

Calcined Neuburg Siliceous Earth in adhesives with high strength based on Kaneka MS Polymer™

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1 Introduction

Apart from the widely introduced silicone and polyurethane systems, the class of Kaneka MS Polymer™ is also a viable option for the preparation of sealants and adhesives. Close-mesh cross-linked polymers which are suitable for formulating high-strength adhesives have been available for some time now.

The formulations prepared are non-hazardously with respect to health and environment and are distinguished by outstanding mechanical properties along with excellent adhesion characteristics.

The standard filler here is calcium carbonate, while surface-treated precipitated calcium carbonate with a higher specific surface area is preferred for highly demanding adhesives.

This study will present Calcined Neuburg Siliceous Earth grades as functional fillers for high-strength adhesives based on Kaneka MS Polymer™.

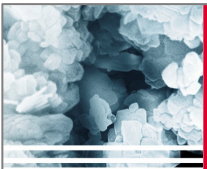

The objective was to improve the strength of the adhesive and take advantage of this effect in order to upgrade traditional compounds formulated with the established filler calcium carbonate.

2 Experimental

2.1 Base Formulation

The tests were conducted using a highly simplified formulation. The employed binding agent is recommended for adhesives with high strength. The filler, a precipitated and surface-treated calcium carbonate is a standard grade, which is often used in moisture curing formulations. Vinyl silane is the chemical drying agent and amino silane is used as an adhesion promoter to the substrate.

Another component is the tin-based catalyst.

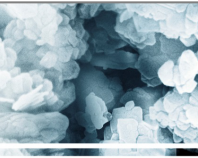
 INTRODUCTION <u>EXPERIMENTAL</u> RESULTS SUMMARY APPENDIX 	Base Formulation			HOFFMANN MINERAL	
			parts by weight [pbw]		
	Kaneka Silyl™ SAX750	MS Polymer™, high strength	42.0		
	Filler PCC s.tr.	Precipitated calcium carbonate, surface treated	52.7		
	Vinyl silane VTMO	Drying agent	2.3		
	Amino silane AMMO	Adhesion promoter	1.5		
	Neostann S1	Catalyst	1.5		
	Total		100.0		
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2.2 Test Design and Formulations

Starting from the basic formulation, the precipitated and surface-treated calcium carbonate (PCC s.tr.) is replaced by Calcined Neuburg Siliceous Earth at equal weight.

It is expected that Calcined Neuburg Siliceous Earth has a lower viscosity in the low shear range (yield point likewise sag resistance). Therefore hydrophobic fumed silica is used for rheology control.

As another variant, a combination of Aktifit AM and other adhesion promoters is tested: the amino silane AMMO (aminopropyltrimethoxy silane) contained in the base formulation with 1.5 pbw is exchanged for a combination of 1.5 pbw amino silane AMEO (aminopropyltriethoxy silane) and 1.5 pbw Dynasylan 1146 (oligomeric diamino silane).



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Test Design

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Weight-equal exchange of PCC s.tr.
by **Calcined Neuburg Siliceous Earth**

PCC s.tr.

➔

Silfit Z 91	Aktifit VM	Aktifit AM	Aktifit PF 115
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+ 1 pbw rheological additive Cab-O-Sil TS 720

Aktifit AM combined with varied / increased adhesion promoter

1.5 pbw amino silane AMMO

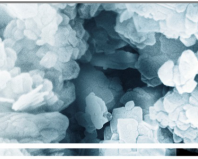
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1.5 pbw amino silane AMEO

1.5 pbw Dynasylan 1146

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This results in the following formulations, which are presented here in a table:



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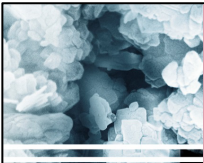


Formulations

	PCC	Calcined Neuburg Siliceous Earth				
	PCC s.tr.	Silfit Z 91	Aktifit VM	Aktifit AM	Aktifit PF 115	Aktifit AM silane varied
MS Polymer™	42.0	42.0	42.0	42.0	42.0	42.0
Rheological additive	---	1.0	1.0	1.0	1.0	1.0
Filler	52.7	52.7	52.7	52.7	52.7	52.7
Drying agent	2.3	2.3	2.3	2.3	2.3	2.3
Adhesion promoter AMMO	1.5	1.5	1.5	1.5	1.5	---
Adhesion promoter AMEO	---	---	---	---	---	1.5
Adhesion promoter Dynasylan 1146	---	---	---	---	---	1.5
Catalyst	1.5	1.5	1.5	1.5	1.5	1.5
Total	100.0	101.0	101.0	101.0	101.0	102.5

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2.3 Fillers and their Characteristics

The table summarizes the most important typical properties of the fillers.

 <p>INTRODUCTION</p> <p><u>EXPERIMENTAL</u></p> <p>RESULTS</p> <p>SUMMARY</p> <p>APPENDIX</p> 	Fillers, Characteristics 					
		PCC	Calcined Neuburg Siliceous Earth			
		PCC s.tr.	Silfit Z 91	Aktifit VM	Aktifit AM	Aktifit PF 115
	Volatile matter At 105 °C	%	0.3	0.2	0.1	0.1
	Oil absorption	g/100g	34	55	55	59
	Specific surface area BET	m ² /g	16	8	7	8
	Functionalization	Fatty acids	---	Vinyl	Amino	Special amino
	Surface character	hydrophobic	hydrophilic	hydrophobic	hydrophilic	hydrophobic
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The precipitated calcium carbonate is a fine type, surface-treated with fatty acids and with a relatively high specific surface, which is frequently used in moisture curing systems.

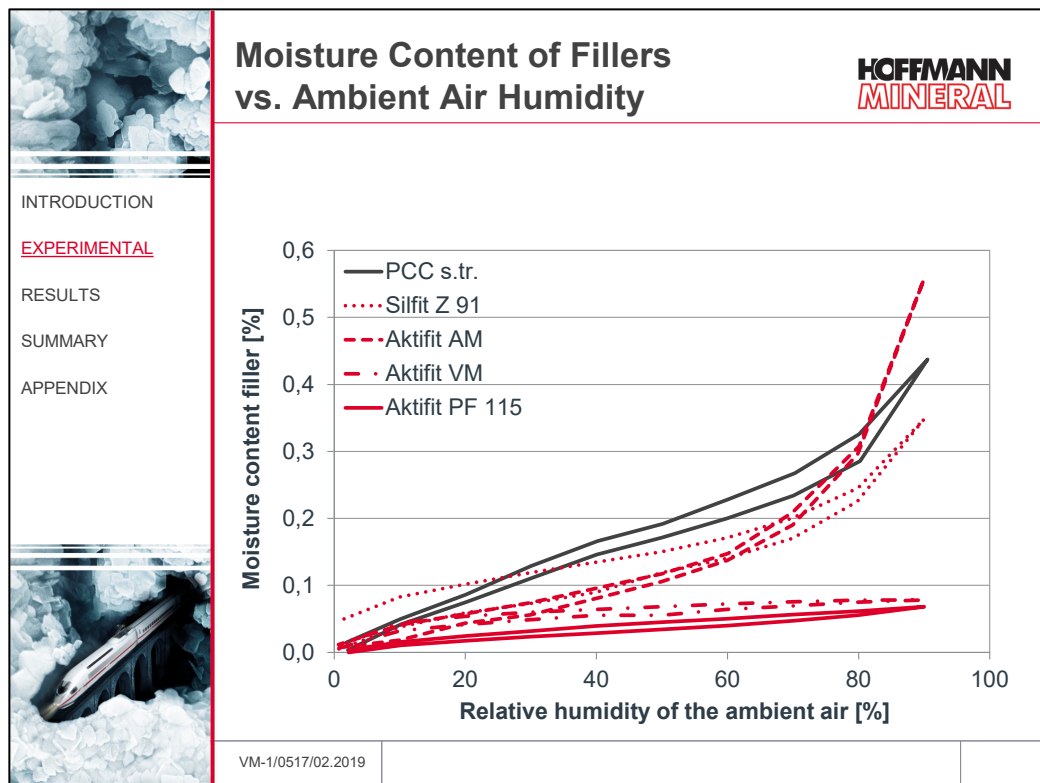
Silfit Z 91, Aktifit VM, Aktifit AM, and Aktifit PF 115 are calcined variants from the Neuburg Siliceous Earth series and are therefore bright and color-neutral products. There are differences with regard to surface character and surface treatment.

Aktifit AM was surface-treated with amino functional groups in order to improve the adhesion properties and thus adhesive strength.

Aktifit VM is hydrophobically treated by a special vinyl functional group.

Thanks to surface treatment with a special amino functional group, Aktifit PF 115 combines both: amino functionality and hydrophobic properties.

Both hydrophobic grades are characterized by a very low volatile content. In addition, they show an extremely low moisture uptake under humid climatic conditions. The following graph illustrates how the (equilibrium) moisture content of the fillers changes with the humidity of the ambient air.



The curves refer to the moisture uptake with increasing humidity of the surrounding air, as well as the moisture loss with decreasing humidity of the ambient air.


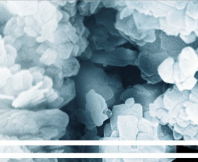
PCC s.tr., Silfit Z 91 and Aktifit AM under dry ambient conditions initially show a markedly low moisture content which only increases with higher ambient air humidity.

Aktifit VM, on the other hand, absorbs much less moisture even with higher ambient air humidity and remains at a value below 0.1% even in very high humidity.

However, Aktifit PF 115, which was calcined and treated with special amino silane deserves particular attention: regardless of the climatic conditions, its moisture content remains at an almost constant level below 0.07 %, even in extremely high air humidity.

With both hydrophobic products, pre-drying of the filler before processing is not necessary.

2.4 Preparation of Batches



Preparation of Batches

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- Planetary mixer
- Dissolver disc, bar blade and scraper
- Batch size approx. 500 ml

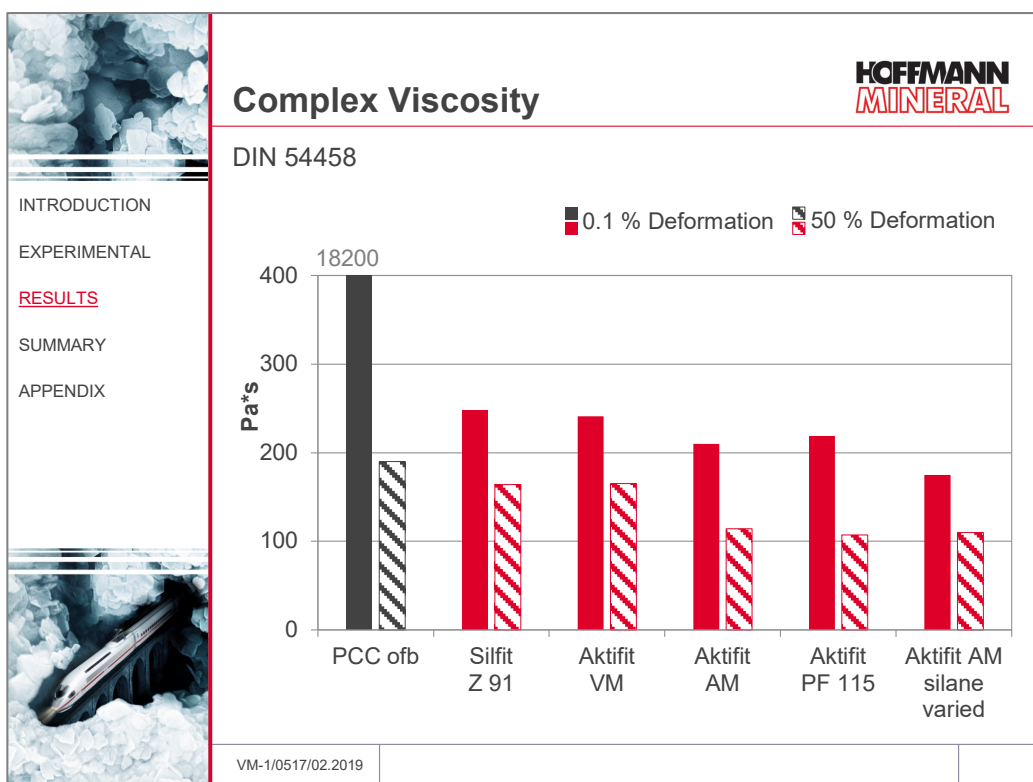
- Feed polymer
- Stir in rheological additive and (undried) filler
 - 10 min at 3000 rpm and 500 rpm, vacuum
 - 20 min at 1500 rpm and 300 rpm, vacuum
 - Cool down to <50 °C
- Add vinyl silane (drying agent)
 - 5 min at 1000 rpm and 200 rpm
- Add amino silane (adhesion promoter)
 - 5 min at 1000 rpm and 200 rpm
- Add catalyst
 - 5 min at 1000 rpm and 200 rpm
- Deaerate
 - 5 min at 500 rpm and 150 rpm
- Fill into cartridge

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3 Results

3.1 Rheology

The complex viscosity was measured with a plate-plate rheometer in a deformation-controlled oscillation mode at a constant frequency of 10 Hz. The measuring plate had a diameter of 25 mm, the gap distance was 0.5 mm according to the standard DIN 54458. During the first days after the preparation of the batches, post-wetting effects still give rise to erratic results. For the overall assessment, therefore, the results after 4 weeks following the preparation were taken into account.



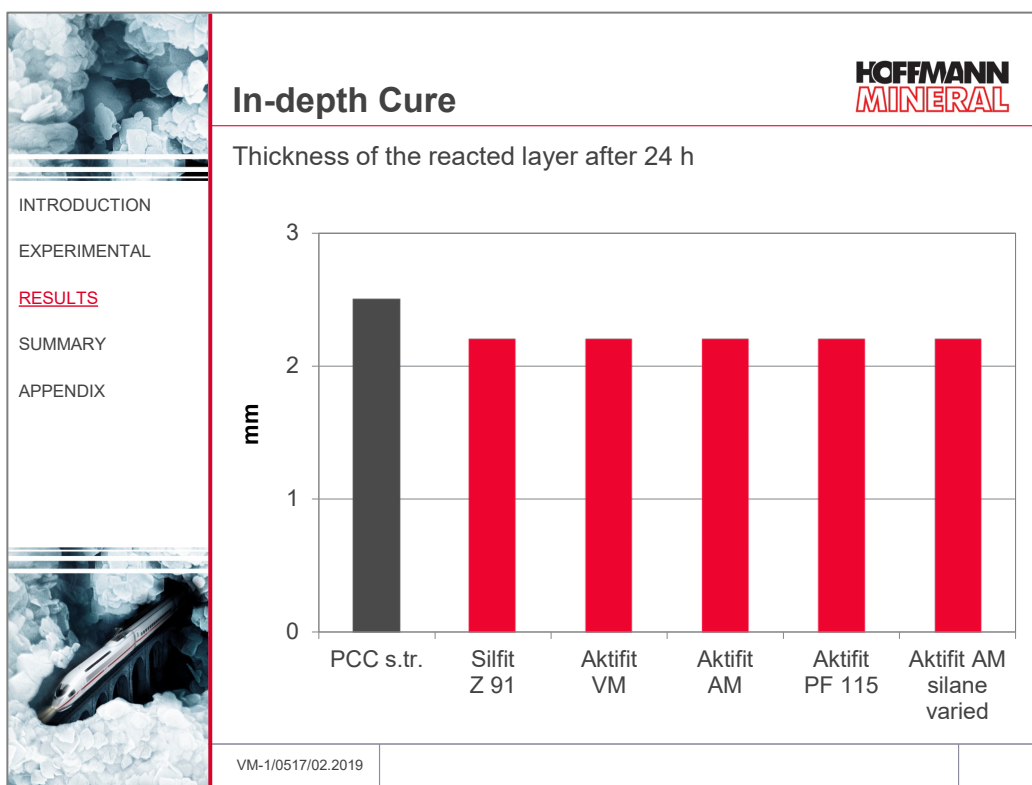
At low deformations, a quasi-static condition is simulated. Here, among others, non-sag properties and the behavior after application can be evaluated.

Despite the addition of a rheological additive, the Calcined Neuburg Siliceous Earth grades yield a lower complex viscosity than PCC s.tr. This indicates a stronger flow tendency, which is, however, easily compensated by increasing the silica addition to 2.5 to 3 parts by weight.

At a higher deformation of 50 %, it is possible to demonstrate the processing behavior, e.g. during extrusion from the cartridge. All formulations with Calcined Neuburg Siliceous Earth grades have a markedly lower complex viscosity than PCC s.tr. Especially the two amino functional grades Aktifit AM and Aktifit PF 115 demonstrate particularly good flow behavior. They are therefore much easier to extrude than the formulation with PCC s.tr.

3.2 Curing

In order to measure the cure rate, approx. 4 ml of the batches were filled into small PE containers (Ø 1.8 cm, height 1.5 cm), and the surface was evenly wiped off. After 24 hours of storage at standard conditions of 23 °C/50 % r.h., the cured layer was taken away, still liquid remainders were removed, and the thickness of the cured layer was determined.



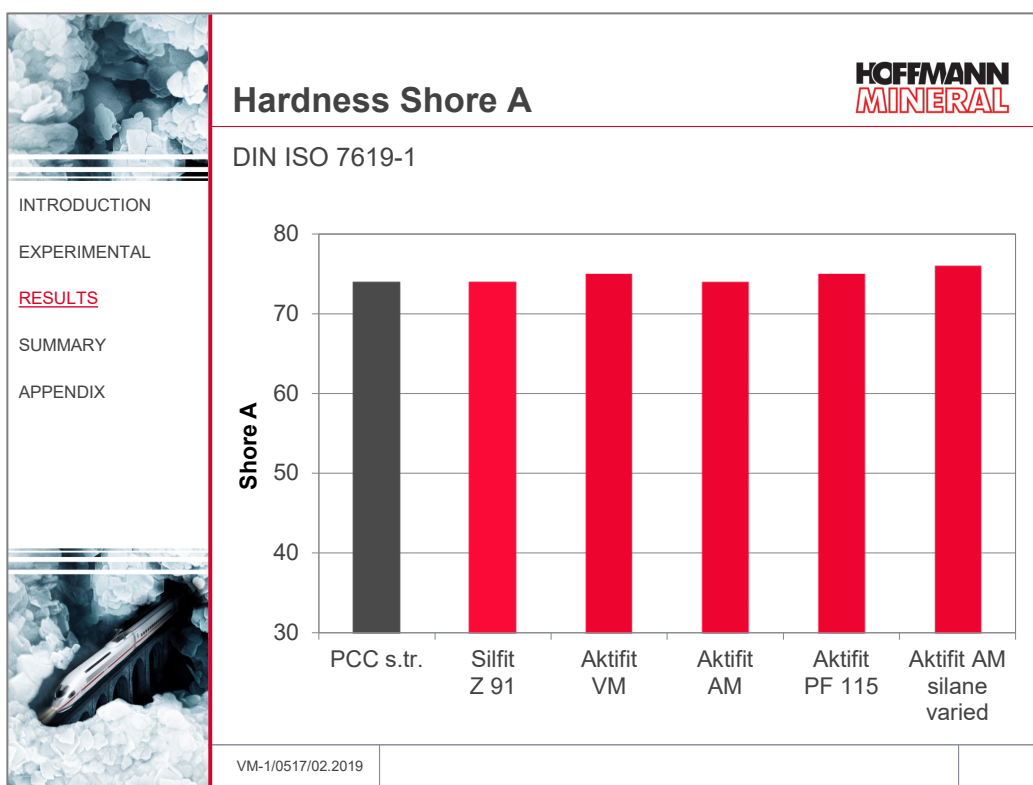
The thickness of the cured layer with Calcined Neuburg Siliceous Earth tends to be somewhat lower. The results, however, are always close to each other, so the minimum differences should not be overestimated.

3.3 Mechanical Properties

To determine the properties of the free film, the required specimens were punched out of a sample sheet of about 2 mm thickness, which was cured for four weeks at standard climate 23 °C/50 % r.h.

a) Hardness Shore A

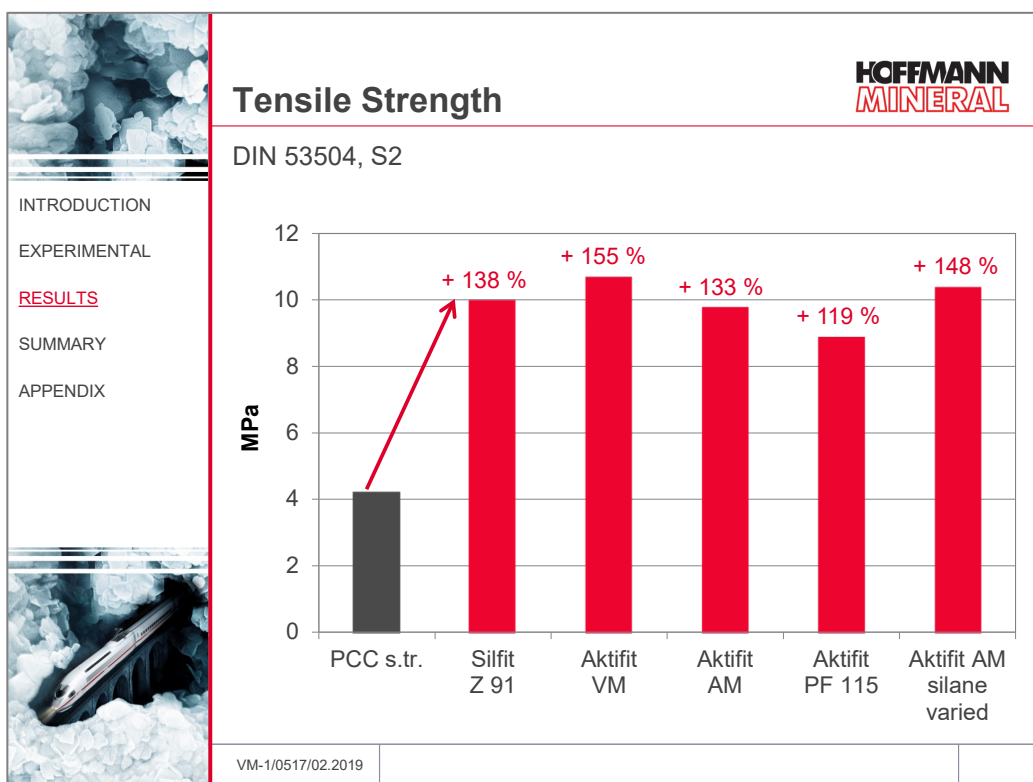
Hardness was measured on piled-up S2 dumbbells (total height approx. 6 mm).



Calcined Neuburg Siliceous Earth yields the same Shore A Hardness as the PCC s.tr. used.

b) Tensile Strength

The cross-head speed for the tests was 200 mm/min.



Compared to PCC s.tr., all the tested Calcined Neuburg Siliceous Earth products produce a significant increase to more than double, up to triple values.

3.4 Adhesive Strength

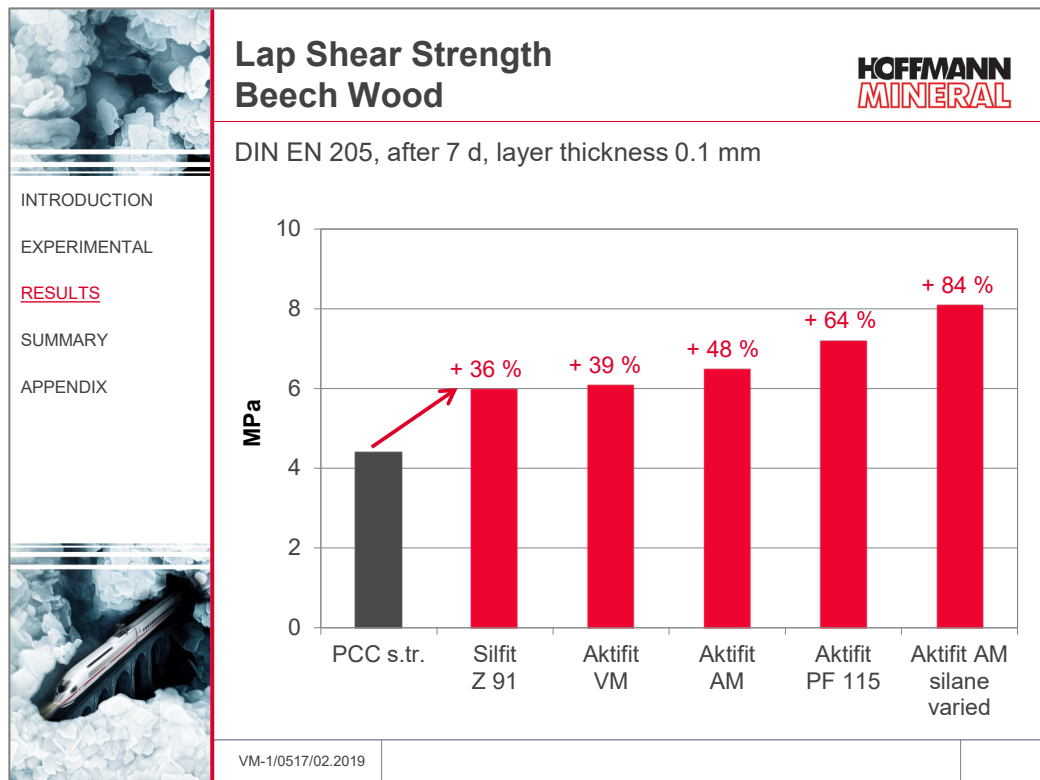
a) Lap Shear Strength on Beech Wood, Thin Adhesive Layer

Beechwood from Rocholl made of steamed, straight-grained beech with a defined angle of annual rings was used for the lap shear strength test (according to DIN EN 205). In contrast to the specifications in the standard, however, the test was not conducted with large wooden plates which are cut to the appropriate dimensions after bonding. Prefabricated wooden slats sized 80 x 20 x 5 mm were used instead, which were bonded overlapping with a bond surface area of 20 x 10 mm (approx. 200 mm²).

Excessive adhesive residues were removed after bonding.

For testing with a thin adhesive layer, the bond surface area was loaded with a 2 kg weight for 1 hour – this corresponds to a pressing power of approx. 0.1 N/mm² and produces an adhesive layer thickness of approx 0.1 mm.

The test was carried out after a curing period of 7 days in normal climate conditions of 23 °C/50 % r. h. at a crosshead speed of 50 mm/min.



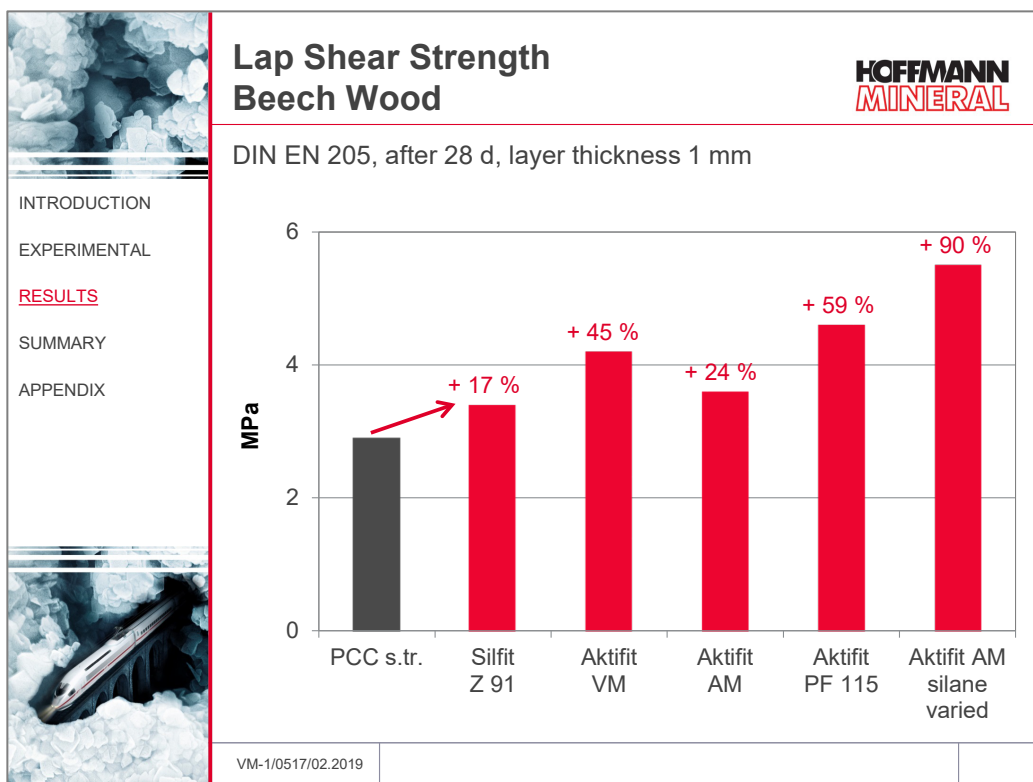
Compared to PCC s.tr., the tested Calcined Neuburg Siliceous Earth grades demonstrated a distinct increase in strength by up to 64 % when bonded in thin layers. The most advantageous in this case are the two amino functional products Aktifit AM and Aktifit PF 115, which yielded the two highest results only due to filler replacement. With Aktifit AM and variation/increase of the adhesion promoter, the strength can be further improved and achieves an increase of more than 80 %. This result clearly shows that the excellent cohesion with Calcined Neuburg Siliceous Earth also requires optimized adhesion in order to utilize the full potential of this functional filler.

Note: by varying the MS polymerTM, the strength on wood substrates can be further increased.

b) Lap Shear Strength on Beech Wood, Thick Adhesive Layer

The test procedure with a thicker adhesive layer was similar to point 3.4 a). The adhesive, however, was applied to the entire bond surface area with a spatula, and the higher adhesive layer thickness of 1 mm was set using appropriate spacers when the wooden slats together were pressed together.

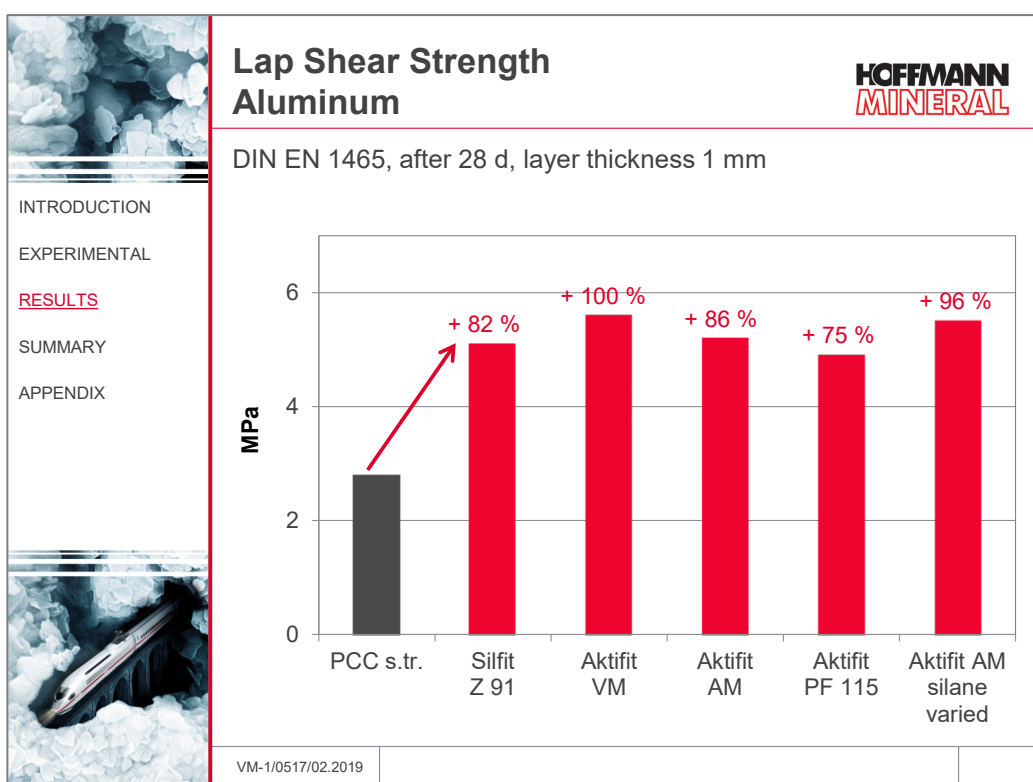
The test was carried out after a curing period of 28 days in normal climate conditions of 23 °C/50 % r. h. at a crosshead speed of 50 mm/min.



Even with a thicker adhesive layer, an increase in strength was noticeable compared to PCC s.tr. With increases of 45 or nearly 60 %, the two hydrophobic products Aktifit VM and Aktifit PF 115 proved to be very effective. With Aktifit AM and the varied/increased adhesion promoter, the lap shear strength is almost doubled, which demonstrates the potential of Calcined Siliceous Earth products with good adhesion.

c) Lap Shear Strength on Aluminum, Thick Adhesive Layer

Two aluminum sample sheets measuring 100 x 25 x 1.5 mm were lap-bonded in an adhesive area of 25 x 12.5 mm (312.5 mm²) with an adhesive layer thickness of 1 mm. The test was carried out after a curing period of 28 days in normal climate conditions of 23 °C/50 % r. h. at a crosshead speed of 10 mm/min.



Compared to PCC s.tr., the lap shear strength is nearly doubled on aluminum from 2.8 to 5 to 5.5 MPa. The highest values are obtained with the formulations with Aktifit VM and Aktifit AM. The formulation with the varied/increased adhesion promoter, however, shows only a minimum further increase in lap shear strength, which can be explained by the already achieved optimal adhesion of the standard formulation with Calcined Neuburg Siliceous Earth on aluminum substrate.

4 Summary

Calcined Neuburg Siliceous Earth is very suitable as a functional filler for high-strength structural adhesives based on Kaneka MS Polymer™.

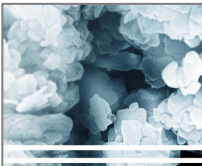

Tensile strength and lap shear strength are distinctly improved compared to precipitated and surface-treated calcium carbonate.

Especially on wood substrates, the full potential of Calcined Neuburg Siliceous Earth can be completely utilized with optimized silane adhesion promoters and thus improved adhesion.

Viscosity and/or rheological behavior can be controlled, from freely flowing to pasty, by an adapted silica content.

Distinguishing Features of the Calcined Neuburg Siliceous Earth Grades:

- | | |
|-----------------------|--|
| Silfit Z 91 | <ul style="list-style-type: none">• Low moisture content• White and color-neutral• Cost-effective• Good mechanical properties |
| Aktifit VM | <ul style="list-style-type: none">• Very low moisture content and extremely low moisture absorption even under humid conditions• White and color-neutral• Especially for thick joints in wood and metal |
| Aktifit AM | <ul style="list-style-type: none">• Low moisture content• White and color-neutral• Low and thereby adjustable viscosity• Especially for thin joints in wood |
| Aktifit PF 115 | <ul style="list-style-type: none">• Very low moisture content and extremely low moisture absorption even under humid conditions• White and color-neutral• Low and thereby adjustable viscosity• For highest requirements on thin joints in wood |

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			PCC	Calcined Neuburg Siliceous Earth					
			PCC s.tr.	Silfit Z 91	Aktifit VM	Aktifit AM	Aktifit PF 115	Aktifit AM silane varied	
	<u>Rheology</u>								
	Complex viscosity	Pa*s	18200	248	241	210	219	175	
	at 0.1 % deformation	Pa*s	190	164	165	114	107	110	
	at 50 % deformation								
	<u>Curing</u>								
	Skin formation	min	5	5	5	5	5	5	
	In-depth cure after 8 h	mm	1.4	1.3	1.3	1.3	1.3	1.3	
	In-depth cure after 24 h	mm	2.5	2.2	2.2	2.2	2.2	2.2	
	<u>Mechanical properties</u>								
	Hardness	Shore A	74	74	75	74	75	76	
	Tensile strength	MPa	4.2	10.0	10.7	9.8	8.9	10.4	
	Elongation at break	%	271	136	148	161	156	155	
	<u>Lap shear strength</u>								
	Beech wood, layer 0.1 mm	MPa	4.4	6.0	6.1	6.5	7.2	8.1	
	Beech wood, layer 1 mm	MPa	2.9	3.4	4.2	3.6	4.6	5.5	
	Aluminum, layer 1 mm	MPa	2.8	5.1	5.6	5.2	4.9	5.5	
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Testing Conditions

Rheology	DIN 54458, MCR 300, PP 25 mm, d: 0.5 mm, Oscillation: deformation 0.01 to 100 %, f = 10 Hz Testing after 28 d		
Hardness Shore A	DIN ISO 7619-1, piled S2 specimens Curing / conditioning: 28 d @ standard conditions 23/50		
Tensile test	DIN 53504, S2 specimens Curing / conditioning: 28 d @ standard conditions 23/50		
Lap shear test Wood	DIN EN 204/205	Substrate: beech wood Adhesive layer: 0.1 mm and 1 mm Curing: 7 resp. 28 d @ standard conditions 23/50 Crosshead speed: 50 mm/min	
Lap shear test Aluminum	DIN EN 1465	Substrate: Aluminum 99.5 % Adhesive layer: 1 mm Curing: 28 d @ standard conditions 23/50 Crosshead speed: 10 mm/min	

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