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Neuburg Siliceous Earth

in Parquet Adhesives based

on Silane-terminated Polyether

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Contents

1 Introduction

Aside from the widely introduced silicone and polyurethane systems also innovative hybrid polymers based on silane-terminated polyethers are able to meet the requirement profile for modern adhesive and sealant applications.

Here it is possible to formulate solvent, isocyanate and tin free, and therefore healthwise and ecologically safe adhesives and sealants which in addition are characterized by excellent adhesion and outstanding mechanical properties.

The present study will present Neuburg Siliceous Earth as a functional filler for (parquet) adhesives based on a silane-terminated polyether.

The objective was to improve the strength of the adhesive compared with the conventional filler calcium carbonate.

2 Experimental

2.1 Base formulation

Base Formulation

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INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

		parts by weight
GENIOSIL® STP-E 10	Polymer Silane-terminated polyether	25.5
Caradol ED 56-200	Plasticizer Polypropylene glycol	15.0
GENIOSIL® XL 10	Drying agent Vinyl silane	2.0
HDK H 18	Rheological additive Fumed silica	2.5
GCC	Filler Ground calcium carbonate	54.0
GENIOSIL® GF 96	Adhesion promoter Amino silane	1.0
Total		**100.0**

VM-0/06.2010

The base formulation used natural calcium carbonate (marble flour, GCC).

2.2 Fillers and their characteristics

The table summarizes the most important filler properties.

Fillers Characteristics

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INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

	Particle size		Oil absorption	Specific surface area BET
	d_{50} [µm]	d_{97} [µm]	[g/100g]	[m²/g]
Ground calcium carbonate (GCC) Marble flour	6.0	25	23	not determined
Sillitin V 85 Neuburg Siliceous Earth (NSE)	4.0	18	45	9
Sillitin Z 86 puriss Neuburg Siliceous Earth, physically after-treated	1.9	7.8	55	11

VM-0/06.2010

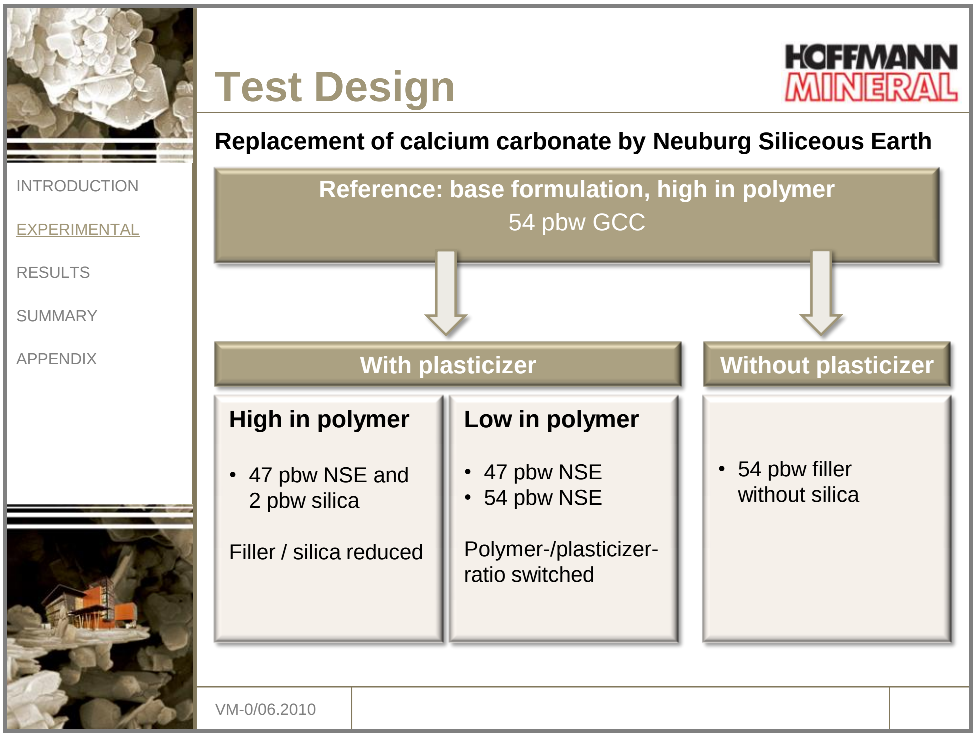
In agreement with the grain size of the competitive material, Sillitin V 85 as the coarsest grade of Neuburg Siliceous Earth was selected.
As a finer grade, Sillitin Z 86 puriss was included, which due to the physical aftertreatment is particularly easy to disperse.

2.3 Test design and formulation variations

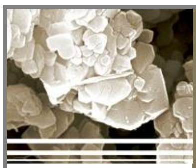
The tests with plasticizer containing formulations were run in two versions:

- „high in polymer“ content, corresponding to the base formulation
- „low in polymer“ content, with a reverse ratio of binder to plasticizer

The formulations without plasticizer were evaluated to verify how high a tensile strength and tensile shear strength could be obtained with Sillitin.



Preliminary tests had already shown that a 1:1 replacement of calcium carbonate with Neuburg Siliceous Earth resulted in a markedly higher viscosity.
Therefore, the filler and fumed silica loadings were reduced in the „high in polymer“ formulation.
The „low in polymer“ version in analogy was also evaluated with a reduced filler addition, however the rheological additive fumed silica in the interest of sag stability was left at the original amount. With Sillitin V 85, also the filler loading could be increased back to 54 pbw without overly affecting the processing properties.



Formulation Variations with Plasticizer

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

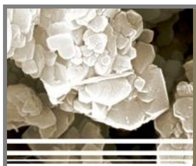
in parts by weight

	High in polymer			Low in polymer		
	GCC	Sillitin V 85	Sillitin Z 86 puriss	Sillitin V 85	Sillitin Z 86 puriss	Sillitin V 85
Polymer	25.5	25.5	25.5	15.5	15.5	15.5
Plasticizer	15.0	15.0	15.0	25.0	25.0	25.0
Drying agent	2.0	2.0	2.0	2.0	2.0	2.0
Rheological additive	2.5	2.0	2.0	2.5	2.5	2.5
GCC	54.0	---	---	---	---	---
Sillitin V 85	---	47.0	---	47.0	---	54.0
Sillitin Z 86 puriss	---	---	47.0	---	47.0	---
Adhesion promoter	1.0	1.0	1.0	1.0	1.0	1.0
Total	**100.0**	**92.5**	**92.5**	**93.0**	**93.0**	**100.0**

VM-0/06.2010

Note: formulation variants in weight percent see Appendix

With the objective to obtain „adhesion under highest possible load transmission“ further studies were carried out with a plasticizer free formulation. In order to assess only the filler effects, the formulation was just made up from polymer, drying agent and adhesion promoter. The rheological additive fumed silica was left out, as it also contributes to the tensile strength and in addition tends to increase the viscosity.



Formulation Variations without Plasticizer

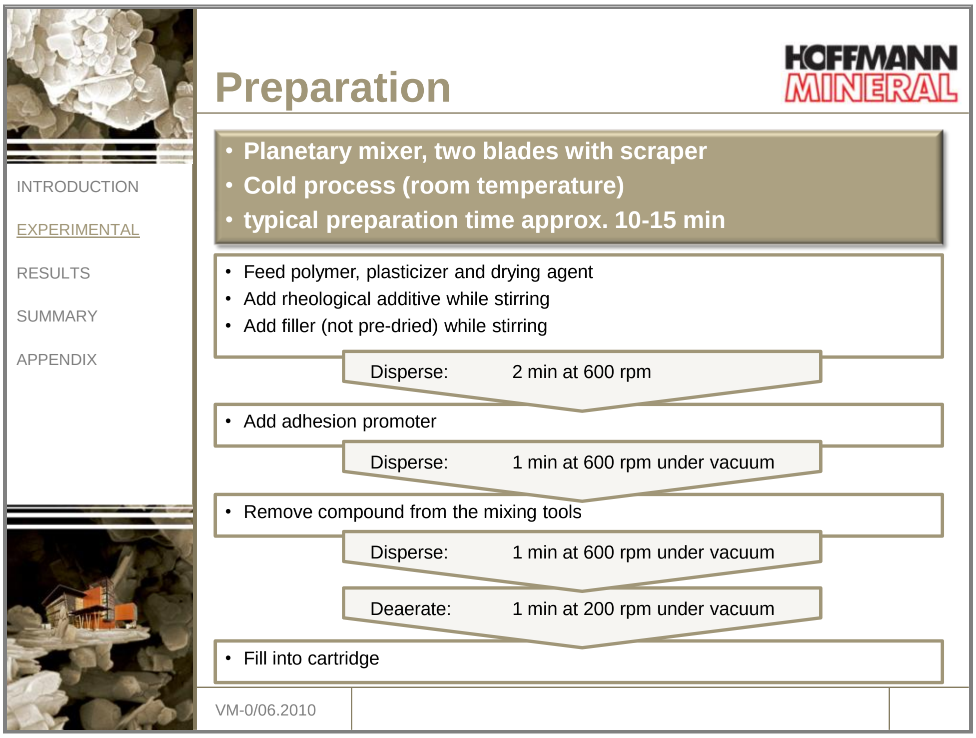
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

in % by weight

	without plasticizer and rheological additive		
	GCC	Sillitin V 85	Sillitin Z 86 puriss
Polymer	42.14	42.14	42.14
Drying agent	2.31	2.31	2.31
GCC	54.38	---	---
Sillitin V 85	---	54.38	---
Sillitin Z 86 puriss	---	---	54.38
Adhesion promoter	1.17	1.17	1.17
Total	**100.00**	**100.00**	**100.00**

VM-0/06.2010

2.4 Preparation

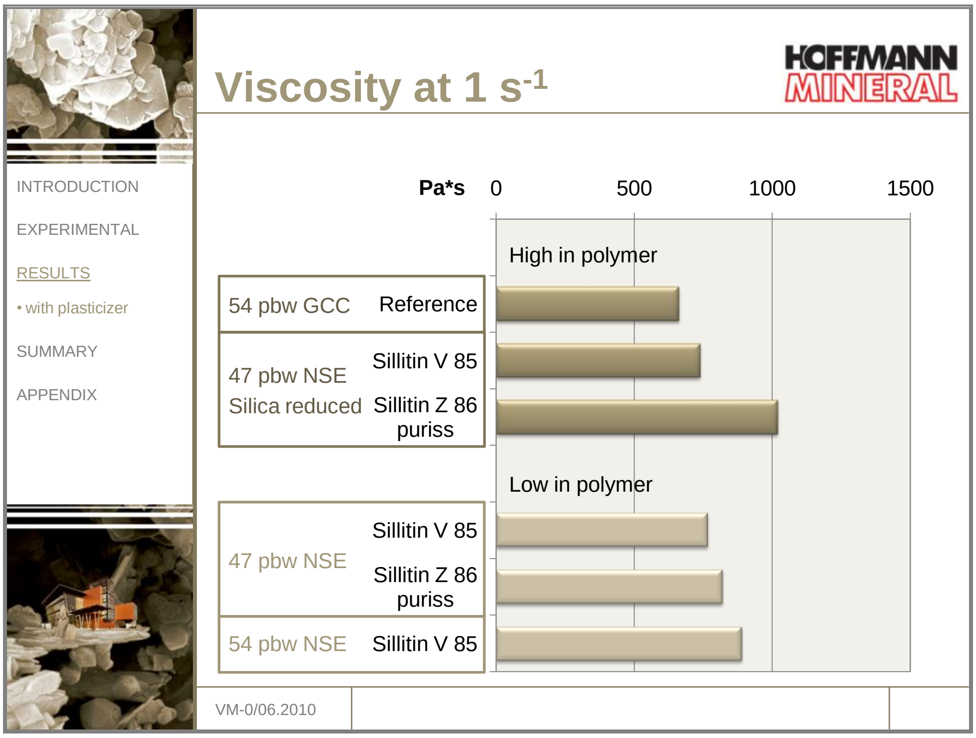


3 Results

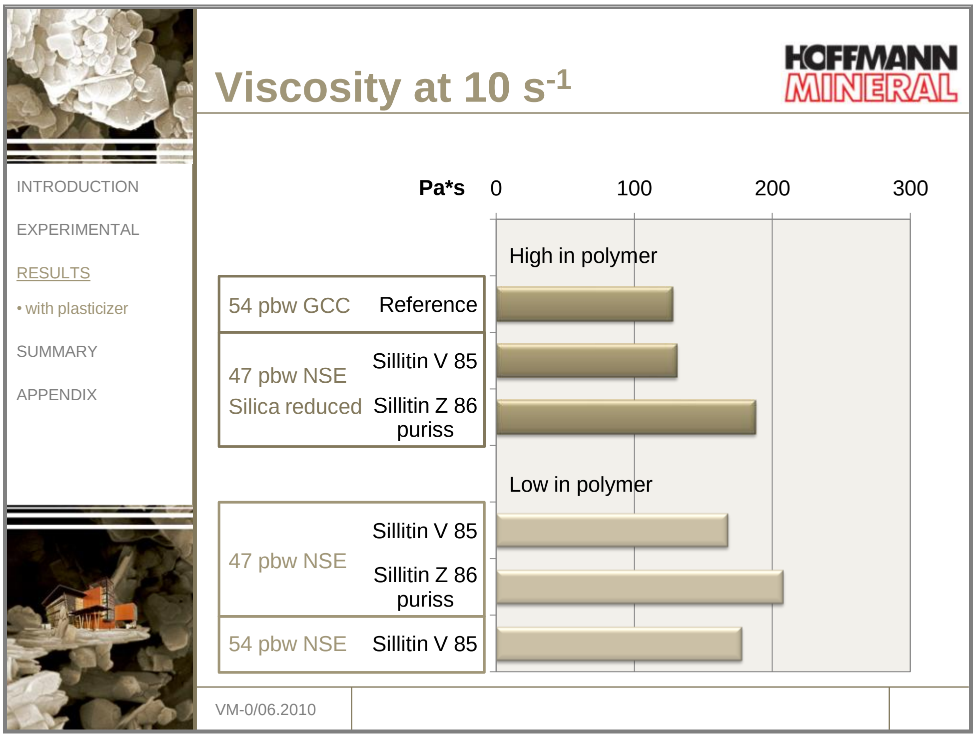
3.1 Formulations with plasticizer

3.1.1 Viscosity

Viscosity measurements were made with a plate-plate rheometer via a shear rate controlled rotation test. The system had a diameter of 25 mm, and a gap distance of 1 mm. The tests were made 4 weeks after the preparation of the samples, as at earlier times post-wetting effects gave rise to some unsteady results.



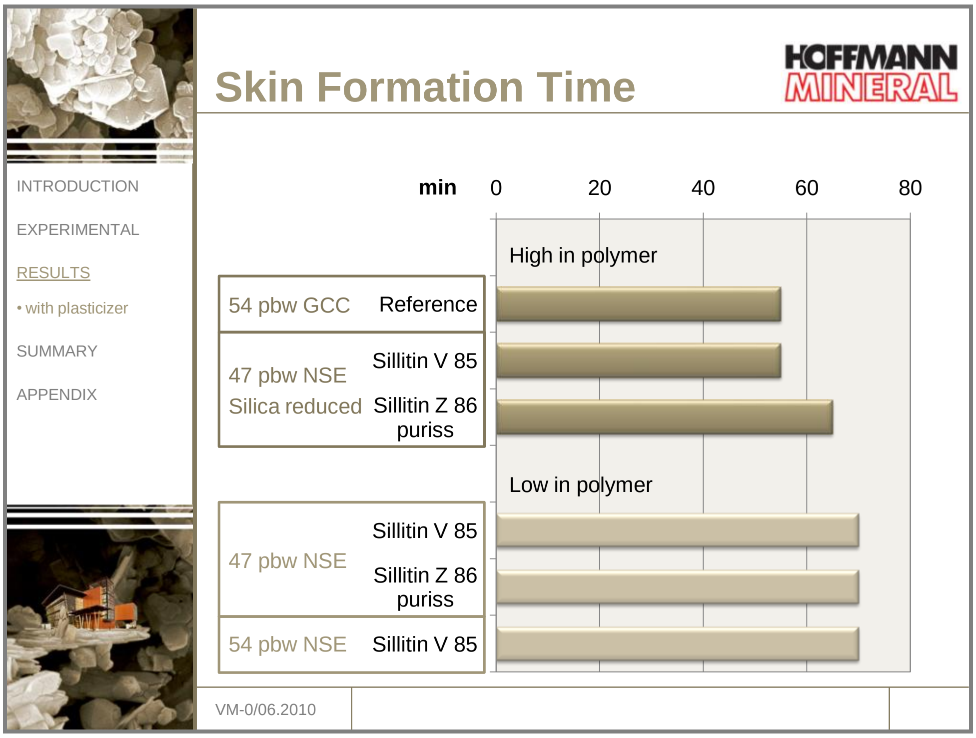
At low shear (at rest), with Sillitin V 85 the viscosity increases only marginally. Sillitin Z 86 puriss, because of its lower particle size, leads to a stronger viscosity increase, in particular in the „high in polymer“ formulation. As demonstrated for the last formulation tested, in the „low in polymer“ variant Sillitin V 85 can be used in the higher amount of 54 pbw without a marked viscosity increase.



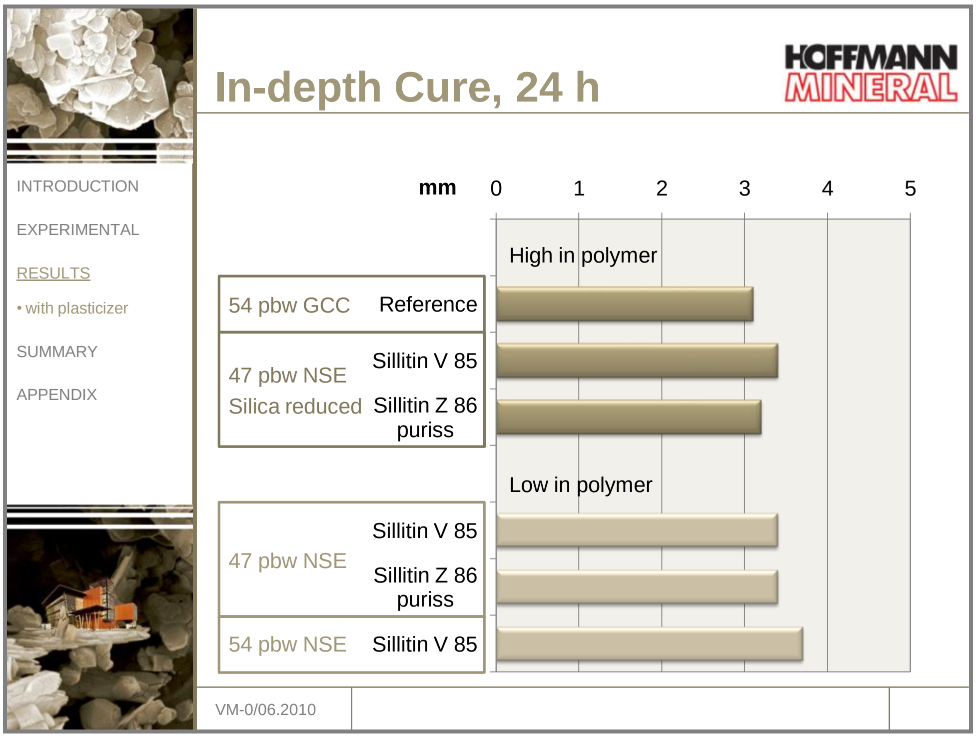
At higher shear rate, the viscosity shows a similar picture. The finer particle size of Sillitin Z 86 puriss gives a somewhat stronger effect.

3.1.2 Skin formation time and curing rate

For the determination of skin formation time, the compounds were squeezed out from a cartridge as strands of approx. 10 mm diameter. Stored at standard 23/50 conditions, the strands were touched with a wooden stick after definite periods of time. The time after which no material residues remained on the sticks was counted as the skin formation time.



Sillitin V 85 shows – in the same formulation – no change of the skin formation time versus the reference compound, while Sillitin Z 86 puriss leads to a somewhat slower onset of the surface reaction and, therefore, to a moderately longer skin formation time.
The longer skin formation time of the „low in polymer“ formulations essentially goes back to the modified polymer/plasticizer ratio, and this without differences between the individual Sillitin grades. Compared to the calcium carbonate control, this means after all a longer time by about 15 minutes which remains available for processing.



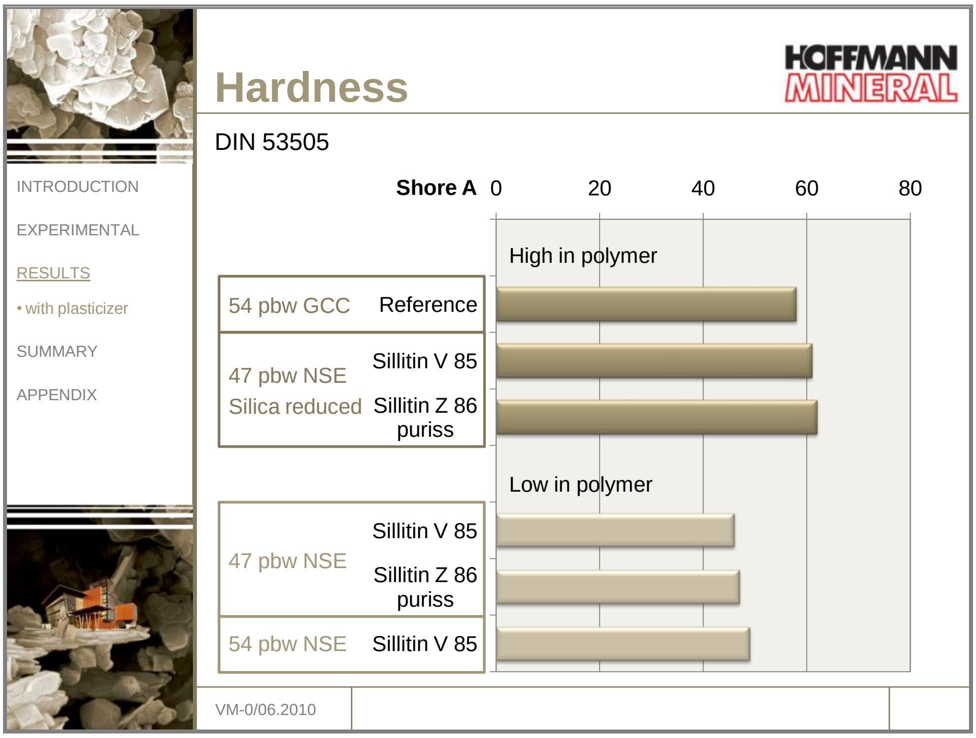
After 24 hours of storage under standard 23/50 conditions, the strand was cut open for determining the thickness of the reacted layer.
Here no marked differences were found between the formulations tested, which in combination with the longer skin formation time has to count as a positive result.

3.1.3 Mechanical properties

Hardness and tensile properties were determined on sample sheets with a thickness of about 2 mm that had been stored in the interest of full cure for 4 weeks at standard 23/50 conditions.

a) Hardness

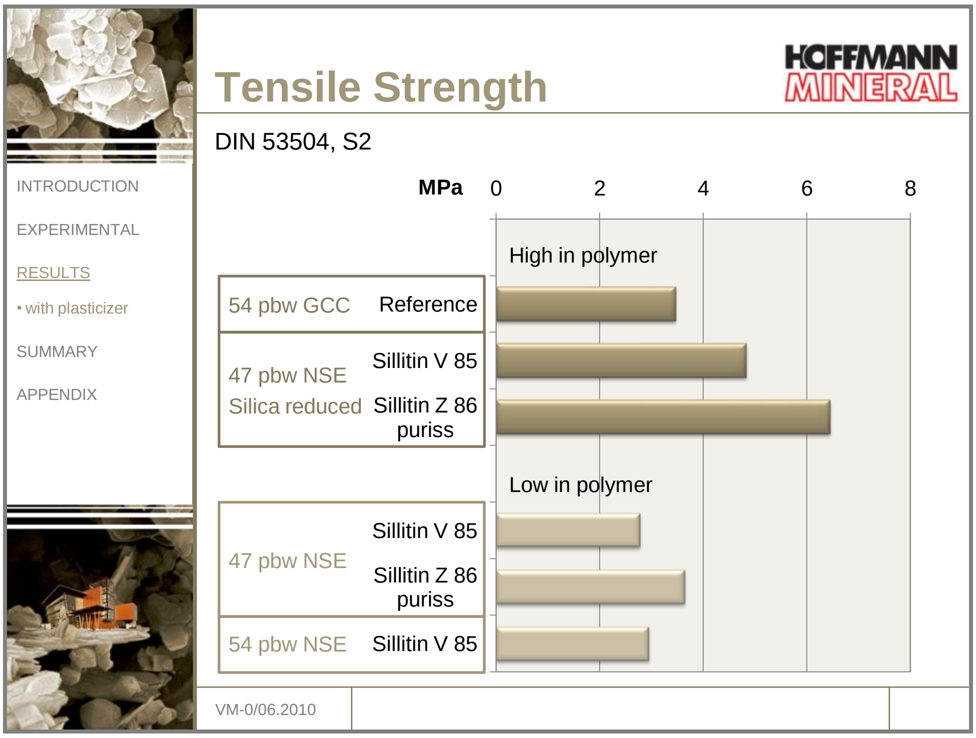
Hardness was determined on piled-up sections cut out from the sample sheet (total height approx. 6 mm).



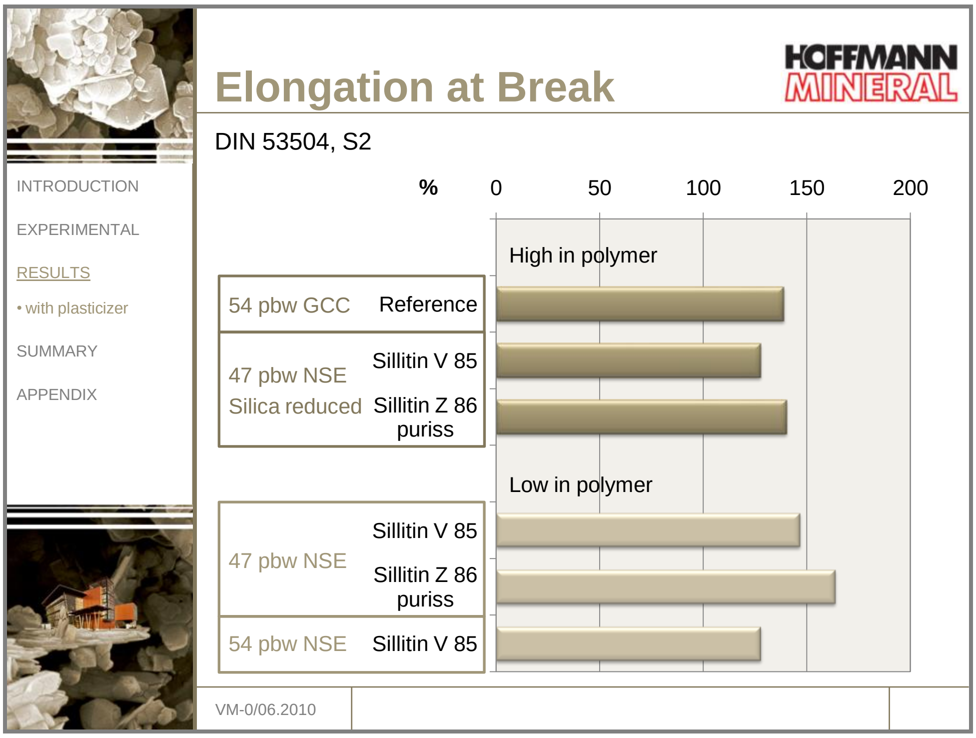
Neuburg Siliceous Earth in the „high in polymer“ formulations, despite the lower filler loading, brings about a higher hardness.
The „low in polymer“ compounds come out at a lower level.
The higher filler addition of the last formulation almost shows no measurable effect.

b) Tensile test

S2 dumbbells were punched out from the sample sheet, and were tested for tensile properties, according to pertinent standards, with a crosshead speed of 200 mm/min.



Despite the lower filler loading, Neuburg Siliceous Earth leads to a significant increase of tensile strength in the „high in polymer" versions. Sillitin Z 86 puriss, the finer grade with improved dispersion properties, even reaches twice the level of the calcium carbonate control.
Although in the „low in polymer" formulations the binder portion was lowered and therefore the crosslinking potential significantly reduced, the compounds with Sillitin V 85 come close, and those with Sillitin Z 86 puriss come up to the level of the „high in polymer" reference formulation.



Elongation at break is hardly affected by the different formulation variations. Sillitin Z 86 puriss leads to a directionally higher elongation compared with Sillitin V 85.

c) Lap shear test

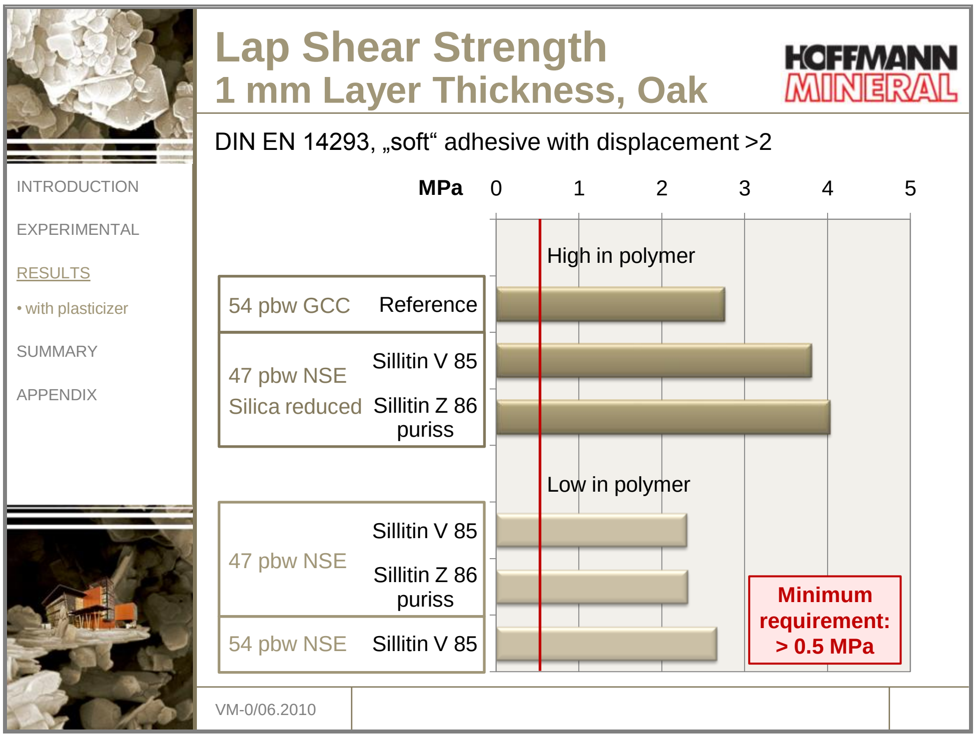
Two oak mosaic parquet slats measuring 160 x 23 x 8 mm were bonded overlapping with a bond surface area of 23 x 26 mm (600 mm²).

For the evaluation as „soft“ adhesive, the sample was applied onto the full surface area with a spatula. The adhesive layer thickness of 1 mm was adjusted with the help of suitable spacers when pressing the parquet slats together.

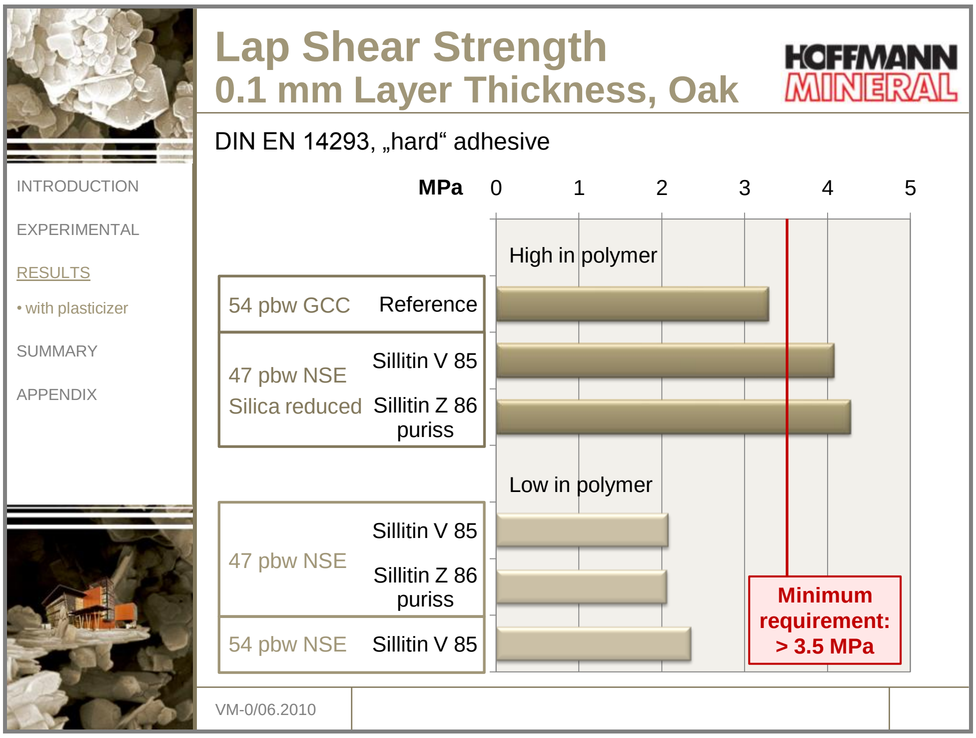
For the evaluation as „hard“ adhesive, the sample was applied with a notched trowel (toothing B3 according to TKB6) at a right angle to the longitudinal direction of the slats, and a second slat laid on top. By loading the bond area with 2 kg for 60 s, an adhesive layer thickness of about 0.1 mm was obtained.

In both tests, excess adhesive residues were removed after the bonding, and the samples stored for 7 days at standard 23/50 conditions + 20 days at 40 °C + 1 day at standard 23/50 conditions.

The test was run according to the standard DIN EN 14293 with a crosshead speed of 20 mm/min.



DIN EN 14293 requires for „soft“ parquet adhesives (defined by a displacement more than 2) a minimum lap shear strength of 0.5 MPa. This minimum level was surpassed without problems by all adhesive formulations of the study, and all also gave evidence of good adhesion on the substrate. Remarkable was the result of the „low in polymer“ formulation with 54 pbw Sillitin V 85, which despite a reversed polymer/plasticizer ratio almost reached the level of the „high in polymer“ control containing calcium carbonate.



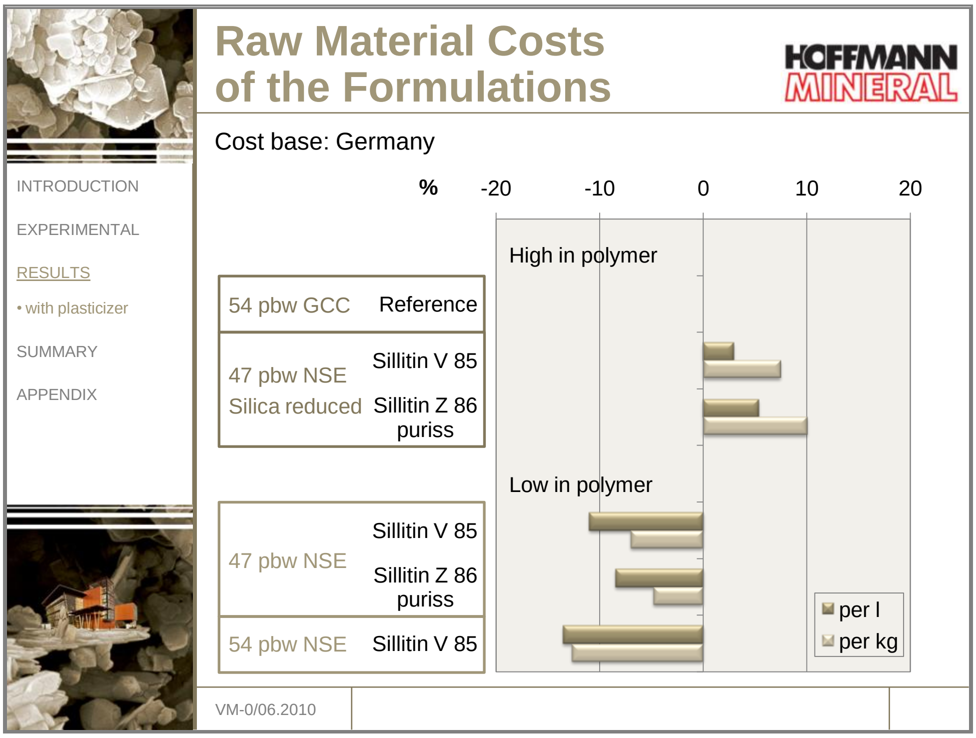
The standard requirement for „hard“ adhesives of at least 3.5 MPa is met only with Neuburg Siliceous Earth in the „high in polymer“ formulations. Here Sillitin Z 86 puriss comes out again slightly better than Sillitin V 85.

3.1.4 Storage stability

After 6 months of storage of the adhesives in a customary standard PE cartridge at room temperature, no premature crosslinking could be observed. The compounds showed no gelling, and could be squeezed out without problems.

3.1.5 Raw material costs

The figure illustrates the raw material costs per liter or kilogram adhesive in comparison with the reference formulation. The calculations were based on raw material prices in Germany in the 3rd quarter of 2009.



The use of Neuburg Siliceous Earth in the „high in polymer“ formulation results in a slight cost increase, but in compensation leads to a marked improvement in the mechanical properties.
The „low in polymer“ version, with properties close to the reference compound, in turn offers possibilities for cost savings.

3.1.6 Conclusion: Formulations with plasticizer

In the „high in polymer“ formulation:

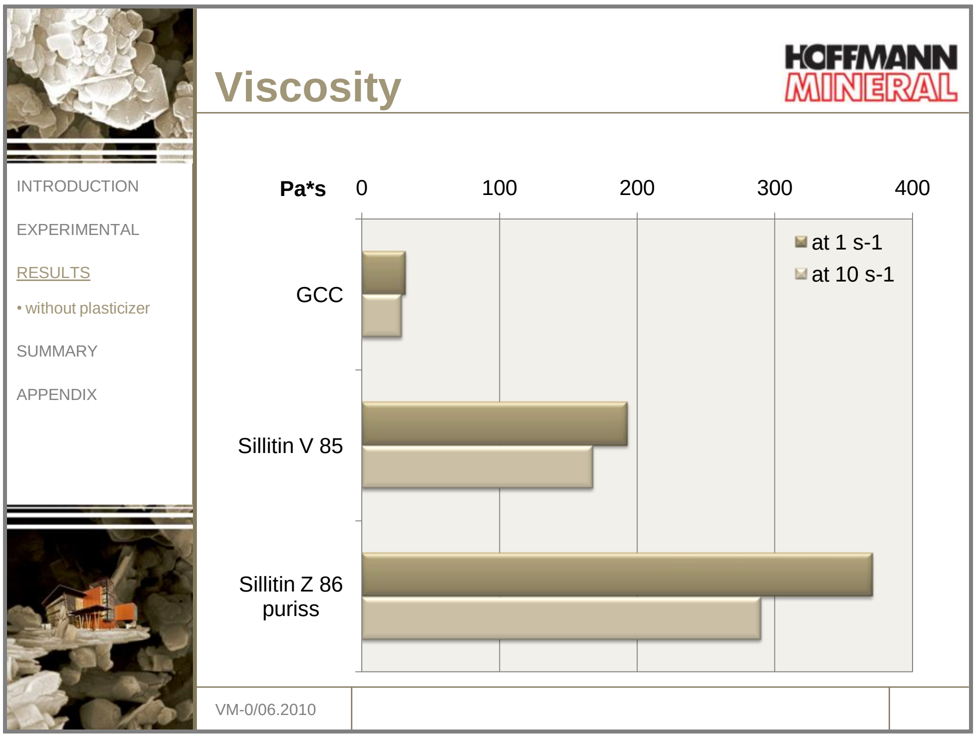
- the higher thickening power of Neuburg Siliceous Earth can be largely compensated by reducing the additions of filler and rheological additive
- comparable or slightly longer skin formation time along with unchanged in-depth cure
- higher tensile strength along with similar elongation at break
- markedly higher lap shear strength
- Neuburg Siliceous Earth allows to meet the standard requirements both for „soft“ as well for „hard“ parquet adhesives

In the „low in polymer“ formulations:

- a rheological property profile similar to the reference (calcium carbonate in „high in polymer“ formulation)
- longer skin formation time without affecting the in-depth cure
- meeting the standard requirements for „soft“ parquet adhesives
- potential cost saving, in particular with Sillitin V 85 at equal weight loading of 54 pbw

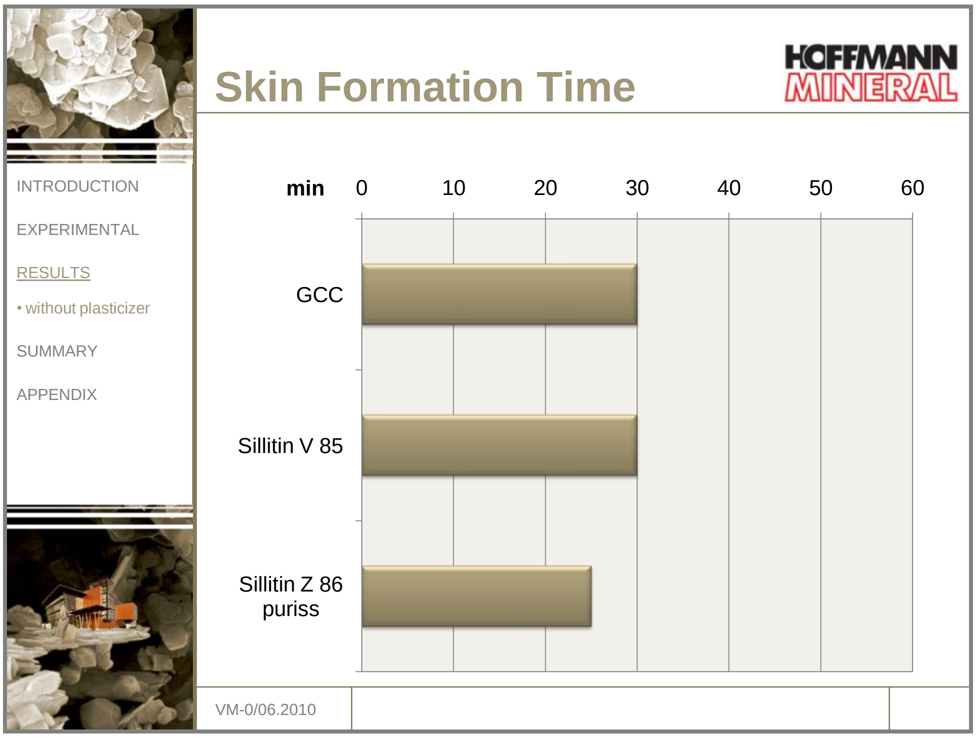
3.2 Formulations without plasticizer

3.2.1 Viscosity

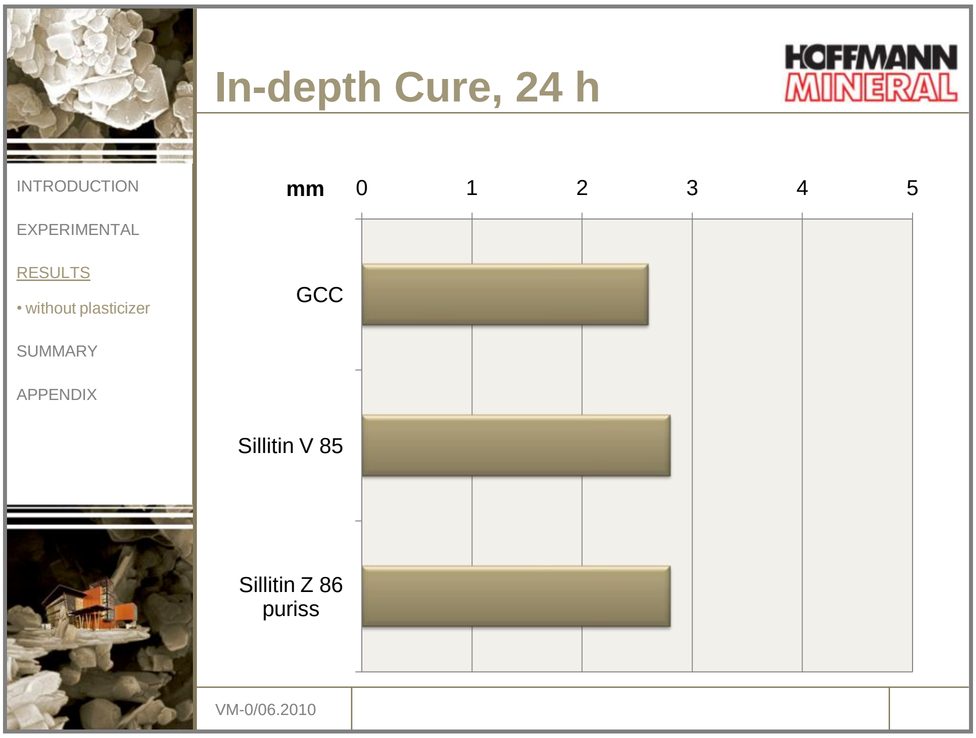


Already with Sillitin V 85 the viscosity is markedly higher than with calcium carbonate, and with Sillitin Z 86 puriss because of its finer particle size there is a further increase. On the other hand, all the compounds give evidence of almost negligible structure and tend to leveling, because no fumed silica was used as a rheological additive.

3.2.2 Skin formation time and in-depth cure



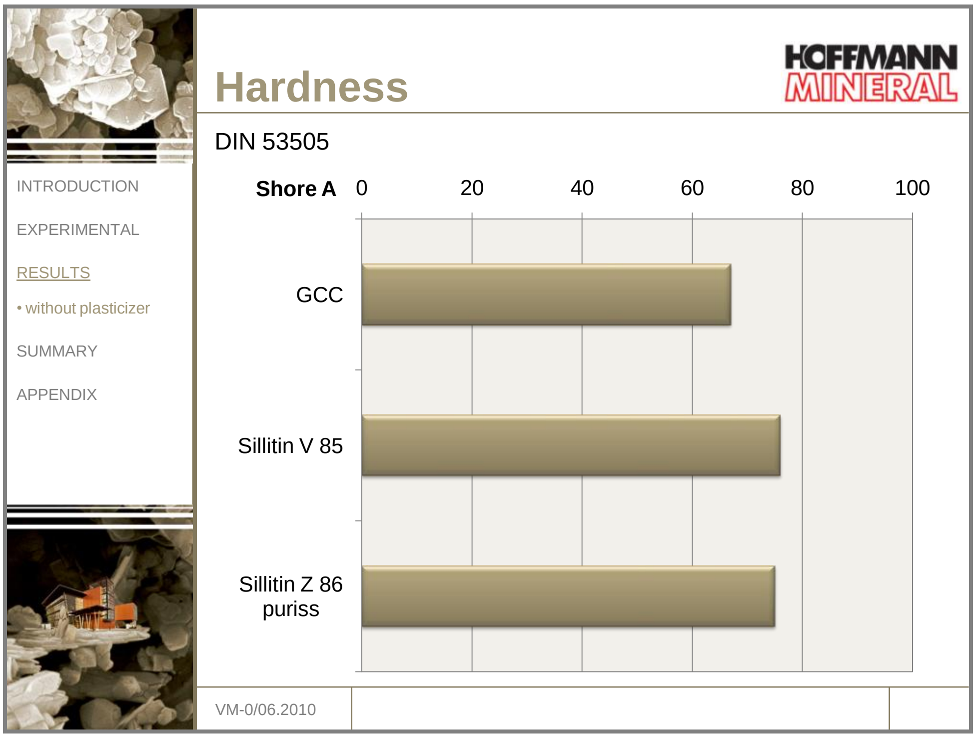
The skin formation time with Neuburg Siliceous Earth is comparable to the results with calcium carbonate, and with Sillitin Z 86 puriss marginally shorter.



Also the in-depth cure remains largely unaffected by the different fillers.

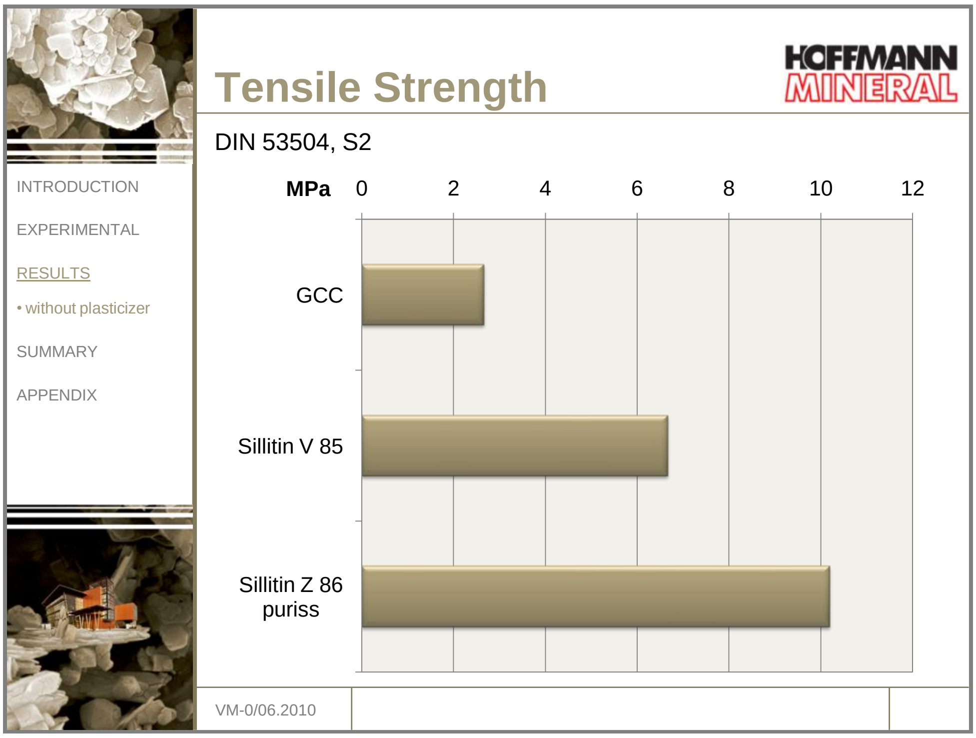
3.2.3 Mechanical properties

a) Hardness

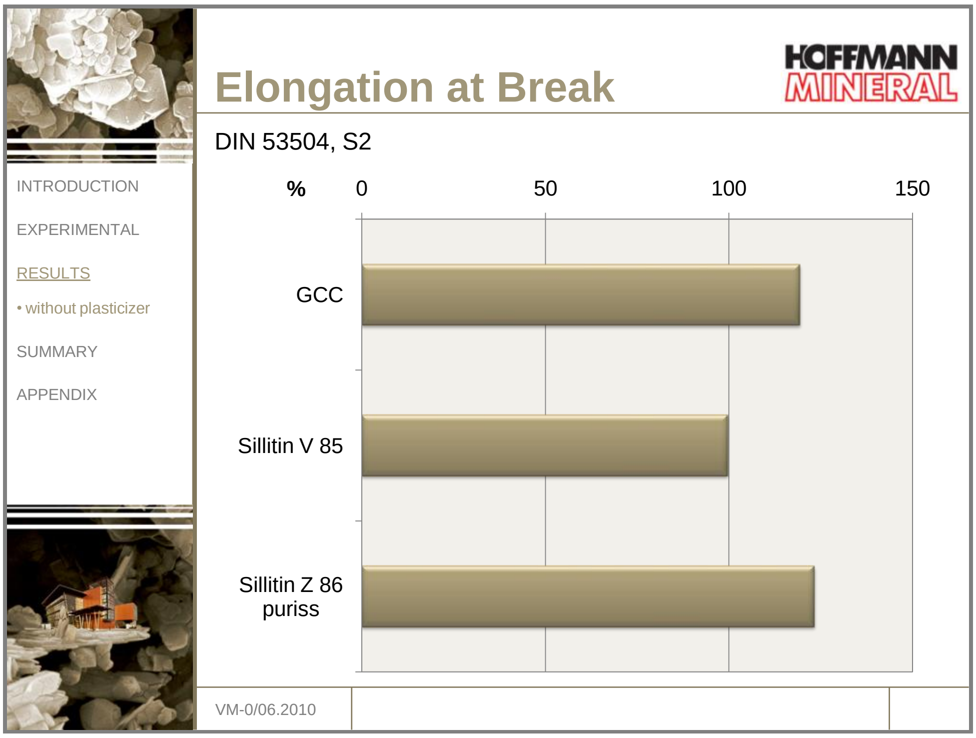


With Neuburg Siliceous Earth, the hardness is about 10 Shore A higher than with calcium carbonate.

b) Tensile test

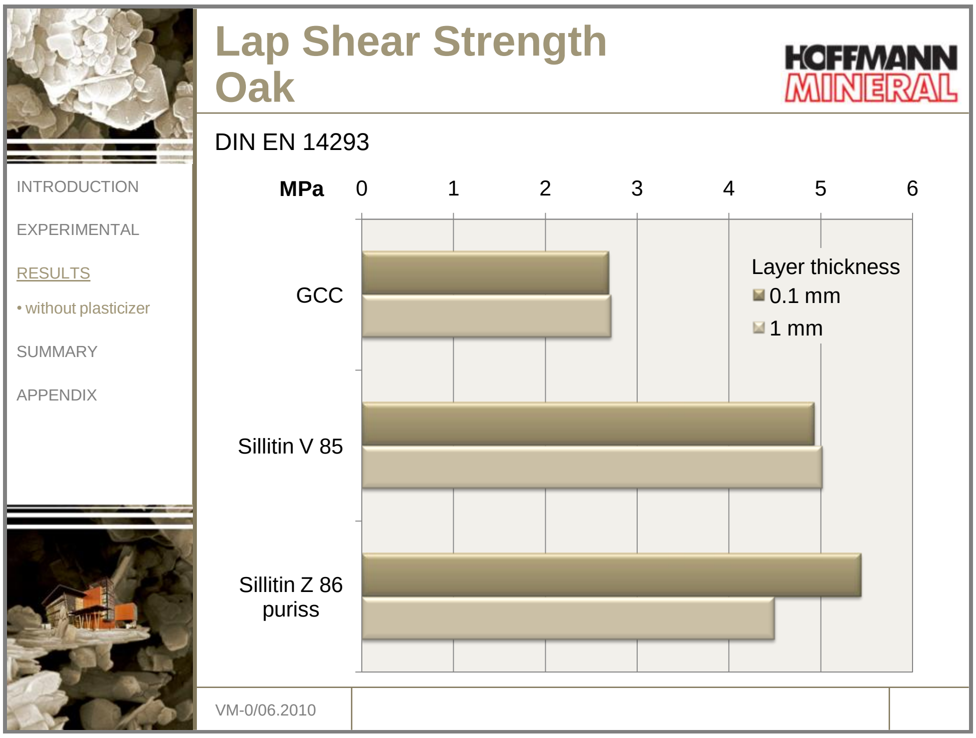


Neuburg Siliceous Earth leads to an extraordinarily high tensile strength on a level unreached so far. Sillitin Z 86 puriss, due to the finer particle size and the improved dispersion, offers a distinct further increase.



The elongation at break is hardly affected at all by the filler selection.

c) Lap shear test



The excellent tensile strength with Neuburg Siliceous Earth, despite very good adhesion, cannot fully be transferred to the substrate. However, compared with calcium carbonate, fairly independent of the adhesive layer thickness the lap shear strength comes out practically twice as high. In fact, the strength of the wood is approached, so that partly wood fiber breakouts are to be seen.

3.2.4 Storage stability

After 6 months of storage of the compounds in customary standard PE cartridges at room temperature, also with the plasticizer-free formulations no premature crosslinking could be observed. The compounds were not gelled, and could be squeezed out without any problems.

3.2.5 Conclusion: Formulations without plasticizer

- high hardness
- extraordinarily high tensile strength up to 10 MPa possible
- elongation at break not affected.
- marked increase of lap shear strength, more than 5 MPa within reach

4 Summary

The „high in polymer“ formulation version loaded with Neuburg Siliceous Earth is able to meet the requirements of DIN EN 14293 as well for „soft“ adhesives with a displacement more than 2 as for „hard“ adhesives with a lap shear strength of at least 3.5 MPa. The higher viscosity can be optimized via a reduced filler and fumed silica content. Of particular advantage versus calcium carbonate is the markedly higher tensile strength and lap shear strength.

The „low in polymer“ formulations allow to produce reasonably priced and easy-to-process compounds which also fulfill the requirements of DIN EN 14293 for „soft“ parquet adhesives.

Formulations without plasticizer reach tensile strength figures on a very high level.

Among the grades in the Neuburg Siliceous Earth range, Sillitin V 85 is particularly suited for parquet adhesive formulations on the base of silane-terminated polyether. For very high requirements with regard to strength, the use of Sillitin Z 86 puriss can be recommended.

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Recommendation

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

in parts by weight

Requirement	Economic parquet adhesive soft	Parquet adhesive with increased strength soft or hard	Adhesive with maximum strength
GENIOSIL® STP-E 10	15.5	25.5	42.1
Caradol ED 56-200	25.0	15.0	---
GENIOSIL® XL 10	2.0	2.0	2.3
HDK H 18	2.0 (- 2.5)	2.0 (- 2.5)	0 (- 2.0)
Sillitin V 85	54.0	47.0	---
Sillitin Z 86 puriss	---	---	54.4
GENIOSIL® GF 96	1.0	1.0	1.2
Total	**99.5**	**92.5**	**100.0**

VM-0/06.2010

5 Appendix

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Formulation Variations with Plasticizer

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in % by weight

	High in polymer			Low in polymer		
	GCC	Sillitin V 85	Sillitin Z 86 puriss	Sillitin V 85	Sillitin Z 86 puriss	Sillitin V 85
Polymer	25.5	27.6	27.6	16.7	16.7	15.5
Plasticizer	15.0	16.2	16.2	26.9	26.9	25.0
Drying agent	2.0	2.2	2.2	2.2	2.2	2.0
Rheological additive	2.5	2.2	2.2	2.7	2.7	2.5
GCC	54.0	---	---	---	---	---
Sillitin V 85	---	50.7	---	50.4	---	54.0
Sillitin Z 86 puriss	---	---	50.7	---	50.4	---
Adhesion promoter	1.0	1.1	1.1	1.1	1.1	1.0
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

VM-0/06.2010

Formulation variants with plasticizer- in weight percent

Suppliers:

GENIOSIL® STP-E 10	Wacker Chemie
Caradol ED 56-200	Shell Chemicals
GENIOSIL® XL 10	Wacker Chemie
HDK H 18	Wacker Chemie
GENIOSIL® GF 96	Wacker Chemie