

High Strength Silane Terminated Polyethers

Introduction

Silane terminated polyethers (STPEs) were already introduced on the market around 40 years ago. The first commercial product, Kaneka MS Polymer™, was launched in 1978 in Japan, mainly for use in low modulus, elastic, construction sealants. Since the introduction of the first polymers continuously new STPE with improved or new properties were developed. To give some milestones.

In 1986 the blending of STPE with random silylated polyacrylates (silyl acryl modified polymers) or with epoxies was introduced. This blending technology opened new markets as the acryl modified polymers enhanced the UV-stability and weatherability and improved the adhesive properties. The epoxy blends combined the properties of the STPE, elasticity, with the properties of the epoxy resin, high strength and water resistance.

In 1997 and 2003 silane terminated polymers with an alternative backbone, polyisobutylene and polyacrylate, were developed and launched on the market. These polymers enabled better chemical and thermal resistance, gas tightness, etc..

Very recently, in 2012, based on the years of experience and combination of different technologies, Kaneka launched a new series of high strength MS Polymer™ in order to further expand the application field of STPEs.

High Strength MS Polymer™

The Kaneka high strength technology is two-fold, or based on silane acryl modified polymers or based on modification of the polyether backbone. In the high strength silane acryl modified polymers, polymers with different structure are combined in order to control the compatibility and Tg. During curing of the blend a change in compatibility occurs and a phase separation will happen between the polyacrylate and the polyether parts ending up with homogeneously distributed acrylic and ether domains. The acrylic domains will provide high strength and good adhesion to plastics, whereas the ether domains will give elasticity to the cured system. The second high strength technology by modification of the polyether backbone will lead to an increased number of branching points on the backbone which result in more entanglements and a denser polymer matrix after curing. The increased number of siloxane bonds will provide the higher strength. When blended with silane acryl modified polymers strength can even be increased to a level of more than 10 MPa (tensile strength at break). In figure 1, a schematic overview of the different sealant and adhesive polymer technologies is

given to show that with the new Kaneka high strength polymers an existing gap is closed and new opportunities are opened.

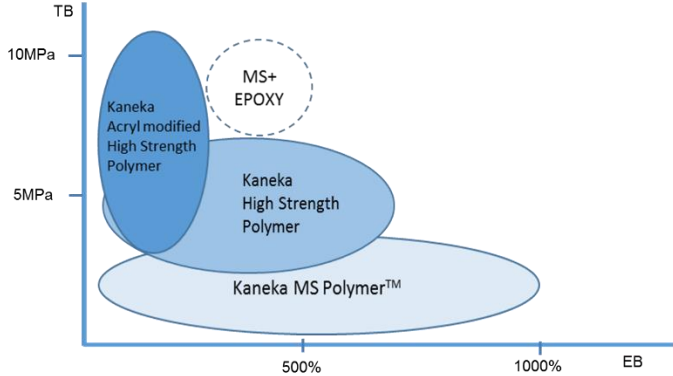


Figure 1 Schematic comparison of the different polymer technologies

In table 1 an overview of the properties of the new high strength polymers are given and shows that especially the polymers A-A, B-A and C-A with modified backbone and blended with polyacrylates combine very high strength, for STPEs, with retention of elongation. The properties of the polymers A, B, D and E with modified backbone without acrylate blending are more or less in line with standard STPE polymers, but it will be shown that by using the right formulation tools end products with increased strength can be formulated. The more standard silane acrylate modified polymers, MA451 and MA480, based on only phase separation technology have properties in between the polymers with modified backbone and with and without acrylate modification.

Type	Grade	Viscosity (Pa.s)	M50 (MPa)	Tb (MPa)	Eb (%)
Acryl Modified HS	Polymer A-A	50	0,62	4,94	153
	Polymer B-A	140	1,03	5,25	167
	Polymer C-A	150	0,63	8,46	168

Table 1 Overview of the properties of the different acryl modified high strength MS Polymers

Comparison with standard STPE

The different “standard” Kaneka MS Polymer™, dimethoxymethylsilane (DMS) and trimethoxysilane (TMS) terminated polyethers, were 1-to-1 compared in a general purpose sealant model formulation with the new high strength polymers. In figure 2, the results of the comparative testing are shown as a relative comparison of the mechanical properties.

Comparing the mid-modulus polymers, Kaneka MS Polymer™ S303H, Kaneka Silyl™ SAX520, Polymer B and the high modulus polymers, Kaneka Silyl™ SAX400, Kaneka Silyl™ SAX580 and Polymer D it is clear that the high strength polymers give an overall improvement of the mechanical properties, especially elastic recovery, tear strength and tensile strength at break.

The conclusion is that the TMS polymers improve elastic recovery combined with faster curing and the new high strength polymers give an overall improvement of the mechanical properties.

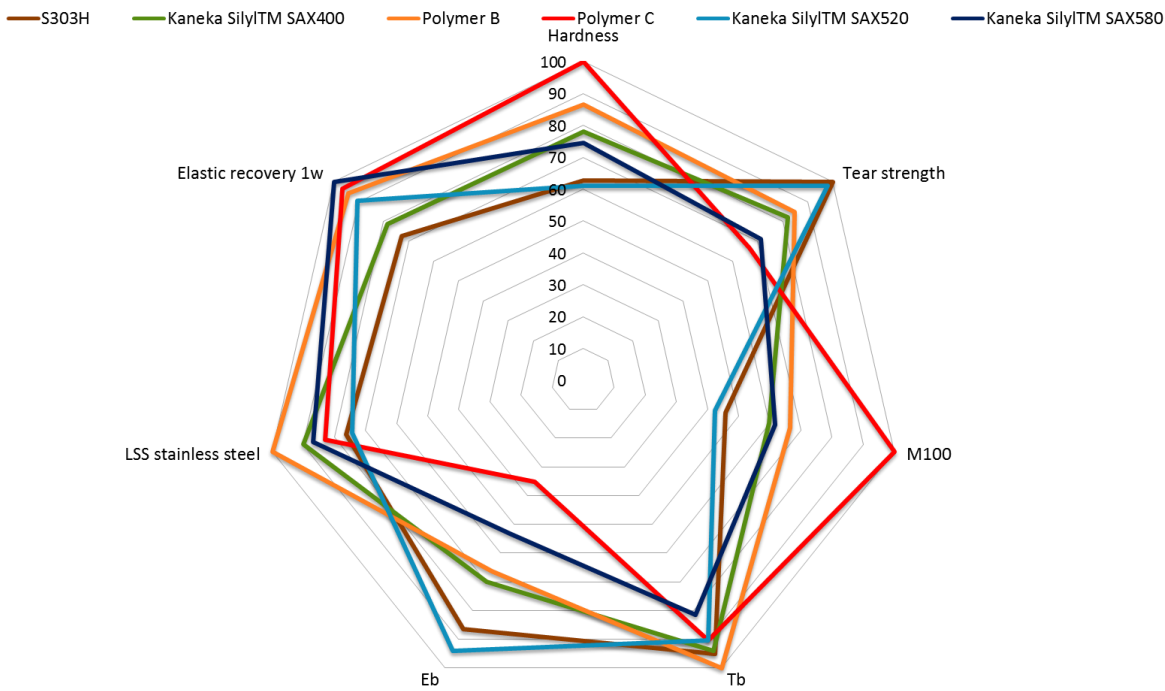


Figure 2 Comparison of the different Kaneka MS Polymer™ types in a general purpose sealant

Formulation examples

To show the capabilities of the new polymer grades a series of formulations were developed within Kaneka for applications up to now out of reach for standard STPEs.

As first was a do-it-yourself high strength or repair adhesive formulated by using an acryl modified polymer which gives phase separation or an acryl and backbone modified high strength polymer. In table 2 the general formulation is given with the initial properties. It can be observed that the viscosity and curing time remains almost constant independent on the selected polymer. More of intrest however is the increase in the modulus (M50) increasing from 2,2 MPa to 6,75 MPa and tensile strength at break (Tb) which increases from 4,2 MPa to 8,7 MPa. Additionally, the tear strength more than doubles to 20 kN/m by using the polymer C-A.

Property	Condition	Unit	TMS-MS	New Polymer	
			MA451	Pol F	Polymer C-A
Viscosity	5 s ⁻¹	Pa.s	139	116	164
	10 s ⁻¹		127	107	151
Skin Formation Time	23°C/50%RH	hh:mm	0:12	0:12	0:11
Residual tack	1d/7d 23°C/50%RH	-	7/7	7/7	7/7
Hardness	7d 23°C/50%RH	Shore A	61/64	68/74	69/72
Tensile properties by dumbbell shape	M50	MPa	2,20	5,80	6,75
	M100		-	-	-
	Tb		4,24	7,01	8,46
	Eb	%	92	59	64
Tear Strength	ISO-34-1-B	kN/m	6,7	10,3	20,0

Formula : MS Polymer (100)/Silica(18)/Silane (10)/Catalyst (1,25)

Table 2 Model formulation and properties of DIY repair adhesive.

In table 3 the general formulation of a (semi-)structural elastic adhesive is given with an overview of the standard properties. As mentioned before and shown in figure 1, the basic high strength polymers with only modification of the backbone did not have very high values for modulus and strength. In a formulation as shown in table 3 however, tensile strength can be up to 8,4 MPa in combination with a high elongation of 229%. These results show that it is possible to formulate (semi-)structural adhesives with the new Kaneka MS Polymer™-grades.

Property	Condition	Unit	Polymer B
Viscosity	5 s ⁻¹	Pa.s	417
	10 s ⁻¹		298
Skin Formation Time	23°C/50%RH	hh:mm	0:10
Residual tack	1d/3d/7d 23°C/50%RH	-	7/7/7
Hardness	1d/3d/7d 23°C/50%RH	Shore A	66/74/75
Tensile properties by dumbbell shape	M50	MPa	2,41
	M100		4,41
	Tb		8,42
	Eb	%	229
Tear Strength	ISO-34-1-B	kN/m	6,7

Formula : MS Polymer (100)/Filler (75) / Silica(20)/Silane (7)/Catalyst (2)

Table 3 Model formulation and properties of (semi-)structural adhesive

Improved properties with high strength polymers

Besides providing high strength the new polymers will also enhance other properties, such as improved weatherability and adhesion to plastics.

The weatherability of the basic high strength polymers was measured in a formulated product in a cyclic test with combination of carbon arc lamp and water spray. After a specific period of time the number of cracks (Q) were counted and the size of the cracks (S) was evaluated and given a score from 0 (good) to 5 (bad) and then multiplied the number and score for the size of the cracks (QS). In table 4 the tested formulation and weatherability results are shown. With the standard dimethoxymethylsilane terminated polymer Kaneka Silyl™ SAX350 after 600 hours exposure a lot of small cracks are formed which keep growing in function of exposure time. With the basic high strength polymer B a smaller number of small cracks are formed after 900 hours. At longer exposure times no more cracks are formed and the existing cracks do not grow. With Polymer A even after 1320 hours of exposure no cracks are formed. It is obvious that by using the new high strength polymers weatherability significantly increases and will result in improved heat/water resistance.

In the same table 4 are also elastic recovery results shown. The test piece was elongated 100% for 24 hours and then released, the recovery was measured after 1 hour and 24 hours. A very high elastic recovery, up to 95%, could be observed with the new polymers.

Another property which was evaluated is the adhesion to different types of plastics, such as hard PVC, fibre reinforced polyester (FRP), polycarbonate (PC), polystyrene (PS), polymethylmethacrylate (PMMA) and ABS. A plastic adhesive model formulation was taken in which the polymer was 1-to-1 replaced and Kaneka MS Polymer™ S303H (DMS), Kaneka

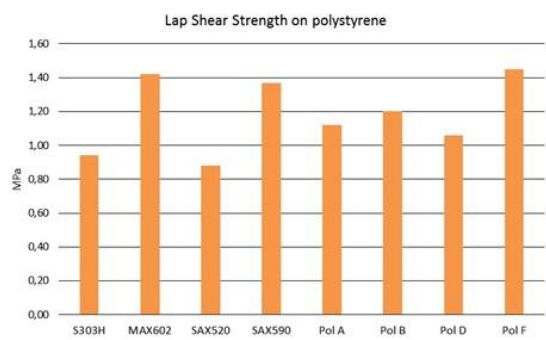
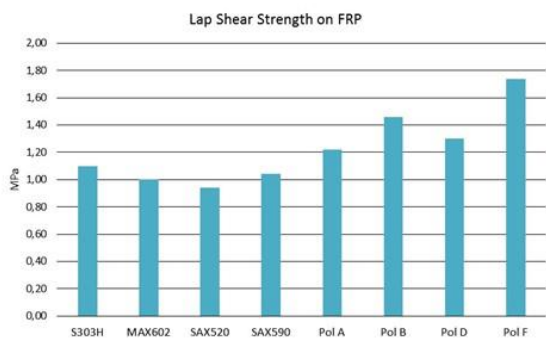
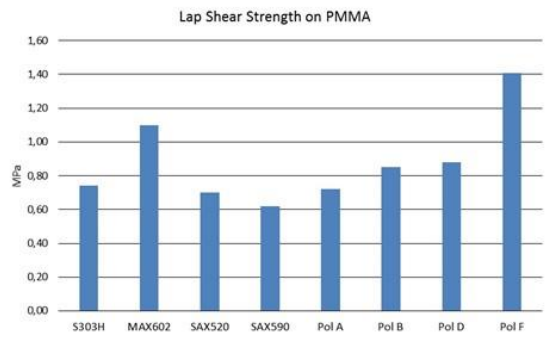
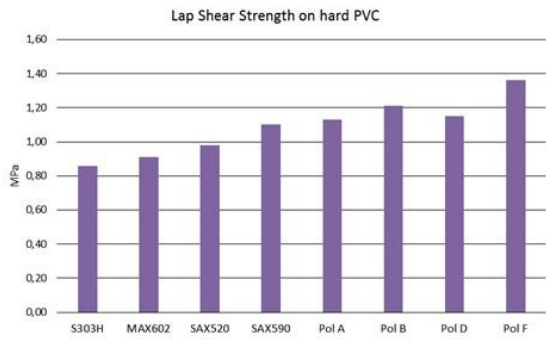
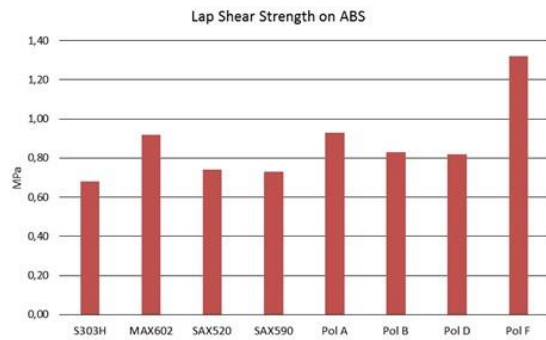
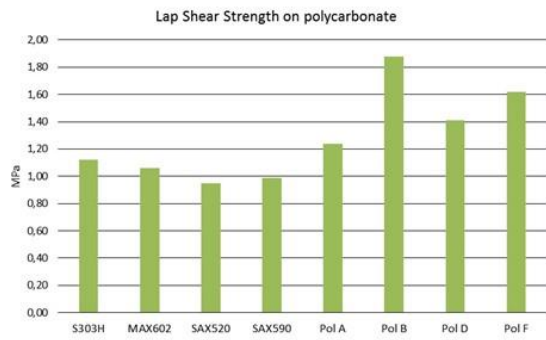
Silyl™ SAX520 (TMS), Kaneka Silyl™ MAX923 (standard acryl modified), Polymer A, B and D (basic high strength) and Polymer F (acryl modified high strength) were compared.

Property	Condition	Unit	New Polymer		DMS-MS
			Polymer A	Polymer B	Kaneka Silyl™ SAX350
Weatherability	600h	Q/S/QS	0/0/0	0/0/0	5/1/5
	900h		0/0/0	3/1/3	5/3/15
	1320h		0/0/0	3/1/3	5/4/20
Elastic recovery	1h	%	86	79	62
	24h		95	89	74

Formula : MS Polymer (100)/Plasticizer (55)/Filler(120)/Pigment (20)/Silane (5)/Catalyst (2)

Table 4 Weatherability and elastic recovery properties of the high strength polymers

In figure 3 the results of the lap shear measurement on the different plastics is shown. Out of all the figures it is obvious that Polymer F provides the overall highest adhesive strength and shows that with 1 polymer strong adhesion to different plastics can be achieved.



14d 23°C/50%RH, 0,2 mm thickness

SAX = Kaneka Silyf™ SAX

Fig 3 Lap shear strength on different plastics in plastic adhesive model formulation

General Conclusion

A new generation of high strength Kaneka MS Polymer™ grades were developed and it is shown that these polymers will improve the overall mechanical properties of the sealants and adhesives compared to the standard STPE. Higher strength and modulus can be achieved up to the level of the polyurethanes. On top also other properties as heat/moisture resistance, elastic recovery, adhesion to plastics, etc. have been improved. It has been shown that these polymers will open new opportunities, such as repair adhesives, (semi-) structural adhesives, etc..