HIGH STRENGTH STARTS HERE: \(\alpha\)-HYBRIDS FOR STRONG BONDING ADHESIVES
High strength bonding is typically used for production of sandwich elements, lamination of surfaces, automotive engineering and woodworking. WACKER's new silane-modified polymer opens this field of application for hybrid adhesives as it enables formulations that produce thermosets with Shore D hardness.
DISCOVER GENIOSIL® XB

Structural bonding has become an indispensable bonding method in virtually all areas of industrial and craft manufacturing. Making high strength, self-supporting adhesive bonds currently involves the use of adhesives based on epoxides or polyurethanes. Over decades they have proven themselves in countless applications such as automotive engineering, production of sandwich elements, lamination of surfaces and in woodworking. However, formulators and end-users of such adhesives do have to accept certain drawbacks.

Polyurethane adhesives have relatively low levels of heat resistance and tend to bubble at high isocyanate concentrations during processing. Epoxy adhesives require two-part formulations and are susceptible to yellowing.

With the new GENIOSIL® XB you can overcome these disadvantages.

High Strength Yet Label-Free
Based on our patented $\alpha$-technology, WACKER experts have now developed a new silane-modified polymer that offers an alternative to the traditional binder materials. GENIOSIL® XB 502 is an $\alpha$-silane-terminated polyether, that is free of isocyanates, cures on contact with atmospheric moisture through silane crosslinking and delivers the strength needed for high strength bonding.

Moreover, this new binder is not subject to labeling according to current EH&S regulations.

GENIOSIL® is a registered trademark of Wacker Chemie AG.
Taking Our Silane-Terminated Polymers One Step Further

Based on α-Silane Technology
Silane-modified polymers generally contain silane components that are coupled to an organic polymer backbone and which can be used for curing through hydrolysis and subsequent condensation. The silane-terminated polyethers from WACKER also belong to this group of hybrid polymers. These have a polyether chain as their organic polymer backbone, with di- or trialkoxysilyl groups at its ends. This structure is achieved through urethane coupling, with an aliphatic bridge positioned between the urethane group and the silane component. In commercially available grades, this aliphatic bridge is either a methylene or a propylene group. The methylene group leads to an α-silane-terminated polyether, the propylene group produces a γ-silane-terminated polyether. Because of their short methylene bridge, α-silane-terminated polyethers can crosslink without the addition of a tin catalyst (α-effect, Figure 1).

State-of-the-Art and Beyond
Silane-terminated polymers have for years served as the binder of choice in a variety of applications. They contain no isocyanates and can be processed in a solvent-free environment. The formulated sealants and adhesives combine the properties of polyurethane with those of silicones to deliver custom-made mechanical properties for many applications. Examples include transparent sealants, wood-flooring adhesives, universal assembly adhesives and industrial adhesives. But existing silane-terminated polyethers were never suitable to formulate adhesives for strong structural adhesive bonds.

![Figure 1: Structure of an α-Dimethoxysilane-Terminated Polyether](image)

![Figure 2: Silane-Modified Polymers Present and Future](image)
GENIOSIL® XB 502 for High Strength Adhesives

To enable the use of silane crosslinking for high strength bonding, research into new hybrid polymers that form close-meshed networks after curing was pursued. The new silane-modified polymer GENIOSIL® XB 502 is the result of this development work. It enables the achievement of tensile lap-shear strengths exceeding 10 N/mm², which are required for structural adhesives.

The new binder is based on α-silane technology and contains a polyether as the organic polymer backbone. It has been optimized for low viscosity while still containing a higher count of silyl groups per unit volume than the elastic STP-E grades.

On curing, the high density of hydrolyzable silyl groups produces a three-dimensional network, consisting of siloxane and polyether segments. The network is far more close-meshed than the one that is formed when conventional silane-terminated polyethers are cured. Formulations with the new hybrid polymer produce thermosets with Shore D hardness. For example, GENIOSIL® XB 502 can be used to generate hardness levels of up to 80 Shore D, which would not have been possible with existing silane-modified polymers to date.
GENIOSIL® XB shows not only a high performance, it is also easy to formulate and comes with many other advantages.

Low Viscosity for Easy Handling
Its low viscosity in the range of 2,000 mPa·s (Brookfield viscometer, spindle 2 at 2.5 rpm, 25 °C) makes the new binder easy to handle and process.

No Need for Plasticizers or Solvents
The low viscosity also leads to the benefit that no solvents or plasticizers are necessary in order to achieve easy workability.

Formulation With or Without Fillers
GENIOSIL® XB 502 can be formulated with a variety of fillers, in amounts up to 70%. The range starts from oxidic materials, such as aluminum trihydroxide, quartz flours or pyrogenic silicas, and extends to coated and uncoated chalks. Of course also unfilled formulations are feasible.

For Tin-Free Formulations
A tin catalyst is not needed, however – quite the opposite: adding an organo-tin compound is in fact counterproductive as it diminishes the shelf life of the formulation. For curing, the addition of an amine catalyst is recommended. GENIOSIL® GF 9 [N-(2-aminoethyl)-3-aminopropyltrimethoxysilane] and GENIOSIL® GF 95 [N-(2-aminoethyl)-3-aminopropyldimethoxysilane] have proven particularly advantageous here.

Fully Compatible with GENIOSIL® STP-E
GENIOSIL® XB 502 is fully compatible with GENIOSIL® STP-E 10, a conventional α-silane-terminated polyether grade. By blending these two hybrid polymers in a formulation, its properties can be modified in terms of viscosity, hardness and elasticity.

Little Tendency to Yellow
Transparent adhesives are essential in many applications, and also a rapidly growing consumer trend. They allow even inexpert users to bond materials without precisely positioned joints. Model formulations of the new binder GENIOSIL® XB 502 were subjected to tests on their phenomenological properties under weathering (see table below). The experiments indicate that transparent, non-yellowing formulations are feasible.

<table>
<thead>
<tr>
<th>GENIOSIL® XB 502 – Phenomenological Properties Under Weathering</th>
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</thead>
<tbody>
<tr>
<td>Before weathering</td>
</tr>
<tr>
<td>L*</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>Model</td>
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<tr>
<td>formulation 1</td>
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<tr>
<td>L*</td>
</tr>
<tr>
<td>formulation 2</td>
</tr>
<tr>
<td>L*</td>
</tr>
</tbody>
</table>

Color values of adhesives, applied to aluminum sheets, after artificial weathering (QVA/water). In the tests, the Delta E value (color difference at particular time intervals before and after weathering, according to ISO 12647 and ISO 13655) shows that the formulation has a constant appearance irrespective of the stabilizer. As shown in model formulation 1, an adhesive can be developed with only a slight yellowing tendency and is not considered perceptible according to the theory (Delta E < 2).

Formulation 1: 95.5% GENIOSIL® XB 502, 2.5% GENIOSIL® GF 9, 2.0% TINUVIN® 123
Formulation 2: 95.5% GENIOSIL® XB 502, 2.5% GENIOSIL® GF 9, 1.0% TINUVIN® 123; 1.0% HOSTAVIN® 3206
With GENIOSIL® XB 502 a high-class adhesive with excellent mechanics can be achieved by simply using some basic components:

### Model Formulations of GENIOSIL® XB 502

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Filled formulation</th>
<th>Unfilled formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>GENIOSIL® XB 502</td>
<td>50%</td>
<td>97.5%</td>
</tr>
<tr>
<td>Aluminum hydroxide (MARTINAL® OL 104)</td>
<td>47.5%</td>
<td>0%</td>
</tr>
<tr>
<td>N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (GENIOSIL® GF 9)</td>
<td>2.5%</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

**Shore hardness of cured formulations**
- 80 D (Filled) 60 D (Unfilled)

**Tensile lap-shear strengths** in N/mm² after 7 days
- Beech/Beech: 11.9 (Filled) 10.5 (Unfilled)
- Aluminum/Aluminum: 8.8 (Filled) 4.8 (Unfilled)

### GENIOSIL® XB 502: Advantages at a Glance

**Formulator advantages:**
- Based on α-silane technology, therefore:
  - No tin catalysts needed
  - Long shelf life
  - No hazardous substance classification
  - Great formulation latitude

Low viscosity, therefore:
- Easy handling and dosing
- Fast compounding process

Water resistant products for wood bonding complying durability classes D1 to D4 (DIN EN 204)

No need for special (e.g. aluminum) cartridges

Good compatibility to GENIOSIL® STP-E for tailor-made adhesives

**End-user advantages:**
- One-part system
- Isocyanate and solvent-free adhesives
- Transparent + filled adhesives feasible
- Fast strength build-up
- No bubbling
- Outstanding resistance to color change
- Excellent adhesion to wood and non-porous substrates like metal, glass and ceramic without primer
ENJOY NEW FORMULATION FREEDOM
Besides its easy handling, GENIOSIL® XB shows high compatibility with many fillers and other α-silane-modified polymers. This results in greater formulation scope and makes it easy to adjust properties.

Adjustment of Strength & Skin Formation Time

Formulations with the new silane-modified polymer produce high levels of adhesive strength. Starting with a model formulation based on 50% polymer and 50% aluminum hydroxide trihydrate (ATH), beech-to-beech bonds containing varying quantities of aminosilane (GENIOSIL® GF 9) were investigated (Figure 4).

The studies showed that high adhesive strength can already be achieved with low quantities of aminosilane, and that adding more aminosilane does not impact adhesive strength, which remains virtually constant.

In contrast, the catalyst quantity used has a substantial impact on skin-formation time, which can be set at between 20 and 120 minutes by adjusting the quantity of catalyst used. Adhesive manufacturers can thus adjust the curing rate by changing the catalyst content, without affecting the adhesive strength.

Additionally curing can be accelerated even further by adding an amine like 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU), which has a strong catalytic effect (Figure 5).
Bonding Performance: Use of Different Fillers
The new binder can be formulated with many different fillers. The figure below illustrates the tensile lap-shear strength of beech-to-beech bonds.

Resistance to Chemicals
Chemical resistance tests showed that cured formulations based on the new silane-modified polymer are resistant to many solvents, acids and alkalis, but that they do swell in tetrahydrofuran, toluene and methyl ethyl ketone (with yellow-brown discoloration in the case of MEK).

Modification of Elasticity and Viscosity
GENIOSIL® XB 502 is fully compatible with GENIOSIL® STP-E 10, a conventional α-silane-terminated polyether grade. By blending these two hybrid polymers in a formulation, its properties can be modified and adjusted in line with requirements. Adding GENIOSIL® STP-E 10 increases elasticity and reduces the hardness of the crosslinked compound. Depending on the substrates to be bonded, this enables considerable control of adhesive strength.

To attain high lap-shear strengths of wood bonding – also after hot water storage – pure formulations of GENIOSIL® XB 502 are recommended. Whereas for bonding of metals like aluminum high values are achieved by making the adhesive more flexible through mixing GENIOSIL® XB 502 with GENIOSIL® STP-E 10 in a ratio of 3:1 (see page 11).

Figure 6: GENIOSIL® XB 502 Lap-Shear Strength Beech/Beech

Filler selection and its effect on adhesive strength, illustrated here by the tensile lap-shear strength of beech-to-beech bonds after seven-day dry conditioning of the bonded test pieces at room temperature. The formulations contained GENIOSIL® XB 502 and a filler in a 1:1 ratio; the content of the GENIOSIL®GF 9 catalyst was 1.5%.
Hardness and viscosity can be adjusted by mixing GENIOSIL® XB 502 with GENIOSIL® STP-E 10.

<table>
<thead>
<tr>
<th>Mixing Ratio</th>
<th>Unfilled Formulations</th>
<th>Filled Formulations</th>
<th>Lap-Shear Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GENIOSIL® XB 502</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 : 1</td>
<td>GENIOSIL® XB 502</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 : 1</td>
<td>GENIOSIL® STP-E 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 : 3</td>
<td>GENIOSIL® STP-E 10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hardness and viscosity can be adjusted by mixing GENIOSIL® XB 502 with GENIOSIL® STP-E 10.
EXPLORE A VAST FIELD OF APPLICATIONS

Sandwich Paneling*
Non Structural Bonding**
Structural Bonding
Assembly Adhesive
Automotive, Truck & Rail
Natural Stone

* Kindly provided by Weiss-Chemie + Technik GmbH & Co.KG
** Kindly provided by UNILUX AG
GENIOSIL® XB is suitable for numerous applications. From wood adhesives to systems for high strength bonding of dissimilar materials. What’s more, adhesives with thermal stability are also achievable.
GENIOSIL® XB 502
FOR WOOD ADHESIVES

Whereas D4 compliant adhesives had been the domain of PVAc, EPI and Polyurethane Systems GENIOSIL® XB 502 now offers an alternative for the formulation of wood adhesives.

Comparison of Technologies for Wood Adhesives:

PVAc
These adhesives are produced by polymerization of polyvinylacetate. They are commonly used as D3 adhesives.

EPI
EPI-adhesives are dispersion based adhesives whereas the polymer base can vary. They are solvent-free but need a relatively large amount of isocyanates (mostly MDI) for crosslinking to achieve high water and thermal stability. Due to their excellent mechanics they are used for D1 – D4 applications and beyond e.g. for conservatories.

Polyurethane
Polyurethane adhesives are used when extraordinary stable and waterproof bonding is desired. PU-adhesives ensure good adhesion to wood yet a multitude of other substrates. However they also crosslink via isocyanates (MDI).

SMP
Silane-modified polymers crosslink without isocyanates. Still, up to now, they could not be used to formulate DIN EN 204 compliant wood adhesives. With GENIOSIL® XB 502 this is now possible for the first time.

| Classification of Non-Structural Wood Adhesives According to DIN EN 204 |
|---------------------------------|----------------------------------------------------------------------------------|
| **Durability classes** | **Examples of climatic conditions and fields of application** |
| D1 | Interior, in which the moisture content of the wood does not exceed 15%. |
| D2 | Interior with occasional short-term exposure to running or condensed water and/or to occasional high humidity provided the moisture content of the wood does not exceed 18%. |
| D3 | Interior with frequent short-term exposure to running or condensed water and/or to heavy exposure to high humidity. Exterior not exposed to weather. |
| D4 | Interior with frequent long-term exposure to running or condensed water. Exterior exposed to weather but with protection by an adequate surface coating. |

Figure 7: Formulations Based on GENIOSIL® XB 502 Exceed the Requirements of DIN EN 204 and Watt 91

Lap-shear strength determination of beech-to-beech bonding displays wood splintering.
Today, many adhesive bonds are used in applications that must withstand high temperatures. For example, resistance up to 100 °C is already state-of-the-art for formulations based on GENIOSIL® STP-E.

There are many examples of applications with such requirements, ranging from adhesive bonds in automotive applications to window construction. Studies on the new GENIOSIL® XB 502 binder have shown that, with suitable additives, continuous service up to 150 °C is possible (Figure 8).

Together with the possibility of bonding different substrates, such as glass, metal, ceramics or even modern materials such as carbon-fiber-reinforced composites, this opens up entirely new applications for adhesives based on silane-modified polymers. Extending from container construction, bonding sandwich panels, facade construction, through to applications in renewable energies.

Aluminum test pieces were bonded using a model formulation consisting of GENIOSIL® XB 502, 2.5% GENIOSIL® GF 9 and a stabilizer in various concentrations. The test pieces were first conditioned for 21 days at room temperature, and then for > 25 days at 150 °C. One surprising finding was that the tensile lap-shear strengths retained two-thirds of their initial measured values where conventional hybrid systems would have disintegrated after just a few days.

High tensile lap-shear strength values are obtained not only for bonding wood. A wide range of other substrates, such as glass, metal or ceramics, can also be perfectly bonded.
## Product Overview

### GENIOSIL® XB for High Strength Adhesives

<table>
<thead>
<tr>
<th>GENIOSIL® XB 502</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer</strong></td>
</tr>
<tr>
<td><strong>Reactive group</strong></td>
</tr>
<tr>
<td><strong>Flash point</strong></td>
</tr>
<tr>
<td><strong>Ignition temperature</strong></td>
</tr>
<tr>
<td><strong>Density at 20 °C</strong></td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
</tr>
</tbody>
</table>

### GENIOSIL® STP-E for Flexible Sealants and Adhesives

<table>
<thead>
<tr>
<th>GENIOSIL® STP-E 10</th>
<th>GENIOSIL® STP-E 30</th>
<th>GENIOSIL® STP-E 15</th>
<th>GENIOSIL® STP-E 35</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer</strong></td>
<td>silane-terminated polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reactive group</strong></td>
<td>α-system</td>
<td>α-system</td>
<td>γ-system</td>
</tr>
<tr>
<td><strong>Flash point</strong></td>
<td>ISO 2719</td>
<td>98 °C</td>
<td>107 °C</td>
</tr>
<tr>
<td><strong>Ignition temperature</strong></td>
<td>DIN 51794</td>
<td>390 °C</td>
<td>380 °C</td>
</tr>
<tr>
<td><strong>Density at 20 °C</strong></td>
<td>DIN 51757</td>
<td>1.0 g/cm³</td>
<td>1.0 g/cm³</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Brookfield, 25 °C</td>
<td>10.000 mPa s</td>
<td>30.000 mPa s</td>
</tr>
</tbody>
</table>
WACKER is one of the world’s leading and most research-intensive chemical companies, with total sales of €4.63 billion. Products range from silicones, binders and polymer additives for diverse industrial sectors to bio-engineered pharmaceutical actives and hyperpure silicon for semiconductor and solar applications. As a technology leader focusing on sustainability, WACKER promotes products and ideas that offer a high value-added potential to ensure that current and future generations enjoy a better quality of life based on energy efficiency and protection of the climate and environment. Spanning the globe with five business divisions, we currently operate 24 production sites worldwide. WACKER is represented by subsidiaries and sales offices in 29 countries in the Americas, Asia, Australia and Europe. With a workforce of 16,300, WACKER sees itself as a reliable innovation partner that develops trailblazing solutions for, and in collaboration with, its customers. WACKER also helps them boost their own success. Our technical centers employ local specialists who assist customers worldwide in the development of products tailored to regional demands, supporting them during every stage of their complex production processes, if required.

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All figures are based on fiscal 2012.
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