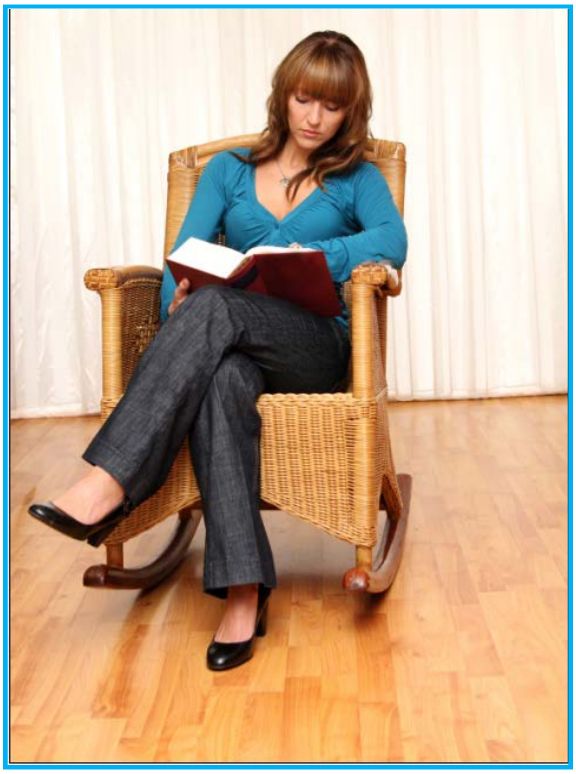
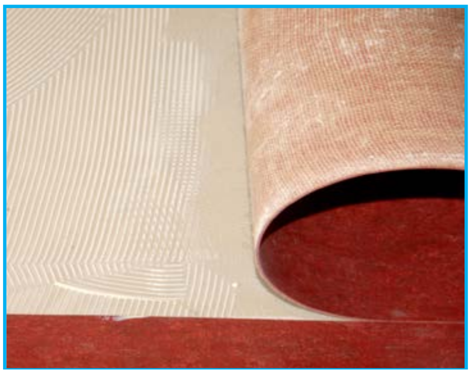




Technical Information

High Performance Fillers in STP Adhesives

HPF The Mineral Engineers
A DIVISION OF QUARZWERKE GROUP

Silane Terminated Prepolymer adhesive systems (STPs) are environmentally compatible, user-friendly alternatives to PU systems and are not subject to compulsory labelling, because they contain neither isocyanate nor solvents. They are used, for example, in the construction, automotive and flooring sectors.

Various fillers and filler combinations were tested in two different formulations in the following procedure. The first formulation is the low-cost formulation of a silane terminated assembly adhesive. In the second series of tests, the fillers were tested in a silane terminated adhesive system for structural bondings.

1. Silane-terminated assembly adhesive

Selection of the fillers

Various filler combinations were tested as to their influence on the mechanical parameters of the adhesive system for the formulation of a low-cost silane-terminated assembly adhesive. In these tests only fine fillers were combined with coarse fillers. Low-water fillers and filler combinations were tested in order to reduce the use of water scavengers and avoid pre-drying of the fillers.

		Mean particle size (µm)		**Top cut (µm)**			**Typical moisture according to Karl Fischer [ppm]**
Filler	**Mineral**	**d50** (Sedigraph)	**L50** (image analysis)	**d95** (Sedigraph)	**d98** (Sedigraph)	**L90** (image analysis)	
Mikhart 15	Calcium carbonate	15	-	-	125	-	400
Calatem C 13 T	Calcium carbonate, surface modified	1.1	-	-	6	-	1300
Calatem C 06T	Calcium carbonate, surface modified	0.65	-	-	3	-	3000
MILLISIL W 12	Quartz	16	-	50	-	-	100
SIKRON SF 600	Quartz	3	-	10	-	-	1000
SIBELITE M 3000	Cristobalite	17	-	50	-	-	600
SIKRON SF 6000	Cristobalite	3.5	-	-	12	-	1300
FS 900L-M10	Feldspar	16	-	50	-	-	400
TREMIN 939-100 USST	Wollastonite, acicular, surface modified	-	39*	-	-	95*	400

Table 1 **L = needle length*

Formulation

The starting formulation of the company Wacker (*Table 2*), being based on a silane-terminated polymer, formed the basis for the test series. The almost 15% of the plasticizer Desmophen 2061 BD that was originally included was replaced by fillers in order to reduce its properties to the mechanical parameters, such as elongation at tear and tensile strength, and in order to be able to better assess the influence of the fillers.

Item	Raw material	Function	Original formulation (wt%)	Tests without plasticizer (wt%)
1.	GENIOSIL® STP-E 10	Silane terminated polyether	12.5	15
2.	GENIOSIL® STP-E 35	Silane terminated polyether	12.5	15
	DESMOPHEN 2061 BD	Plasticizer	14.7	-
	Marble powder	Filler	53.3	
3.	Coarse filler (d50 > 5 µm)	**Filler**	-	**33.5***
4.	Fine filler (d50 < 5 µm)	**Filler**	-	**33.5***
	HDK H 18	Rheological additive pyrogenic silicic acid	4	-
5.	GENIOSIL® GF 96	Adhesion promoter aminosilane	1	1
6.	GENIOSIL® XL 10	Dessicant vinylsilane	1.5	1.5
7.	Tinuvin 770	Catalyst	0.5	0.5
	Total		100	100
	***Degree of filling**		**53.3**	**67**

Table 2

Production of the test specimens

Adhesive skins without plasticizer
Production by means of a SpeedMixer:
Item 1 + 2: weigh-in in the container, mix for 1 min at 2200 rpm
Item 3: weigh in the coarse filler, stir with a wooden spatula, then mix for 2 min at 2300 rpm
Item 4: weigh in the fine filler, stir with a wooden spatula, then mix for 2 min at 2300 rpm
Item 5–7: weigh in, then mix for 2 min at 2300 rpm

The temperature of the mixture is increased to approx. 50°C.

The adhesive compound is spread into a mould (18 x 20 cm) with a 2 mm high border, cured for 24 hours at room temperature, removed from the mould and stored for 14 days at 23°C/50% relative humidity in a climatic cabinet. For performance of the tensile test, ten S2 shouldered test strips were stamped out in the direction of application and tested in accordance with DIN 53504 for tensile strength and elongation at tear.

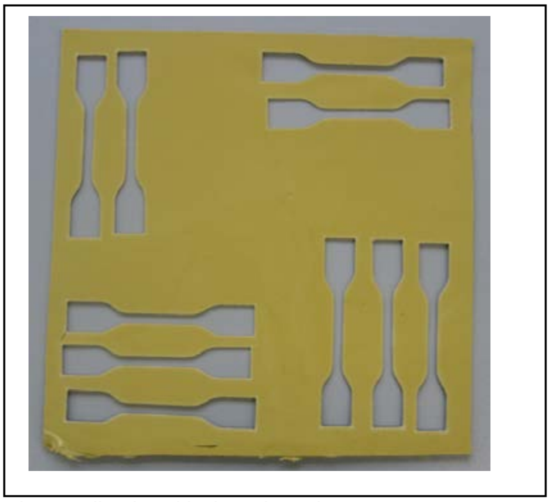


Fig. 1: Adhesive skin (membrane)

Application direction ↓

☞ The influence of the anisotropy of the fillers on the measuring results depending on the stamping direction of the test bars in application direction (doctor blade) was conspicuous.

Bonding with a layer thickness of 2 mm:
The aluminium platelets (aluminium test specimen 3.1364T351, plated alloy 2024 100 x 25 x 1.6 mm from the company Rocholl GmbH) are cleaned with ethanol for the shear tension test.

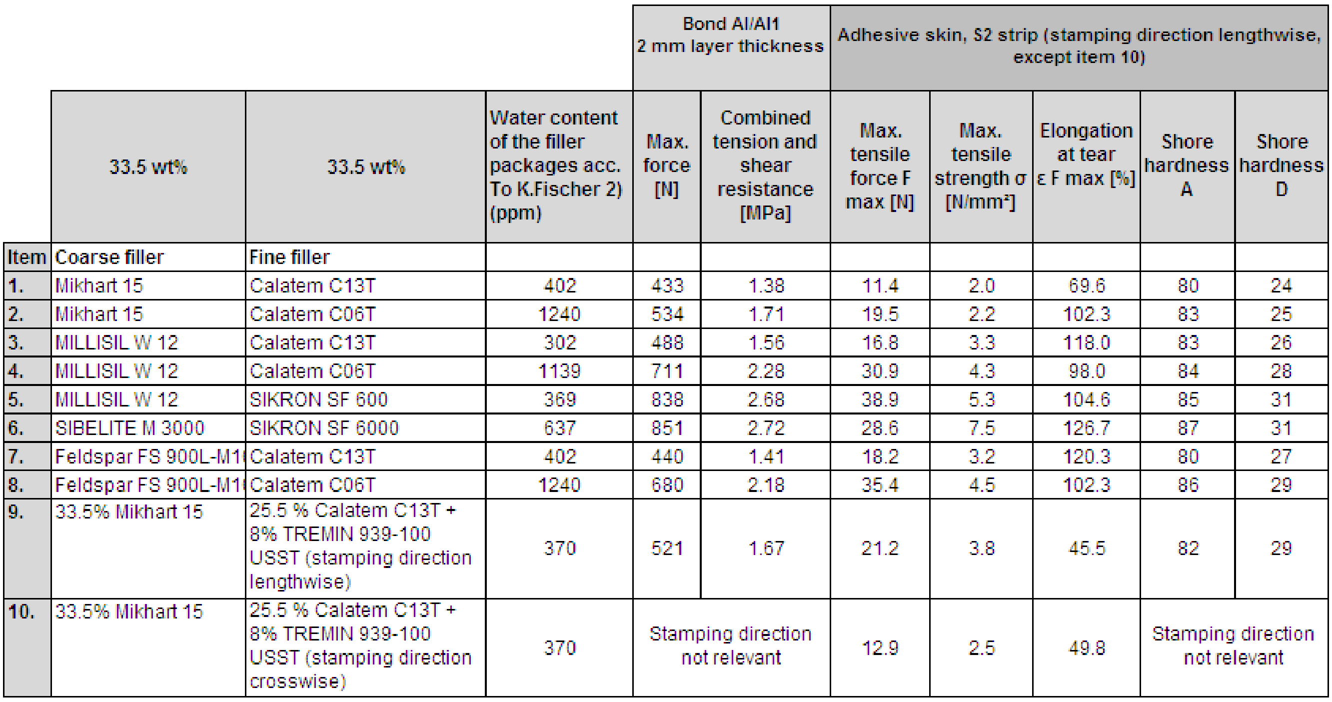
The bonding is produced in a holder that ensures an overlap of 12.5 +/- 0.25 mm. For this purpose, the front quarter of the bottom platelet is coated with adhesive using a wooden spatula, inserted into the holder and the upper platelet is also inserted overlapping into the holder. A spacer plate is placed under the upper platelet to achieve a layer thickness of 2 mm. The bonding is subjected to a weight of 781 g and cured for about 12 hours.

After two weeks of storage at 23°C and 50% relative humidity the testing of the combined tension and shear resistance is performed in accordance with DIN EN 1465 on 10 specimens each.

Results

Fracture behaviour

Cohesive failure occurs in the case of the filler combination Mikhart 15, Calatem C13T + TREMIN 939-100 USST. An adhesive failure occurred in the case of all the other filler combinations investigated.



				Bond Al/Al[1] 2 mm layer thickness		Adhesive skin, S2 strip (stamping direction lengthwise, except item 10)				
	33.5 wt%	33.5 wt%	Water content of the filler packages acc. To K.Fischer 2) (ppm)	Max. force [N]	Combined tension and shear resistance [MPa]	Max. tensile force F max [N]	Max. tensile strength σ $[N/mm^2]$	Elongation at tear ε F max [%]	Shore hardness A	Shore hardness D
Item	Coarse filler	Fine filler								
1.	Mikhart 15	Calatem C13T	402	433	1.38	11.4	2.0	69.6	80	24
2.	Mikhart 15	Calatem C06T	1240	534	1.71	19.5	2.2	102.3	83	25
3.	MILLISIL W 12	Calatem C13T	302	488	1.56	16.8	3.3	118.0	83	26
4.	MILLISIL W 12	Calatem C06T	1139	711	2.28	30.9	4.3	98.0	84	28
5.	MILLISIL W 12	SIKRON SF 600	369	838	2.68	38.9	5.3	104.6	85	31
6.	SIBELITE M 3000	SIKRON SF 6000	637	851	2.72	28.6	7.5	126.7	87	31
7.	Feldspar FS 900L-M1	Calatem C13T	402	440	1.41	18.2	3.2	120.3	80	27
8.	Feldspar FS 900L-M1	Calatem C06T	1240	680	2.18	35.4	4.5	102.3	86	29
9.	33.5% Mikhart 15	25.5 % Calatem C13T + 8% TREMIN 939-100 USST (stamping direction lengthwise)	370	521	1.67	21.2	3.8	45.5	82	29
10.	33.5% Mikhart 15	25.5 % Calatem C13T + 8% TREMIN 939-100 USST (stamping direction crosswise)	370	Stamping direction not relevant		12.9	2.5	49.8	Stamping direction not relevant	

Table 3

1) Pretreatment of the aluminium specimens: degreasing with ethanol
2) Relative to the overall formulation

Influence of the fineness on the combined tension and shear resistances:

The combined tension and shear resistance increases with decreasing particle size of the $CaCO_3$ fine fraction. Compared to the filler combinations that contain $CaCO_3$ the combined tension and shear resistance for pure SiO_2-based filler combinations is increased again by 18% *(Diagram 1)*.

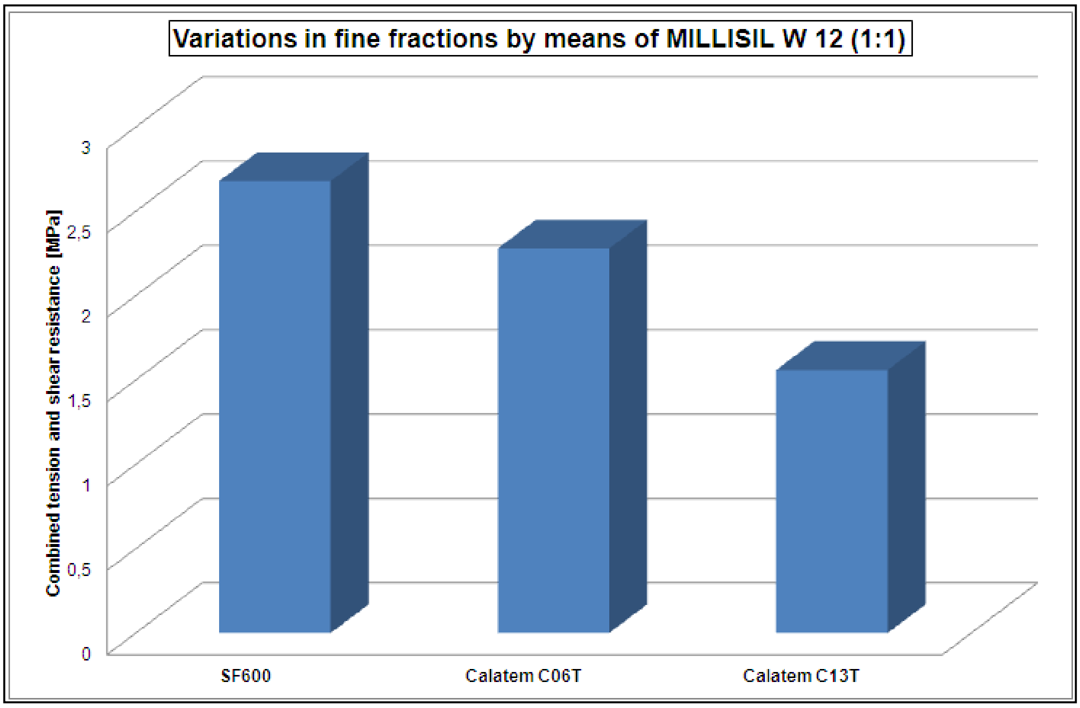


Diagram 1:

Influence of the raw material basis on the combined tension and shear resistances:

The combined tension and shear resistances of a filler combination based on SiO_2 are higher than the lower-priced $CaCO_3$ combinations *(Diagram 2)*.

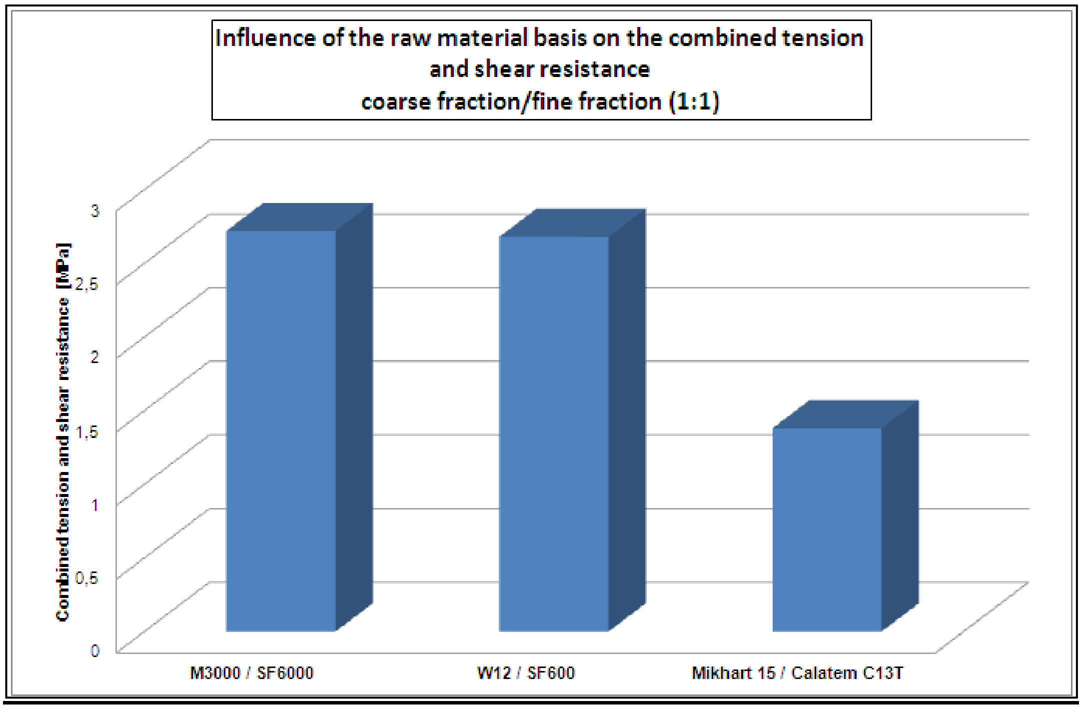


Diagram 2:

Replacement of the $CaCO_3$ coarse fraction by quartz; influence on the combined tension and shear resistances:

If the coarse fraction of $CaCO_3$ is replaced by the quartz powder MILLISIL W 12, significant increases in the combined tension and shear resistance are still perceivable. Calcium carbonate Calatem C06T combined with MILLISIL W 12 provides the best results in this case (*Diagram 3*).

A customary precipitated and surface treated $CaCO_3$ type (PCC) was included in this study. This type has a mean particle size of d_{50} = 0.1 µm.

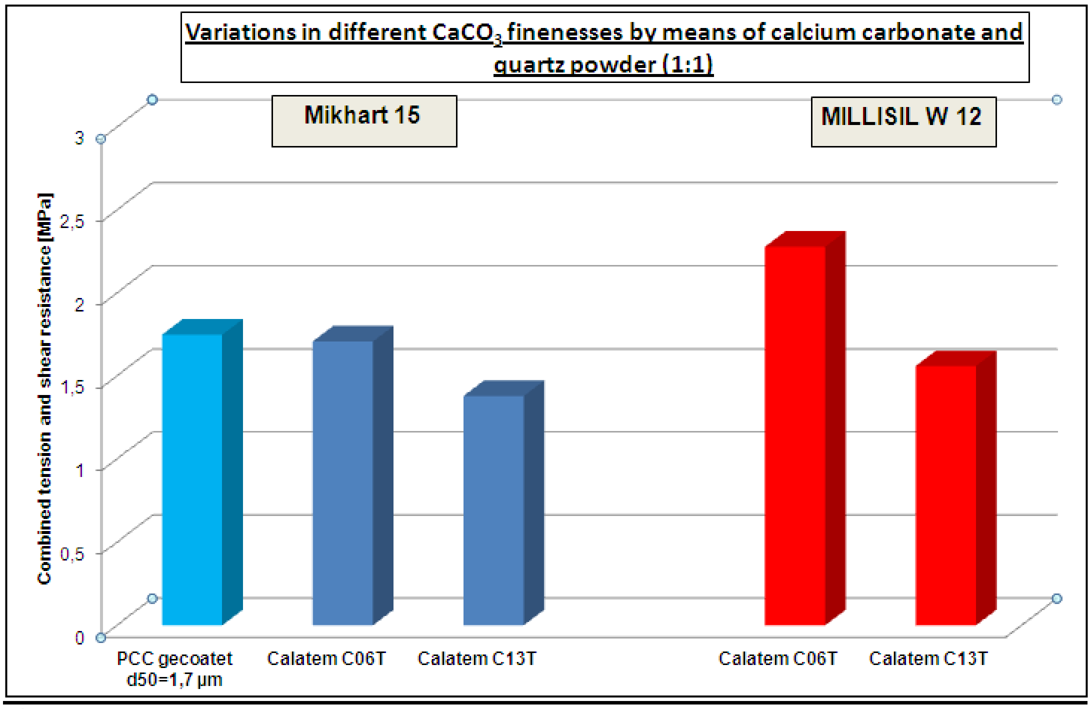


Diagram 3

Summary:

- Through the combination of different minerals and grain distributions, the mechanical parameters, e.g. the combined tension and shear resistances, elongation at tear and Shore hardness, can be significantly influenced without varying the bonding agent or special additives.
- In addition, Calatem C06T is an interesting filler alternative to precipitated, coated $CaCO_3$.

2. Silane terminated adhesive system for structural bonding

Selection of the fillers

In the series of experiments described below various fillers were tested in a silane adhesive system for high strength bonds. In particular the influence of fillers with an aspect ratio, such as surface treated TREMIN® wollastonite and surface treated TREMICA® muscovite mica, was determined in comparison to the chalk that is normally used. The test series was supplemented by the admixing of TREMIN®to the reference filler chalk and a type of calcium carbonate on a marble basis.

In collaboration with a polymer manufacturer a preselection of suitable reinforcing fillers was elaborated by screening fillers in a hard elastic adhesive system, which improved the efficiency of the adhesive system. As a filler the starting formulation contained natural, surface treated chalk, various variants of which were substituted for higher performance filler.

In the starting formulation, TREMIN®939-100 AST/2 and TREMICA®I155-010 AST significantly improved the tensile strength of the adhesive skin, the Shore hardness and the combined tension and shear resistance of a beech/beech bond. The elasticity of the systems worsened due to the use of these fillers and expressed itself in a low elongation at tear.

Filler parameters

Filler	Mineral	Medium particle size [µm] d_{50} (Sedigraph) L_{50} (image analysis)	Topcut [µm] d_{90} (Sedigraph)	Topcut [µm] d_{98} (Sedigraph)	Topcut [µm] L_{90} (image analysis)	Structure
Chalk	calcium carbonate surface modified	1	-	3.5	-	nodular
TREMIN® 939-100 AST/2	wollastonite surface modified	39*****	-	-	95*****	acicular
TREMICA® 1155-010 AST	muskovite surface modified	4.6	12.5	-	-	flaky
Mikhart MU08T	marble powder surface modified	0.9	-	5	-	nodular

Table 4 ****** L = needle length*

One-component STP adhesive formulation

The starting formulation of the company Bayer Material Science AG *(Table 5)*, based on an aliphatic silane-terminated prepolymer, formed the basis for the series of tests in which the 63.4 wt% of surface-modified chalk included was replaced by weight with high-performance fillers from our range of products. On account of excessively high viscosity the replacement with TREMIN® 939-100 AST/2 and TREMICA® 1155-010 AST succeeded with the same processability with only 54.9 wt% and 51.2 wt%.

Components	**Description**	**Manufacturer**	**Wt% target**	**Wt% actual**
Stage one:				
Desmoseal® S XP 2749	Binding agent	BMS	30.41	30.41
Irganox 1135	Antioxidant	BASF	0.46	0.46
Bayferrox 415	Pigment	Lanxess	0.28	0.28
Cab-O-Sil TS 720	Thixotropizing agent	Cabot Corporation	0.94	0.94
Surface treated chalk	Reference filler	-	**63.4**	**63.4**
Filler alternatives:				
TREMIN® 939-100 AST/2	Wollastonite filler	Quarzwerke	**63.4**	**54.9**
TREMICA® 1155-010 AST	Muscovite filler	Quarzwerke	**63.4**	**51.2**
8% TREMIN® 939-100 AST/2 55.4% surface treated chalk	Filler mixture	Quarzwerke Reference	**63.4**	**63.4**
Mikhart MU08T	$CaCO_3$ filler	Provençale	**63.4**	**63.4**
Dynasylan VTMO	Dehydrating agent	Evonik	2.6	2.6
Lupragen N 700	Catalyst	BASF	0.14	0.14
Stage 2:				
Dynasylan 1146	Adhesion promoter	Evonik	1.77	1.77

Table 5: Starting formulation of the company Bayer Material Science AG for a hard elastic adhesive

Production

All fillers are pre-dried for approx. 16 h at 100°C. The production of the adhesives took place with a vacuum dissolver without a wall doctor.

Stage 1:
Components 1–4 are weighed together and the thixotropizing agent and the filler are added in metered portions and homogenized while being stirred. Shortly prior to dispersion the dehydration agent and catalyst are added. Dispersion takes place subject to cooling (product temperature < 60°C):

- approx. 10 min at 3000 rpm (static vacuum < 200 mbar)
- approx. 10 min at 1000 rpm (static vacuum < 200 mbar)

Stage 2:
The bonding agent is homogenized with the mixture from stage 1. Dispersion takes place again subject to cooling (product temperature < 60°C):

- approx. 10 min at 1000 rpm (static vacuum < 200 mbar)
- approx. 5 min at 1000 rpm (dynamic vacuum)

Measurement

Adhesive skins approx. 2 mm in thickness (17 x 17 cm) were produced for performance of the tensile test. After curing the adhesive skins for 14 days in a standard atmosphere (23°C / 50% rel. air humidity) five S2 shouldered strips were stamped out crosswise and lengthwise to application direction and tested for tensile strength and elongation at tear in accordance with DIN 53504. For the Shore hardness a partial amount of the liquid adhesive was filled into a plastic beaker 1.5 cm in height and determination was also performed after 14 days of storage in a standard atmosphere.

Results

Filler	Stamping direction relative to applic. direction	F max	Tensile strength	Elongation at tear	Shore hardness	Shore hardness
	S2 strip	[N]	[N/mm^2]	[%]	A	D
Surface treated chalk	Crossw.	20.7	4.9	33	85	23
	Lengthw.	16.4	4.5	27		
TREMIN® 939-100 AST/2	Crossw.	25.8	7.2	27	89	27
	Lengthw.	43.0	11.7	19		
TREMICA® 1155-010 AST	Crossw.	29.9	6.6	32	85	22
	Lengthw.	29.9	7.2	32		
8% TREMIN® 939-100 AST/2 55.4% chalk	Crossw.	23.9	5.4	31	87	26
	Lengthw.	29.1	6.9	22		
Mikhart MU08T	Crossw.	21.4	5.2	37	86	25
	Lengthw.	21.8	5.4	36		

Table 6: Results of the tensile strength, elongation at tear and Shore hardness tests

Summary:

- All high-performance fillers used increase the tensile strength in the adhesive system
- The anistropy of the fillers influences the measured results by way of their alignment lengthwise with the direction of application (doctor blade)
- TREMIN® 939-100 AST/2 increases the tensile strength most intensely with a lower degree of filling
- TREMICA® 1155-010 AST increases the tensile strength significantly with a comparable elongation at tear with a lower degree of filling
- An 8% admixture of TREMIN 939-100 AST/2 to the reference product increases the tensile strength, while the elongation at tear is slightly worse
- Calcium carbonate MU08T creates better tensile strengths with a clearly increased elongation at tear

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