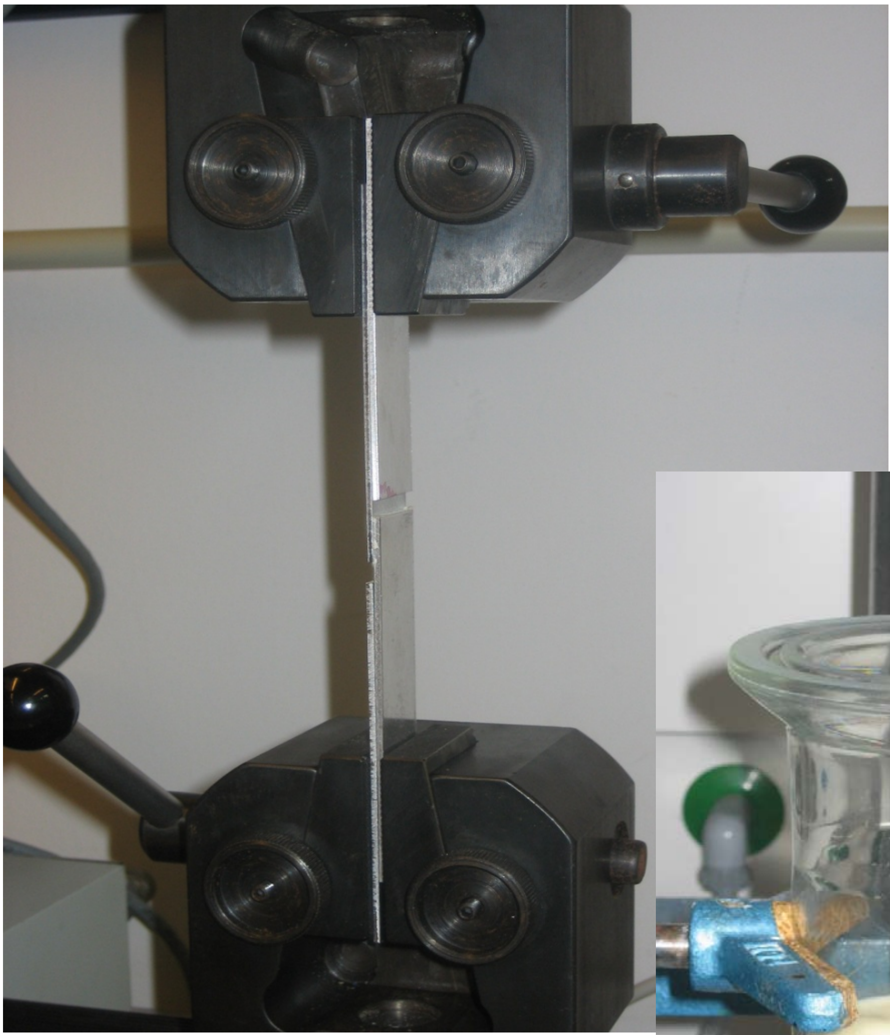

Technical Information

High Performance Fillers as Reinforcing Additives in Two-Component PU Adhesive for Structural Bonding

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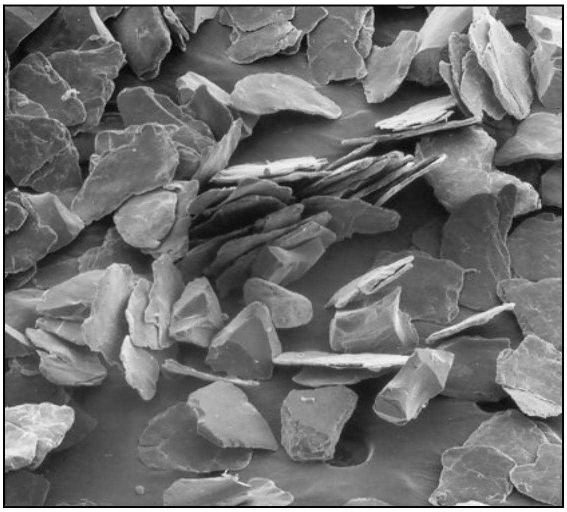
Introduction:

Two-component PU systems are classic addition polymerization adhesives that are widely used in the field of structural bonding, for example, in the automobile and railway vehicle industry. Their properties can be set within broad limits from brittle/hard to plastic/elastic by selection of the components and fillers. In general they have very good adhesion properties and exhibit no embrittlement even at low temperatures (typical Tg -40 to -60 °C). Classically calcium carbonate is used as the filler in this case. It does, however, act only as filler and not as a functional additive.

In the test series described below flaky Quarzwerke **TREMICA®** muscovite mica and needle-shaped Quarzwerke **TREMIN®** wollastonite were used to test in terms of applications engineering to what extent the performance profile of the bonding can be improved through the use of these high performance fillers in comparison to a classic filler.



TREMICA® 1155 muscovite mica,
Quarzwerke GmbH
chem. formula $KAl_2[AlSi_3O_{18}](OH)_2$
distinct platelet structure

TREMIN® 939 wollastonite,
Quarzwerke GmbH
chem. formula $CaSiO_3$
distinct needle structure

Description of the recipe and investigations

The guide formulation of the company BAYER Material Science AG (table 1), which is based on a two-component polyurethane (PU), formed the basis for the test series, in which the 46.73 % by weight of the surface-modified filler Calcium Carbonate that is contained in it was replaced in weight by Quarzwerke fillers. Table 2 shows the properties of the filler in comparison to the high performance fillers.

Component	Material class	Material	Manufacturer	Parts by weight	% by weight
C1 polyol component	Polyol	Desmophen® 1380 BT	Bayer Material Science AG	50	23.36
	Polyol	Desmophen® 1110 BD	Bayer Material Science AG	20	9.35
	"Polyol"	Castor oil		30	14.02
	Na-K-Ca-A zeolite	Baylith® UOP L-paste	Kurt Obermeier GmbH	10	4.67
	Filler	**Calcium Carbonate**		100	46.73
	Alternative Quarzwerke filler	**TREMIN® 939-600 AST**	Quarzwerke GmbH	100	46.73
	Alternative Quarzwerke filler	**TREMICA 1155-010 AST**	Quarzwerke GmbH	100	46.73
	Rheolog. additive	Aerosil® 200	Evonik Degussa GmbH	4	1.87
Total				214	**100.00**
C2 isocyanate component	Isocyanate	Desmodur® VKS 20 F	Bayer Material Science AG	81.3	37.99

Table 1: Guide formulation of the company Bayer Material Science AG with substitution of the calcium carbonate used as a filler by Quarzwerke high performance fillers

Filler / high performance filler	Mineral	Mean particle size [µm]	Top cut [µm]	Structure
Calcium Carbonate	Calcium carbonate, surface modified	2.4	20	Nodular
TREMIN® 939-600 AST**	Wollastonite, surface modified	23	53	Needle-shaped
TREMICA® 1155-4.6 AST***	Muscovite, surface modified	4.6	14	Platelet-shaped

*Manufacturer's specifications; ** particle size specified as the needle length; ***Sedigraph measurements

Table 2: Properties of the filler used in comparison to the high performance fillers

Influence of TREMICA® muscovite mica and TREMIN® wollastonite on the bonding properties

Preparation / application / measurement:

The filler and the high performance fillers are pre-dried for approx. 12 h at 80 °C.
The liquid materials of component 1 are mixed in the speed mixer. The filler and the rheological additive are initially dispersed in the mixture by hand and then by means of a dissolver. After the homogenization of component 1, component 2 is also mixed in the dissolver, avoiding the dragging-in of moisture. To ensure identical layer thickness of the bonds 1 % of solid glass balls 200-212 µm are incorporated into the formulation. The processing is performed quickly after the mixture has been made.

The aluminium platelets (aluminium test specimen 3.1364T351, alloy 2024 plated 100 x 25 x 1.6 mm from the company Rocholl GmbH) for the tensile shear strength test are initially cleaned for 5 mins. in a vertical position in MEK (methyl ethyl ketone) in an ultrasonic bath and dried in the air. The front third of the platelets is roughened uniformly by diagonally grinding it with 80 grade sandpaper. They are then cleaned again for 5 mins. in MEK in the ultrasonic bath. To be able to describe the mechanical properties of the adhesive better, the adhesion surface of the aluminium platelet is primed with aminosilane to prevent adhesion breakage. To do so the polished area is immersed for 10 secs. in a 1:10 aminopropyl-triethoxysilane : ethanol mixture and after draining is dried for 1 h at room temperature.

The bonding is performed in a holder that ensures an overlap of 12.5±0.25 mm. To do so, the front quarter of the bottom platelet is coated with adhesive using a wooden spatula, inserted into the holder and the top platelet is also fitted overlapping into the holder. The bond is subjected to a load with a weight of 781 g and cured for approx. 12 h. After a week of storage at 23 °C and in a relative air humidity of 50 % testing of the tensile shear strength in accordance with DIN EN 1465 is performed on 10 specimens each.

Result:

The Quarzwerke high performance fillers can be incorporated without difficulty into the recipe.

The tensile shear strengths achieved in accordance with DIN EN 1465 are summarized in Table 3.

Filler / high performance filler	Max. force [N]	Tensile shear strength [Mpa]
Calcium Carbonate	2790	8.91
TREMIN® 939-600 AST	2860	9.17
TREMICA® 1155-010 AST	3390	10.8

Table 3: Comparison of the results of the tensile shear strength test in accordance with DIN EN 1465 on the formulations

The distinct increases in strength of the adhesive formulations or of the bond with high performance fillers are clearly recognizable by the maximum forces and the tensile shear strength. In particular the surface-coated muscovite mica **TREMICA®** 1155-010 AST improves the tensile shear strength by 21 %. If **TREMIN®** 939-600 AST is used, the tensile shear strength increases by still 3 % in comparison to Calcium Carbonate. Diagram 1 shows a comparison of the data of the tensile shear strength test.

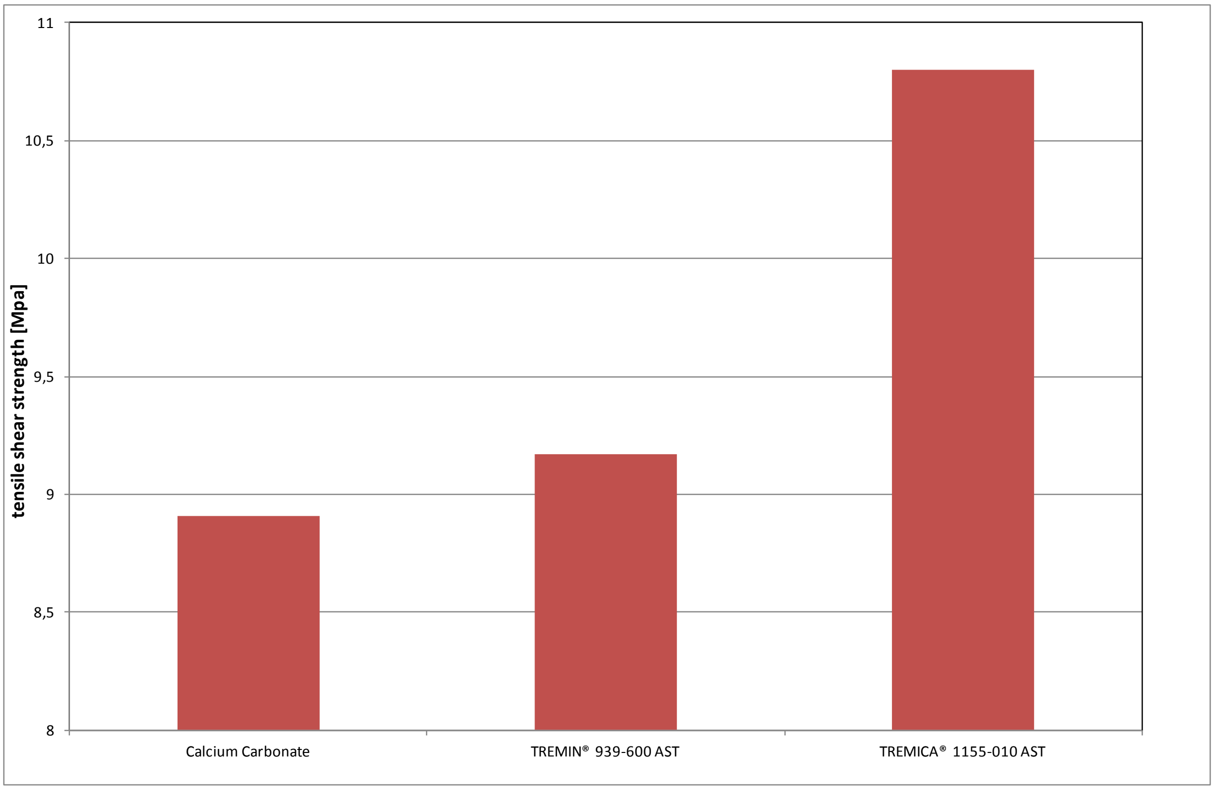
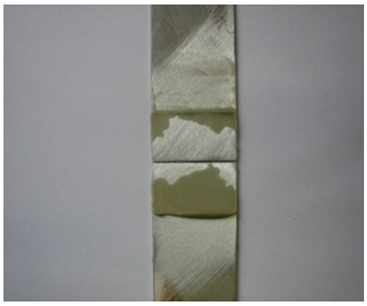


Diagram 1: Comparison of the results of the tensile shear strength test in accordance with DIN EN 1465 on the formulations

The formulation with surface-treated calcium carbonate clearly shows cohesion failure, whereas (despite the substrate being primed in the same way for all bonds) the high performance fillers exhibit uniform adhesion failure with increased tensile shear strength. This shows that the cohesion of the adhesive has been clearly improved by using the high performance fillers.

Cohesion breakage of the formulation with **Calcium Carbonate**

Uniform adhesion breakage of the formulation with **TREMIN® 939-600 AST**



Uniform adhesion breakage of the formulation with **TREMICA® 1155-010 AST**

In addition, a tendency to ductile behavior can be observed in the case of the formulation with **TREMIN®** 939-600 AST (slight increase in the initial area of the shear stress/path curve) in comparison to Calcium Carbonate. The breaking elongation tends to be greater in the case of the formulation with **TREMICA®** 1155-010 AST. No embrittling through the use of high performance fillers in comparison to the classic filler was observed.

Summary:

- Replacement of the surface-modified filler calcium carbonate with surface-modified Quarzwerke high performance fillers in a reactive two-component PU (polyurethane) adhesive system is possible without any difficulty and results in a distinctly better performance of the adhesive bond.

- The use of **TREMIN®** 939-600 AST results in a 3 % increase in the tensile shear strength of the bond in comparison to the classic filler. The breaking mechanism changes from cohesion failure in the case of the calcium carbonate to adhesion failure in the case of **TREMIN®** 939-600 AST. The shear stress/path curves indicate a higher degree of ductility in the case of **TREMIN®** 939-600 AST. The bond does not become brittle.

- The use of **TREMICA®** 1155-010 AST results in a 21 % increase in the tensile shear strength of the bond in comparison to the classic filler. The breaking mechanism changes from cohesion failure in the case of the calcium carbonate to adhesion failure in the case of **TREMICA®** 1155-010 AST. The shear stress/path curves indicate a higher degree of breaking elongation in the case of **TREMICA®** 1155-010 AST. The bond does not become brittle.