

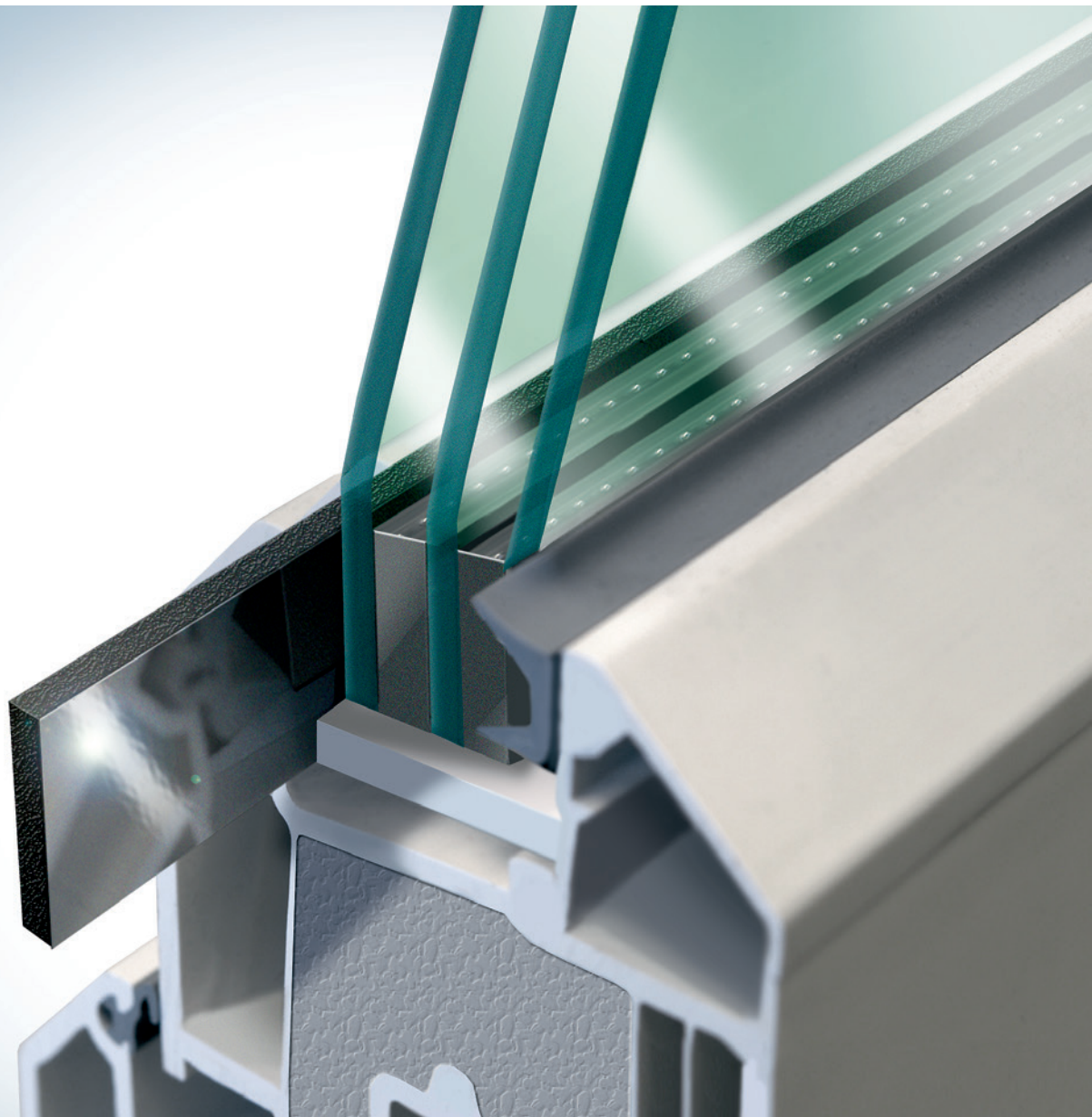
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ADHESIVES &
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NEW SILANE-TERMINATED POLYETHERS

Tear-Resistant and Highly Elastic Formulations



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For bonded joints and coatings under high dynamic loads, polyurethane systems are generally the technology of choice. Silane crosslinking can now also be used for these types of applications, thanks to a new class of modified silane-terminated polyethers.

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Silane-terminated polymers have been used as binders for sealants, adhesives, and coatings for over 30 years due to many reasons. They can, for example, be formulated into one-component, isocyanate-free products where, due to their low viscosity, solvents can be excluded. It is beneficial that the products cure without bubble formation even under unfavorable

weather conditions. Nowadays, many wood-flooring adhesives are based on silane-terminated polymers, as are several assembly adhesives and exterior waterproofing systems. In these kinds of applications, the elasticity of the cured materials and their wide adhesion profile are of particular importance.

Applications in which bonded joints or waterproofing membranes are exposed to high dynamic loads still remain the domain of polyurethane technolo-

gy. A large proportion of the adhesives used in the automotive or white goods industry are for example polyurethane-based, including waterproofing membranes for roofs, balconies, and patios. After curing, all of these industrial adhesives and coatings are highly elastic and have high tear and tensile strength. Minor damage as encountered in practice when exposed to extreme loads does not lead to the complete deterioration of the layer.

A new class of silane-terminated polyethers (Geniosil XT) yields, for the first time, binders that can be formulated, by silane crosslinking, to shear-resistant materials of high tensile strength which are both highly elastic and extremely tear resistant (Figure 1).

Alpha- and Gamma-Silane-Terminated Polyethers

All commercially available silane-modified polymers contain alkoxysilyl groups and are thus able to crosslink in the presence of moisture /1/. They differ in their organic structure, notably the manner the silyl groups are linked to the polymer backbone and the distance between the silyl groups and the backbone. In the case of silane-terminated polyethers (Geniosil STP-E), the silyl groups are coupled to the ends of

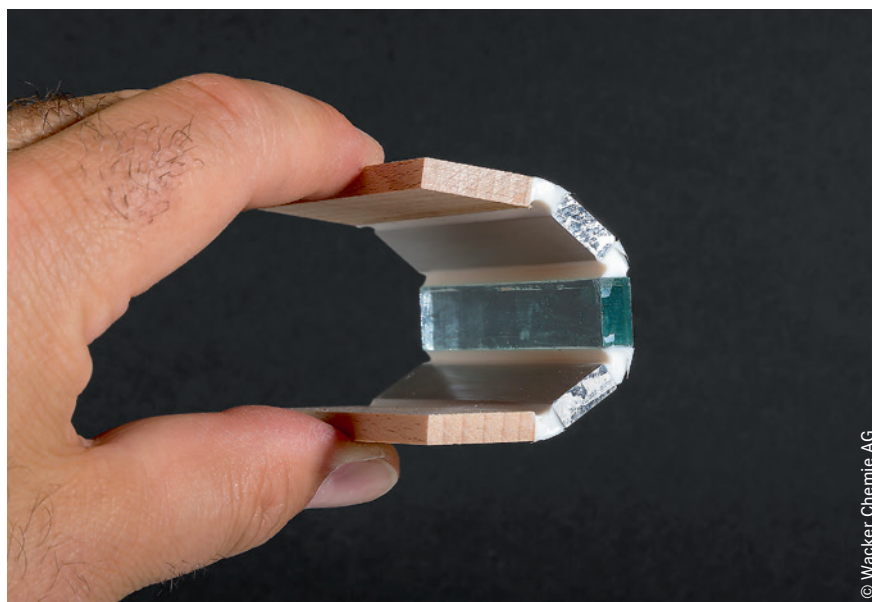


Figure 1: The bending test clearly illustrates the high flexibility of adhesives now possible using WACKER's new range of silane terminated polyethers.

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the polyether backbone via an alkylene unit and a urethane group (Figure 2). The alkylene unit can either be a methylene group, in which case it is an α -silane-terminated polyether, or a propylene group, in which case it is a γ -silane-terminated polyether.

The length of the alkylene unit influences the reactivity of the alkoxy silyl groups toward moisture /2, 3/. Formulations of α -silane-terminated polyethers cure rapidly without needing a tin catalyst; the presence of a catalytic primary amino compound will suffice to kick off the catalytic reaction. In the case of γ -silane-terminated polyethers, however, a tin catalyst or a strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is always required.

Both types of silane-terminated polyethers have specific advantages. γ -Silane technology yields products that feature particularly high elastic recovery. In the case of α -silane technology, the wide formulation latitude is very much in the forefront by virtue of the fact that formulations require no tin catalyst. This allows the use of ester-based plasticizers, for example, since in the absence of the tin catalyst there is no risk of ester hydrolysis. There is also a positive impact on the shelf life of the formulations. Furthermore, the absence of organotin compounds is equally beneficial for environmental and health reasons.

Modification of Silane-Terminated Polyethers

The STP-E polyethers that have been available since 2005 can achieve tensile strength values of up to 3 N/mm² and elongation-at-break data of up to around 600%. These polymers thus meet elastic bonding and sealing requirements. However, it is by no means possible to formulate exceptionally hard or tear-resistant adhesives using standard STP-E grades. To obtain these properties, new silane-terminated polymers had to be developed.

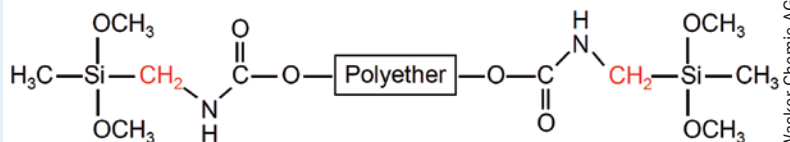


Figure 2: Structure of an α -dimethoxysilane-terminated polyether. The terminal silyl groups (silane end groups) are each connected to the polyether backbone via a methylene group (red) and a urethane group. The N atom attachment of the urethane groups is at α to the Si atom of the end group in each case.



Figure 3: Schematic representation of the end-group modification concept. By selecting different silane modifiers, the properties of the polymer can be varied.

Development work led to the concept of end-group modification, which is illustrated schematically in Figure 3. Here, the polymers were optimized so as to have both a low viscosity as well as a high number of crosslinkable silyl groups per unit volume. In general, the silane end groups are modified using organosilicon intermediates developed specifically with this in mind.

The first α -silane-terminated polyether to be modified in this way was launched on the market in 2012 with the designation Geniosil XB 502. Silane crosslinking could now also be used for high-strength structural bonding /4/. In this case, silane modifiers that provide the end groups with methyl-dominated units were selected for the modification. Crosslinking yields a close-meshed, rigid network of siloxane and polyether segments. Formulations based on this hy-

brid polymer cure to form thermosets with low elongation-at-break values.

To broaden the application potential, the next step was to try to develop silane-terminated polyethers that achieve not only high strength values, but also demonstrate high elasticity. Here, it became clear that varying the organosilicon intermediate from a methyl-dominated structure to a phenyl-dominated one alters the mechanical properties of the cured silane-terminated polyether significantly.

Exceptionally High Tear Strength

With these findings, two new silane-terminated polyether grades were developed. One of the grades is based on α -silane technology (Geniosil XT 50), the other on γ -silane technology (Geniosil XT 55). Both are colorless, transparent liquids that are easy to process due

Formulation, concentrations in % (relative to the overall polymer content)			
Geniosil XB 502	75	-	-
Geniosil XT 50	-	75	-
Geniosil XT 55	-	-	75
Geniosil STP-E 10	25	25	25
Aminopropyltrimethoxysilane (Geniosil GF 96)	2.5	2.5	2.5
Diocetyl tin dilaurate	-	-	0,2
Mechanical Properties			
Elongation at break in % DIN 53504 (ASTM D412)	50	275	220
Tensile strength in N/mm ² DIN 53504 (ASTM D412)	12	6.7	6.3
Shore hardness DIN 53505-A-87	D 35	A 80	A 75
Tear strength in N/mm DIN ISO 34-1 C (ASTM D624 B)	20	35	37

Table 1: Basic formulations and mechanical properties of the cured materials. (Quelle: Wacker Chemie AG)

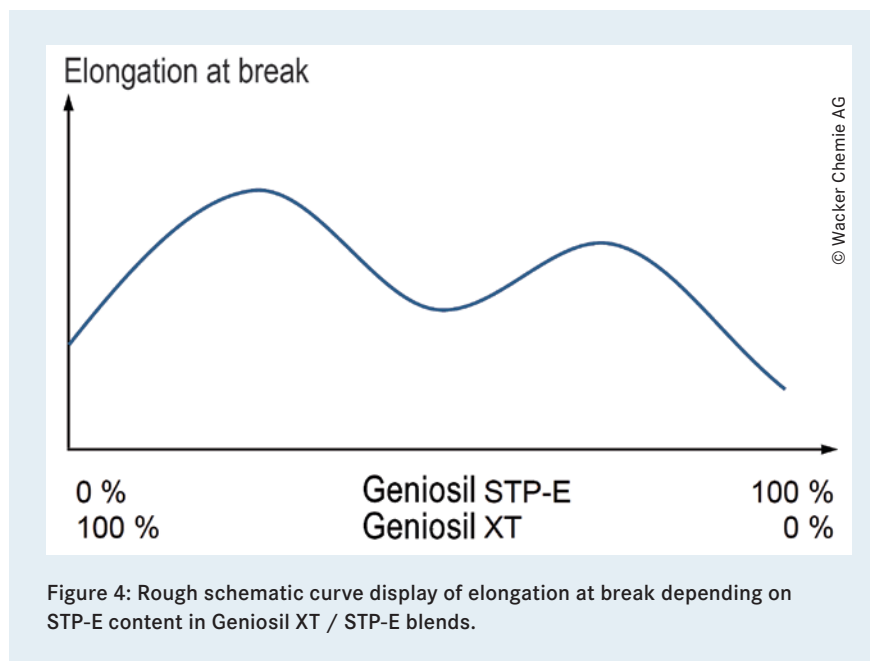


Figure 4: Rough schematic curve display of elongation at break depending on STP-E content in Geniosil XT / STP-E blends.

to their low viscosity (500 mPa·s and 1,200 mPa·s) without the added need for solvent.

Tests on the cured new grades show that, while the altered end-group modifiers see a reduction in the cohesive strength compared to Geniosil XB 502, the elongation at break has increased considerably (Table 1). What is more

striking and unusual for silane-modified polymers is the exceptionally high tear strength that the two new grades can achieve. The tear strength of the cured unfilled grades is – at the most extreme – a factor of almost 7 greater than for a silane-terminated polymer such as Geniosil STP-E10 (40 N/mm as opposed to 6 N/mm) and is thus in the range of poly-

urethane systems. To capture this special feature in the product name, the two new polymers have been designated XT (for extra tear resistant).

Furthermore, blending of the new polymers is decisive for the end properties of the cured sealant or adhesive. Figure 4 illustrates the properties of the new self-reinforcing polymers with data on mechanics of various blends that were cured using an aminosilane as the catalyst. The elongation at break initially increases with increasing amounts of STP-E, then reaches a peak, drops again and reaches a second peak with the addition of more STP-E. At the peaks, the elongation at break clearly exceeds the values achievable when using the new pure grades only.

The position of the two peaks depends greatly on the formulation and cannot be generalized, but must always be determined experimentally. In the lab, elongation-at-break values of almost 300% were measured with tear strength of over 35 N/mm. If the XT grades are to be used, a ratio of of 3:1 is a good start for formulation optimization.

As to the mechanical properties of the cured polymers, no notable difference could be determined between the α and the γ versions. Selection depends on the application. The use of a catalyst can be one criteria, for example. For coatings, it often makes sense to use a tin-free catalyst and hence use the α grade to avoid yellowing. Very good elastic recovery, on the other hand, is easier to achieve with the γ grade.

Use in Industrial Adhesives

To demonstrate the suitability of the XT grades as binder components in adhesives, a sample formulation with a γ -STP-E as the base polymer was selected. The aim was to obtain an adhesive with good elastic recovery, as is to be expected with formulations based on γ -silane-terminated polyethers. Accordingly, a blend containing Geniosil STP-

E 35 as the base with Geniosil XT 55 as an additive was screened. Additionally the plasticizer type was varied to establish its impact on properties. The resultant tests included a formulation described as SMP I (Table 2) containing a polypropylene glycol, SMP II a trimellitate and SMP III an acrylate. Table 3

References

- /1/ Pröbster, M., Silane-modified polyether sealants and elastic adhesives (Part I): Versatile backbones for high-tech sealants and adhesives. Adhesion Adhesives & Sealants 9/2009, 2–6
- /2/ Schindler, W., Fast and reliable. α -silane-terminated polyethers as moisture-curing base polymers for elastic adhesives. European Coatings Journal 4/2007, 98–105
- /3/ Stanjek, V., und Weidner, R., Alpha-Silanes. In: Proceedings of the conference “Silicon for the Chemical and Solar Industry X”, Ålesund-Geiranger/Norway, June 28–July 02, 2010, pp. 157–168
- /4/ Bichler, K., und Zander, L., Alpha-silanterminierte Polyether. Innovative Hybridpolymere für hochfeste Klebstoffe. Adhäsion Kleben & Dichten 9/2012, 32–36
- /5/ Crewdson, M., Outdoor weathering must verify accelerated testing. Technical paper presented at The Waterborne Symposium, 2008, New Orleans. <http://www.q-lab.com/documents/public/9d677625-3d76-47a0-8099-daf3b24290fc.pdf>
- /6/ Bichler, K., und Bauer, A., Schnell vernetzt. Neue Bindemitteltechnik für Flüssigabdichtungen, Farbe und Lack, 2013, 119 (4), 128–133

Formulation		
	Components	% by Mass
A	Geniosil XT 55	14
	PPG 2000	14.8
	Vinyltrimethoxysilane (Geniosil XL 10)	2
B	Hakuenka CCR S10	46.5
C	Geniosil STP-E 35	21
	Tinuvin B 75	0.5
	Dibutyltin dilaurate (TIB KAT 216)	0.2
	N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Geniosil GF 91)	1
Procedure		
Prepare A. Mix in B, followed by the components of C in the given order.		
Table 2: Test formulation SMP I. This silane-terminated-polyether-based formulation is a guide formulation for a highly elastic, tear-resistant adhesive. (Quelle: Wacker Chemie AG)		

demonstrates the influence of the plasticizer on the mechanical properties. The results stem from a benchmark test in which three formulations based on silane-modified polymers (SMP) were compared with three commercially available industrial polyurethane adhesives (PU I, PU II and PU III).

SMP and polyurethane technologies yield comparable mechanical properties. While the SMP formulations do not quite attain the same level of tensile strength

as the polyurethane-based adhesives, they clearly outperform them in terms of elongation at break. Such extremely high elongation values are particularly advantageous for bonded joints that are repeatedly exposed to high dynamic loads, as is the case for road and rail vehicles or white goods.

The adhesion profile of SMP formulations are superior to those of the polyurethane-based products (Table 4). Depending on the formulation – for exam-

Properties	Reference Products			Test Formulations		
	PU I	PU II	PU III	SMP I	SMP II	SMP III
Skin-over time in minutes	57	36	38	95	68	134
Elongation at break in %	583	305	404	713	328	587
Modulus of elasticity at 100 % elongation (E100) in N/mm ²	1.1	3.4	2.2	1.7	2.3	1.9
Tensile strength in N/mm ² (DIN 53504, S1 test specimen)	3.2	9.1	8	5.4	4	3.9
Hardness, Shore A	42	60	51	56	62	59
Tear strength in N/mm (DIN ISO 34-1 C)	15.7	21.9	32.5	31	15	28
Elastic recovery in % DIN EN ISO 7389 – aluminum	95	Not determined	Not determined	76	84	73

Table 3: Properties of Geniosil XT 55 adhesive formulations compared to the properties of commercially available polyurethane-based industrial adhesives. (Quelle: Wacker Chemie AG)

Substrate	Reference Products						Test Formulations					
	PU I		PU II		PU III		SMP I		SMP II		SMP III	
	A	B	A	B	A	B	A	B	A	B	A	B
AlMg1	-	-	-	-	-	+	-	+	+	+	-	-
AlMg, anodized	-	-	-	-	-	-	-	-	+	+	-	-
Copper	-	-	-	-	-	-	+	-	+	+	+	o
Zinc	+	+	-	-	-	-	+	+	+	+	-	-
Stainless steel	-	-	-	-	-	-	+	-	+	+	-	-
Steel, DC 04	+	o	-	-	-	-	o	-	+	+	-	-
Steel, DC 05, galvanized	+	+	+	+	+	o	+	+	+	+	+	+
Steel, DP 600	o	+	-	-	-	-	o	+	-	+	-	+
French concrete	o	o	-	-	-	-	-	-	-	-	-	-
Glass	+	+	+	+	+	+	+	+	+	+	+	+
Tiles	-	+	-	-	+	+	+	+	+	+	+	+
Beech	+	-	-	-	-	-	+	-	+	-	+	-
PMMA	-	-	-	-	-	-	-	-	-	-	+	+
PMMA, filled	-	-	-	-	-	-	-	-	-	-	+	+
ABS	-	-	-	-	-	-	-	-	-	-	-	-
Flexible PVC	-	-	-	-	-	-	o	o	-	-	-	+
Rigid PVC (transparent, Simona)	-	+	-	-	-	-	-	-	-	-	-	-
Polycarbonate	-	+	+	-	-	-	-	-	+	+	+	+
PS	-	-	-	-	-	-	-	-	-	-	+	+

Table 4: Adhesion to various substrates. Comparison of the SMP test formulations with commercially available polyurethane-based industrial adhesives (PU). The A columns give the adhesion after two weeks of dry storage, the B columns after two weeks of dry storage followed by two weeks of storage in water. The measurements were taken at room temperature. The color markings in the table specify the type of removal (green: cohesive, yellow: partially cohesive, and white: adhesive). (Quelle: Wacker Chemie AG)

ple on the plasticizer used – they adhere to many common materials without the need for priming. Unlike conventional polyurethane adhesives, they achieve adhesion to aluminum-magnesium alloys, copper, beech, polymethyl methacrylates and polycarbonate without primer.

Accelerated aging tests show that SMP formulations must always be stabilized against UV- and temperature-induced oxidative degeneration in order to obtain durable products. The choice of stabilizer and the amount used depend on the end use /5/. A blend of various stabilizers, as contained in Tinuvin B 75, can maintain the mechanical

properties of the test formulations in Table 3 at an average level of around 60% of their initial values after 2,000 h in a QUV-A test.

Overall, the test results prove that the two new silane-terminated polyethers allow the formulation of adhesives which are at least a technically comparable alternative to polyurethane-based industrial adhesives. They are superior to the isocyanate-crosslinked systems in two particular aspects. On the one hand, due to their low viscosity, they are easier to handle even at lower temperatures, and, on the other, their good adhesion profile provides greater reliability in bonding.

Use in Coatings

Polyurethane technology also dominates liquid coating materials as used to waterproof roofs, patios and balconies. The products cure to form solid materials that adhere well to the substrate and yield a joint- and seam-less waterproof membrane. As a rule, a nonwoven polyester fabric is incorporated during the application of the liquid waterproofing system to reinforce the membrane. If patios and roofs are to be sealed to retain their original appearance, transparent coatings are essential.

For some years now, silane-terminated polyethers have been used as binders in liquid waterproofing systems.

Properties	Reference Products			Test Formulations	
	PUR 1, transparent, without nonwoven	PUR 2, filled, without nonwoven	PUR 3, filled, with nonwoven	XT 1, filled, without nonwoven	XT 2, unfilled, without nonwoven
Shore hardness	D 32	A 60	D 20	D 45	D 36
Elongation at break in %	280	240	40	60	250
Tensile strength in N/mm ²	7.7	2.6	8.1	9.5	8.8
Tear strength (ASTM D 624 B-91) in N/mm	26	18.2	68	41	50
Skin-over time in minutes	120	85	Not determined	40	95
Water uptake after 28 h in %	Not determined	Not determined	Not determined	< 0.5	< 0.5
Viscosity in mPa·s	500	2500	Not determined	12000	800

Table 5: Comparison of the properties of liquid waterproofing systems based on Geniosil XT 50 (XT 1 and XT 2), processed without nonwovens, and commercially available polyurethane-based liquid waterproofing systems (PUR 1, PUR 2 and PUR 3). (Quelle: Wacker Chemie AG)

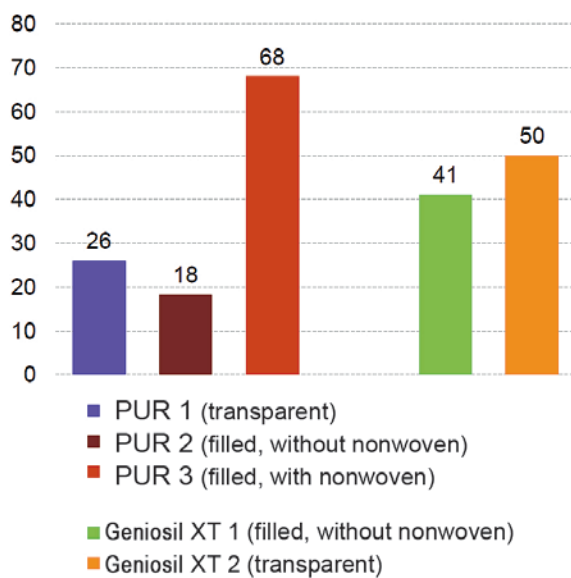
With the appropriate formulation, ETAG-005-compliant long-lasting waterproofing membrane products with good adhesion can be manufactured [6]. However, the silane-terminated polyethers known to date were unable to yield transparent

products, as these do not exhibit the required mechanical strength.

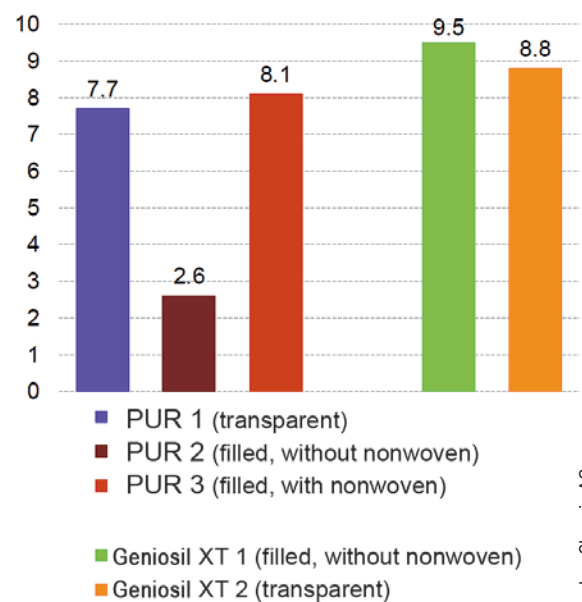
The new silane-terminated polyethers alter the situation in several respects, as illustrated in a benchmark test using the α grade (Table 5, Figure 5).

Two tin-free formulations were tested, one highly filled with aluminum hydroxide and calcium carbonate and the other unfilled (XT 1 and XT 2, respectively), both were processed without a nonwoven fabric. These test formulations

Tear strength (ASTM D 624 B-91) in N/mm



Tensile strength in N/mm



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Figure 5: A Comparison of Polyurethane and GENIOSIL® Formulations



Figure 6: Application of a transparent waterproofing membrane based on Geniosil XT 50.

corresponded to the second peak of the curve represented in Figure 4: they contained Geniosil XT 50 as the main binder and Geniosil STP-E 30 as an additive. A transparent liquid waterproofing system based on an aliphatic polyurethane (PUR 1) and a filled polyurethane-based liquid waterproofing system served as reference products; both are commercially available products. The latter was processed both without (PUR 2) and with (PUR 3) a nonwoven.

The test shows that unfilled α -grade formulations can yield transparent membranes that are not only highly elastic (elongation at break: 250%), but also have very high tear and tensile strength. With tear strengths of 50 N/mm, these kinds of coatings outperform commercially available, transparent liquid waterproofing systems based on aliphatic polyurethane. Unlike polyurethane systems, there is no risk of undesirable secondary reactions with water with such systems. They will cure in damp environments, unhindered, with no bubble

formation. Due to their low viscosity of 800 mPa·s, the unfilled formulations are pourable or can be applied by brush and roller (Figure 6).

A comparison of the filled formulations (PUR 2, PUR 3 and XT 1) shows that, even without nonwoven reinforcement, highly filled formulations of the α grade attain comparable mechanical properties as is the case where polyurethane-based liquid waterproofing systems are both filled and further strengthened with a nonwoven.

For surface coating formulations, a light stabilizer – such as Tinuvin B 75 – was determined necessary to achieve good aging resistance of the membranes; the concentrations to be used must be determined on a case-by-case basis.

Conclusion

The new silane-crosslinking Geniosil XT binders can be used in formulations for adhesives and surface coatings which, when cured, exhibit elastic and mechanical properties that are at least on

a par with those of commercially available polyurethane-based products. They outperform polyurethane-based products especially in terms of adhesion profile and handling.

It is now possible to benefit from the advantages of silane crosslinking in numerous applications hitherto closed to silane-terminated polymer use. The new polymers can now find application in formulations requiring high elasticity, outstanding tear strength and exhibiting good adhesion profile – for industrial adhesives exposed to high dynamic loads as well as for crackbridging coatings used as waterproofing membranes in the construction industry. ■

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