MS Polymers in "Hybrid" Sealants

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Introduction

"Hybrid" sealants are of increasing interest because they can be formulated to provide the best properties of two or more families of polymeric materials while limiting their individual inherent weaknesses. For example, a polyether or a polyurethane polymer can be terminated with silyl groups (related to silicone polymers) to yield a high performance sealant having many of the beneficial characteristics of both polyurethanes and silicones without many of the disadvantages.

There are two main types of hybrid sealants: silyl-modified polyethers (known as MS polymers) and silyl-modified polyurethanes (known as SPUR polymers). They have closely associated chemistry and many common features. Because of the similarity of their polymer backbones, collectively these polymers are sometimes referred to as silyl-terminated oligomers. The main application for these materials is as sealants in the building and construction industry; however, other possible applications exist.

Hybrid sealants are claimed to combine the strength of polyurethanes with the weathering resistance of silicones. In addition to their high performance properties, these sealants are achieving popularity due to their solvent-free and isocyanate-free nature and due to their formulation versatility that allows the customization of viscosity and early strength development for various applications.

This article reviews the advantages and disadvantages of silylated polyether (MS polymers) when used in sealant formulations. This type of sealant is also sometimes referred to as modified urethane, modified silicone (MS), hybrid, or silyl terminated polypropylene oxide. Such synonyms often lead to confusion.

Trends in Construction Sealants

Sealants have grown in sophistication in recent years as the markets have grown more demanding. The emergence of new materials has spawned a range of sealant types as varied as their applications.

Sealants cover a wide range of materials, from low cost oil and butyl based mastics, for use around doors and windows, to considerably more costly one and two part polyurethanes and silicones used to seal joints in high rise structures. In between is a range of other materials, all with their own unique characteristics and preferred applications.

The anemic new home construction market has had an adverse affect on the sealant markets in a generally sagging economy. However, there is a trend to higher performance sealants due to recent regulations resulting from hurricanes, floods, mold, and other natural events. Impediments to market growth are the generally fragmented nature of the industry and lack of consistent standards for differentiating sealants. Another is the rising cost of raw materials and the increasing number of environmental regulations regarding solvent emissions, out-gassing, and toxicity.

Conventional "High Performance" Sealants

Polyurethane and silicone sealants are often referred to as "high performance" sealants in that they provide significant adhesion, movement capability, and durability. However, even these adhesives have certain disadvantages that can limit their use. Comparison of the common properties of these sealants is shown in Table 1.

Table 1: Comparison of Properties for Polyurethane and Silicone Construction Sealants

Property	***Silicone***	***Polyurethane***
Recovery from stress	++	++
UV resistance	++	+
Cure rate (one component sealant)	++	- to ++
Low temperature gunnability	++	-
Tear resistance	-	++
Cost	-	++
Paintability	--	++
Available in colors	-	++
Unprimed adhesion to concrete	-	++
Resistance to hydrolysis	++	-
Non-bubbling	++	-
Self-leveling formulations	-	++

Scale: -- very poor; - poor; + moderate; ++ good

Although silicone and polyurethane sealants account for nearly 51% of the U.S. sealant market, hybrid construction adhesives have increased in prevalence due to their many advantages and recent improvements in performance. As a group, hybrid sealants represent only about 9% of the market by volume and MS sealants represent only 1.6% although they are growing faster than their more conventional counterparts. MS sealants are considered to be competitively priced with polyurethanes and oxime-cured silicones. The MS polymers have found applications mainly in sealants although they are also being used in adhesives that have high tack (acrylic modified MS) and excellent toughness and flexibility (MS-epoxy blends).

Although the use of MS sealants has been relatively slow to develop in the U.S. and European markets, they are the most used type of sealant in Japan since their introduction nearly 30 years ago. MS sealants were originally developed to solve some of the bleeding and staining issues that occur with highly plasticized sealants. With continuous improvements in weatherability, MS sealants have taken shares from both the urethane and the silicone sealant markets.

MS Polymer Characteristics

The structure of an MS polymer consists of a polyether backbone and silane terminal functionality (Figure 1). The MS polymer is prepared from high molecular weight polypropylene oxide. It is end capped with allyl groups, followed by hdrosilylation to produce a polyether end-capped with methyldimethoxysilane groups.

Figure 1: MS polymer structure.

$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ CH_3O - & Si & - \text{Polyether} - & Si & - OCH_3 \\ & CH_3 & & CH_3 & \end{array}$$

It does not have urethane, urea, or other functional groups that are typical in polyurethane sealants. MS polymer’s polyether main chain provides low viscosity, low glass transition temperature, flexibility over a wide temperature range, and low color and odor. Since the main chain does not contain any highly cohesive segments, these polymers do not generally need solvent nor plasticizer.

Several types of MS polymer are commercially available. The leading supplier is Kaneka in Japan. Linear MS polymers produce a very soft, low modulus sealant with superior workability and adhesion. Slightly branched MS polymer structures provide a higher modulus that yield a fast and uniform cure. Blends of the two main types of MS polymers are often used to provide “engineered” properties that are matched to specific applications.

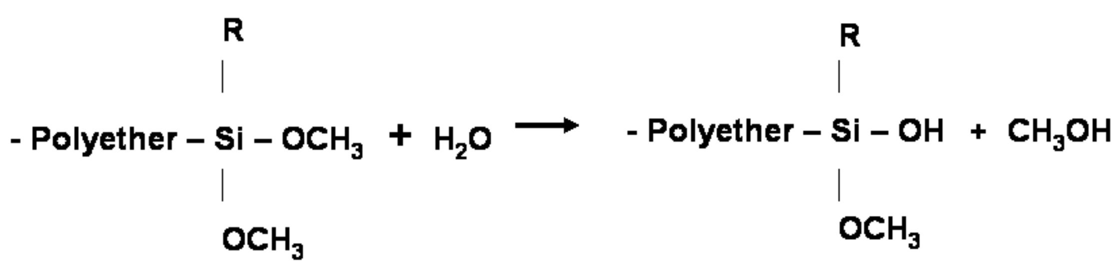
MS polymers offer a low viscosity in the range of 8,000-12,000 cps despite their high molecular weight. The viscosity is relatively stable throughout a wide range of temperatures. As a result, compounding is generally easy and straight-forward. Processes are used similar to formulating a polyurethane adhesive. Fillers and pigments must be pre-dried, and mixing should be under vacuum in order to maintain moisture content to less than 800 ppm. Chemical driers and water scavengers are sometimes employed. Good quality packaging is required to enhance the shelf life of the sealant.

The silane groups provide a non-isocyanate curing mechanism, good adhesion to various substrates, and good storage stability. The silyl reactive end-groups cure in the presence of moisture and an appropriate catalyst by means of an alkoxy reaction that is different than the conventional silicone cure mechanism.

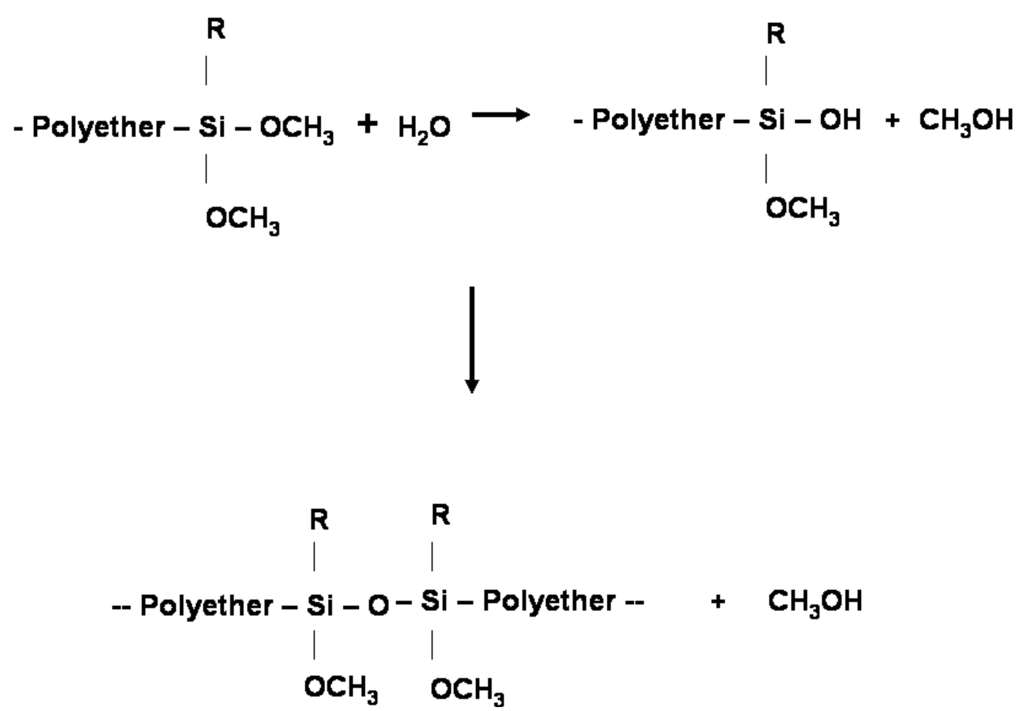
In the presence of appropriate catalyst, the methoxysilane group can be cured by moisture. The water reacts with the silane group to liberate methanol and produce a silanol. Further reaction of the silanol with either another silanol or methoxysilane produces siloxane linkages. The crosslinking reaction proceeds in two steps that are illustrated in Figure 2.

Figure 2: MS polymer crosslinking reactions.

Step 1: Conversion from Methoxysilane to Silanol



Step 2: Condensation of Silanol and Methoxysilane to Form Siloxane Crosslink



Similar to other sealants, MS polymers can be formulated with various plasticizers, fillers, and other additives to provide a wide range of properties depending on the application. Single-part formulations are most common, but two-part formulations are also possible.

Formulation Guide

A typical one-component MS sealant formulation is presented in Table 2. One-component systems have advantages in workability and adhesion. Typical properties of this formulation with three different grades of MS polymer are given in Table 3.

Table 2: One-Component MS Sealant Formulation[1]

Component	*Parts by Weight*
MS polymer	100
Plasticizer (e.g., DIUP)	55
Calcium carbonate	120
Titanium oxide	20
Thixotrope (e.g., fumed silica)	2
Antioxidant	1
UV absorber	1
Dehydration agent	2
Adhesion promoter (e.g., aminosilane)	3
Hardening catalyst (e.g., dibutyl tin)	2

Table 3: Typical Properties of One-Component Sealant Formulations Compared to a Commercial Polyurethane[1]

Property	*MS Polymer Grade Used in Formulation from Table 2*			*Commercial Polyurethane*
	S203H	*S303H*	*SAX400*	
Viscosity, Pa·s	760	890	1030	880
Tack free time, min	60	30	15	35
Cure depth, mm, at 23°C and 50%RH				
• 1 day	3.3	3.3	3.5	3.7
• 7 days	9.0	8.7	8.9	8.4
Tensile shear strength, MPa	1.1	1.3	1.7	0.4
T-peel strength, N/25mm	41	53	74	70

Calcium carbonate is generally selected as filler because of its desirable effect on modulus, tensile strength, and elongation. Many different types of plasticizers can be used as rheology modifiers. Tin and amine compounds are used as catalysts to speed the curing reaction. Moisture scavengers are sometimes added to the formulation. Adhesion promoters can be added although the silane groups function as adhesion promoters in themselves.

Two-component MS sealant formulations are also possible. These eliminate the need for dehydration or moisture control during compounding. They exhibit a fast, uniform cure (pot life is 8 hrs) and good environmental durability. Other properties are approximately equivalent to the one-component system. However, a primer is generally necessary with the two-component sealant for maximum adhesion.

MS Sealants – Extending the Value Proposition

The rise in MS sealant popularity has been primarily due to its versatility and well-balanced properties. MS sealants are suitable for a wide range of applications. Formulations commonly provide a hardness of around 40 Shore A, elongation at break of 150-350%, elastic recovery higher than 70%, tensile strength of 1MPa, and a modulus of 0.8 MPa. Movement capability in construction joints is generally +/- 25%, which places these materials in the category of "high performance sealants".

MS sealants meet the requirements of ASTM CC920 Class 25, as well as those of Federal Specification TT-S-00230C Type II, Class A as a one-component sealant and Specification TT-S099227E Type II, Class A as a two-component sealant. MS sealants also meet ISO Standard 11600G, Class 25HM (high modulus).

Table 4 compares the performance of silicone rubber, polyurethane, and MS sealants. Compared with the other two types of sealants, MS sealants have well balanced properties and performance. Some of the unique properties of MS sealants are:

- Environmental friendliness (solvent-free and isocyanate-free)
- Low temperature gunnability: the viscosity of MS sealants is less dependent on temperature changes
- Storage stability: shelf life is excellent although sealant must be protected from moisture
- Weather resistance and durability: MS sealant shows no cracking, splitting, discoloration or adhesion failure after seven years of testing in desert climate
- Stain resistance: MS sealants do not stain as some silicone sealants do because of low molecular weight silicon materials that bleed from the surface of sealed joints
- Paintability: MS sealants provide good paintability unlike silicone sealants
- Adhesion: MS sealants provide adhesion to various substrates including metals, plastics, wood, and ceramics.

Table 4: Performance Comparison of MS, Polyurethane, and Silicone Sealants[2]

Property	*MS Polymer*	*Polyurethane*	*Silicone*
Environmental friendliness	10	5	9
Non-bubbling	10	6	10
Low temperature gunnability	10	8	10
Slump resistance	10	10	10
Quick cure	10	7	10
Storage stability	10	7	9
Body (tooling)	8	10	8
Weather resistance	8	6	10
Adhesion to various substrates	10	5	8
Mechanical properties	10	10	10
Heat resistance, mechanical stability	9	8	10
Non-dirt pickup	10	10	5
Stain resistance	8	8	5
Paintability with water-based paint	10	10	3

Scale: 10=excellent; 1=very poor

The MS sealants have high performance capabilities with many of the same characteristics as a urethane sealant. However, the one-part MS sealants cure much faster than a one-part urethane sealant and find use in the construction industry where property development speed is important. The skin formation (15-20 mins) occurs much faster with MS sealants than with silicones and urethanes, therefore they exhibit very little dirt pickup. They can also cure in much deeper sections than polyurethane.

MS sealants do have several drawbacks. The initial adhesion of MS sealants onto glass is good, but its exposure to sunlight or UV over a long period of time generates bond strength deterioration. MS sealants, therefore, should not be used for glass glazing. MS sealants, like polyurethane sealants, should not be used at temperatures greater than 85°C. MS sealants also provide excellent paintability with water based acrylic paints. With oil based alkyd type paints it has been noted that the drying time for the paint is increased. However, this problem has been overcome by the use of selection of plasticizer.[1]

Perhaps the most compelling value proposition associated with MS sealants is their lack of isocyanates in the formulation. MS sealants are based on a polymer, which is already silyl-terminated, eliminating isocyanate content to only those that may be involved in the manufacturing process.

Isocyanates are highly reactive chemicals which to a certain extent explains their effectiveness in various sealant applications. Consequently, sealant formulations containing isocyanates must have reasonable protection from contact with agents that combine with the isocyanate group including moisture as this will drastically decrease shelf life. The presence of isocyanates also provides a tendency for bubbling during cure. Isocyanates are considered to be hazardous materials to use. Reasonable caution must also be exerted in the use of materials containing isocyanate including adequate ventilation and prompt washing of body areas coming in contact.

The absence of isocyanates eliminates the problems outlined above and, additionally, broadens the range of formulation possibilities. MS sealant formulations also allow the use of aminosilane adhesion promoters and hindered amine light stabilizers which are not otherwise employed in one-part sealants containing isocyanate groups.

References:

[1] *Silyl-Terminated Polyether Sealants and Adhesives of a New Generation*, Kaneka Corporation.
[2] Hashimoto, K., "Silyl-Terminated Polyethers for Sealant Use: Performance Updates", *Adhesives Age*, August 1998.
[3] US Patent Application 2002/0198308, December 26, 2002.