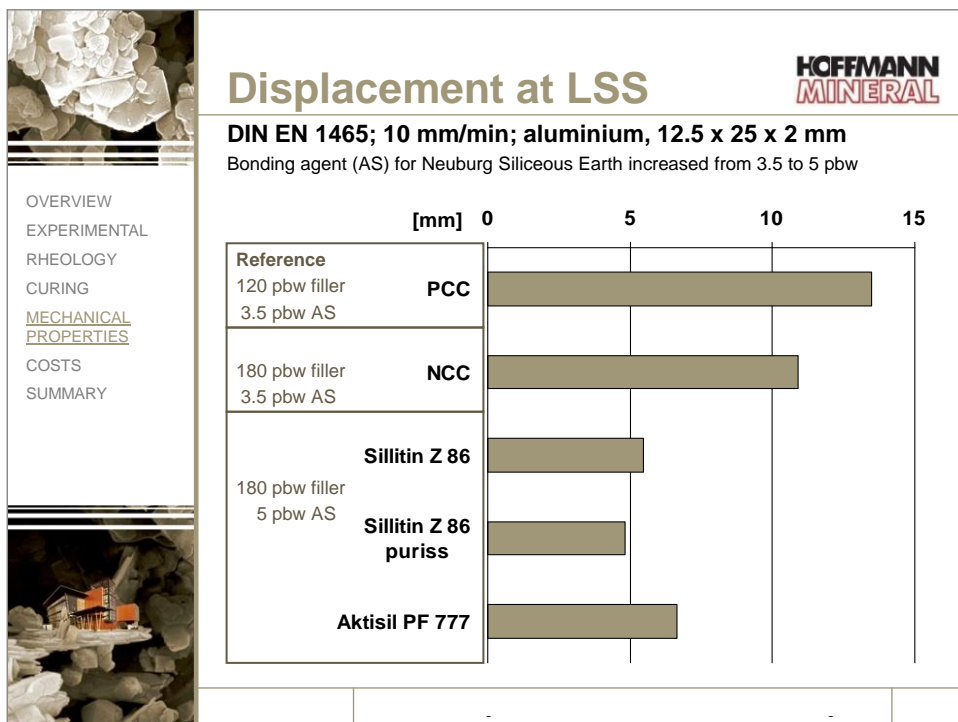
Lap shear test (DIN EN 1465)

Neuburg Siliceous Earth allows to markedly increase the lap shear strength. Different from the tensile test, Aktisil PF 777 also joins the high level of the grades without surface modification.



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.

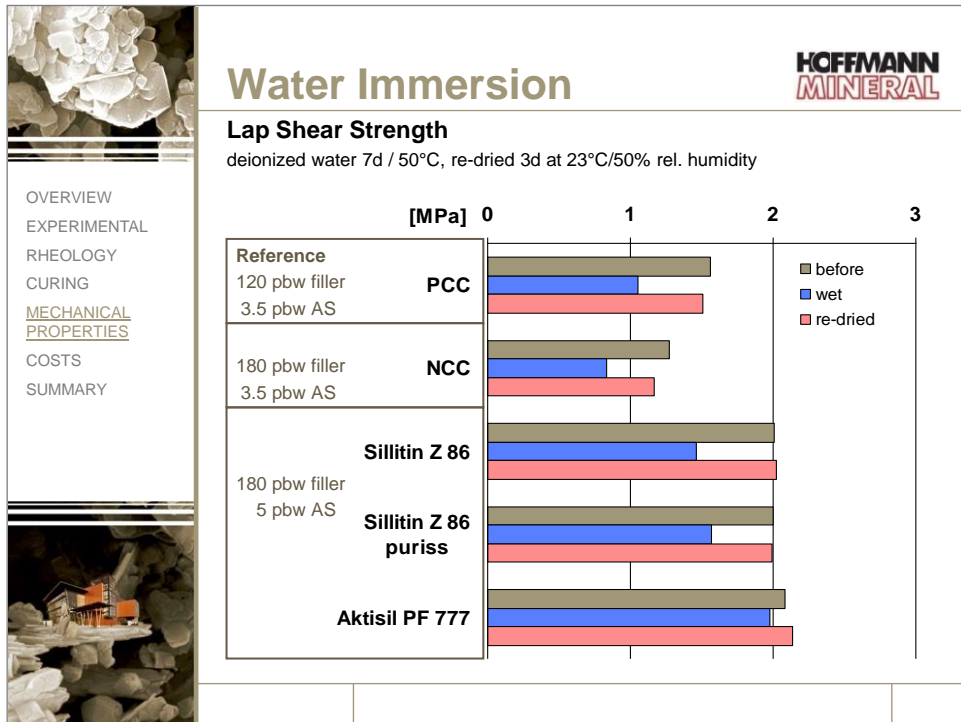
All the same, the measured shift distance of 5 mm at an adhesive joint thickness of 2 mm still corresponds to a potential deformability of 250 %.



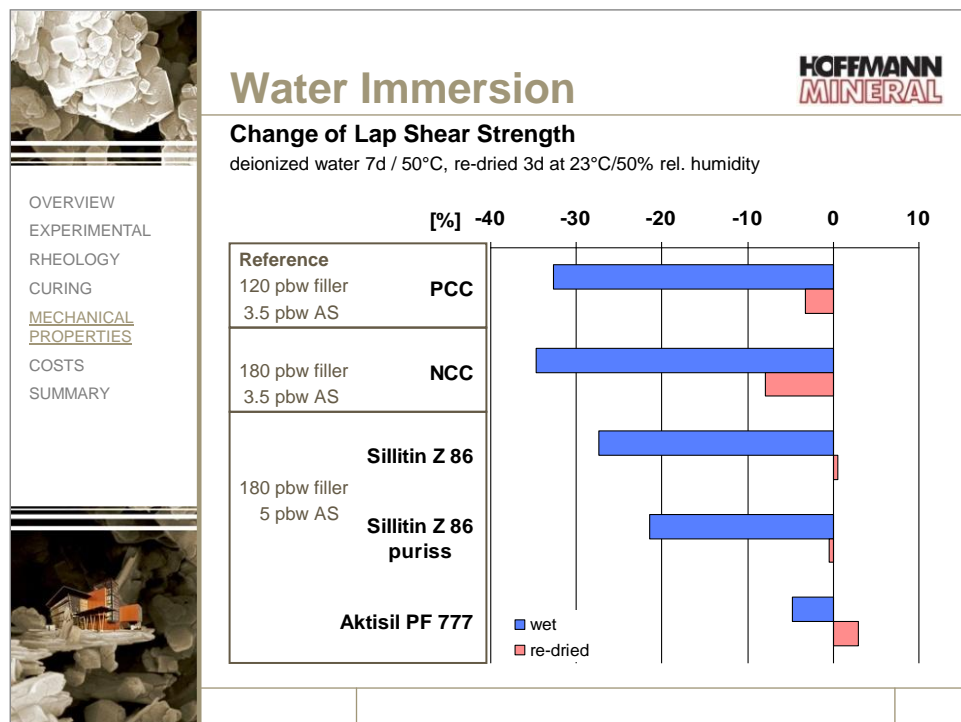
Warm water resistance

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, but come back to their original level after re-drying. Aktisil PF 777 comes off markedly more stable than the other fillers.



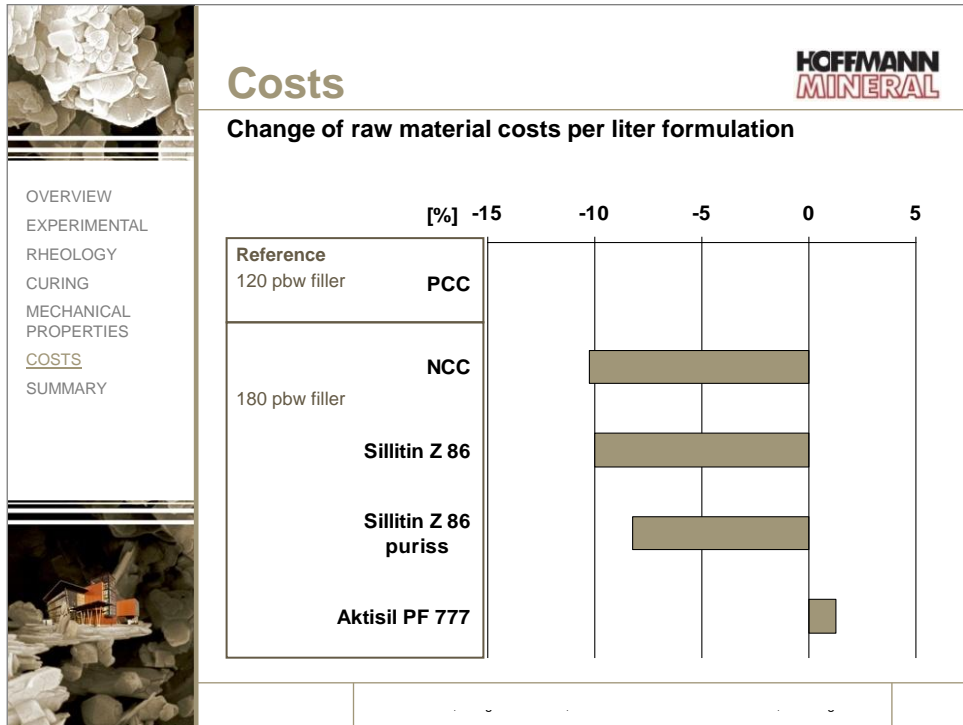
Particularly when comparing the percentual changes this becomes apparent: Aktisil PF 777 increases the resistance in wet condition to warm water considerably.



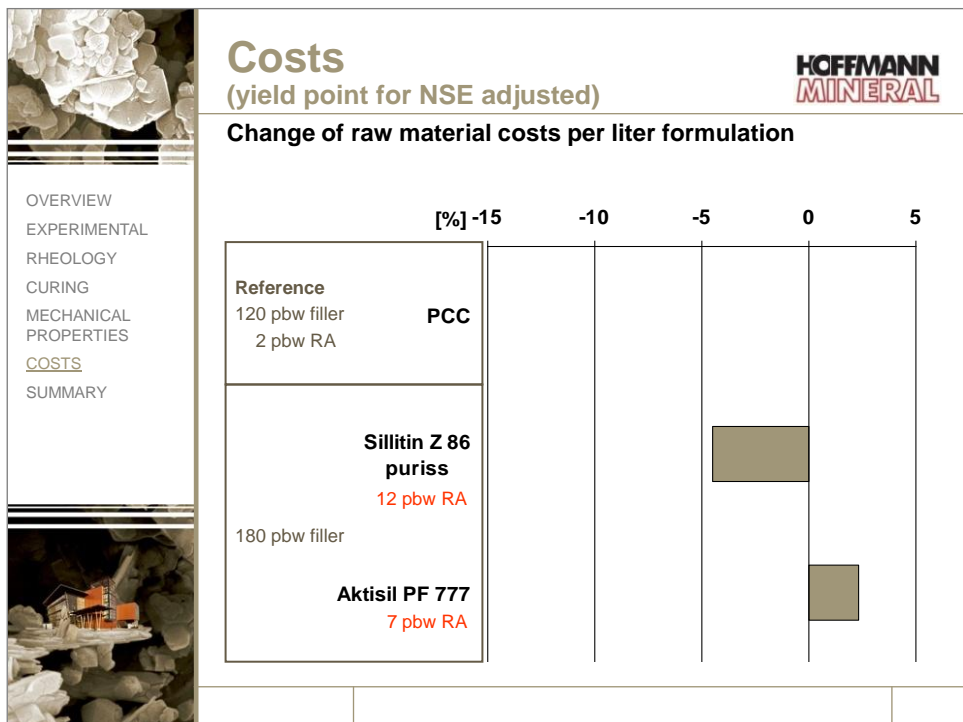
4 Costs

The diagram shows the raw material costs per liter of formulation in comparison with the reference formulation containing 120 pbw precipitated calcium carbonate.³⁾

With Neuburg Siliceous Earth as well as with natural calcium carbonate, it is possible to make up more priceworthy formulations. Aktisil PF 777, because of the additional surface treatment, demands a higher raw material price, and therefore in the formulations tested remains more or less cost-neutral.



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

Compared with calcium carbonate, Neuburg Siliceous Earth in MS based elastic adhesives 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)
- similar viscosity along with lower yield point with Sillitin grades, Aktisil PF 777 close to natural calcium carbonate
- yield point to be adjusted via dosing of rheological additive
- lower elongation at break
- **with Sillitin grades higher tensile strength, Aktisil PF 777 close to reference**
- **higher tensile moduli**
- **increased lap shear strength**
- **markedly higher hardness**
- **improved warm water resistance, especially with Aktisil PF 777**
- **potential cost advantages**

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