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Calcined Neuburg Siliceous Earth in adhesives with high strength based on silane terminated polyurethane (STP-U)

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Contents

1 Introduction

Apart from the widely introduced silicone and polyurethane systems, also hybrid prepolymers based on silane terminated polyurethanes (STP-U) offer themselves for the preparation of sealants and adhesives. They combine the benefits of a polyurethane base structure with a silane based curing mechanism.

The formulations prepared are non-hazardous 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, and for highly demanding adhesives in preference precipitated calcium carbonate (PCC) with a higher specific surface area.

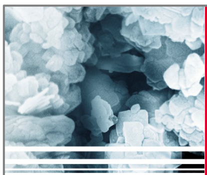
This study will present Calcined Neuburg Siliceous Earth grades as functional fillers for high strength adhesives based on silane terminated polyurethanes.

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

2 Experimental

2.1 Base Formulation

The tests were conducted using a guide formulation from Covestro. The employed binding agent is recommended for structural adhesives with high tensile strength and lap shear strength. The basic formulation contains precipitated calcium carbonate as a filler. Hydrophobic fumed silica is used for rheology control. Vinyl silane is the chemical drying agent and the two amino silanes are used as an adhesion promoter to the substrate. DBU (diazabicycloundecene) is used as catalyst. Further ingredients of the formulation include a yellow pigment and an antioxidant.



INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Formulation

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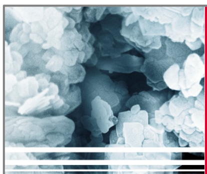
Basis: Guide formulation BBB 7507 from Covestro

		parts or % by weight
Desmoseal S XP 2821	Polymer: silane terminated polyurethane	38.88
Irganox 1135	Antioxidant	0.46
Bayferrox Gelb 415	Pigment	0.28
Cab-O-Sil TS 720	Rheological additive: fumed silica	0.95
Filler		**53.71**
Dynasylan VTMO	Drying agent: vinyl silane	2.61
DBU	Catalyst: diazabicycloundecene	0.11
Dynasylan 1146	Adhesion promoter: amino silane	1.50
Dynasylan AMEO	Adhesion promoter: amino silane	1.50
Total		**100.00**

2.2 Fillers and their Characteristics

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



INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Fillers, Characteristics

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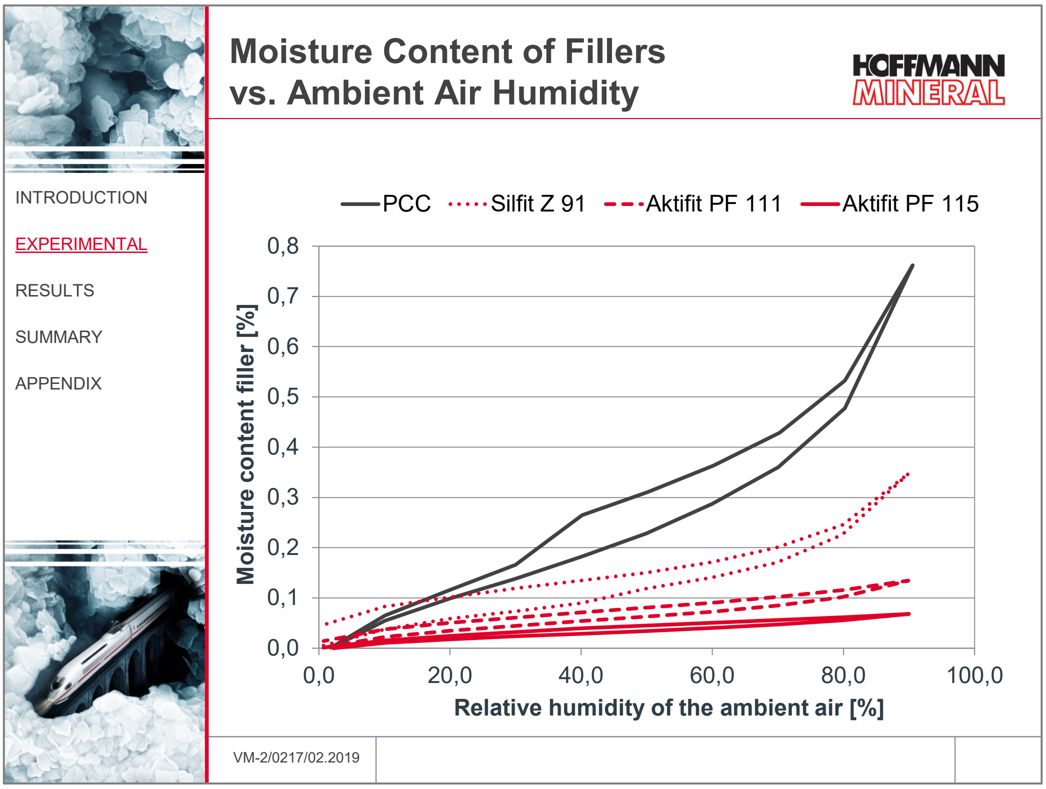
		PCC	Calcined Neuburg Siliceous Earth		
			Silfit Z 91	Aktifit PF 111	Aktifit PF 115
Volatile matter at 105 °C	%	0.5	0.2	0.2	0.1
Oil absorption	g/100g	44	55	49	59
Specific surface area BET	m²/g	11	8	7	8
Surface treatment		---	---	Alkyl silane	Special amino silane
Surface character		hydrophilic	hydrophilic	hydrophobic	hydrophobic

The precipitated calcium carbonate in the guide formulation from Covestro is a fine type with a special grain shape. In this category of PCCs, maximum mechanical properties can be achieved with this type.

Silfit Z 91, Aktifit PF 111, 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.
As an untreated variant, Silfit Z 91 can be classified as hydrophilic, whereas Aktifit PF 111 treated with alkyl silane and Aktifit PF 115 treated with a special amino silane are hydrophobic.
The purpose of the special surface treatment of Aktifit PF 111 with alkyl silane is to enable rheology control: viscosity in the low shear range is increased, thus improving the stability of the adhesive bead without increasing viscosity in the process-relevant high shear range. With Aktifit PF 115, adhesion and adhesive strength will be further improved through functionalization with a special amino silane.

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.



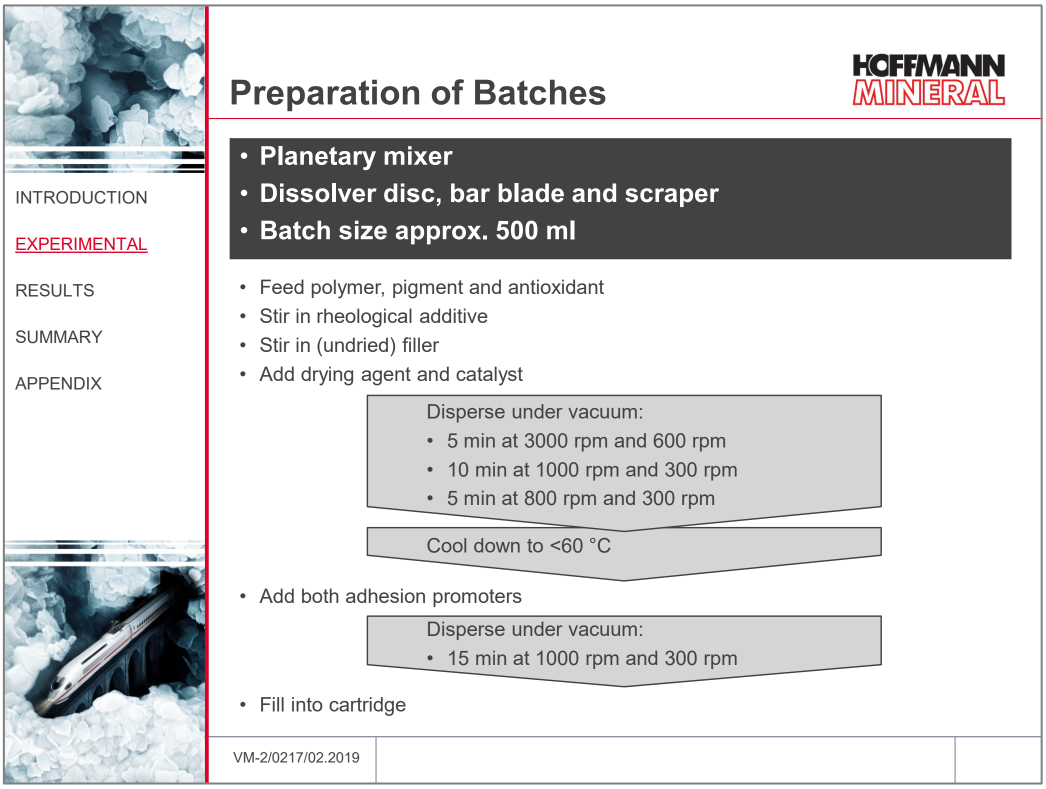
The curves refer to the moisture uptake with increasing humidity of the surrounding air, as well as the moisture loss with decreasing humidity of the ambient air. PCC gives evidence of a distinct dependence of the filler moisture content on the ambient climate – at high ambient air humidity, it absorbs relatively much moisture up to 0.75%. Silfit Z 91, however, under dry ambient conditions shows a markedly low moisture content which only increases with higher ambient air humidity. Aktifit PF 111, on the other hand, absorbs much less moisture even with higher ambient air humidity.

Particular attention, however, deserves the calcined and with special amino silane treated Aktifit PF 115: independent on the climatic conditions its moisture content remains at an almost constant level below 0.07 %, even with extremely high air humidity. This means a pre-drying of the filler prior to its use can be left out.

2.3 Test Design

The calcium carbonate was exchanged 1:1 weight-equal by the different types of calcined Neuburger Siliceous Earth.

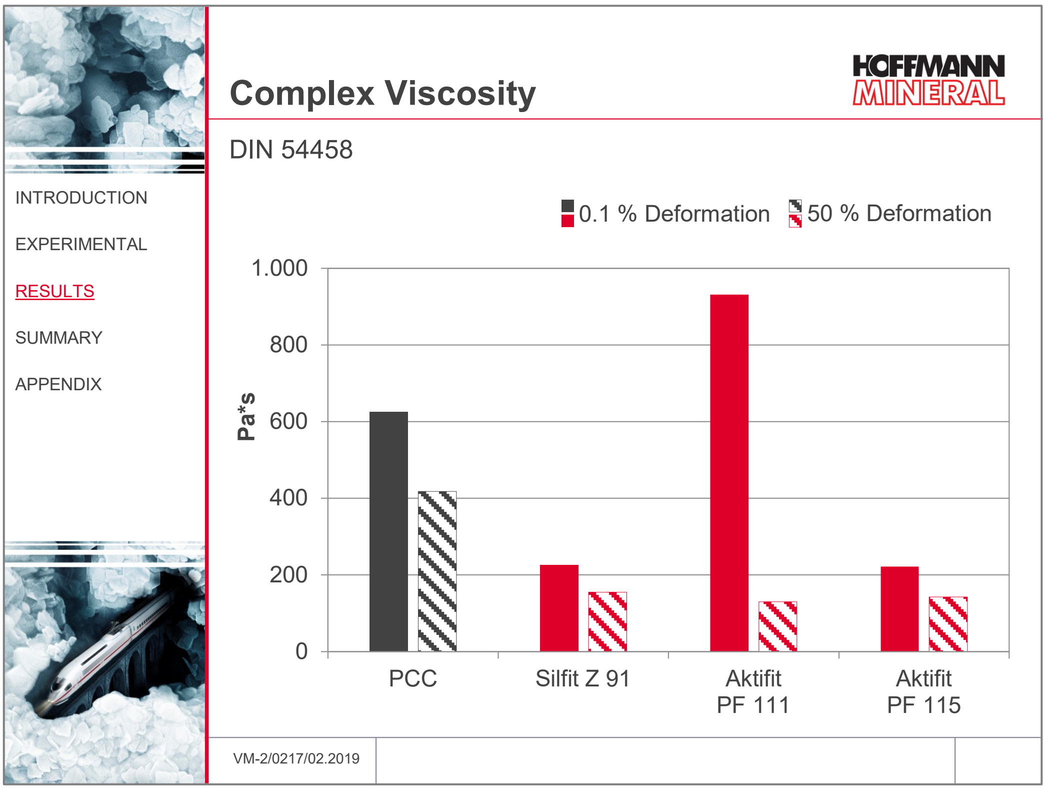
2.4 Preparation of Batches



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. 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.



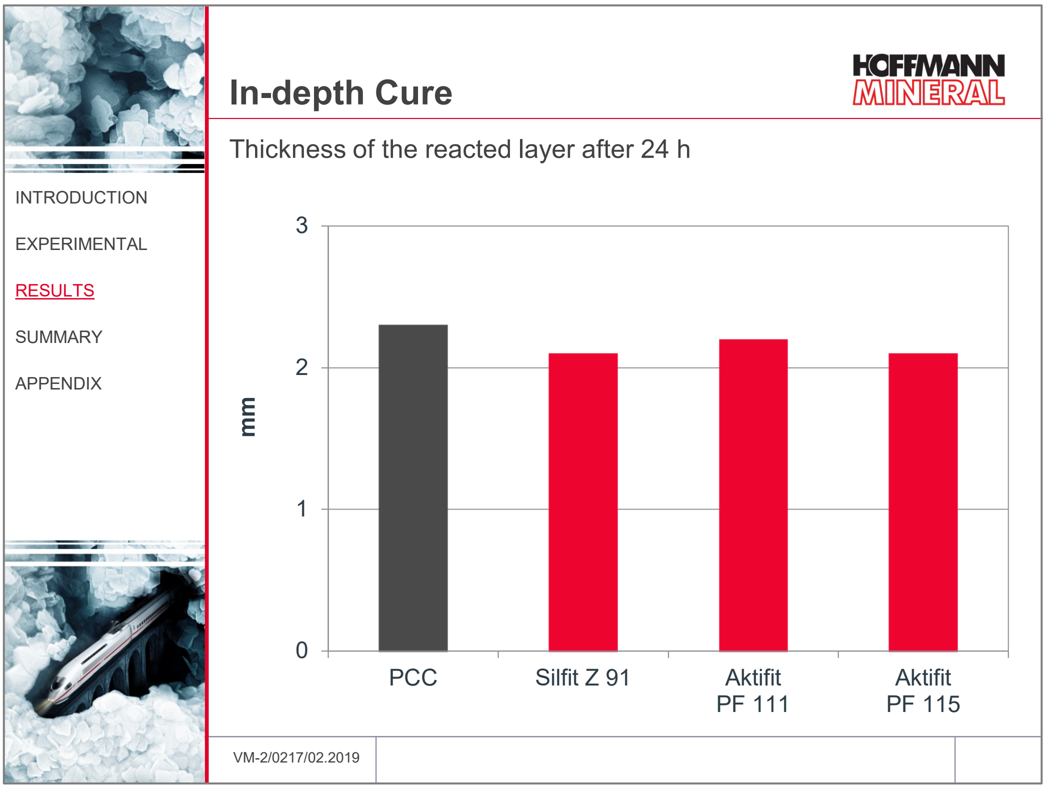
At low deformations, a quasi-static condition is simulated. Here, among others, non-sag properties and the behavior after application can be evaluated. With the exception of Aktifit PF 111, the Neuburg Siliceous Earth grades give a lower complex viscosity than the calcium carbonate. This indicates a stronger flow tendency, which is, however, easily compensated by increasing the silica addition to 2.5 to 3 parts by weight.

Aktifit PF 111, by contrast, gives rise to a markedly higher complex viscosity, indicating superior non-sag properties. Here the rheological additive fumed silica can be left out, or at least much reduced in concentration.

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 calcium carbonate. They are therefore easier to extrude than the formulation with PCC.

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 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.



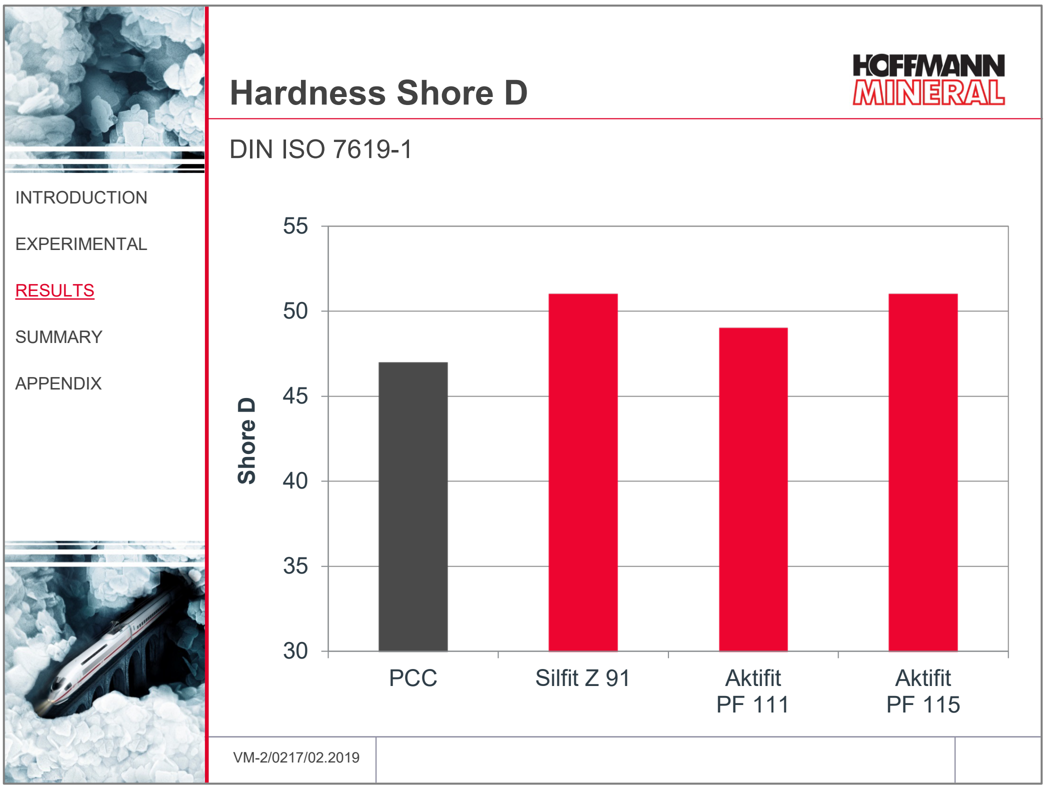
The thickness of the cured layer with Calcined Neuburg Siliceous Earth differed slightly. The results, however, are always close to each other, so the minimum differences should not be overestimated.

3.3 Mechanical Properties

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

a) Hardness Shore D

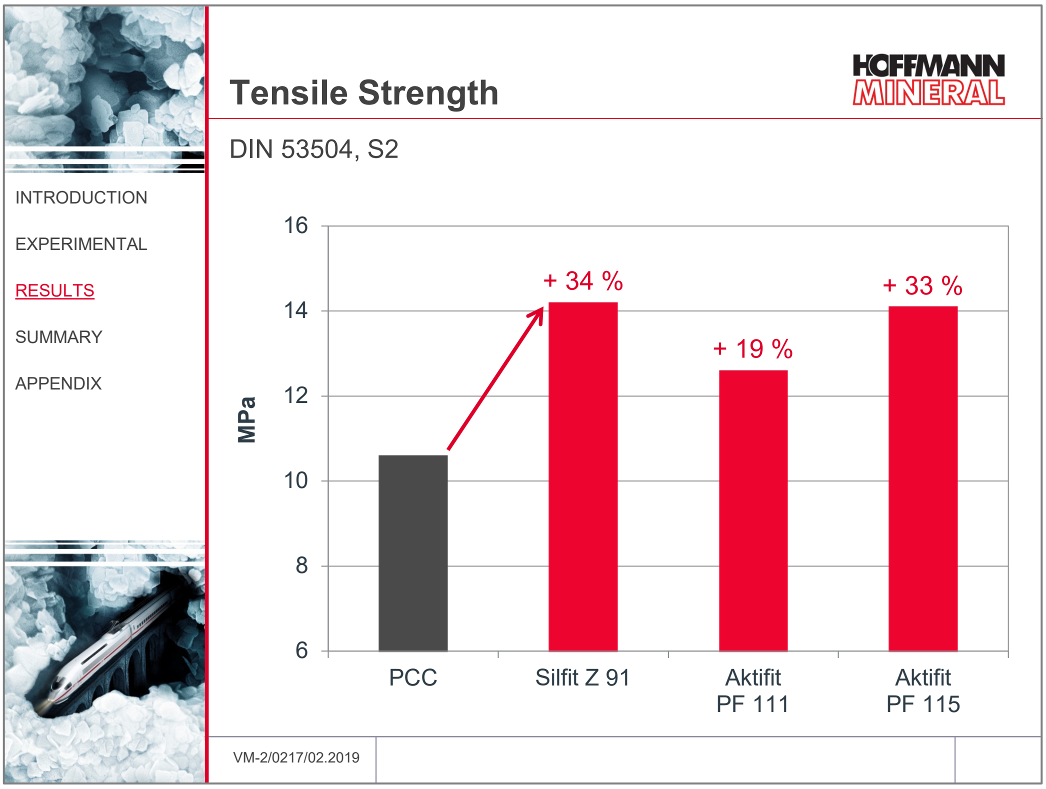
Hardness was measured on piled-up S2 dumbbells (total height approx. 6 mm).



Calcined Neuburg Siliceous Earth produces a hardness increase of 2-4 Shore D.

b) Tensile Strength

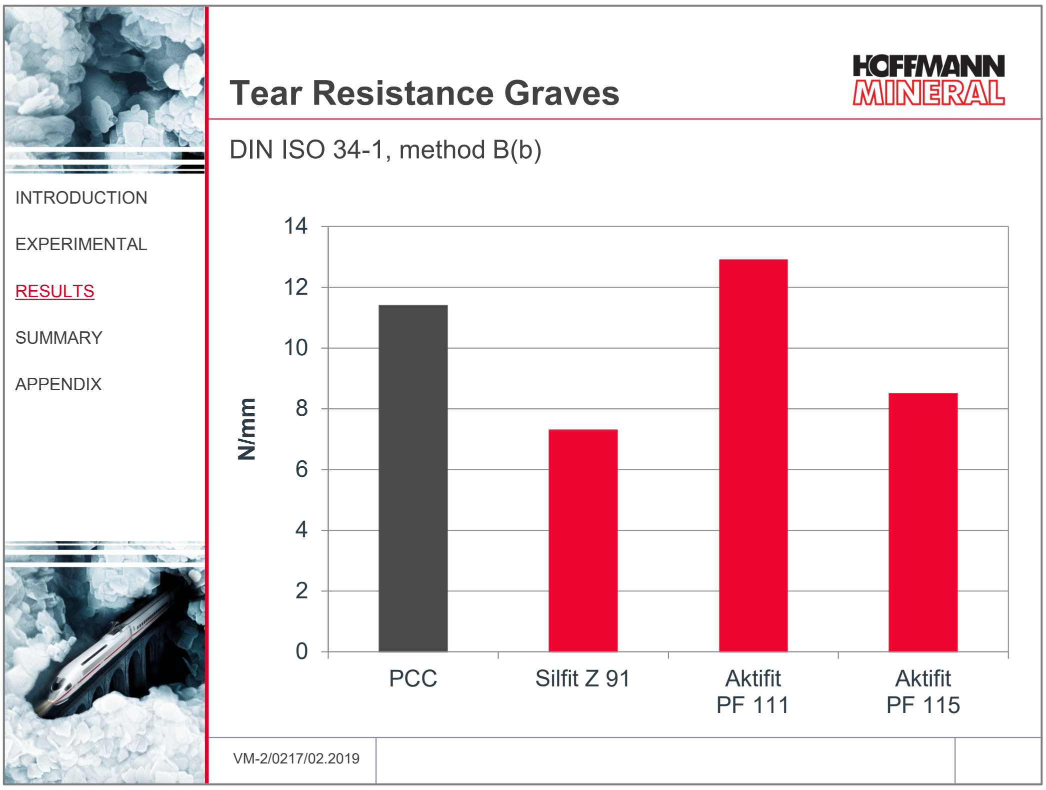
The cross-head speed for the tests was 200 mm/min.



Compared to precipitated calcium carbonate, all the tested calcined Neuburg Siliceous Earth products produce a significant increase in strength of up to 34 %, which is a bit lower only with Aktifit PF 111.

c) Tear Resistance

The test items according to procedure B(b) of the standard (angled specimen with nick, known as "Graves") were tested at a crosshead speed of 500 mm/min.



With regard to tear resistance, Silfit Z 91 and Aktifit PF 115 do not have quite as high values. Aktifit PF 111 instead yields a slight increase compared to precipitated calcium carbonate.

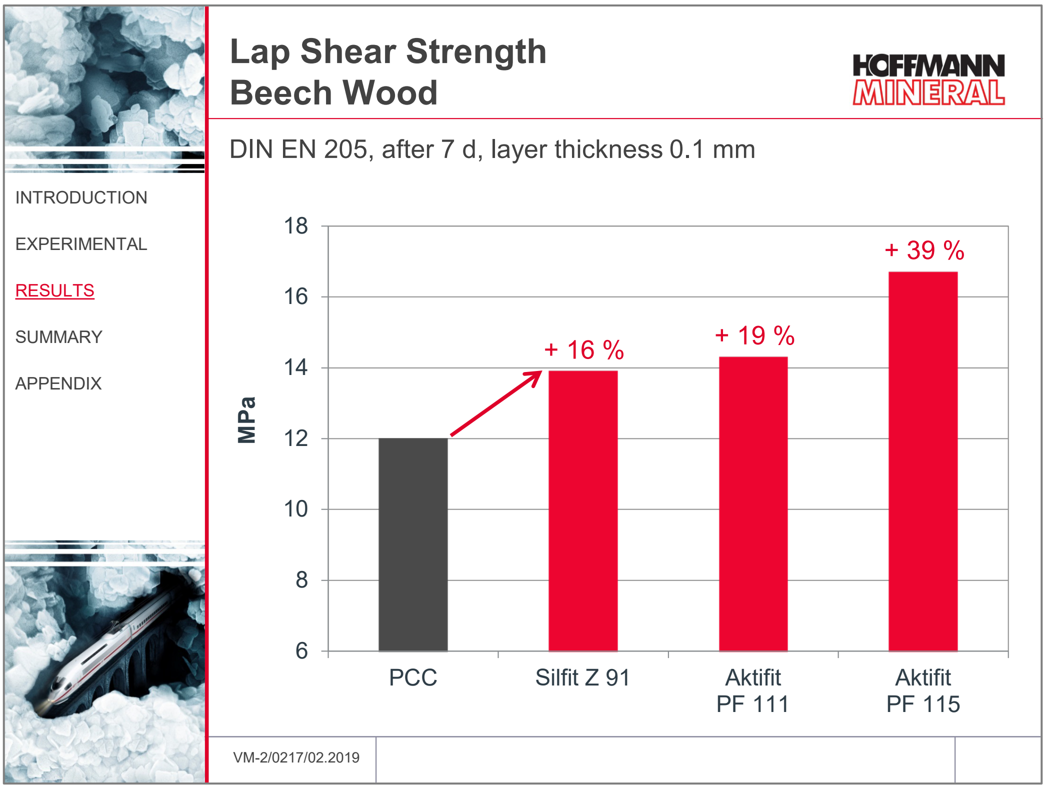
3.4 Adhesive Strength

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.

Two wooden slats respectively were bonded overlapping with a bond surface area of 20 x 10 mm (approx. 200 mm²). 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.

Excessive adhesive residues were removed after bonding.

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



Calcined Neuburg Siliceous Earth produces a marked increase in strength here. It is 15 to 20 % with Silfit Z 91 and Aktifit PF 111.

Aktifit PF 115 with a special amino silane surface treatment achieves a lap shear strength of nearly 17 MPa, which means an increase of almost 40 %.

4 Summary

Calcined Neuburg Siliceous Earth is very suitable as a functional filler for high-strength structural adhesives based on silane-terminated polyurethanes (STP-U).

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

Viscosity and/or rheological behavior can be optimized by an adjusted silica content.

Special surface modifications of Neuburg Siliceous Earth grades offer potential for further increase in strength and improvement of additional properties such as sag resistance of the adhesive rope and tear resistance.

Distinguishing Features of the Calcined Neuburg Siliceous Earth Grades:

Silfit Z 91

- Low moisture content
- White and color-neutral
- Cost effective
- Good mechanical properties

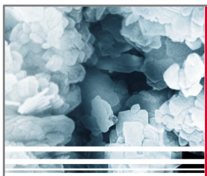
Aktifit PF 115

- Very low moisture content and extremely low moisture absorption even under humid conditions
- White and color-neutral
- For highest requirements on tensile strength and lap shear strength

Aktifit PF 111

- Very low moisture content and very low moisture absorption even under humid conditions
- White and color-neutral
- Rheology control along with high strength, high elongation at break and high tear resistance

5 Appendix



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Table of Results

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		PCC	Calcined Neuburg Siliceous Earth		
			Silfit Z 91	Aktifit PF 111	Aktifit PF 115
Rheology					
Complex viscosity at 0.1 % deformation	Pa*s	626	227	931	222
Complex viscosity at 50 % deformation	Pa*s	418	155	130	143
Curing					
Skin formation	min	25	45	25	35
In-depth cure after 8 h	mm	1.4	1.2	1.3	1.3
In-depth cure after 24 h	mm	2.3	2.1	2.2	2.1
Mechanical properties					
Hardness	Shore D	47	51	49	51
Tensile strength	MPa	10.6	14.2	12.6	14.1
Elongation at break	%	38	20	30	22
Tear resistance Graves	N/mm	11.4	7.3	12.9	8.5
Lap shear strength					
Beech wood, layer 0.1 mm	MPa	12.0	13.9	14.3	16.7

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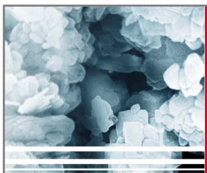

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Testing Conditions

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Rheology	DIN 54458, MCR 300, PP 25 mm, d: 0.5 mm, Oscillation: deformation 0.01 to 100 %, f = 10 Hz
Hardness Shore D	DIN ISO 7619-1, piled S2 specimens Curing / conditioning: 4 weeks @ standard conditions 23/50
Tensile test	DIN 53504, S2 specimens Curing / conditioning: 4 weeks @ standard conditions 23/50
Tear resistance Graves	DIN ISO 34-1, method B (b) Curing / conditioning: 4 weeks @ standard conditions 23/50
Lap shear test	DIN EN 205 Substrate: beech wood Adhesive layer: 0.1 mm Curing: 7 d @ standard conditions 23/50 Crosshead speed: 50 mm/min

VM-2/0217/02.2019

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