

The future of moisture curable silane polymer technology

The continuation of a success story

In 1978, the first generation of silyl-terminated polyethers (hereinafter “STPE”), Kaneka MS Polymer™, was developed for Japanese construction sealant market. Since then, through continuous research, new generations of Kaneka MS Polymer™ have been developed to broaden the application fields towards adhesives and to enable the penetration into European and US markets.

Based on the more than 30-year experience, a toolbox of reactive technology has become available. By selecting the right tools, different Kaneka MS Polymer™ types can be designed depending on the required specifications or polymer properties. In Table 1, the general toolbox is shown which is built around three vertical blocks, 1) Polymer or Backbone Design, 2) Functionalization and 3) Combination/Modification of Polymers. Through a careful combination of the different tools, three new Kaneka MS Polymer™ technologies have been developed: 1) Low Viscosity Technology, 2) High Strength Technology, 3) Fast Curing Technology. These three new technologies will be discussed more in detail.

Polymer Design	Functionalization	Combination/Modification of Polymers
<p>Polymerization technology</p> <ul style="list-style-type: none"> ⇒ living anionic ⇒ living cationic ⇒ living radical 	<p>Functional groups</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---} \\ \\ \text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$ <p>DMS*¹</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{OCH}_3 \\ \\ \text{---Si---} \\ \\ \text{OCH}_3 \\ \\ \text{OCH}_3 \end{array}$ <p>TMS*²</p> </div> </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="text-align: center;"> ---CH=CH_2 <p>Alpha-olefine</p> </div> <div style="text-align: center;"> ---O---C(=O)--- <p>Acrylic olefine</p> </div> </div>	<p>Kaneka STPE*³ (Kaneka MS Polymer™)</p> <p>Kaneka STPIB*⁴</p> <p>Kaneka STPA*⁵</p> <p>Silylated acrylate Epoxy resin...</p>
<p>Molecular control</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\text{Si} \sim \sim \sim \text{Si}$ <p>High Mn</p> </div> <div style="text-align: center;"> $\text{Si} \sim \text{Si}$ <p>Low Mn</p> </div> </div>	<p>Location functionality</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\text{Si} \text{---} \text{Si}$ <p>Telechelic</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{Si} \\ \\ \text{---} \\ \\ \text{Si} \end{array}$ <p>Side chain</p> </div> </div> <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="text-align: center;"> $\text{Si} \text{---}$ <p>One Side</p> </div> </div>	<p>*1:Dimethoxymethylsilyl group *2:Trimethoxysilyl group *3:Silyl terminated polyether *4:Silyl terminated polyisobutylene *5:silyl terminated polyacrylate</p>
<p>Backbone</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{Si} \\ \\ \text{---} \\ / \quad \backslash \\ \text{Si} \quad \text{Si} \end{array}$ <p>Branched</p> </div> <div style="text-align: center;"> $\text{Si} \text{---} \text{Si}$ <p>Linear</p> </div> </div>		

Table 1 : Toolbox used to design new Kaneka MS Polymer™ technologies

1) Low Viscosity Technology

In the sealant and adhesive business, a lot of plasticizers are still used to reduce viscosity despite the impact on the properties of sealants or adhesives: mechanical properties, hardness,, will drop, and the risk of plasticizer's incompatibility with the system leading to migration of the plasticizer and leaving greasy markings on the adhered surfaces. Reactive diluents, low molecular weight Kaneka MS Polymer™, can overcome these issues. Two reactive diluents have been developed, one combining low viscosity with increased strength and hardness, through the design of a low molecular weight branched backbone and the other combining low viscosity with retention of the mechanical properties, through the design of a low molecular weight linear backbone.

In figure 1, lap shear strength build up according to DIN EN 14293 is shown.

Replacing PPG with Kaneka MS Polymer™ B (a branched reactive diluent), or with Kaneka MS Polymer™ C (a linear reactive diluent), the initial strength build-up becomes significantly faster and even the final strength will be positively influenced. As observed in figure 2, replacing the plasticizer with a reactive diluent does not end up in higher viscosity, but contrary in a lower viscous system with an improved workability. Also the hardness significantly increases from 60 Shore A to 80 Shore A by incorporating the reactive diluent in parquet (*wood floor) adhesive formulations.

Component		Formulation		
		1	2	3
Base polymer	Kaneka MS Polymer™ A	100	100	70
Reactive diluent	Kaneka MS Polymer™ B		50	30
	Kaneka MS Polymer™ C			50
Plasticizer	PPG	50		

Table 2 Polymer/plasticizer or reactive diluent ratio in the parquet adhesive formulations.

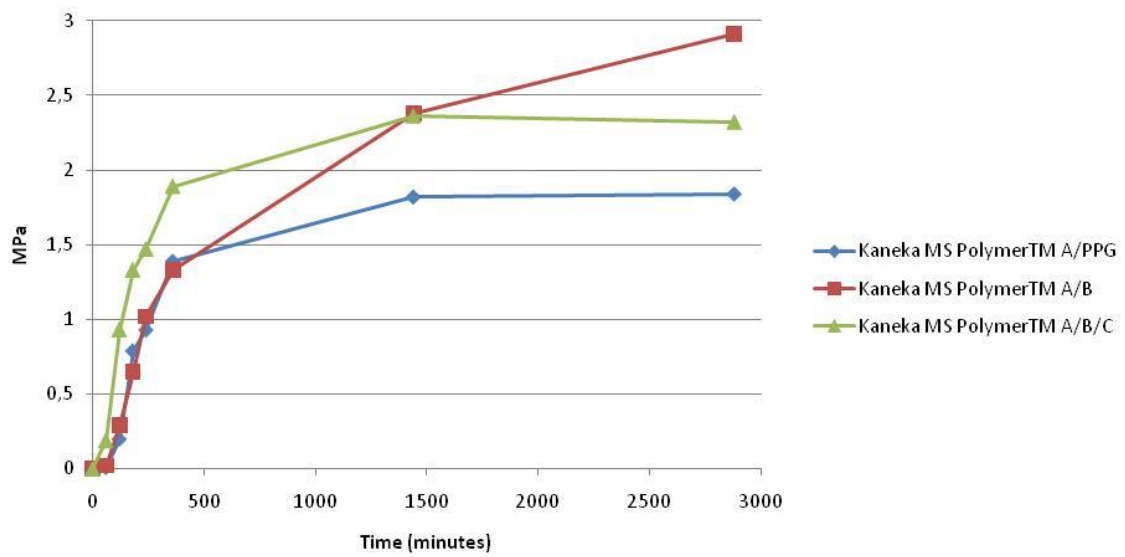


Fig. 1 Lap shear strength build-up in function of time according to DIN EN 14293

All polymers for this evaluation were made by Kaneka Co. All data were obtained at Kaneka's laboratory. No guarantee is provided.

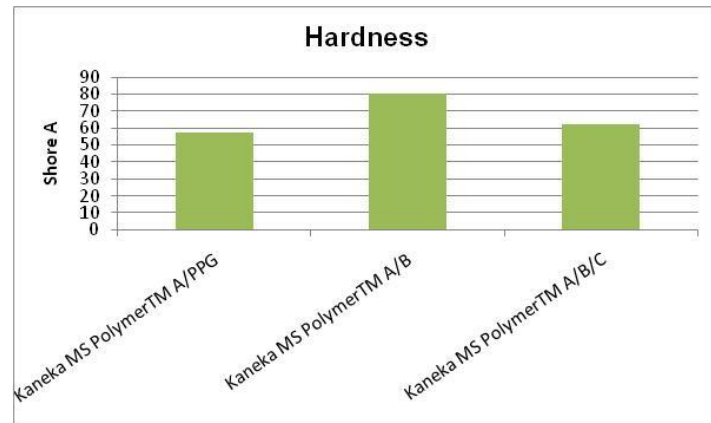
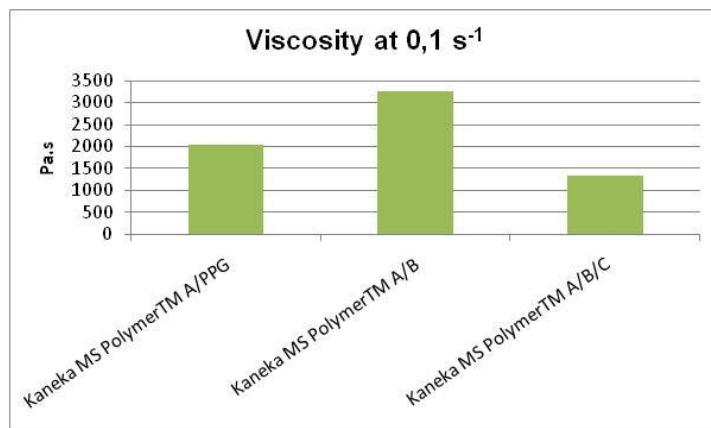
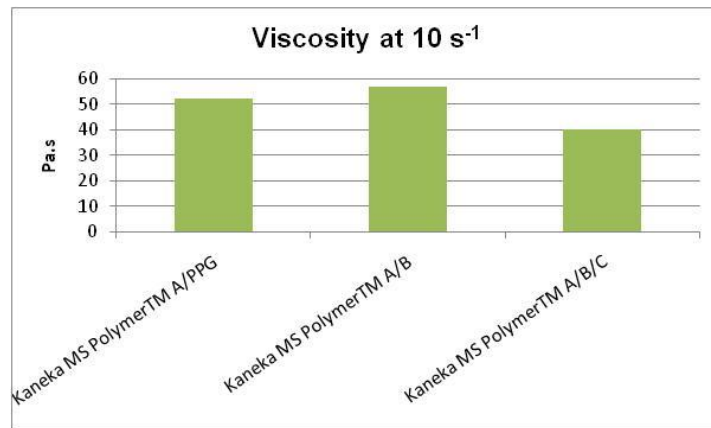


Fig. 2 Viscosity at low (0,1s⁻¹) and high (10 s⁻¹) shear and hardness of parquet formulation with plasticizer replaced with reactive diluent (polymer/plasticizer-reactive diluent ratio in table 2).

All polymers for this evaluation were made by Kaneka Co. All data were obtained at Kaneka's laboratory. No guarantee is provided.

By synthesizing a polymer with low molecular weight mono-functionality, a low viscous, low modulus, non-bleeding reactive diluent was developed. As shown in table 3 (partial), the replacement of standard plasticizers with Kaneka MS Polymer™ E (a mono-functional reactive diluent) works to formulate a non-bleeding sealant proven by paintability test. The plasticizer is not migrating, and the viscosity and mechanical properties are kept in line with the standard sealant. Moreover, a slight reduction of modulus 100% is observed which can help the formulation of sealants pass ISO 11600 25LM. Sealants using DIDP or PPG plasticizer are sometimes on the borderline of modulus for the ISO 11600 25LM and a slight decrease has been desired.

Component		Formulation			
		1	2	3	4
Base polymer	Kaneka MS Polymer™ D	100	100	100	100
Reactive Diluent	Kaneka MS Polymer™ E			55	27,5
Plasticizer	DIDP	55			27,5
	PPG		55		
Viscosity (2rpm)	Pa.s	341	413	432	368
Dumbbell property					
M100	MPa	0,42	0,41	0,35	0,38
Eb	%	990	945	1040	1055
Paintability	(Plasticizer migration)	D	C	A	A

A ↑ good
B
C
D ↓ bad

Kaneka MS Polymer™ D is a linear low modulus grade

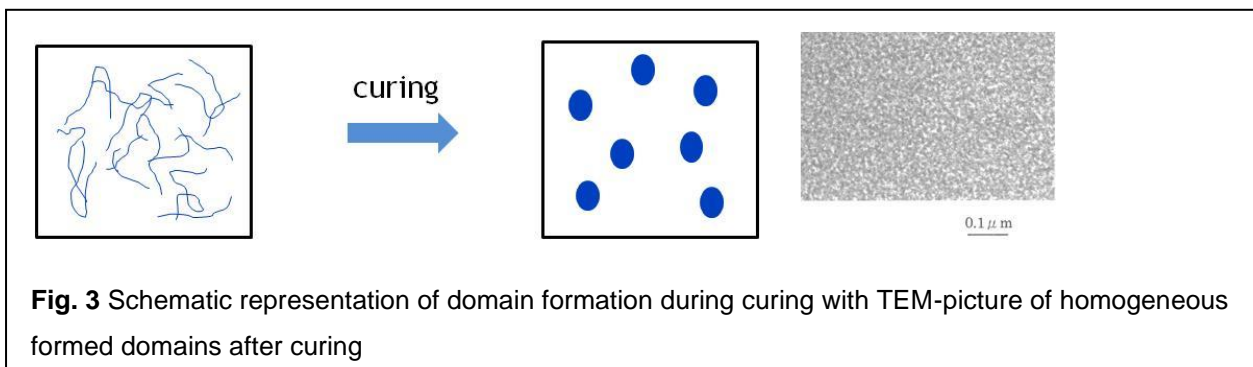
Kaneka MS Polymer™ E is a branched low molecular weight grade

Table 3 (Partial) Replacement of standard plasticizers with a reactive diluent results in a non-bleeding sealant.

All polymers for this evaluation were made by Kaneka Co. All data were obtained at Kaneka's laboratory. No guarantee is provided.

2) High strength technology

The second generation Kaneka MS Polymer™ modified with polyacrylate is able to control the morphology. By redesigning of the backbone and polymer structure, Tg of the polymer can be controlled and consequently the compatibility of the polymers before and after curing can be manipulated. As schematically shown in figure 3, both polymers are in non-cured state fully compatible and a phase separation occurs during curing. Acrylic domains are formed in a polyether matrix and these acrylic domains enhance the strength significantly. Moreover the acrylic domains will provide an improved adhesion to plastic substrates. In figure 4 and table 4, an overview of the progress made on the tensile strength increase of the Kaneka MS Polymer™ is shown. In comparison with a formulated adhesive based on a standard Kaneka MS Polymer™, the new polyacrylate modified Kaneka MS Polymer™ clearly shows the improvement steps under which the lap shear strength can reach a level of a commercial 1K polyurethane (hereinafter “PU”) adhesive. The recent further improvement of this technology resulted in a polymer with a tensile strength above 10 MPa. In table 5, some first preliminary results of the newly developed polymer are given. The lap shear strength on beech wood showed 12 MPa. Those high lap shear strength is important for formulation of high demanding adhesives, such as D4-adhesives which require DIN-EN 204 conformity.



Strength build-up

Conditions (Lap shear)	High strength adhesive of MS		Commercial 1K PU adhesive
	Kaneka MS Polymer™	New polyacrylate modified Kaneka MS Polymer™	
after 1 h	0,7 MPa	4,2 MPa	2,5 MPa
after 2 hrs	2,6 MPa	6,5 MPa	5,6 MPa

Tensile Strength after aging

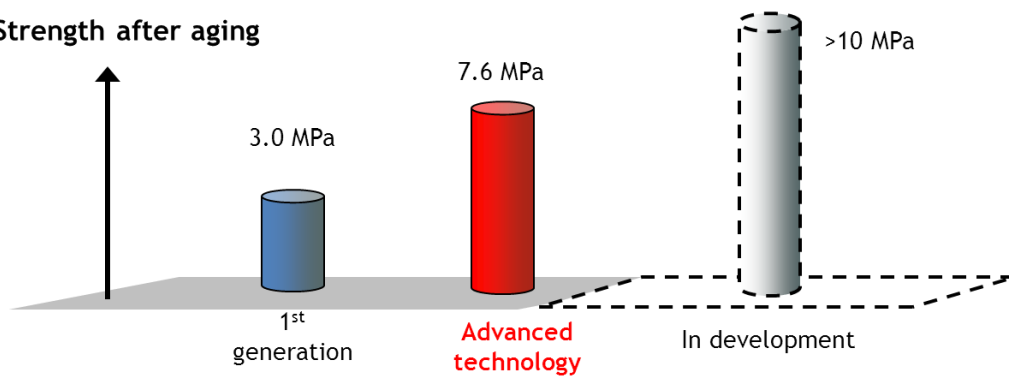


Table 4 Comparison of lap shear strength between the conventional Kaneka MS Polymer™, the new polyacrylate modified high strength Kaneka MS Polymer™ and a commercial 1K PU adhesive

Fig. 4 Schematic overview of the continuous progress made to develop Kaneka MS Polymer™ with higher tensile strength

All polymers for this evaluation were made by Kaneka Co. All data were obtained at Kaneka's laboratory. No guarantee is provided.

Polymer			New polyacrylate modified Kaneka MS Polymer™	In development
Skin formation time		min	25	20
Tensile properties by dumbbell shape 3d 23 °C /50% RH + 4d 50 °C	M50	MPa	3,3	5,3
	Tb		6,5	12
	Eb	%	80	80
Lap shear strength on beech wood 14d 23 °C, 50% RH			10,5	12

Table 5 Comparison of the new acryl modified high strength Kaneka MS Polymer™ with the increased strength polymers which are in development.

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3) Fast Curing Technology

Modification of the silane functional group is another tool to improve the properties of the silane-terminated polyethers. The current market trend requires adhesives with very fast strength build-up and faster curing. Drawback of these systems is however that most of these adhesives lack in elongation or elasticity. The first generation of Kaneka MS Polymer™ with the dimethoxymethylsilyl end groups (hereinafter "DMS-MS") has an excellent elastic behavior, but are relatively low in reactivity. Faster curing systems were later developed by replacing the dimethoxymethyl silyl group with trimethoxysilyl groups, as consequence that elongation dropped, certainly with the silylated polyurethane (hereinafter "SIPU") types. The next step was the development of very fast curing systems, such as the α -type SIPU's, which keeps the inherent low elongation, resulting in more brittle products.

Recently a Kaneka MS Polymer™ with a new type of silane functional group incorporated, has been developed by Kaneka and it shows very fast curing speed while keeping the similar elastic behavior of DMS-MS. The Kaneka MS Polymer™ having such a fast curing silane group is called "Fast-Cure-MS" herein after. Figure 5 demonstrates the lap shear strength build-up and in Figure 6, the strength-strain curves of the different polymer systems are shown. The lap shear strength behavior shows that the standard DMS-MS system using tin catalyst slowly picks up in strength, while the strength build-up is obviously improved with the

trimethoxysilyl type Kaneka MS Polymer™ (herein after “TMS-MS”) systems using tin catalyst. The α -type SIPU with non-tin catalyst is comparable to TMS-MS with tin catalyst in terms of strength build-up speed. This type of strength build up behavior can now be achieved with the newly developed Fast-Cure-MS system using the same type of non-tin catalyst.

On the other hand the strength-strain curves clearly show in figure 6 that the α -type SIPU and TMS-MS systems are more rigid and have a limited elastic behavior. On the contrary, the Fast-Cure-MS show a distinct elastic behavior, comparable to the DMS-MS systems.

Thus, Fast-Cure-MS polymer is a new fast curing polymer having high elasticity.

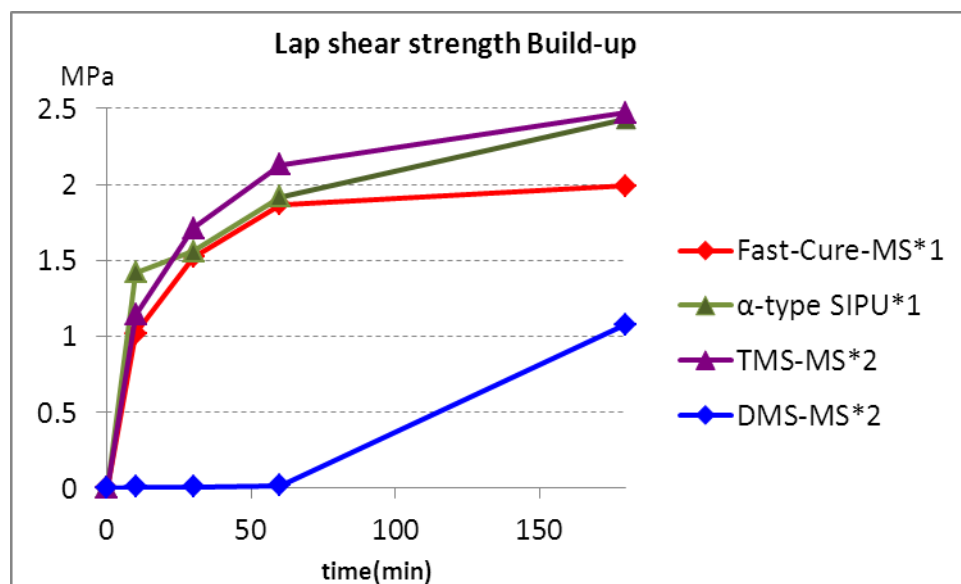


Fig.5 Lap shear strength build-up of the different polymer technologies in comparison with the new Fast-Cure-MS.

All Kaneka MS Polymer™ for this evaluation were made by Kaneka Co. All data were obtained at Kaneka’s laboratory and no guarantee is provided.

Test condition: Test piece was aluminum plates and made at 23°C and 50%RH. Adhesion area was 25mm*25mm and thickness was 100 μ m. Lap shear strength was measured in each set after taking 2 minutes as open time and sticking together .

*1.Curing catalyst was a phenyl guanidine. *2. Curing catalysts were organotin compounds.

Strength-Strain Curve

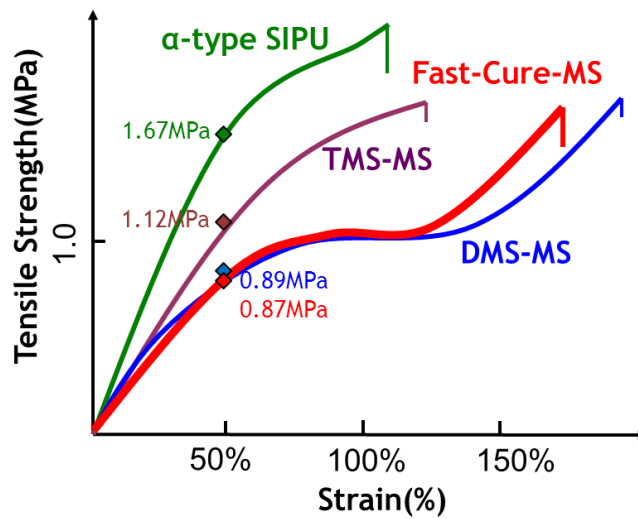


Fig.6 Strength-strain curve of the different polymer technologies in comparison with the new developed Fast-Cure-MS.

All Kaneka MS Polymer™ for this evaluation were made by Kaneka Co. All data were obtained at Kaneka’s laboratory and no guarantee is provided. The test piece was dumbbell shape of JIS K6301-3 with 3 mm thickness. The strain test speed was 200mm/min.

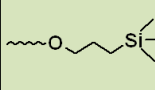
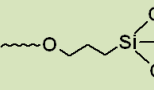
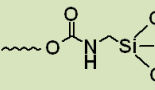
				Fast-Cure-MS
	DMS-MS	TMS-MS	α-type SIPU	
Reactivity (Skin formation time)	40 min	10 min	5 min	5 min
Strength build-up	STD	faster	faster	faster
Modulus (M100)	0.9 MPa	1.1 MPa	1.7 MPa (brittler)	0.9 MPa
Elongation (Eb)	200%	120%	110%	170%

Table 6 Comparison of the different polymer technologies in comparison with the new developed Fast-Cure-MS.

All Kaneka MS Polymer™ for this evaluation were made by Kaneka Co. All data were obtained at Kaneka’s laboratory and no guarantee is provided.

Conclusion

As shown in all the data, it is obvious that when an extended, well-equipped toolbox is available, combining of the different tools can lead to a flexible development of new polymer technologies whenever the market or customers ask for it. In order to cope with the current and future market demands, three new silane-terminated polymer technologies have been developed, low viscous reactive diluents, polyacrylate modified high strength polymers and fast curing elastic polymers.

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