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Silylated Polyurethane Technology Suitable for Constructon Applications

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Abstract

Organofunctional silane capped polyurethane (SPUR+*) prepolymers[1,2] have been employed in adhesive and sealant formulations for many years. SPUR+ prepolymer technology provides NCO-free prepolymers with good durability and excellent adhesion performance.[3] SPUR+ prepolymer technology also provides the ability to tailor polymers with high or low modulus for different applications. This presentation will describe the formulation of a low modulus sealant, using SPUR+ prepolymers, for construction applications.

Introduction

Similarly to conventional polyurethane chemistry, SPUR+ prepolymer-based precursors can be built up for different inherent properties, using various types of polyols and diisocyanates with a wide range of molar ratios.[4] Here the typical structure-property relation of polyurethane hard-and-soft-segments particularly impact physical properties such as modulus, flexibility and strength. The addition of an organofunctional silane endcapper further extends the range of tailor-made prepolymers,[5] whereas the organo-functional group on the silane plays an important role in the reaction with the urethane intermediates, affecting the properties of the prepolymers.

Silylated polyurethanes can be formulated to make sealants that offer a good balance between physical properties and application-oriented benefits like immediate paintability, improved UV stability and weather stability, and superior adhesion to inorganic and organic substrates. The nature of silane cure chemistry allows one-part polyurethane-based sealants to include a wide range of additives, including adhesion promoters and stabilizer packages that are normally not usable in systems that contain isocyanate. Recently developed silylated polyurethane prepolymers (incorporating new silanes as adhesion promoters) have further extended the potential of SPUR+ prepolymer-based formulations in highly demanding applications like low modulus, flexible construction sealants.

Experimental

Preparation of Silylated Polyurethane Prepolyers

Silylated urethane prepolymers were typically synthesized in a two-step reaction sequence. First, a urethane prepolymer intermediate was prepared in the conventional manner from the reaction of a diisocyanate and a high molecular weight polyol.[4] Diisocyanates (such as TDI or IPDI) and an 8000 mw polypropylene-diol, were employed in the syntheses, using a ratio between 1.3 to 1.5 of NCO/OH. Then, the urethane intermediate was endcapped by N-ethyl-γ-aminoisobutyl trimethoxysilane (Silquest* A-Link* 15 silane) mentioned in a previous article.[6] The reactions were maintained at 120°C for TDI and at 65°C for IPDI, respectively. All the reactions were under nitrogen protection until no free isocyanate was detected by titration.[7] To accelerate the reactions, a tin catalyst was optionally added in ppm quantities.

Sealant Preparation

Sealant samples were prepared in a conventional manner using an one quart double planetary Molteni mixer equipped with a water-jacketed mix kettle. To assure good shelf-stability, all fillers were pre-dried for a minimum of 24 hours at 120°C prior to use. Typically, the silylated urethane prepolymer, calcium carbonate fillers, titanium dioxide thixotropic agent, plasticizer, UV stabilizer, and moisture scavenger were mixed at 60°C for 120 minutes under nitrogen protection. After cooling the mixture to 50°C, the silane adhesion promoter and moisture cure catalyst were added, and the mixture was then stirred for additional 30 minutes under vacuum.

Property Testing

Physical properties of the prepolymers and sealants were measured by standard ASTM methods. Data from tensile strength and elongation at break, modulus (ASTM D 412), Shore A hardness (ASTM C 661) and tear (ASTM D 624) testing were obtained on samples cured according to the following schedule: three days at 23°C and 50% relative humidity (RH), followed by four days in an oven at 50°C.

The adhesion-in-peel testing was conducted in accordance with the ASTM C 794 test procedure. The substrates (3'' x 6'' coupons) were initially cleaned with isopropanol, followed by a detergent (0.1% solution) washing. The substrates were then rinsed with distilled water and allowed to air dry prior to preparation of the test specimen.

The adhesion-in-peel samples were prepared as follows: the experimental sealant was spread over 4'' x 3'' portion of the substrate coupon to a depth of approximately 1/16''. The substrate was covered with a 6'' x 3'' sheet of 30 mesh aluminum screen and then covered by an additional 1/16'' layer of the sealant. Specimens were cured for a total of 28 days, according to the following schedule: Seven days at 23°C and 50% RH; seven days at 38°C and 95% RH; seven days at 23°C and 50% RH; and final seven day water immersion.

Viscosities were obtained using a Brookfield cone-plate viscometer. Readings were typically taken at 25°C with torque around 50%.

Table 1: Aminosilanes Used in This Study

Silquest Silane	Structure
Silquest A-1110	γ-Aminopropyltrimethoxysilane
Silquest A-1120	N-b-(Aminoethyl)-γ-aminopropyltrimethoxysilane
Silquest A-2120	N-b-(Aminoethyl)-γ-aminopropylmethyldimethoxysilane
Silquest A-1170	bis-(γ-Trimethoxysilylpropyl)amine
Silquest A-Link 15	N-ethyl-γ-aminoisobutyltrimethoxysilane
Silquest Y-11637	4-(trimethoxysilyl)-2,2-dimethylbutanamine
Silquest Y-11639	4-(dimethoxysilylmethyl)-2,2-dimethylbutanamine

Results and Discussion

Table 2: Mechanical Properties of Silquest* A-Link* 15 Silane Capped SPUR+* Prepolymers

SPUR+ Prepolymer			Viscosity	Mechanical Properties			Shore A Hardness
	Chain Extender	NCO/OH Ratio	(cps)	Tensile Str. (psi)	Modulus @ 100% (psi)	Elongation (%)	
A	TDI	1.3	44,000	48	22	294	10
B	IPDI	1.5	40,000	88	53	222	21
C	IPDI	1.3	53,000	67	22	565	10

Low Modulus Silylated Prepolymers

SPUR+ prepolymer technology has recently developed silylated polyurethane prepolymers with low modulus and high flexibility particularly suitable for highly demanding construction sealant applications. The mechanical properties of several cured SPUR+ prepolymers are summarized in Table 2 above.

The results in Table 2 show that relatively low viscosity SPUR+ prepolymers can be made from diisocyanates having two isocyanate groups with differing reactivity, such as TDI and IPDI, since the molecular weight distribution of the prepolymer can be controlled by the differentiated reaction rates of the two isocyanate groups. With high MW polyols (8000 mw, low monol), as starting materials, low modulus SPUR+ prepolymers can be synthesized using a ratio between 1.3 and 1.5 of NCO/OH.

In general, the viscosity of the SPUR+ prepolymers increases significantly following the addition of aminosilanes as endcappers, particularly when primary aminosilanes are applied. However, using Silquest A-Link 15 silane as endcapper, the viscosity of the prepolymer can be controlled within an acceptable range. This secondary aminosilane reacts quickly with the remaining isocyanates and reduces the chance of side reactions. The resultant prepolymers have similar modulus at 100% elongation, and improved flexibility, compared to silyated polyether polymers.

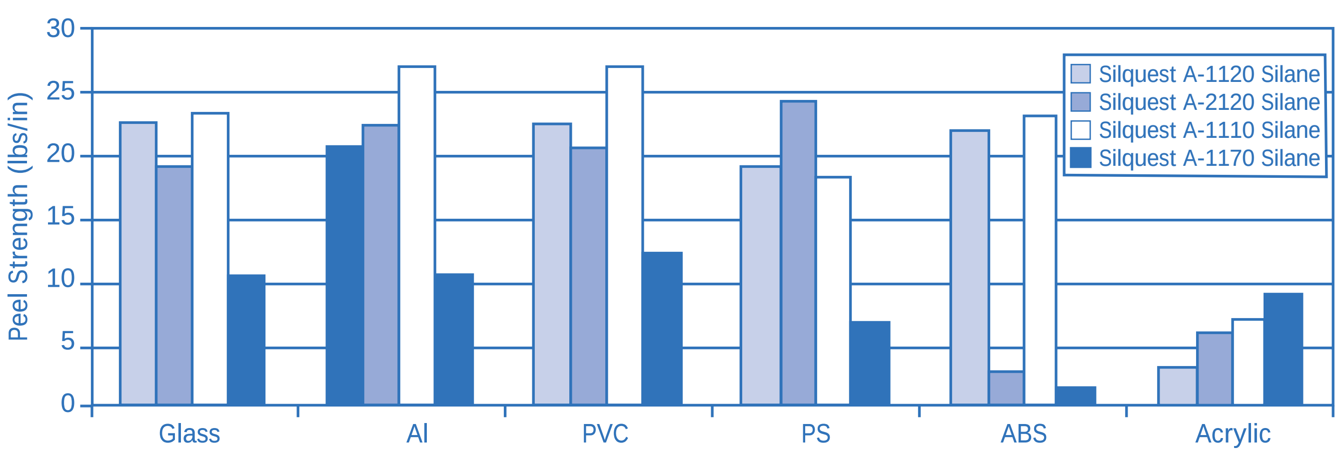
Silanes Used as Adhesion Promoters Improve Sealant Properties

Organosilanes traditionally have been used as adhesion promoters for adhering to difficult substrates. For example, silylated polyurethane-based sealant formulations (incorporating a typical 1.5 phr of aminosilanes) were shown to offer good adhesion to glass, aluminum and primed concrete substrates. These aminosilanes included Silquest A-1120 silane, Silquest A-1110 silane and Silquest A-2120 silane.

To address the increasing interest in adhesion to plastic substrates, these silanes were tested as adhesion promoters on several plastic substrates. Surprisingly, the testing results showed that the sealants adhered to all substrates except acrylic (Figure 1).[7] These sealants demonstrated superior peel strength with cohesive failure, except on an acrylic substrate. The adhesion to acrylic substrates could be improved by using the secondary aminosilane Silquest A-1170 silane.[7]

These results indicate that a combination of different silanes may promote adhesion to a broad range of difficult substrates.

Figure 1: Adhesion of the SPUR+ Prepolymer-based Sealants



Silane loading levels were at 1.5 phr. The data were cited from the reference.[3]

Results and Discussion (continued)

Formulation of Low Modulus Sealants with Different Silane Adhesion Promoters

Recent study has proved that the organosilanes can improve the adhesion and the mechanical properties (particularly the flexibility) of sealants. In this experiment, several low modulus sealants were formulated with a highly filled model formulation. The content of SPUR+* prepolymer in this formulation was only about 23% by weight, but the sealant provided excellent adhesion and mechanical properties. The model of high filled sealant formulation is shown in Table 3, below.

The SPUR+ prepolymer B (Table 2, page 3) was used to make sealants in this study. In the formulation, different aminosilanes were evaluated as adhesion promoters, at loading level of 2.5 parts per 100 parts of the prepolymer (i.e., about 0.57% of total sealant weight). The experimental results are summarized in Table 4, below.

Table 3: Highly Filled Sealant Formulation

Ingredients	phr	Weight %
SPUR+ Prepolymer	100	22.94
Plasticizer	80	18.35
Moisture Scavenger (Silquest A-171* silane)	1.5	0.34
Calcium Carbonate	240	55.05
UV Stabilizers	2	0.46
Thixotropic Agent	5	1.15
TiO_2	5	1.15
Silane Adhesion Promoter	2.5	0.57
Tin Catalyst (Fomrez* SUL 4)	0.12	0.03

Table 4: Properties of SPUR+ Prepolymer-based Sealants Based on the Prepolymer B

Silane Adhesion Promoter	Silquest* A-1120 Silane	Silquest A-Link* 15 Silane	Silquest Y-11637 Silane	Silquest Y-11639 Silane
Tensile Str. (psi)	155	228	166	194
Young's Modulus (psi)	115	95	103	79
Modulus at 100% (psi)	96	59	89	61
Elongation (%)	297	932	506	950
Tear Resistance (lb/in) 31	37	40	46	
Hardness Shore A	38	28	36	30
Tack free time (hrs)	7	7	8.5	11
Adhesion (lbs/in /failure)				
Glass	21/100%CF	20/100%CF	31/95%CF	42/90%CF

Results and Discussion (continued)

Clearly, the silanes promoted adhesion, and also affected the sealant mechanical properties. The aminosilanes with branched bridge between the amine and the silane groups, such as Silquest* A-Link* 15 silane, Silquest Y-11637 silane and Silquest Y-11639 silane, gave the sealants higher elongation compared to those having linear bridge, like Silquest A-1120 silane and Silquest A-1110 silane. The branched silanes also provide sealants relatively low modulus at 100% elongation. Moreover, the curing time of these sealants was essentially the same as sealants that contain Silquest A-1120 silane. All the above mentioned improvements are highly applicable to construction sealant applications.

The SPUR+* prepolymer B used in the above experiments has a theoretical average molecular weight of about 16,000. Prepolymer C, shown in Table 2, page 3, is a high molecular weight prepolymer that was used in the formulation to further reduce the modulus at 100% elongation. Prepolymer C has a theoretical average molecular weight of about 24,000. Table 5 contains the comparison of the sealants made from prepolymers B and C, respectively. The two sealants had similar tensile strength, but the sealant containing prepolymer C was more flexible. Its elongation was more than 1400%, and modulus was less than 50 psi at 100% elongation, demonstrating performance demanded by construction applications.

Table 5: Properties of SPUR+ Prepolymer-based Sealants (Silquest A-Link 15 Silane was used as Adhesion Promoter)

	Sealants Using Prepolymer B	Sealants Using Prepolymer C
Viscosity @ 25°C (cps)	174,000	212,000
Tensile Strength (psi)	228	216
Young’s Modulus (psi)	95	42
Modulus at 100% (psi)	59	44
Elongation (%)	932	1457
Resilience (lbs/in)	37	40
Hardness Shore A	28	15

Conclusion

The properties of SPUR^{+}* prepolymers can be tailor made by changing the polyols, the ratios of NCO/OH, and the silane endcappers. Using Silquest A-Link 15 silane, low modulus and low viscosity prepolymers can be made at the NCO/OH ratio of 1.3 – 1.5. Consequently, the sealants (made from SPUR^{+} prepolymers and a series of new aminosilanes as adhesion promoters) can achieve the excellent flexibility, adhesion and low modulus that is particularly suitable for construction applications. Moreover, for economy, these SPUR^{+} prepolymers were designed for high-filled sealant formulation.

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