Momentive
Performance
Materials

A New Low Viscosity SPUR^{+}* Prepolymer Without Added Plasticizers

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Abstract

Low viscosity SPUR^{+} prepolymers without an added plasticizer have long been sought in the marketplace. Momentive Performance Materials presents the first in a series of new SPUR^{+} prepolymers designed to meet this need. In addition to detailing the properties of the new SPUR^{+} prepolymers, this paper will describe the performance of representative starting formulations of SPUR^{+} based hybrid sealants which may be excellent candidates for use in construction or industrial applications.

Also discussed is a new class of silanes developed to improve SPUR^{+} sealant adhesion to wet concrete.

The SPUR^{+} Prepolymer Technology

Silane-terminated polyurethanes (SPUR^{+} prepolymers) have become increasingly attractive to manufacturers of adhesives, sealants and coatings. This hybrid technology appeals to users because of the synergy between the silane-curing mechanism and the polyurethane backbone properties.

Formulations developed using this technology offer fast room-temperature cure and good durability, and the sealants or adhesives they produce are free of un-reacted isocyanates allowing them to have a less harmful impact on the environment. Benefits of the resulting products also include:

- No bubbling during cure, and
- A broadening of the formulation latitude compared to conventional polyurethane technologies.

These prepolymers allow the formulator to utilize a wide variety of additives and adhesion promoters to meet end users' performance needs, such as:

1) Good elasticity and durability
2) Primerless adhesion to both organic and inorganic, porous and non-porous substrates
3) Superior chemical resistance to chemicals such as to automotive fluids (e.g., glycols, motor and transmission fluids)
4) Minimal shrinkage
5) Excellent weatherability
6) Immediate paintability
7) No staining on porous substrates

The SPUR+ Prepolymer Technology (continued)

The production of SPUR+ prepolymers offering both low viscosity and good balance of properties has been a primary challenge to resin producers. Many approaches to the preparation of these polymers have been reported. Most of those works focused on amino alkoxysilanes reacting with a conventional isocyanate-terminated prepolymer. This approach has been employed by researchers to prepare hybrid polymers containing both difunctional and trifunctional organosilane endcappers.[1] Many of these polymers were either too brittle or offered curing profiles that were unsuitable for most sealant applications.

Reviewing Momentive Performance Materials development of SPUR+ prepolymers, we published our first technical article ten years ago.[2] That article contrasted different silane endcappers to the properties of resultant SPUR+ prepolymers. Among those potential endcappers (mercaptosilane, ureidosilane and aminosilanes) a secondary aminosilane, Silquest* Y-9669 (phenylaminopropyltrimethoxysilane) demonstrated the best balance of durability and curing rate. That was Momentive Performance Materials' first generation of SPUR+ prepolymer technology.

Since then we have focused our efforts on continuing development of SPUR+ polymer technology. In 1997 we reported on the superior adhesion of SPUR+ based sealants to a wide range of plastic substrates.[3] We further improved the SPUR+ process in 1999 with the introduction of a second generation endcapper Silquest A-Link* 15 silane (a new aliphatic aminosilane) which was designed to address the slow reactivity of Silquest Y-9669.[4] Silquest A-Link 15 silane reacts twice as fast as Silquest Y-9669 silane with -NCO terminus of the polyurethane prepolymer, thereby offering dramatically improved process efficiency.

Though the technology of the second generation of SPUR+ overcame many deficiencies associated with earlier versions, the viscosity of the aminosilane capped SPUR+ prepolymer remained above 100K cP for a desired molecular length. For ease of handling, the prepolymers have often been diluted with a plasticizer. However, presence of the diluent has, in many instances limited the utility of these polymers.

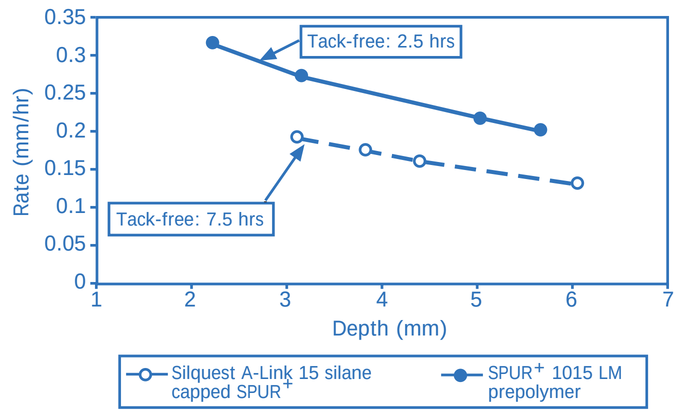
A low viscosity, SPUR+ prepolymer without added plasticizers has therefore become more important, as formulators seek to improve the performance of their products by selecting different plasticizers, or to optimize their properties by mixing thixotropic agents with the prepolymer before addition of the plasticizer. To meet the industry demand, we present in this paper one of the next generation of silylated polyurethane resins: SPUR+ 1015 LM prepolymer, low modulus resin.

Next Generation of SPUR+ Prepolymers

The SPUR+ 1015 LM prepolymer, the first and premier product in this line, is obtained from the reaction of a -OH terminated SPUR+ prepolymer which has been capped by an isocyanatosilane.[5] In comparison to SPUR+ polymers obtained using aminosilane capping groups, resins prepared using isocyanate silanes have fewer isocyanate hard segments, thereby reducing the potential for the intermolecular hydrogen bonding that results in lower polymer viscosity.

The SPUR+ 1015 LM prepolymer is a clear liquid resin. It has a viscosity of ~ 50K cP and it is free of any added plasticizer. The polymer is easily handled, as it is freely flowable at room temperature. As shown in Figure 1, the SPUR+ 1015 LM prepolymer resin offers faster tack-free performance, compared to similar resins prepared using secondary aminosilane capping groups. When mixed with 1 wt% dibutyltin dilaurate, in the absence of added fillers, the SPUR+ 1015 LM prepolymer is three times as fast in tack-free time and there is about a 50% enhancement in the rate of deep section cure under ambient conditions.

Figure 1: Curing Rates of SPUR+ Prepolymers



In general, surface cure can be accelerated by the combination of a tin catalyst and co-catalyst(s). But the deep section cure is more dependent on the nature of the prepolymers. Here, the SPUR+ 1015 LM prepolymer clearly demonstrates the ability to cure-through faster. That unique characteristic can be a benefit to many applications where a thick layer of adhesive or sealant is used.

Next Generation of SPUR+ Prepolymer (continued)

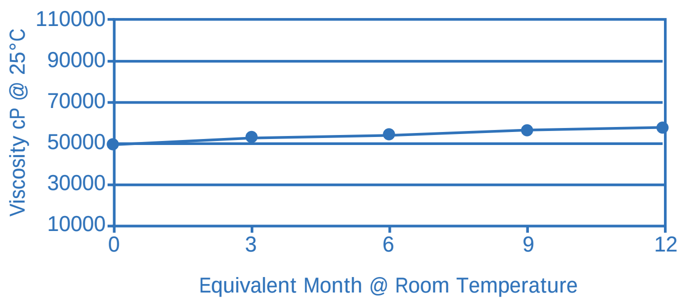
Additionally, the new generation SPUR+ prepolymer provides balanced mechanical properties (Table 1) makes it an excellent choice for the formulation of products for construction, industrial and consumer applications.

Table 1: Mechanical Properties of SPUR+ 1015 LM Prepolymer

Tensile Strength (MPa)	0.58
Young's modulus (MPa)	0.41
Modulus @ 100% (MPa)	0.31
Elongation @ break (%)	300
Shore A Hardness	15

Shelf-life of a reactive polymer is often a concern. This fast cure SPUR+ prepolymer is quite stable in the absence of moisture, as shown in Figure 2. An accelerated aging test was conducted in an oven at 50°C for four weeks, which corresponds to a year at room temperature.

Figure 2: Shelf Life of SPUR+ 1015 LM Prepolymer



Performance of SPUR+ 1015 LM Prepolymer in Sealants

Our SPUR+ strategic platform is built on technologies in both SPUR+ prepolymers and silane additives. By combining the SPUR+ 1015 LM prepolymer with desired silane adhesion promoters, we can tailor the sealant properties for different applications. This ability can be demonstrated here by way of a generic formulation shown in Table 2.

Table 2: SPUR+ Sealant Formulation

Ingredients	Wt %
SPUR+ 1015 LM prepolymer	22.94
Plasticizer (DIDP)	18.35
Moisture Scavenger (Silquest A-171* silane)	0.34
Calcium carbonate	55.05
UV stabilizers	0.46
Fumed Silica	1.115
TiO_2	1.15
Adhesion Promoter	0.57
Tin catalyst	0.03
Total	100.0

Performance of SPUR+ 1015 LM Prepolymer in Sealants (continued)

Selected silane adhesion promoters are described in Table 3 at right. Evaluations followed ASTM test methods (ASTM D-412, C-661, C-794) and European test methods (ISO 34, 37, 868, 4578, 9046, 7389).All the adhesion data presented in Table 5 is the result after seven day immersion in water, unless stated otherwise.

For the construction market, sealant flexibility is a fundamental requirement for the ASTM C-920 standard. For the industrial and consumer sectors, modulus and tensile strength are emphasized. Non-yellowing is often important when formulating a white or clear sealant. As demonstrated here, selection of the silane adhesion promoter has a dramatic impact on the sealant's performance characteristics.

Table 3: Organofunctional Silane Adhesion Promoters

Adhesion Promoter	Structure
Silquest* A-1120 silane	N-ß-(aminoethyl)-γ-aminopropyltrimethoxysilane
Silquest A-1110 silane	γ-aminopropyltrimethoxysilane
Silquest A-Link* 15 silane	N-ethyl-γ-aminoisobutyltrimethoxysilane
Silquest A-1637 silane	4-amino-3,3-dimethylbutyltrimethoxysilane
Silquest Y-15710 silane	Proprietary
Silquest Y-15713 silane	Proprietary

Table 4: SPUR+ Sealant Properties Tailored by Amino Silane Adhesion Promoters

Silquest* Silane as Adhesion Promoter	Silquest A-1120 silane	Silquest A-1110 silane	Silquest A-Link 15 silane	Silquest A-1637 silane
Tensile Strength (MPa)	1.11	1.21	1.11	1.25
Elongation at Break (%)	651	626	1150	1073
100% Modulus (MPa)	0.4	0.39	0.29	0.27
Tear Resistance (N/mm)	7.97	7.08	5.39	7.81
Hardness Shore A	20	22	13	13

Minimizing Yellowing

Table 5: SPUR+ Sealant Adhesion to a Wide Range of Substrates (N/mm/% of cohesive failure)

Substrate	Silquest A-1120 silane	Silquest A-1110 silane	Silquest A-Link 15 silane	Silquest A-1637 silane
Glass	3.7 / 100%	4.6 / 100%	3.0 / 100%	3.3 / 100%
Aluminium	3.3 / 100%	3.2 / 100%	3.0 / 100%	2.8 / 100%
ABS	3.9 / 100%	3.5 / 100%	3.0 / 100%	3.3 / 100%
PVC	2.8 / 100%	3.0 / 100%	3.5 / 85%	2.6 / 100%
Polystyrene	3.7 / 80%	4.0 / 100%	3.0 / 100%	3.2 / 100%
Nylon	4.6 / 100%	4.2 / 100%	2.8 / 10%	2.8 / 100%

Performance of SPUR+ 1015 LM Prepolymer in Sealants (continued)

Adhesion to wet concrete without primer, whether applied on wet concrete or tested after water immersion, has been highly sought after by formulators. As a result of the high pH of the wet surface of concrete, until now the only reliable method to achieve good adhesion required initial application of a primer. To satisfy contractor needs, many formulators are striving to gain adhesion without primer.

We present here new silane adhesion promoters, Silquest* Y-15710 silane and Silquest Y-15713 silane (Table 3). When used in combination with a SPUR+ 1015 LM prepolymer based sealant formulation, these new adhesion promoters offer primerless adhesion to wet concrete. Using only 0.58% of Silquest Y-15710 silane or Silquest Y-15713 silane in the formulation (Table 2), the resultant SPUR+ sealant demonstrates good adhesion to glass, aluminium and plastic (Table 6, at right) as well as improved adhesion to concrete, under all test conditions. The tests were carried out on different kinds of concrete, smooth and flat surfaced or rough and porous surfaced. The adhesion obtained with new Silquest Y-15710 silane and new Silquest Y-15713 silane is significantly improved, compared to a conventional silane, Silquest A-1110 silane, without primer (Figures 3 and 4).

Figure 3: Adhesion on Rough Concrete

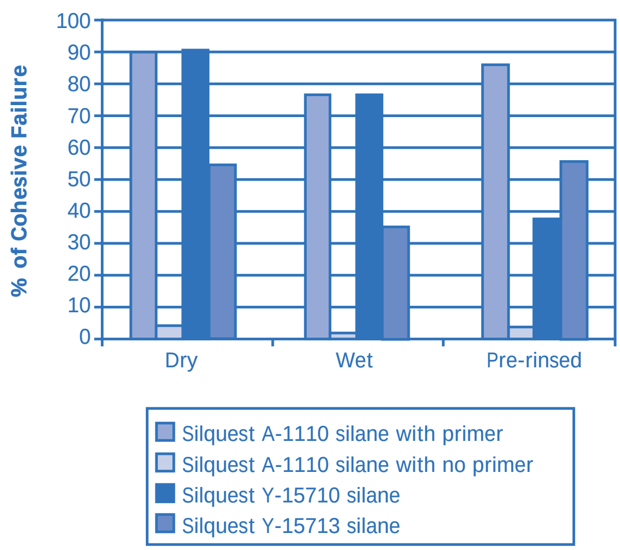
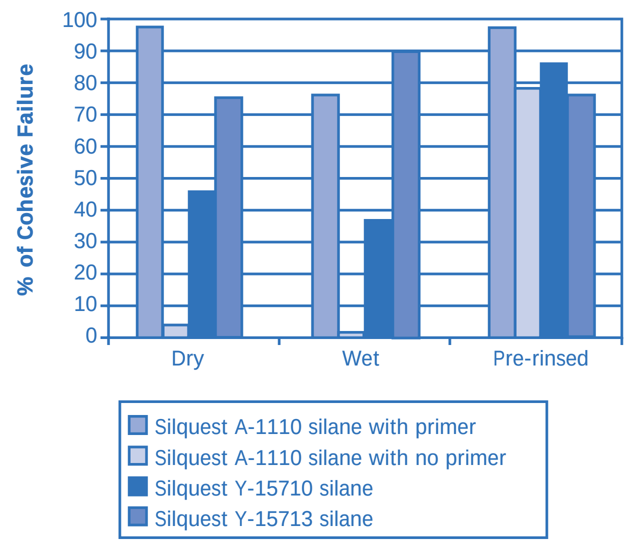


Table 6: Silquest Y-15710 Silane and Silquest Y-15713 Silane Adhesion to Various Substrates (N/mm/% of cohesive failure)

Substrates	Silquest Y-15710 Silane	Silquest Y-15713 Silane
Glass	4.0 / 100%	6.1 / 100%
Aluminium	3.85 / 100%	1.3 / 25%
ABS	2.63 / 100%	NA
PVC	2.45 / 100%	NA
Nylon	2.63 / 90%	NA

NA - Not yet available

Figure 4: Adhesion on Smooth Concrete



Dry – Specimens were tested dry after the standard curing cycle of 2 weeks at 23°C, 50% RH

Wet – Specimens were tested after immersion in water for one day followed by equalizing at room temperature for one day before test

Pre-rinsed – Sealant was applied on wet concrete, and then cured under the standard curing cycle.

Performance of SPUR+ 1015 LM Prepolymer in Sealants (continued)

Conclusion

The development of the next generation of SPUR+ resin technology has resulted in a low viscosity SPUR+ prepolymer without added plasticizers that is the flagship product in a new generation of SPUR+ prepolymers. In addition to the well known advantages of SPUR+ prepolymers, the new SPUR+ 1015 LM prepolymer provides additional features: non-yellowing, improved tack free, and deep section cure performance. These performance advantages provide formulators with more latitude to optimize their products for industry needs.

Combined with new silane technology, adhesives and sealants formulated with this new SPUR+ prepolymer can provide adhesion to many difficult substrates, including wet concrete. This new development in silane technology helps enable adhesion to wet concrete without use of a primer.

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