Neuburg Siliceous Earth
in adhesives based on silane-terminated polyether
e.g. for parquet and industry

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Contents

Status Quo

- 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 adhesives and sealants which are free from solvents, isocyanates and tin, therefore healthwise and ecologically safe, and which in addition are distinguished by excellent adhesion and outstanding mechanical properties.

- As a conventional filler calcium carbonate is used.

Objective

The present study will present Neuburg Siliceous Earth and Calcined Neuburg Siliceous Earth grades as functional fillers for (parquet) adhesives based on a silane terminated polyether.

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.

Fillers
Characteristics

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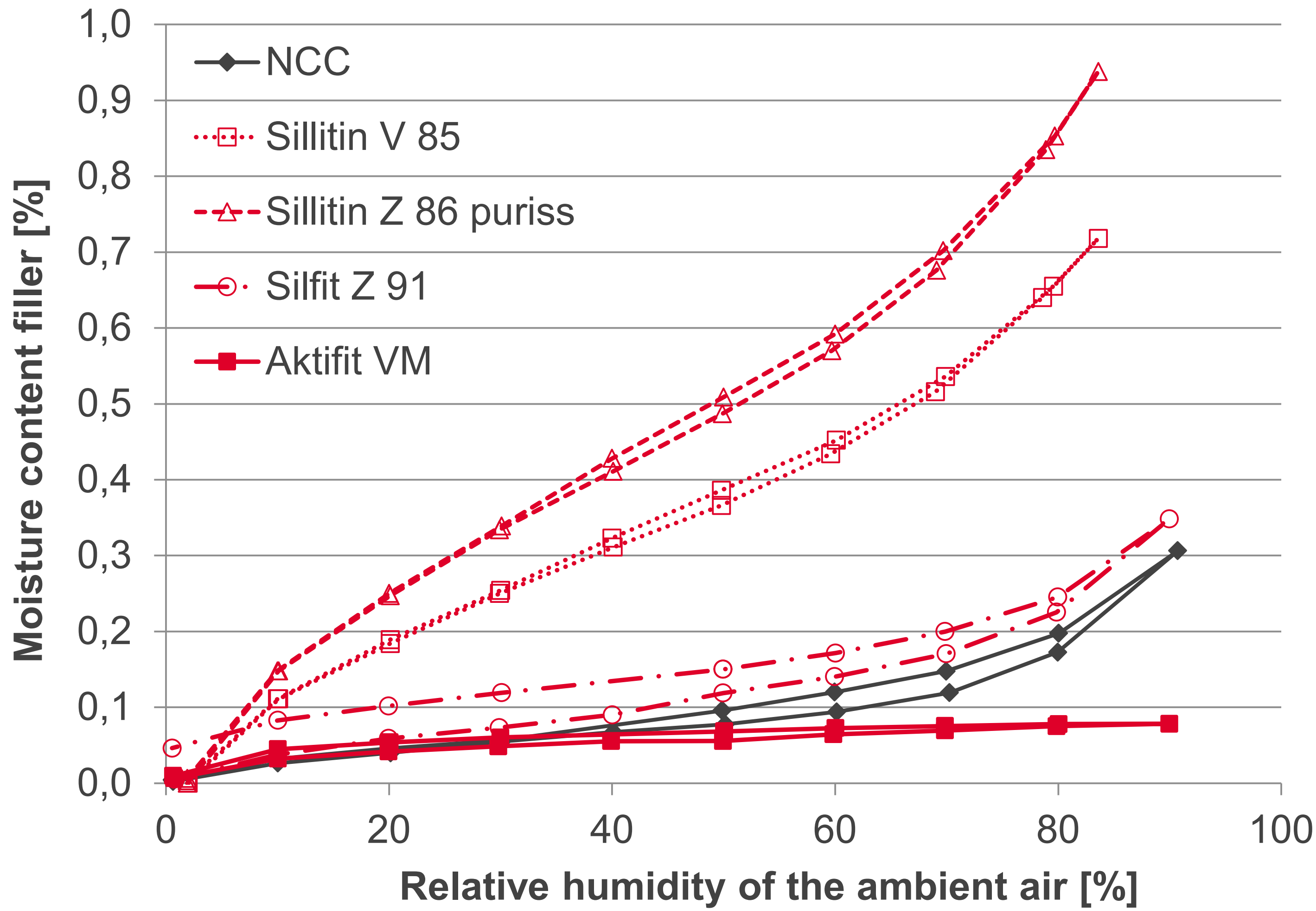
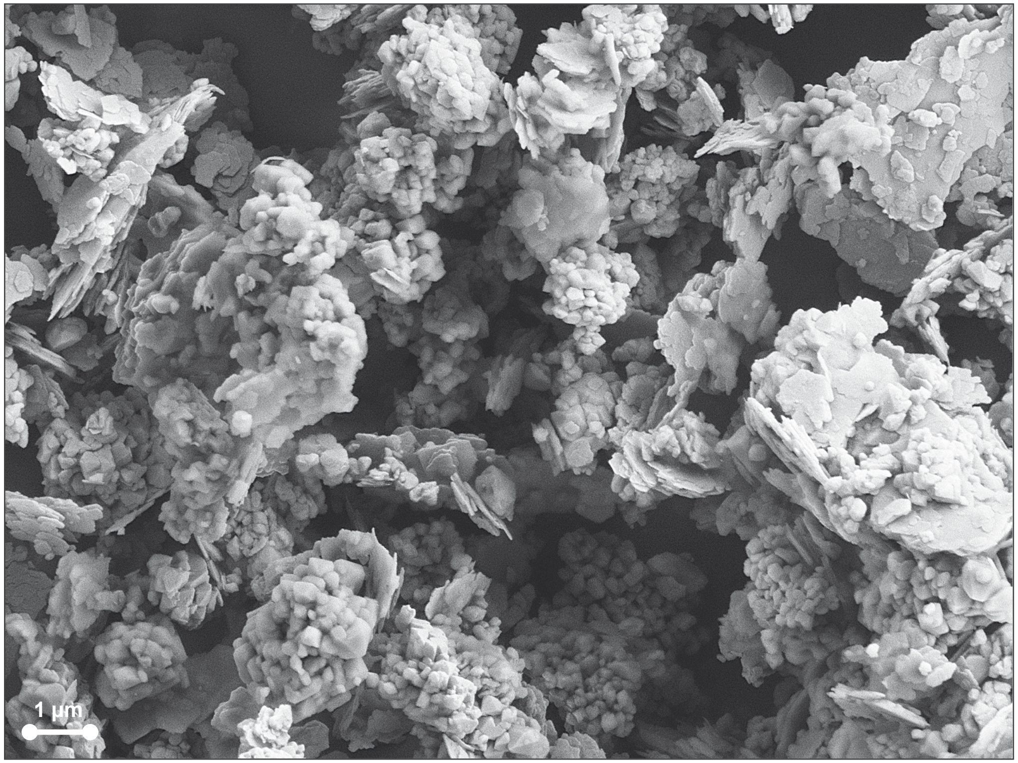
		GCC	Neuburg Siliceous Earth		Calcined Neuburg Siliceous Earth	
			Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91	Aktifit VM
Volatile matter at 105 °C	[%]	0.1	0.4	0.6	0.2	0.1
Particle size d_{50}	[µm]	5	4	1.8	2	2
Particle size d_{97}	[µm]	21	18	8	10	9
Oil absorption	[g/100g]	20	40	50	57	52
Specific Surface Area BET	[m²/g]	2.4	7	10	7.9	7.9
Functionalisation		---	---	---	---	Vinyl
		hydrophilic				hydro-phobic

Moisture Content of Fillers vs. Ambient Air Humidity



What is
Neuburg Siliceous Earth?

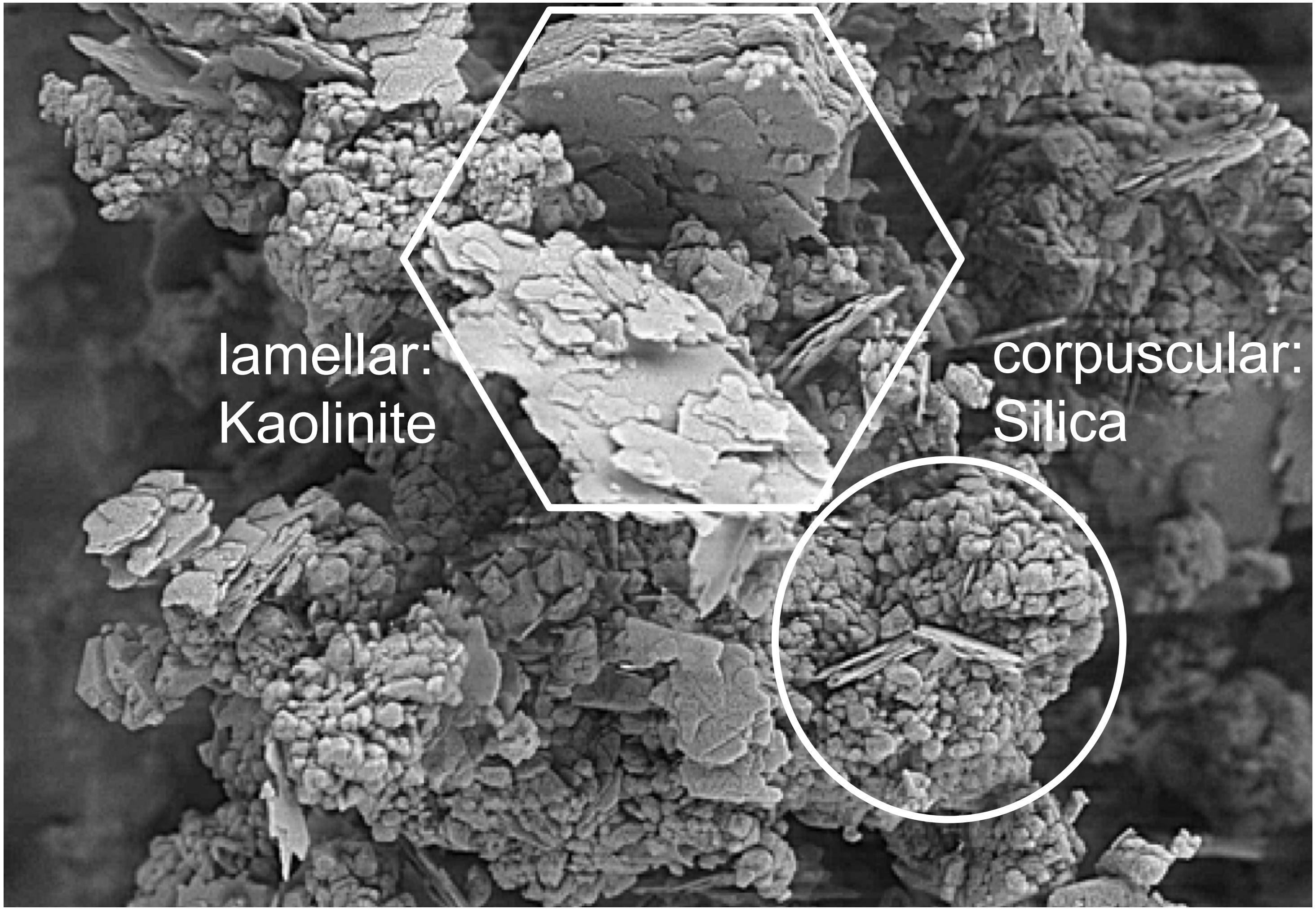


A natural combination of corpuscular Neuburg silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods.

The silica portion exhibits a round grain shape and consists of aggregated primary particles of about 200 nm diameter.

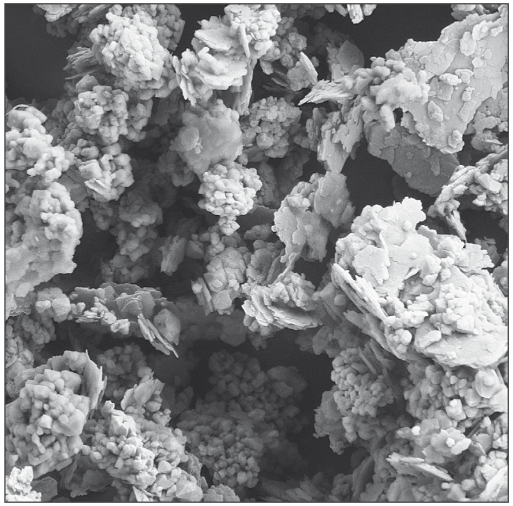
Morphology of Neuburg Siliceous Earth

Magnification 10.000x



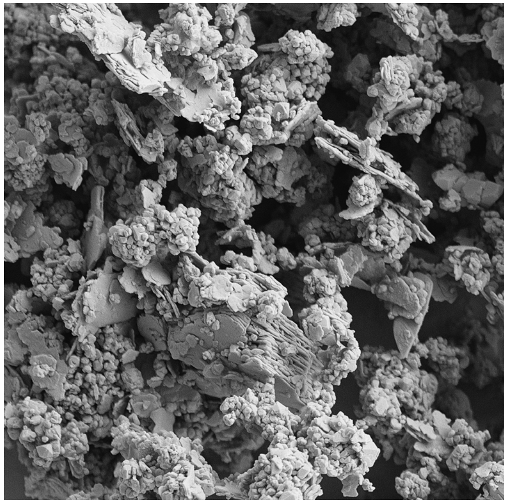
Calcined Neuburg Siliceous Earth

A downstream thermal process lead to the calcined products Silfit and Aktifit, based on SILLITIN Z 86.



Neuburg Siliceous Earth

Calcination Process →



Calcined Neuburg Siliceous Earth

Additional application benefits, as well as the removing of crystal water included in the kaolinite. The silica part remains inert.

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Base Formulation

		parts or % 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**

Formulation Variations

Replacement of calcium carbonate by Neuburg Siliceous Earth

Control: base formulation with
54 pbw GCC
2.5 pbw silica

Value-Driven Approach	**Cost-Driven Approach**	**Maximum Performance Approach**
Filler + silica loading reduced	Polymer/plasiticizer-ratio inverted	without plasiticizer
47 pbw NSE 2 pbw silica	47 pbw NSE 2.5 pbw silica	54 pbw filler without silica

Value-Driven Approach

Value-Driven Approach

Filler + silica loading reduced

47 pbw NSE
2 pbw silica

- Sillitin V 85
- Silfit Z 91
- Aktifit VM

Formulation Variations
Value-Driven Approach

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	GCC	Neuburg Siliceous Earth	
	pbw or weight-%	pbw	weight-%
Polymer	25.5	25.5	27.6
Plasticizer	15.0	15.0	16.2
Drying agent	2.0	2.0	2.2
Rheological additive	2.5	2.0	2.2
Filler	54.0	47.0	50.7
Adhesion promoter	1.0	1.0	1.1
Total	**100.0**	**92.5**	**100.0**

Complex Viscosity at 50 % deformation

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DIN 54458, [Pas]

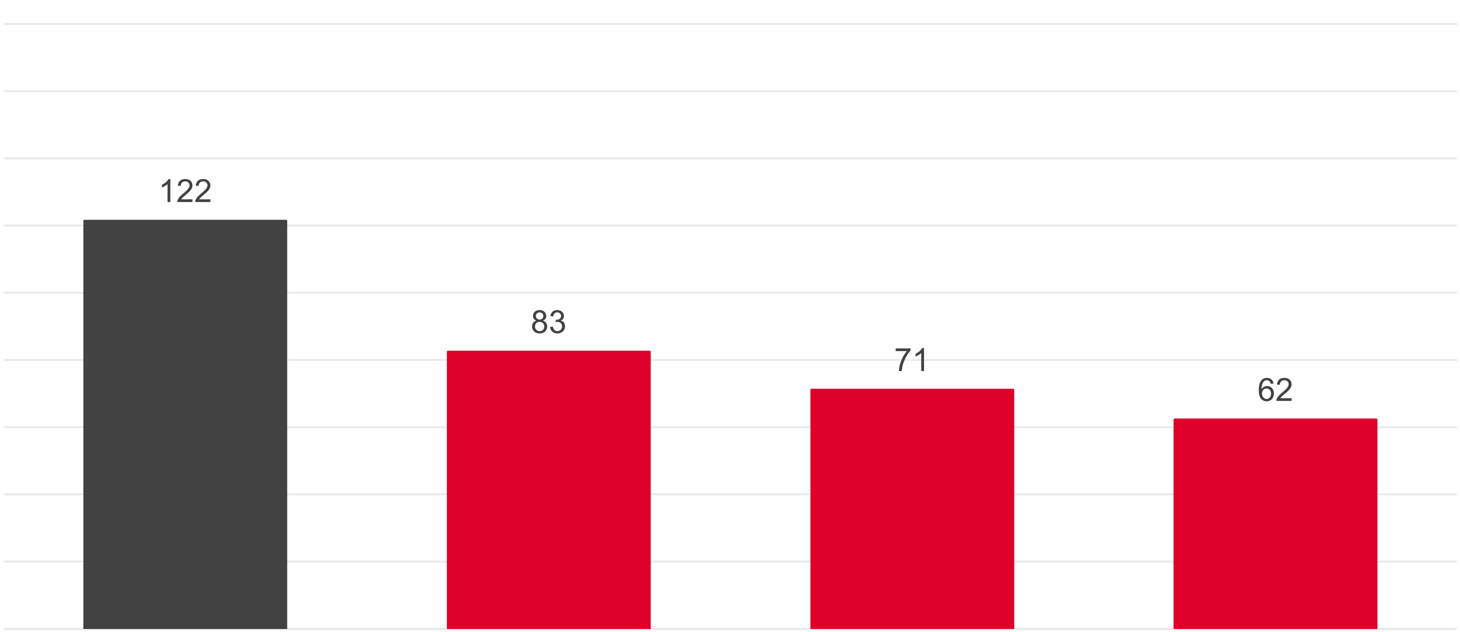
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

54 pbw	47 pbw, less rheological additive		

Complex Viscosity at 0.1 % deformation

DIN 54458, [Pas]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

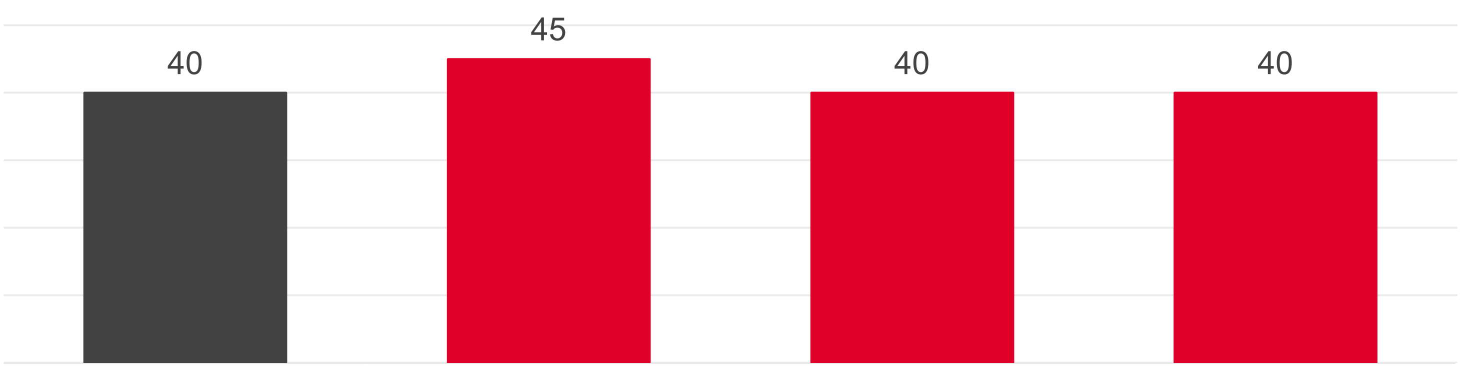


54 pbw	47 pbw, less rheological additive		

Skin Formation Time

Touched with a wooden stick, [min]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

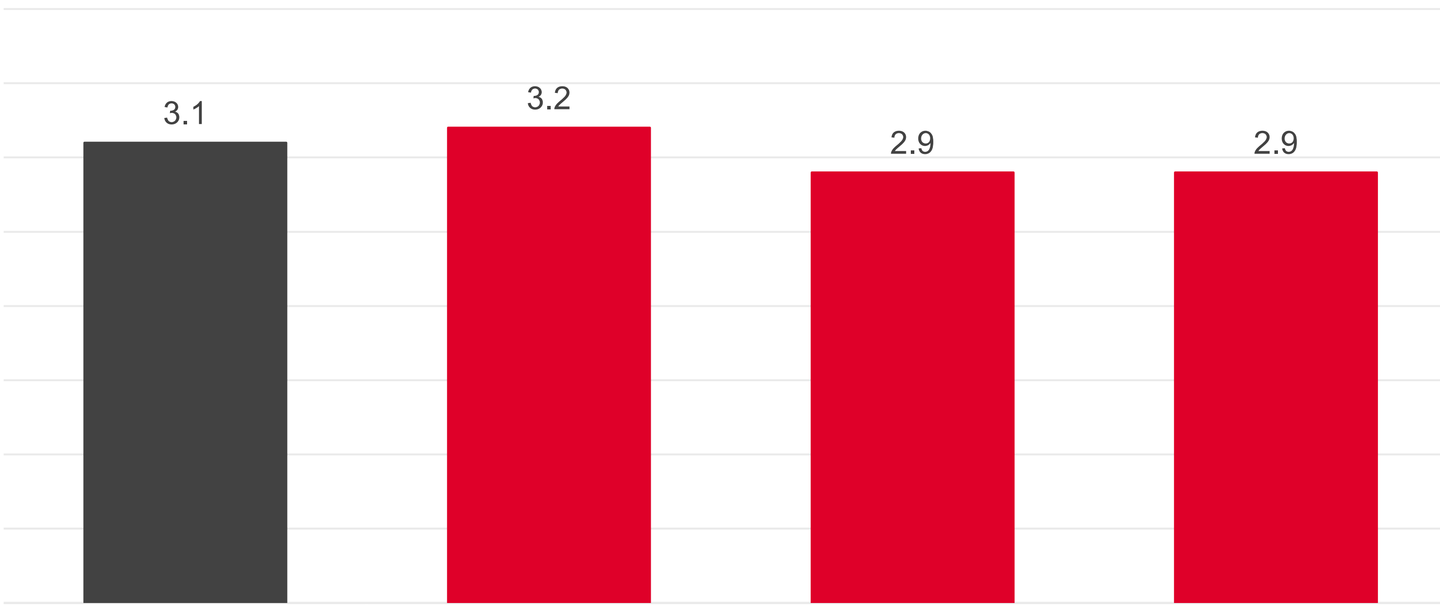


54 pbw	47 pbw, less rheological additive		

In-depth Cure

Thickness of the reacted layer after 24 h, [mm]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

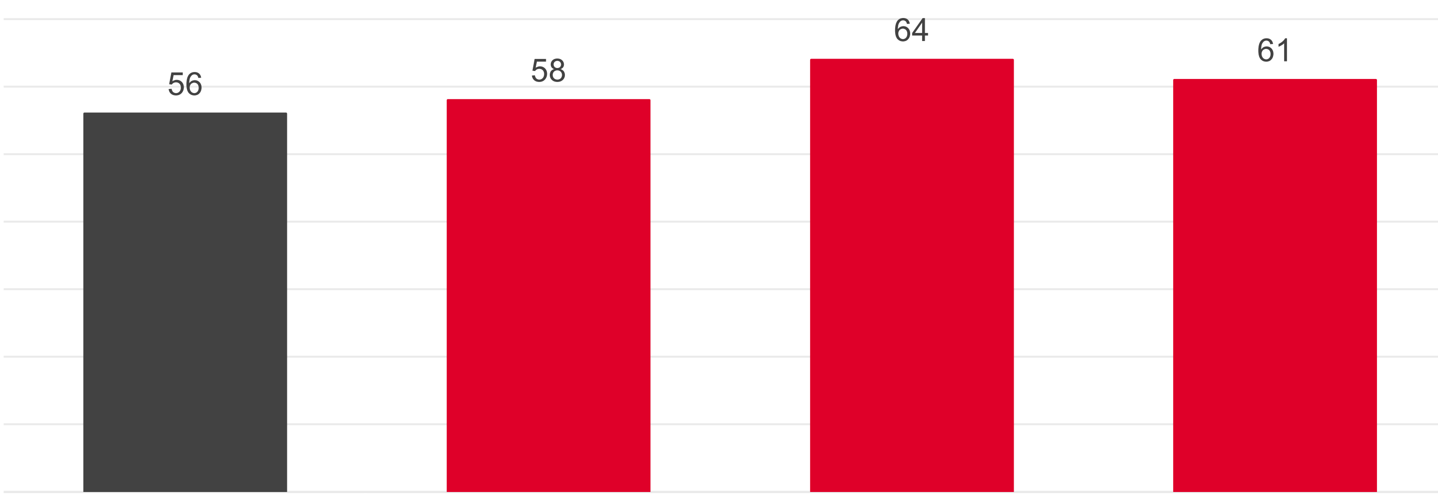


54 pbw	47 pbw, less rheological additive		

Hardness

DIN ISO 7619-1, [Shore A]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive		

Tensile Strength

DIN 53504, S2 dumbbell, [MPa]

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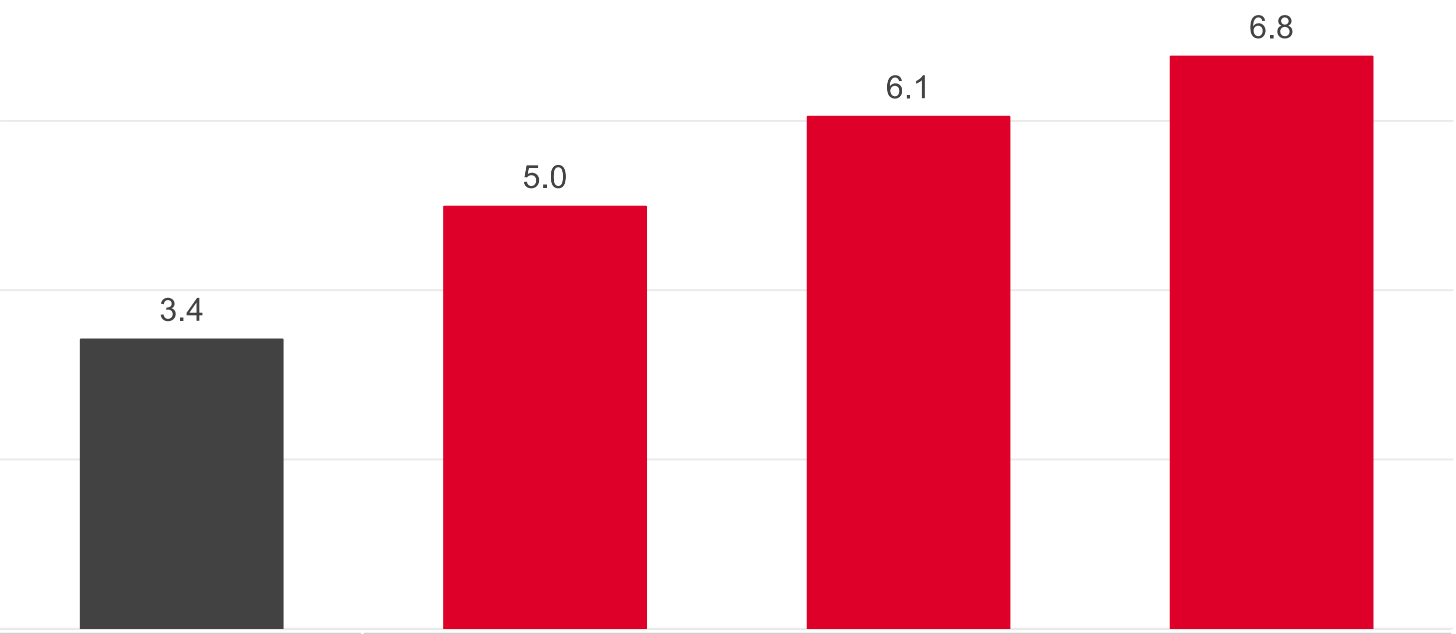
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

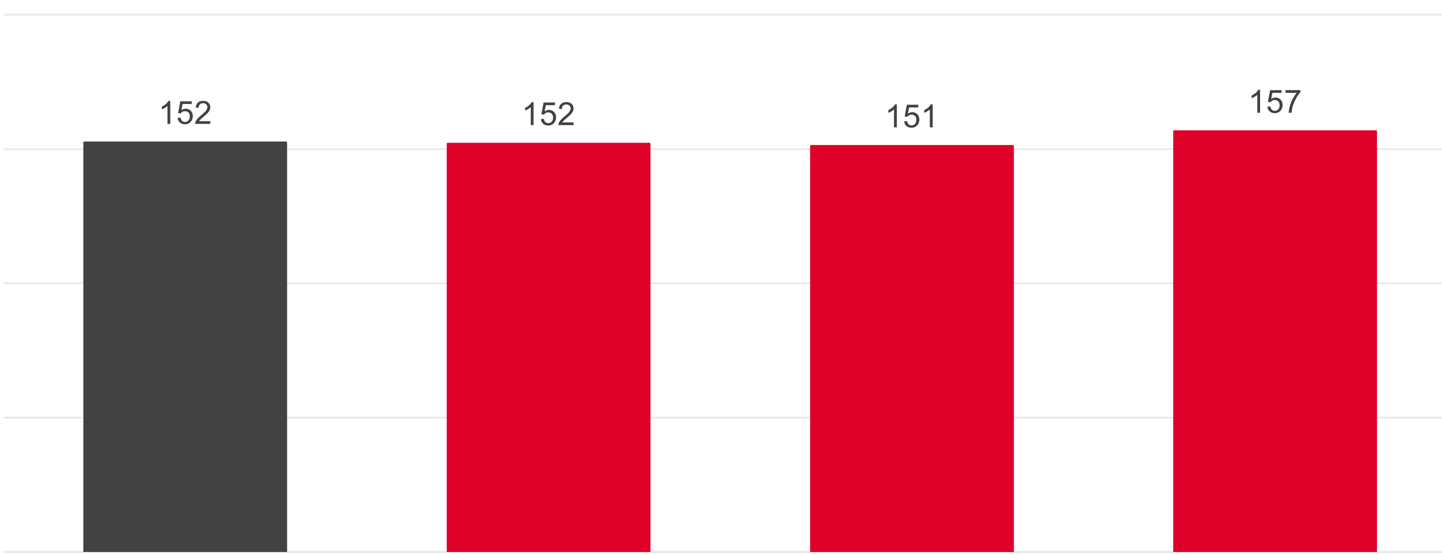


54 pbw	47 pbw, less rheological additive		

Elongation at Break

DIN 53504, S2 dumbbell, [%]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive		

Lap Shear Strength
Oak wood, 1 mm layer

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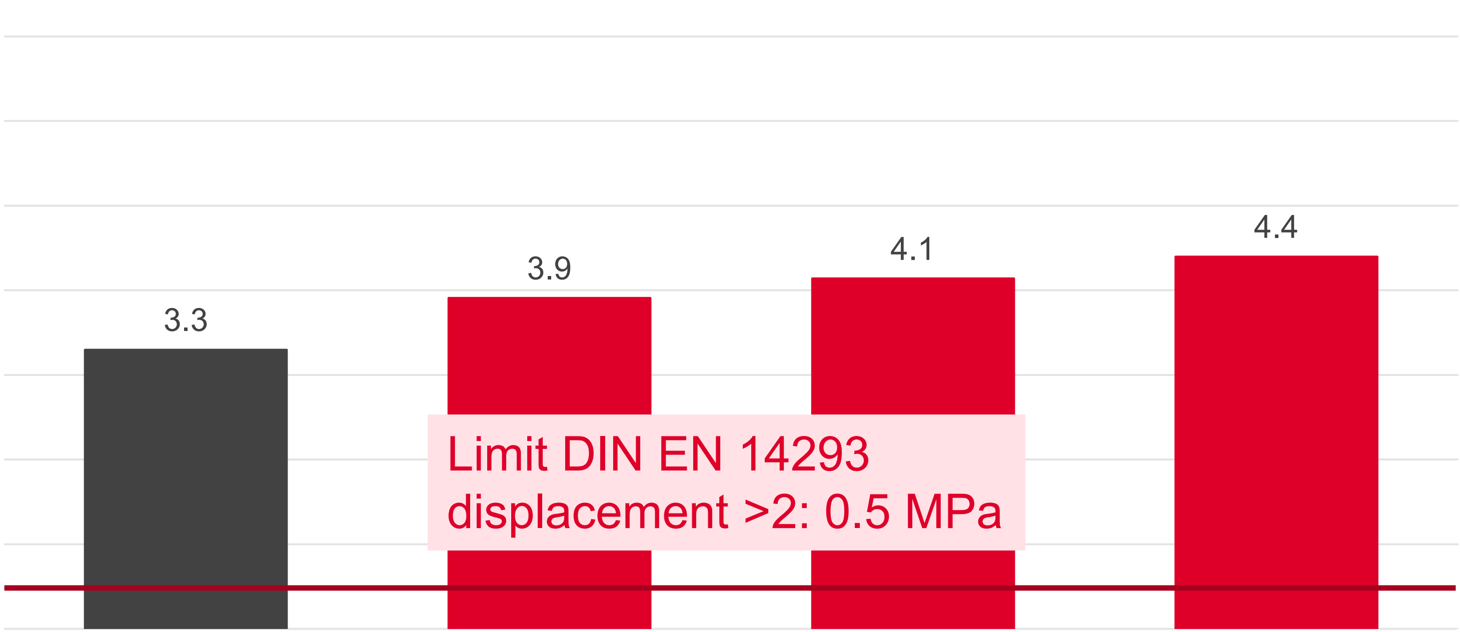
28 d, 23/40/23 °C, DIN EN 14293, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM

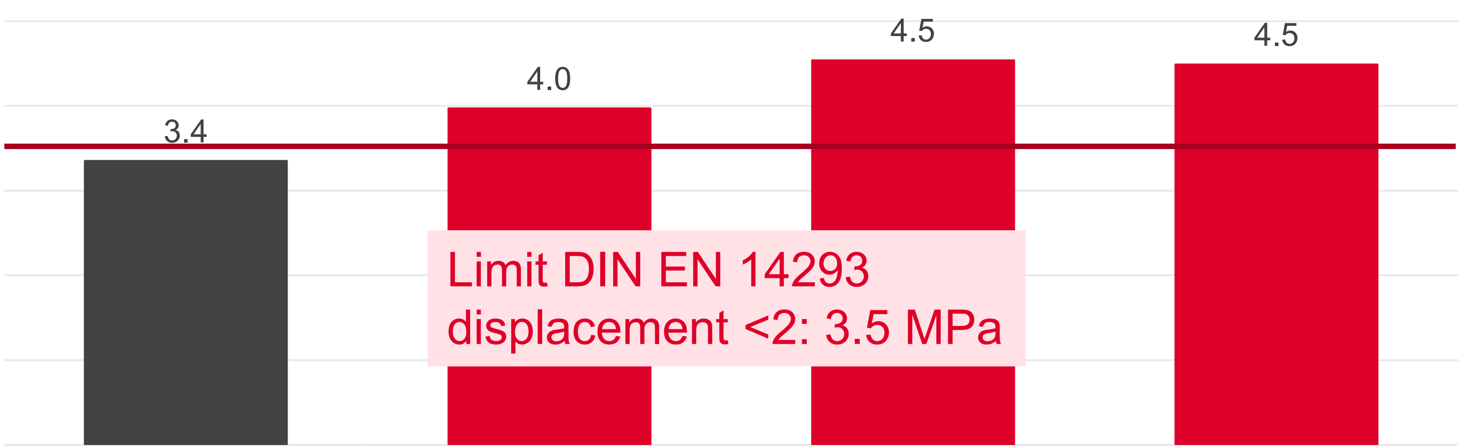


54 pbw	47 pbw, less rheological additive

Lap Shear Strength
Oak wood, 0.1 mm layer

28 d, 23/40/23 °C, DIN EN 14293, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive		

Lap Shear Strength
Oak wood, 0.1 mm, early stage

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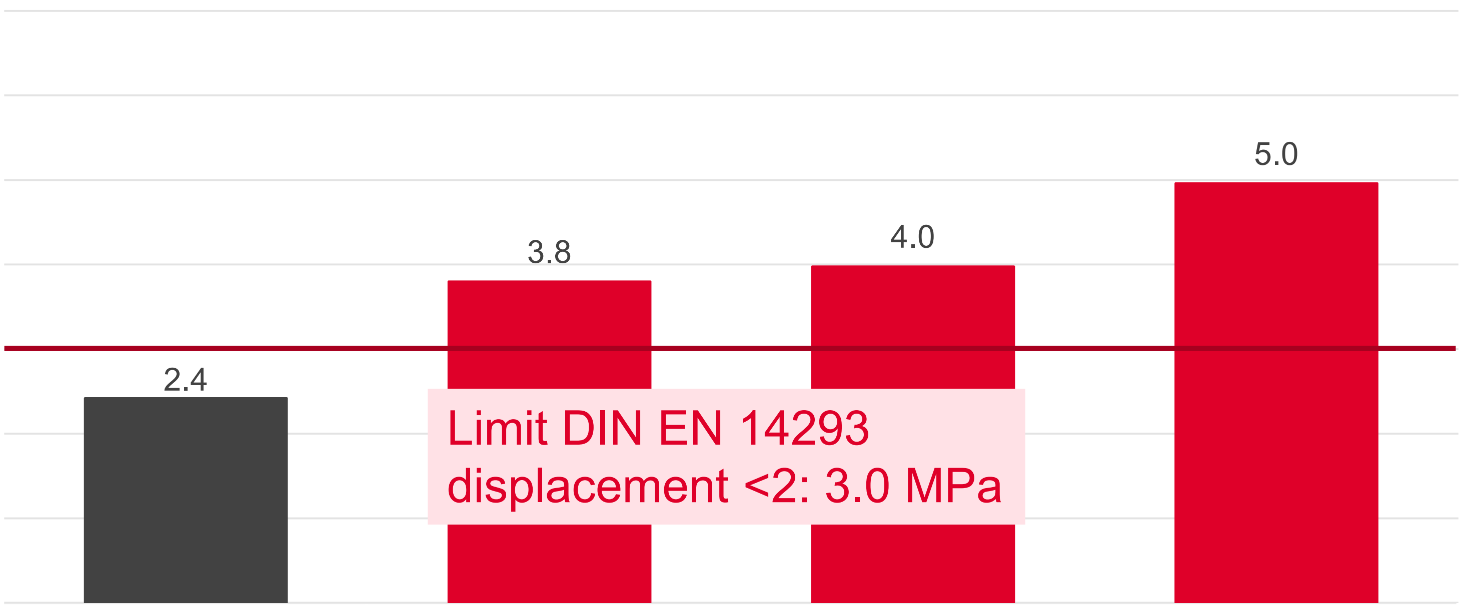
3 d, 23 °C, DIN EN 14293, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive

Lap Shear Strength
Aluminum, 2 mm layer

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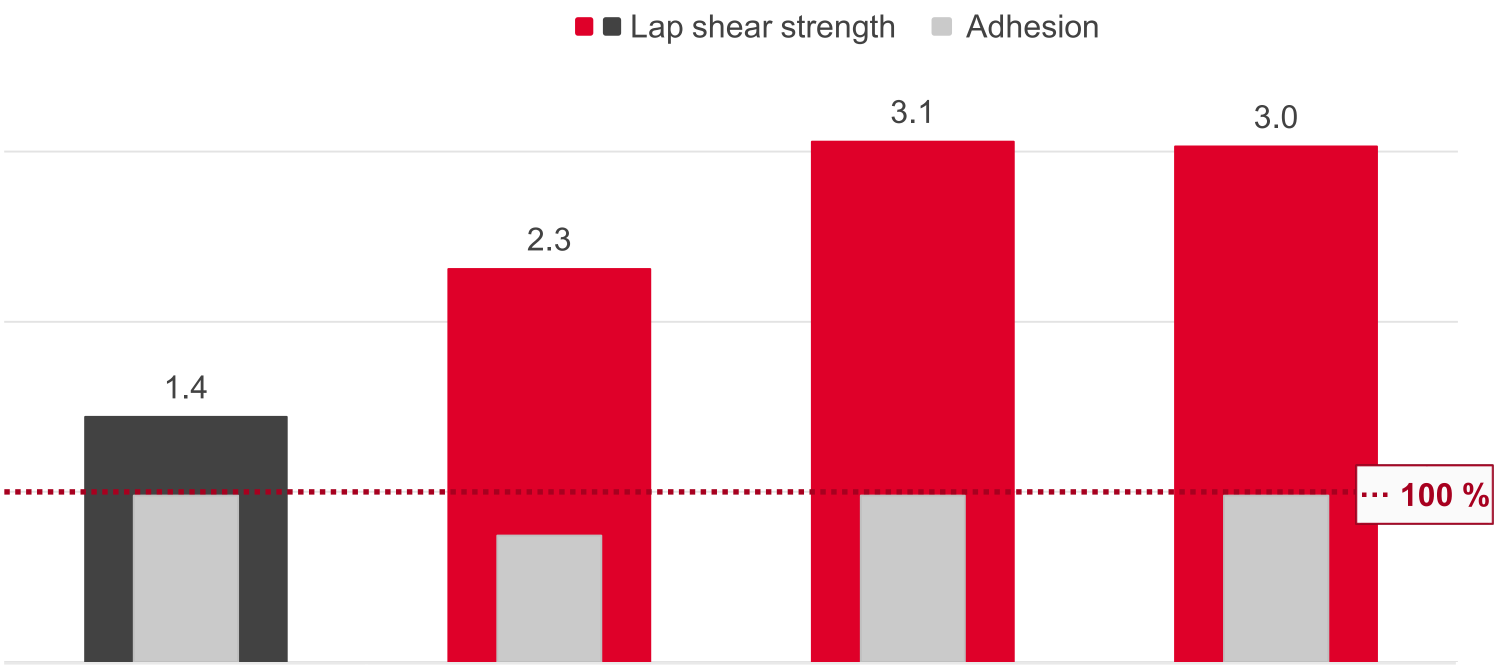
According to DIN EN 204, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive

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Hot Water Test 95 °C after Immersion

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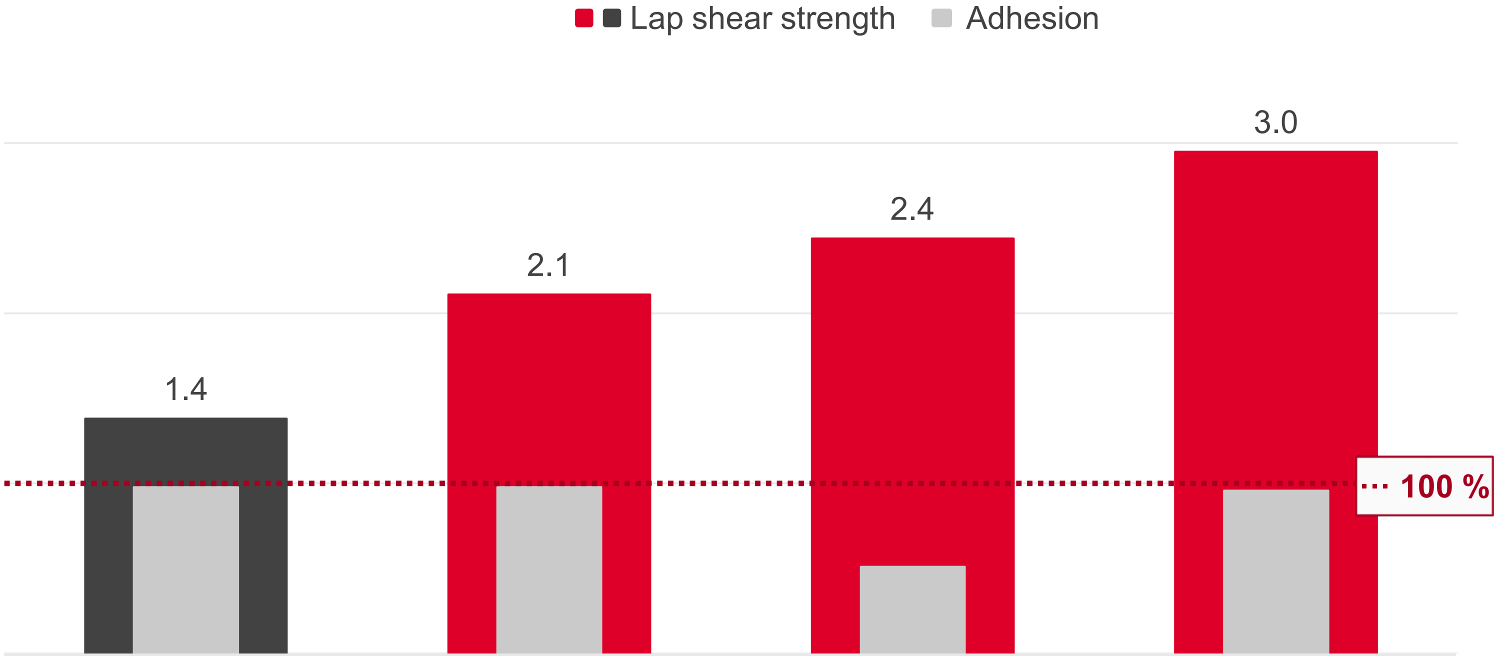
Lap shear strength on aluminum, acc. to DIN EN 204, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



54 pbw	47 pbw, less rheological additive		

Storage Stability
6 Months at Room Temperature

Storing in standard PE cartridges

The adhesives were stored for 6 months in customary PE cartridges at standard 23/50 conditions.

After this time, the formulations showed no gelling.

All formulations could be squeezed out without problems.

Conclusion
Value-Driven Approach

Compared to the standard filler GCC:

- Control of rheology via filler and fumed silica loading
- Higher tensile strength without losses in elongation at break
- Markedly higher lap shear strength
- High lap shear strength even after immersion in hot water
- Formulations with Neuburg Siliceous Earth meet the requirements of DIN EN 14293 for “soft” as well as “hard” adhesives

Cost-Driven Approach

Cost-Driven Approach

Polymer/plasticizer-ratio inverted

47 pbw NSE
2.5 pbw silica

- Sillitin V 85
- Sillitin Z 86 puriss
- Silfit Z 91

Formulation Variations
Cost-Driven Approach

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	Control with GCC high in polymer	Neuburg Siliceous Earth low in polymer	
	pbw or weight-%	pbw	weight-%
Polymer	25.5	15.5	16.7
Plasticizer	15.0	25.0	26.9
Drying agent	2.0	2.0	2.2
Rheological additive	2.5	2.5	2.7
Filler	54.0	47.0	50.4
Adhesion promoter	1.0	1.0	1.1
Total	**100.0**	**93.0**	**100.0**

Complex Viscosity at 50 % deformation

DIN 54458, [Pas]

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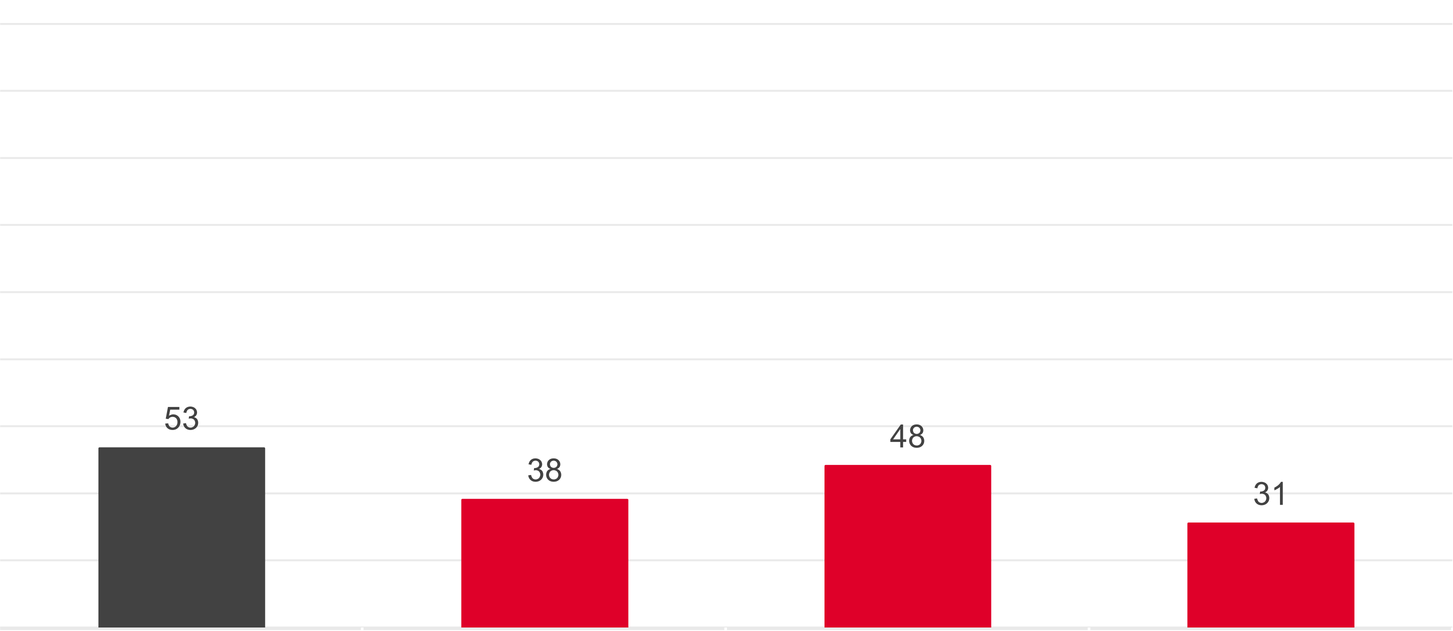
Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91



54 pbw	47 pbw		

Complex Viscosity at 0.1 % deformation

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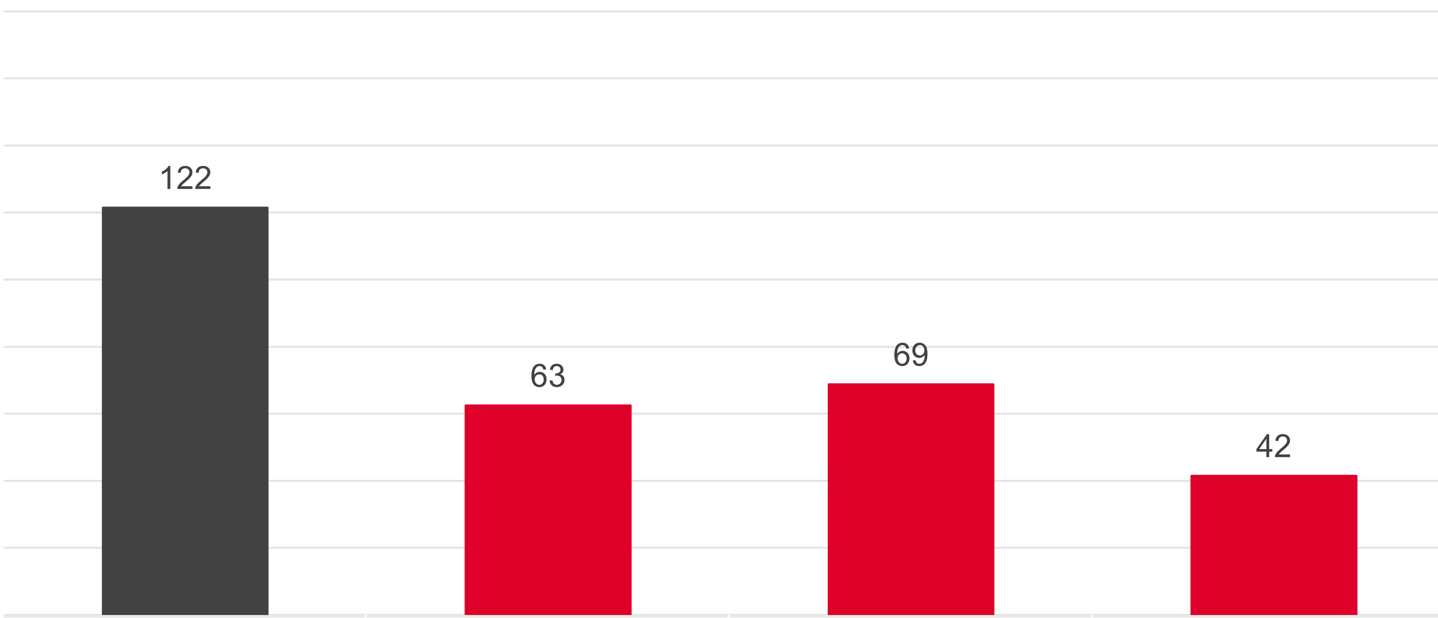
DIN 54458, [Pas]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91



54 pbw	47 pbw

Skin Formation Time

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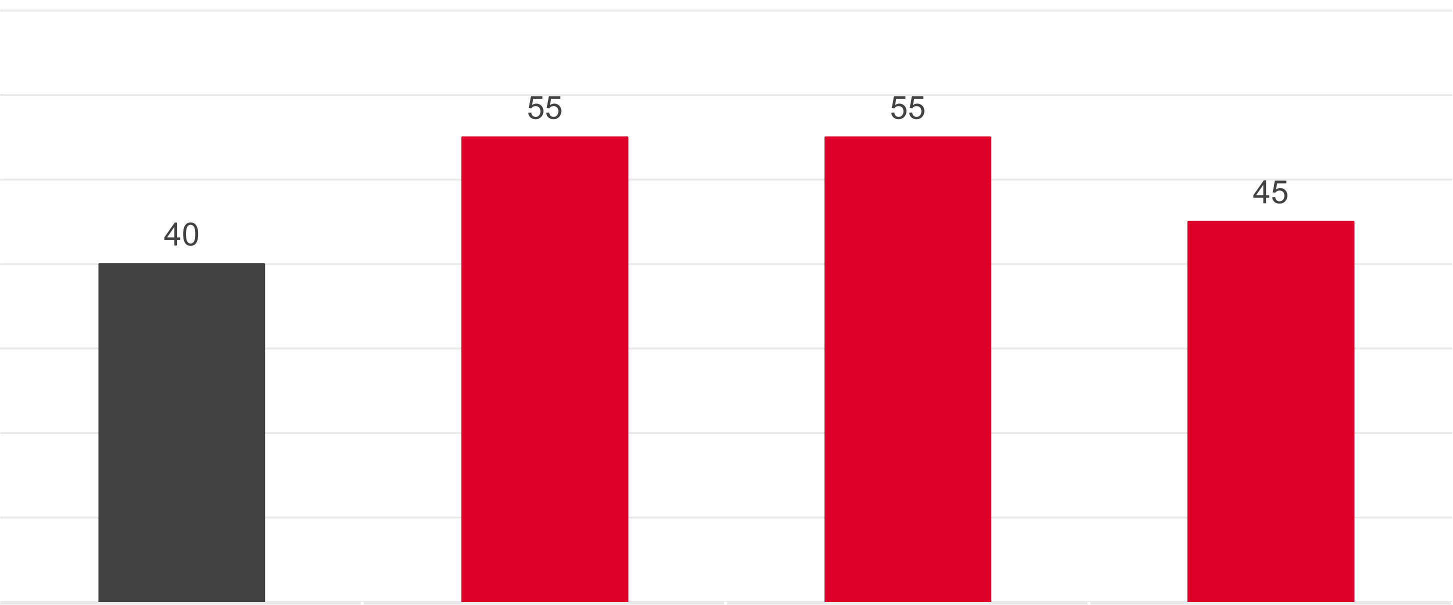
Touched with a wooden stick, [min]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91

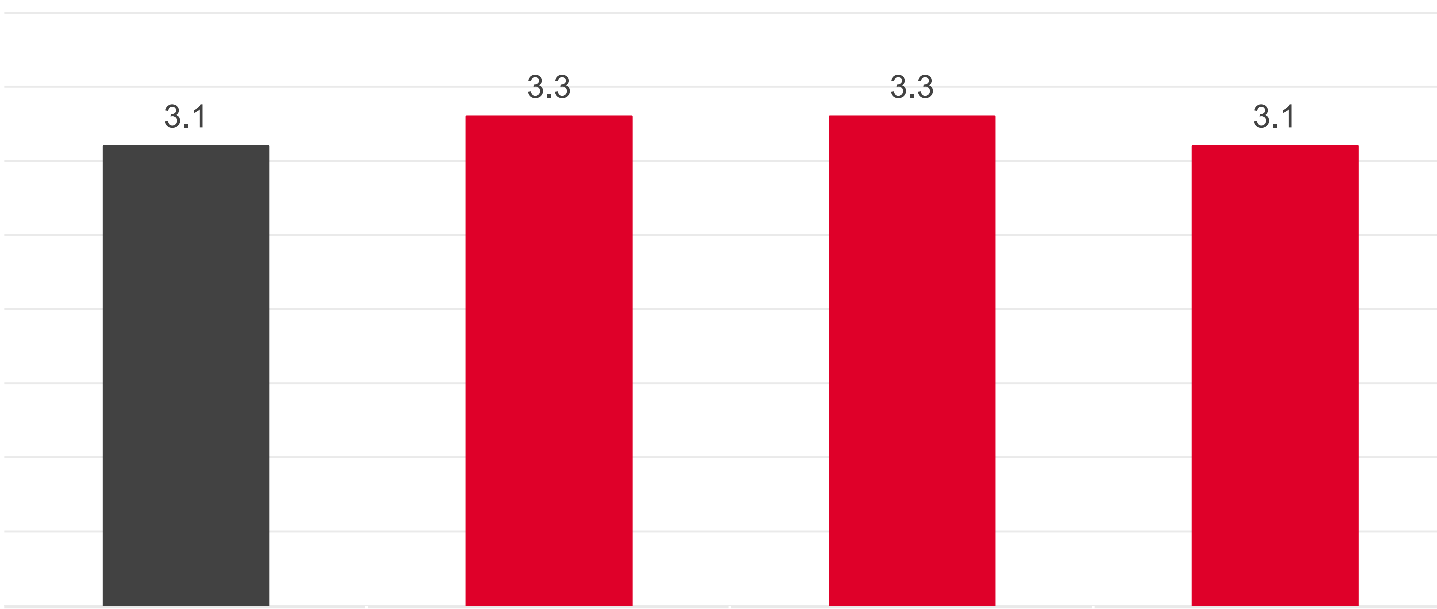


54 pbw	47 pbw		

In-depth Cure

Thickness of the reacted layer after 24 h, [mm]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91
54 pbw	47 pbw		



Hardness

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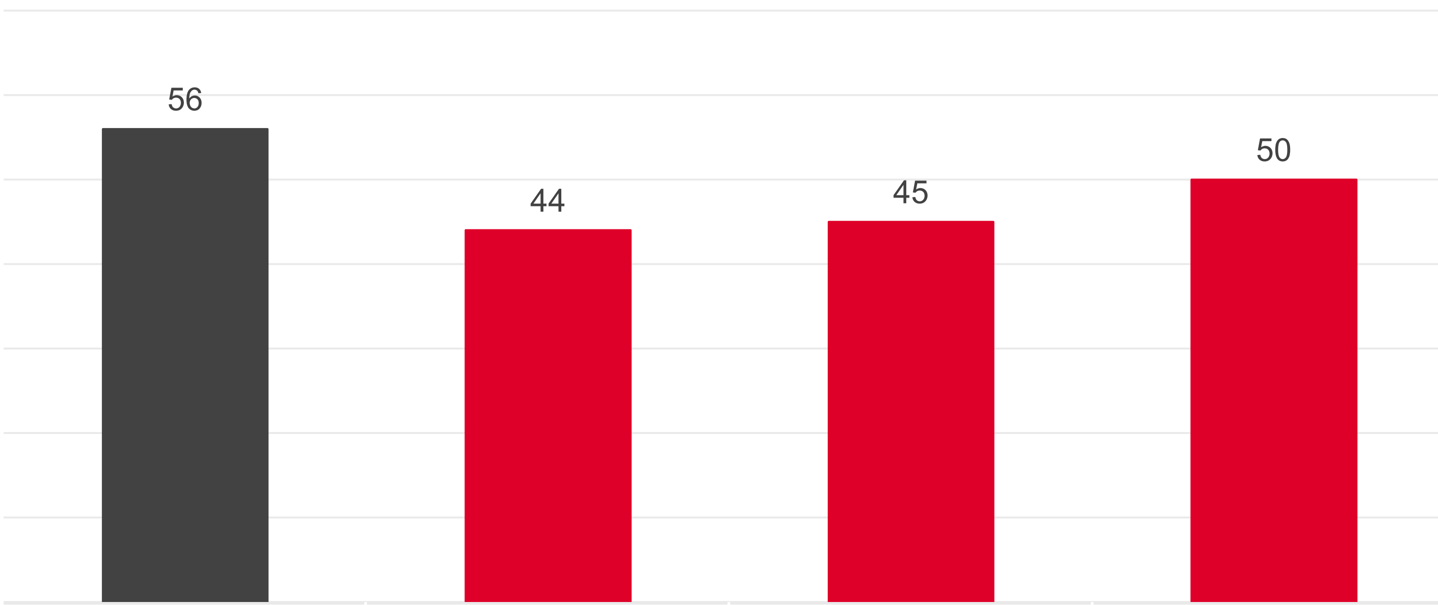
DIN ISO 7619-1, [Shore A]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91



54 pbw	47 pbw		

Tensile Strength

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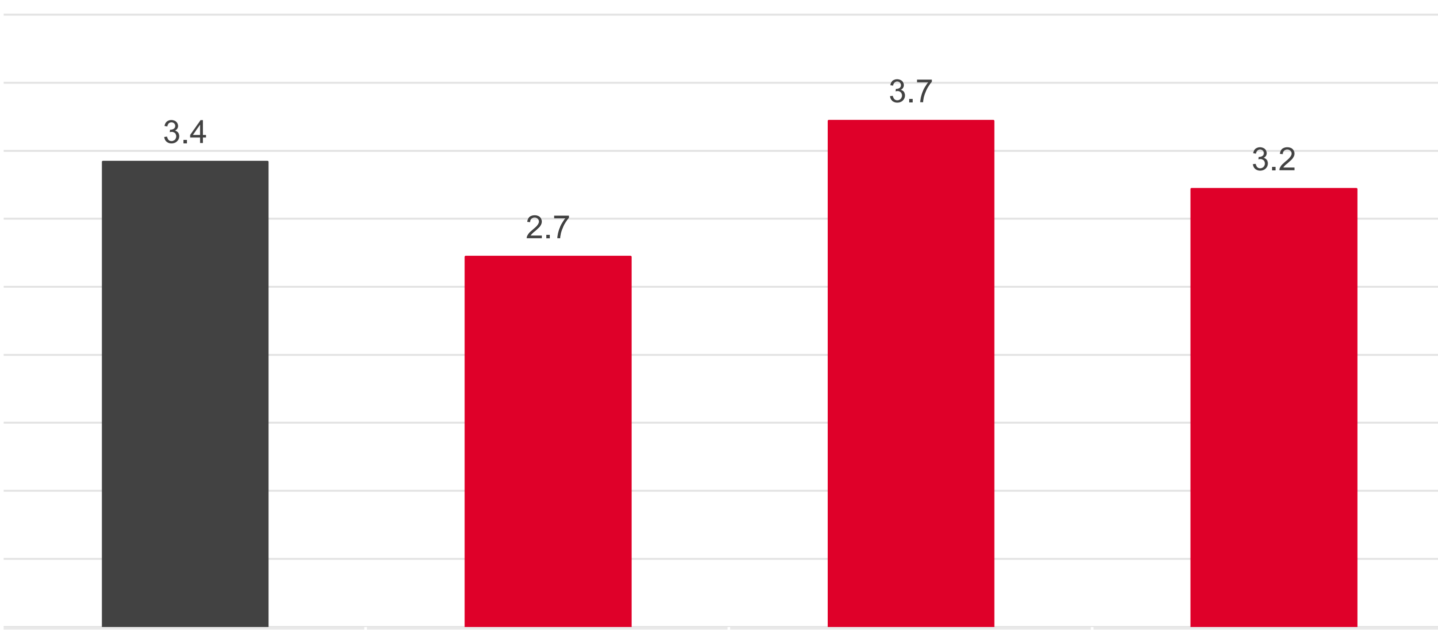
DIN 53504, S2 dumbbell, [MPa]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91

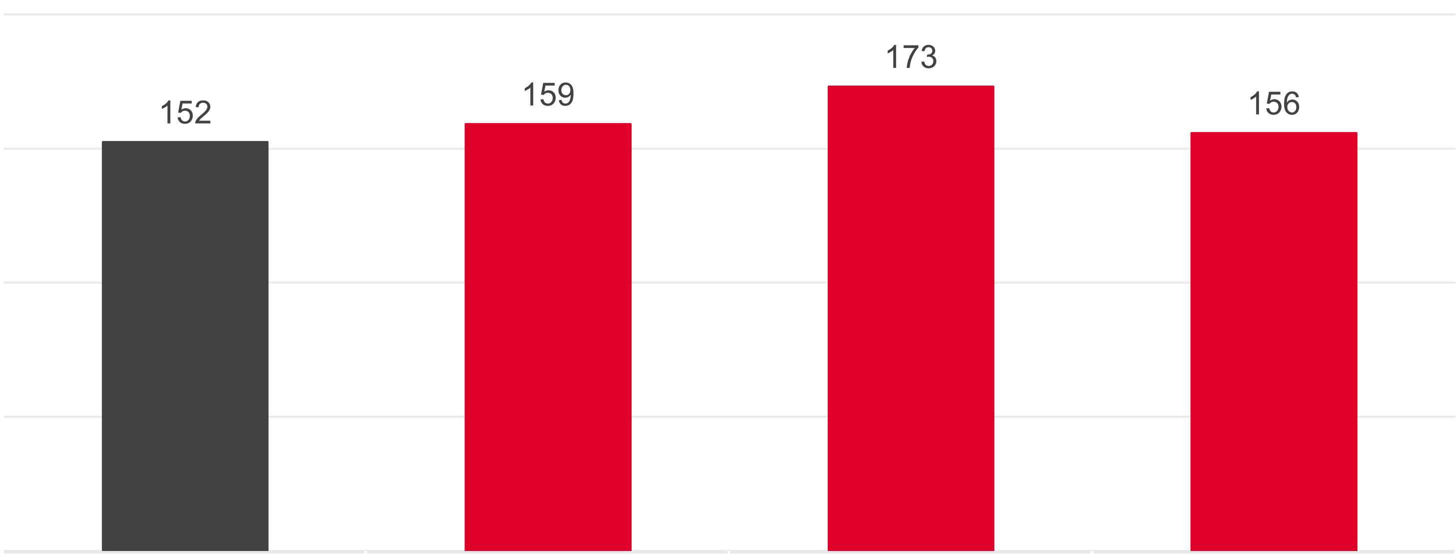


54 pbw	47 pbw

Elongation at Break

DIN 53504, S2 dumbbell, [%]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91



54 pbw	47 pbw		

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Lap Shear Strength
Oak wood, 1 mm layer

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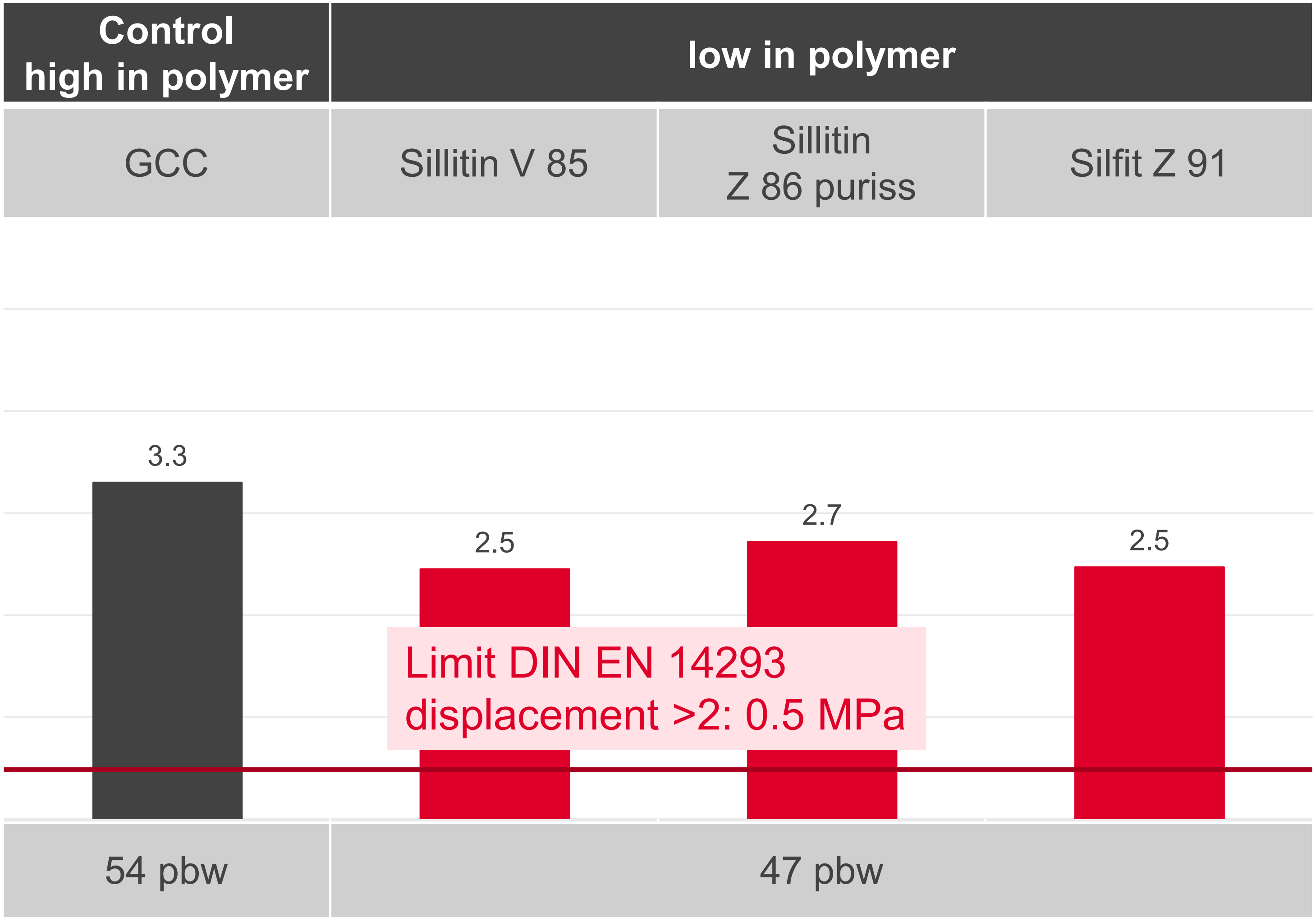
28 d, 23/40/23 °C, DIN EN 14293, [MPa]



Storage Stability
6 Months at Room Temperature

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Storing in standard PE cartridges

The adhesives were stored for 6 months in customary PE cartridges at standard 23/50 conditions.

After this time, the formulations showed no gelling.

All formulations could be squeezed out without problems.

With Sillitin Z 86 puriss, a slight increase in viscosity was noticed.

Raw Material Costs Germany 2012

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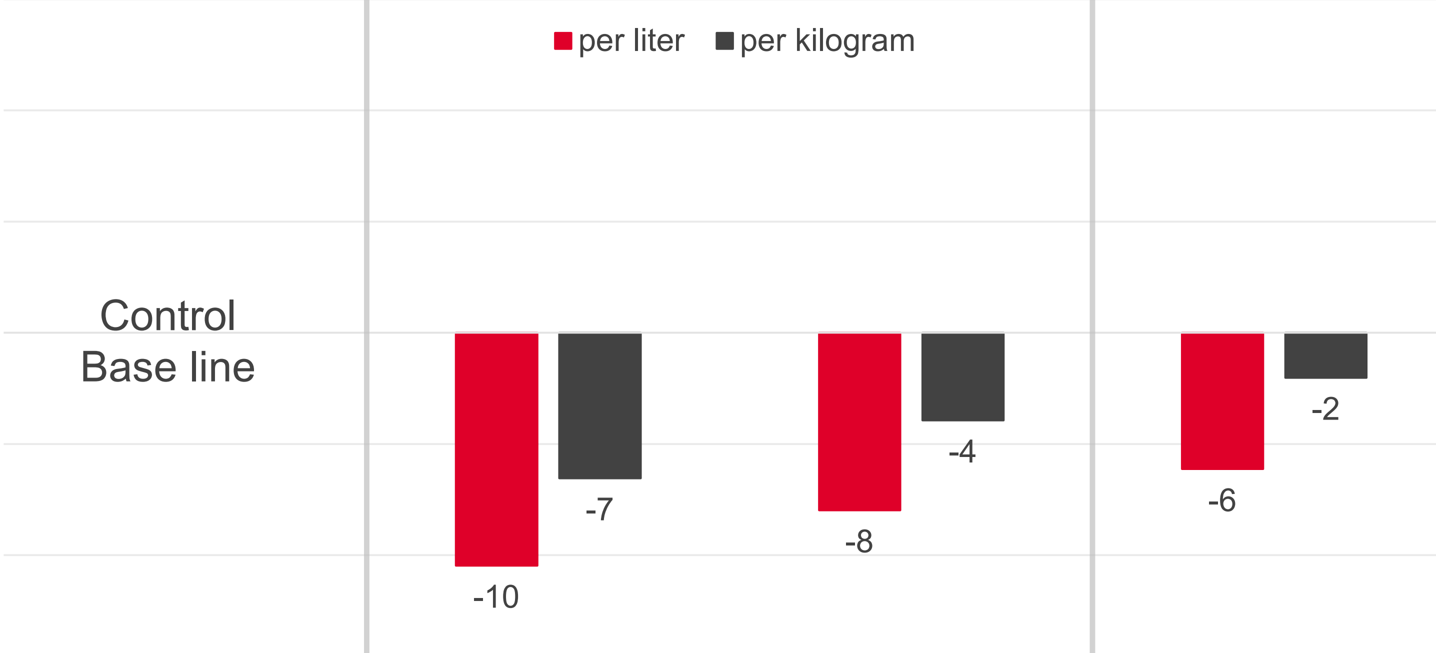
Compared to the control formulation, [%]

Control high in polymer	low in polymer		
GCC	Sillitin V 85	Sillitin Z 86 puriss	Silfit Z 91



54 pbw	47 pbw

Conclusion
Cost-Driven Approach

Compared to the control formulation (high in polymer):

- Similar tensile strength and elongation at break
- Somewhat lower lap shear strength
- Compliance with the requirements for “soft” parquet adhesives
- Cost saving potential by reduced polymer / increased plasticizer content

Maximum Performance Approach

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Maximum Performance Approach

without plasticizer

54 pbw filler
without silica

- Sillitin V 85
- Silfit Z 91
- Aktifit VM

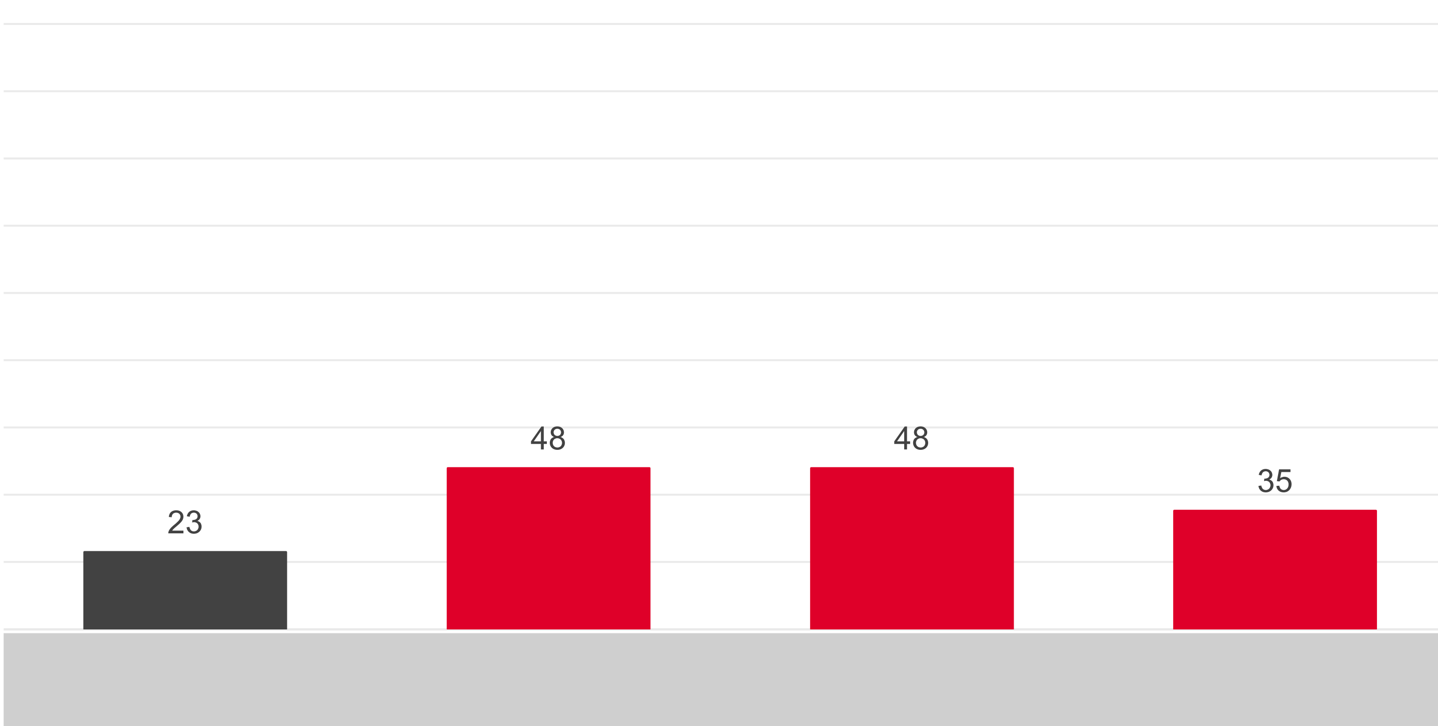
Formulation Variations
Maximum Performance

	without plasticizer pbw or weight-%
Polymer	42.14
Plasticizer	---
Drying agent	2.31
Rheological additive	---
Filler	54.38
Adhesion promoter	1.17
Total	100.00

Complex Viscosity at 50 % deformation

DIN 54458, [Pas]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Complex Viscosity at 0.1 % deformation

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DIN 54458, [Pas]

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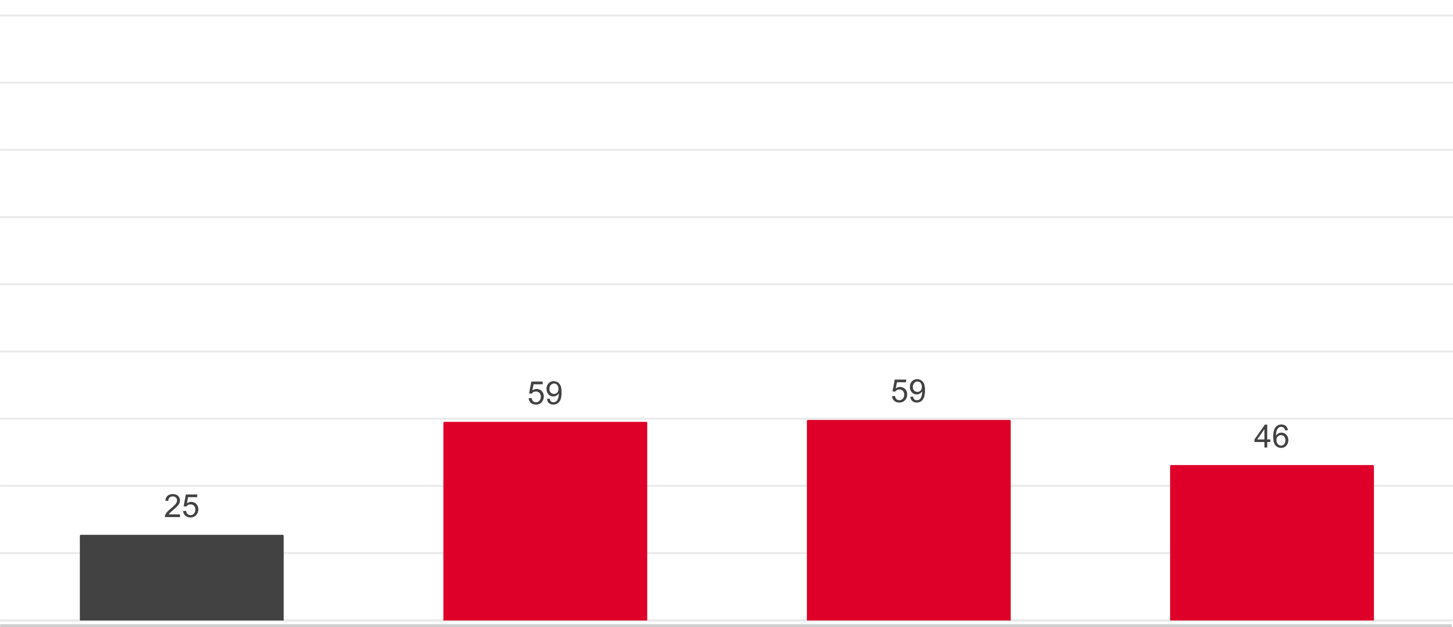
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Skin Formation Time

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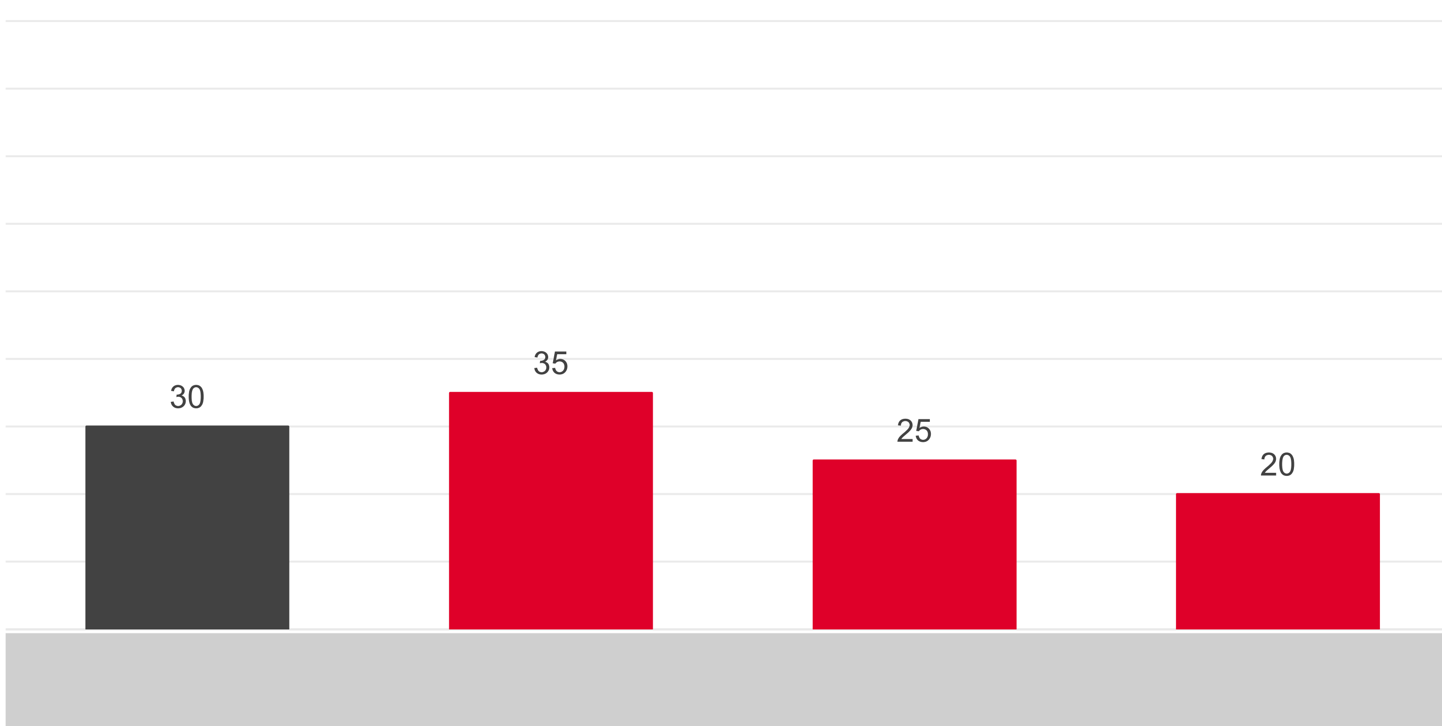
Touched with a wooden stick, [min]

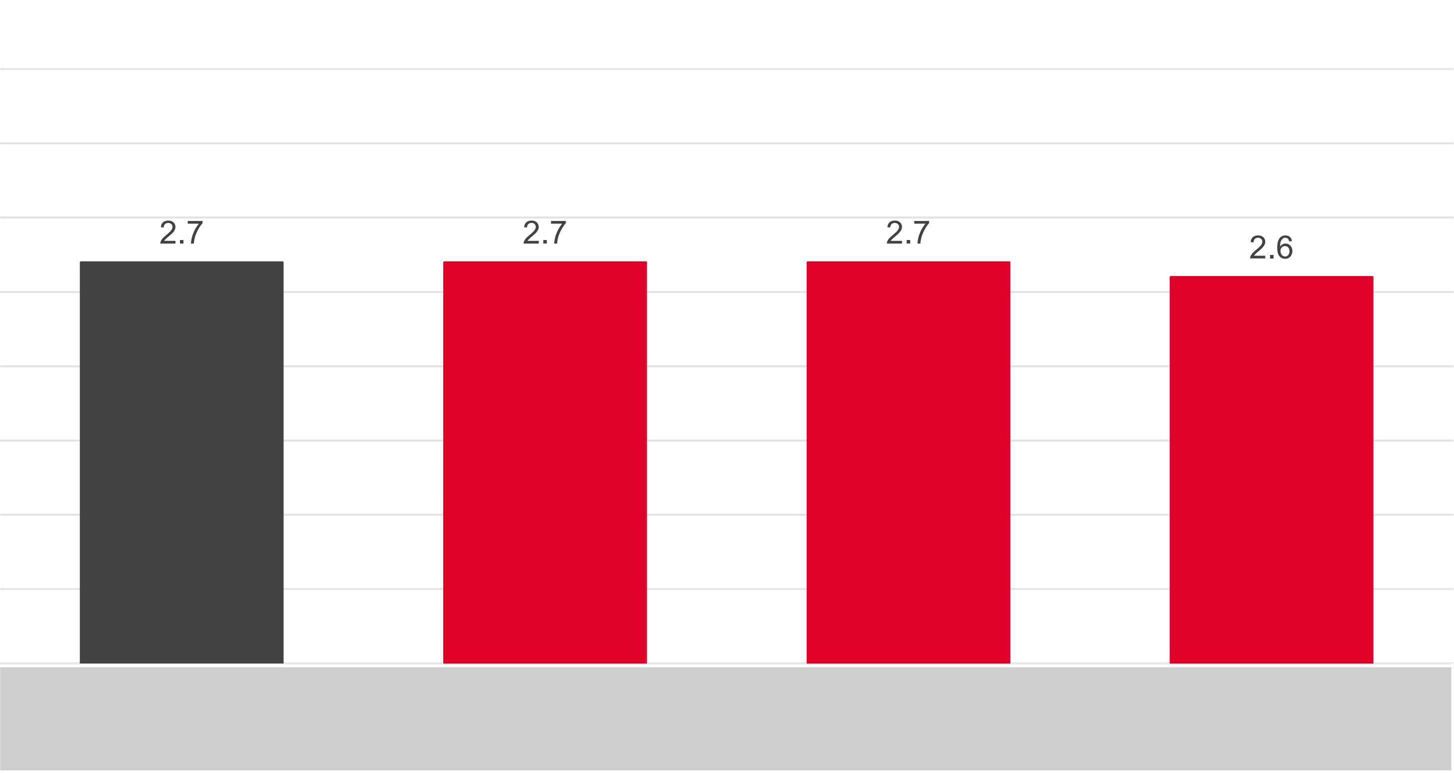
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



In-depth Cure

Thickness of the reacted layer after 24 h, [mm]

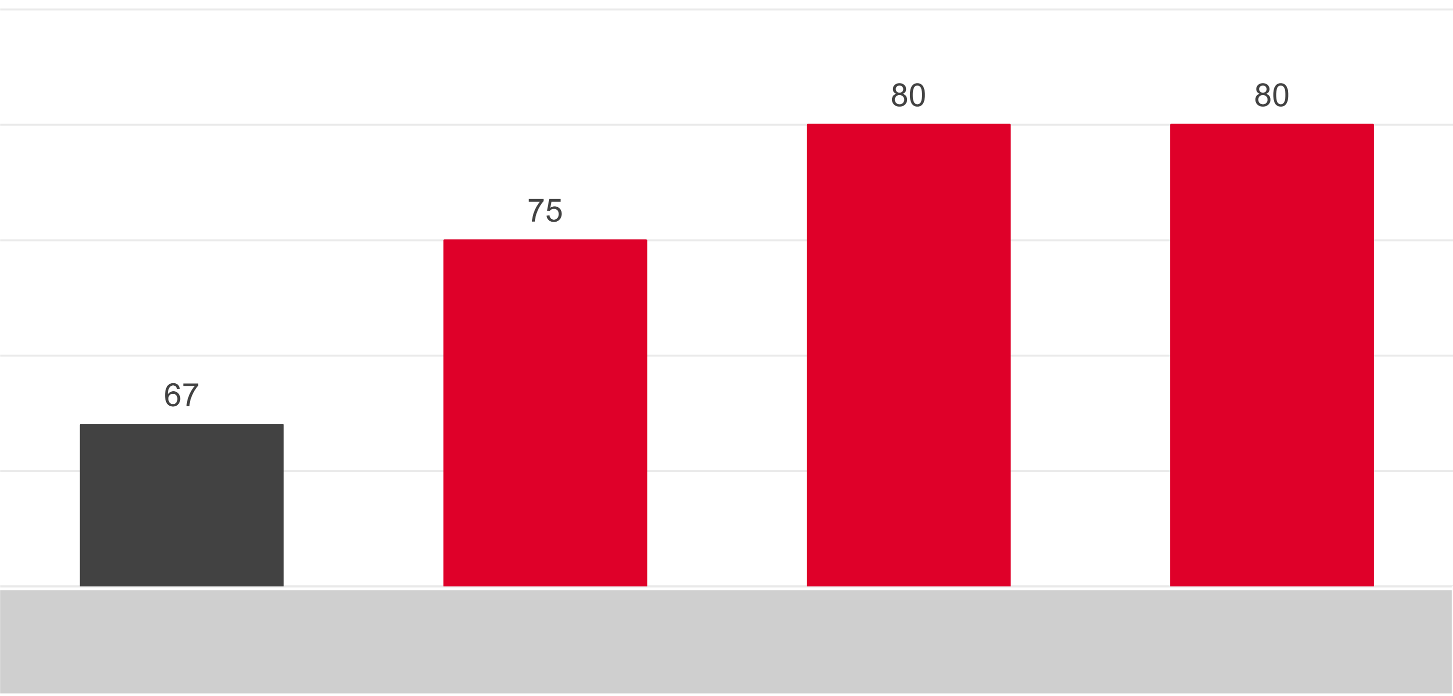
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Hardness

DIN ISO 7619-1, [Shore A]

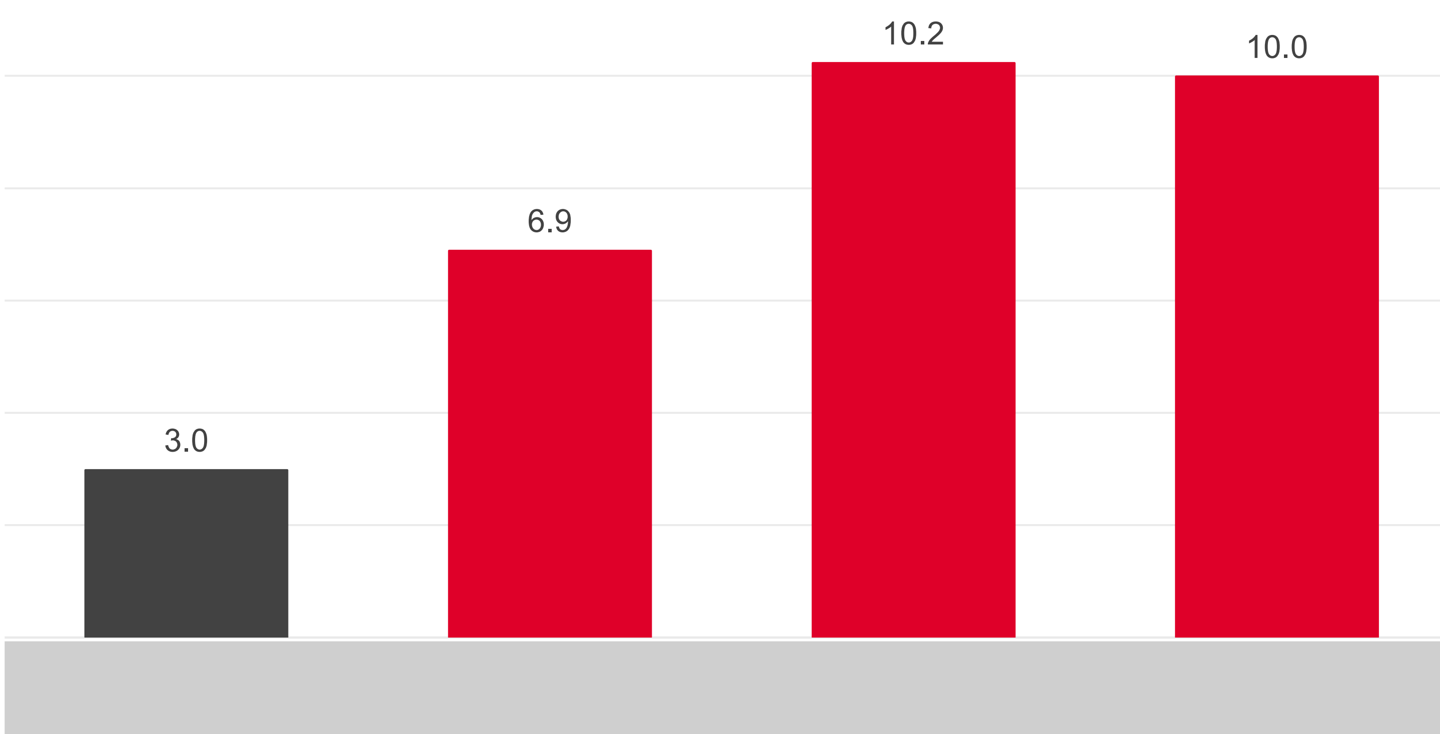
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Tensile Strength

DIN 53504, S2 dumbbell, [MPa]

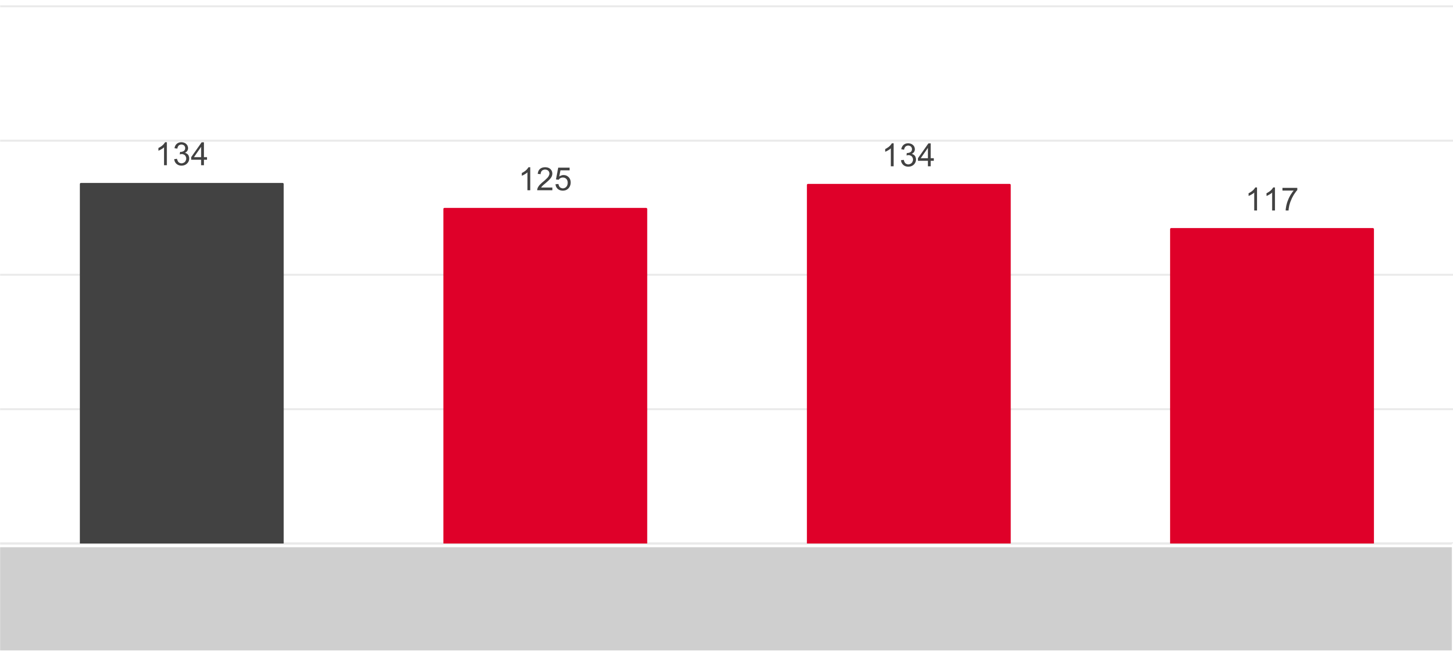
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Elongation at Break

DIN 53504, S2 dumbbell, [%]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Lap Shear Strength
Oak wood, 1 mm layer

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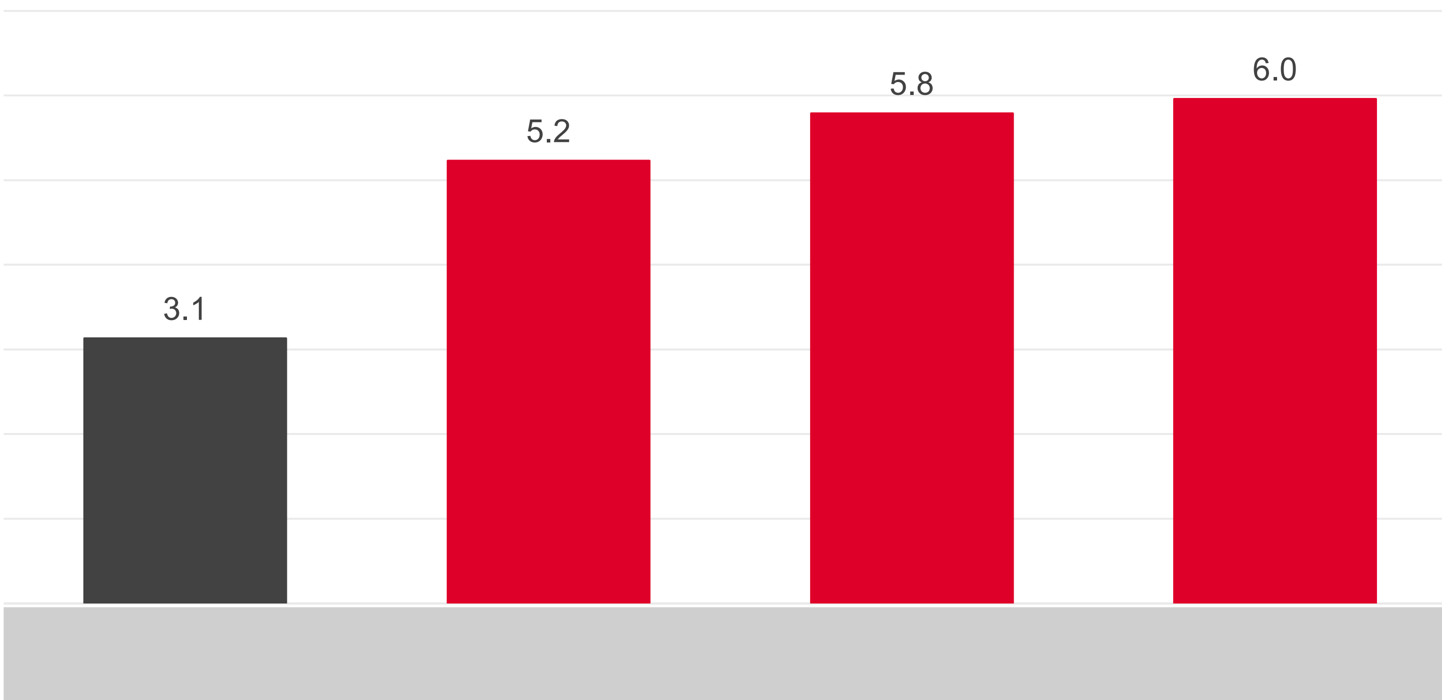
28 d, 23/40/23 °C, DIN EN 14293, [MPa]

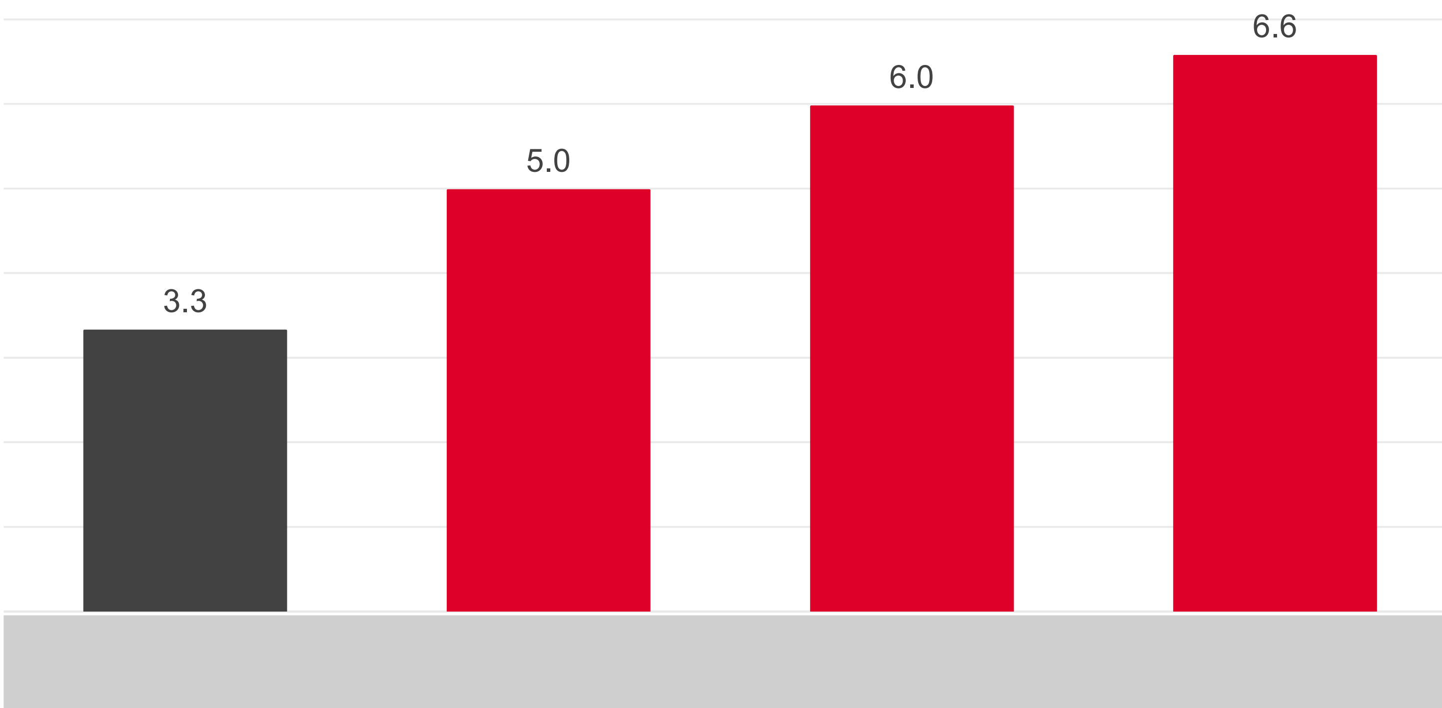
Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Lap Shear Strength
Oak wood, 0.1 mm layer

28 d, 23/40/23 °C, DIN EN 14293, [MPa]

Control	Standard NSE	Calcined Neuburg Siliceous Earth	
GCC	Sillitin V 85	Silfit Z 91	Aktifit VM



Storage Stability
6 Months at Room Temperature

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Storing in standard PE cartridges

The adhesives were stored for 6 months in customary PE cartridges at standard 23/50 conditions.

After this time, the formulations showed no gelling.

All formulations could be squeezed out without problems.

Conclusion
Maximum Performance

- High hardness
- Extraordinarily high tensile strength up to 10 MPa
- Almost unchanged elongation at break
- Marked increase of lap shear strength, more than 5 MPa appear possible

Summary

Value-Driven Approach

- Control of rheology via filler and fumed silica loading
- Similar deformability as measured by the elongation at break
- Higher tensile strength and lap shear strength
- High lap shear strength remains even after immersion in hot water
- Formulations with Neuburg Siliceous Earth meet the requirements of DIN EN 14293 for “soft” as well as “hard” adhesives

Summary

Cost-Driven Approach

- Similar tensile strength and elongation at break as control
- Compliance with the requirements for “soft” adhesives
- Cost saving potential by reduced polymer / increased plasticizer content

Maximum Performance Approach

- Extraordinarily high strength on a level unreached so far

Distinguishing Features of the NSE Grades

HOFFMANN MINERAL

• Silltin V 85	Very cost-effective, high strength
• Silltin Z 86 puriss	Cost effective, higher strength
• Silfit Z 91	Low moisture content, white and color-neutral, cost effective, very high strength
• Aktifit VM	Very low moisture content and extremely low moisture absorption even under humid conditions, white and color-neutral, very high strength, excellent hot water resistance and adhesion on aluminum

We supply material for good ideas!

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Start Formulations

parts by weight

Requirement	Parquet adhesive with increased strength "soft" or "hard"	Economic parquet adhesive "soft"	Adhesive with maximum strength
GENIOSIL® STP-E 10	25.5	15.5	42.1
Caradol ED 56-200	15.0	25.0	---
GENIOSIL® XL 10	2.0	2.0	2.3
HDK H 18	2.5	3.0 – 2.0	0 – 2.0
Sillitin / Silfit	---	47.0 – 54.0	---
Sillitin / Silfit / Aktifit	47.0	---	54.4
GENIOSIL® GF 96	1.0	1.0	1.2

Preparation of Batches

- **Planetary mixer, two bar blades with scraper**
- **Cold process (room temperature)**
- **typical preparation time approx. 10-15 min**

- Feed polymer, plasticizer and drying agent
- Add rheological additive while stirring
- Add filler (not pre-dried) while stirring

Disperse: 2 min at 600 rpm

- Add adhesion promoter

Disperse: 1 min at 600 rpm under vacuum

- Remove compound from the mixing tools

Disperse: 1 min at 600 rpm under vacuum

Deaerate: 1 min at 200 rpm under vacuum

- Fill into cartridge

Testing Conditions

Rheology	DIN 54458, MCR 300, PP 25 mm, d: 0.5 mm, Oscillation: deformation from 0.01 to 100 %, f = 10 Hz
Hardness	DIN ISO 7619-1, piled S2 specimen Curing / conditioning: 4 weeks @ standard conditions 23/50
Tensile test	DIN 53504, S2 specimen Curing / conditioning: 4 weeks @ standard conditions 23/50
Lap shear test	DIN EN 14293, substrate oak wood - Adhesive layer about 0.1 mm Curing a) 7d @ 23/50 + 20d @ 40°C + 1d @ 23/50 b) 3d @ 23/50 - Adhesive layer 1 mm Curing 7d @ 23/50 + 20d @ 40°C + 1d @ 23/50
Hot water test	Substrate aluminum 99.5 Adhesive layer 2 mm Curing 14d @ 23/50 Hot water test according to DIN EN 204 6h @ 95°C + 2h @ 20°C in deionized water Testing DIN EN 1465 - before - immediately after immersion