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New Developments in Silylated Polyurethane Technology

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Abstract

Silylated polyurethane (SPUR+*) prepolymer technology is an extension of conventional hybrid polymer technology. Silquest* silanes and SPUR+ prepolymer technology allow for tailor-made prepolymers that may make them excellent candidates for formulations ranging from low to high modulus. This presentation will provide a brief overview of recent developments in novel silane endcappers. These new silane endcappers can not only reduce cost, but also improve UV resistance and color stability of the SPUR+ prepolymer.

Introduction

Silane terminated polyurethanes are receiving increased attention as raw materials for sealant and adhesive applications.[1] A properly selected organofunctional silane will react with a conventional urethane prepolymer[2] to form a shelf stable silane "endcapped" or silylated polyurethane (SPUR+) prepolymer. These termination agents replace the isocyanate crosslink mechanism with a silane crosslink mechanism. In the presence of moisture and an appropriate cure catalyst, the reactive alkoxy silane endgroups of the modified polyurethanes undergo hydrolysis, followed by condensation, to form a stable siloxane (Si-O-Si) crosslink network.[3]

Standard polyurethane chemistry remains a means for building prepolymer precursors of different inherent properties, using various types of polyols and diisocyanates at a wide range of molar ratios. The usual polyurethane hard- and soft-segments structure-property relationships come into play impacting physical properties such as modulus, flexibility and strength. The addition of organofunctional silane endcappers can extend the performance range of tailor-made prepolymers. Whereas the organic group on the silane plays a key role in the reaction with the prepolymer intermediate and affects the prepolymer properties, the alkoxy functionality on the silicon governs the crosslinking kinetics and the physical properties of the final SPUR+-based system.

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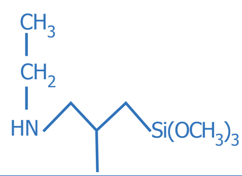
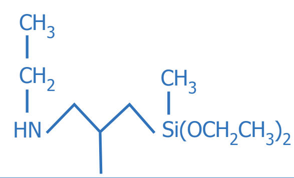
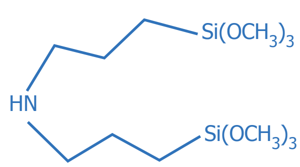
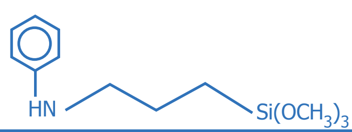
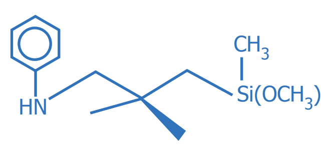
Introduction (continued)

Silylated polyurethane technology allows for formulating systems that offer a good balance of physical properties and application-oriented benefits, such as:

(1) isocyanate (NCO) free moisture curable systems,
(2) superior adhesion to both organic and inorganic substrates,[6]
(3) enhanced resistance to automotive fluids,[5]
(4) immediate paintability,
(5) improved UV stability and,
(6) weatherability.

The NCO-free nature of a silane crosslinked system allows a formulator to incorporate a broader range of additives into their urethane sealant that cannot be used in isocyanate systems. Examples include amino silane adhesion promoters providing superior adhesion to plastics, and hindered amine light stabilizer packages capable of dramatically enhancing UV resistance. Recent developments in silylated polyurethane prepolymers further extend the potential of SPUR+ prepolymer-based formulations in applications, such as low modulus, flexible building construction sealants and tough high modulus automotive sealants or elastomeric adhesives. This presentation will focus on how to improve UV stability of the prepolymer through new silane endcappers.

Table 1: Identification of Silane Endcapper

Designation in This Article	Structure	Mw	Name
Silane Endcapper 1		222	Silquest* A Link* 15 Silane
Silane Endcapper 2		223	Experimental
Silane Endcapper 3		341	Silquest A-1170 Silane
Silane Endcapper 4		255	Silquest Y-9669 Silane
Silane Endcapper 5		267	Experimental

Preparation of Silylated Polyurethane Prepolymers

Silylated polyurethanes prepared according to SPUR+* prepolymer technology, discussed here, are synthesized in a two-step reaction sequence.

(1) A urethane prepolymer is prepared from the reaction of a diphenylmethane diisocyanate (MDI) and a conventional 4000 molecular weight of polypropylene glycol using a NCO/OH ratio of 1.5.[2]

(2) The synthesized polyurethane intermediate is then silylated. A hydrogen active organofunctional silane, such as amino silanes with secondary amine structures, are used to endcap the isocyanate terminated prepolymer.

The reactions are typically maintained at 65-70°C under a protective blanket of nitrogen until no free isocyanate is detected by titration. To accelerate the reactions, a catalyst such as dibutyltin dilaurate (Fomrez SUL 4 catalyst) might be employed in ppm quantities.

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Sealant Preparation

Table 2: SPUR+ Prepolymer-based Sealant Formulations

Formulation Ingredient	phr
SPUR+ Prepolymer	100
Plasticizer (DIDP)	40
Fillers[a] ($CaCO_3$, 0.07µ/13-5µ)	100
Thixotrope[a] (SiO_2)	6
UV Stabilizers	2
TiO_2	2
Silquest A-171* silane	1
Silquest* A-1120 silane	1.5
Fomrez* SUL 4 tin catalyst	0.2

(a) Surface treated

Sealants based on SPUR+ prepolymer technology were prepared in a conventional manner using a one liter, double planetary mixer equipped with a water-jacketed mix kettle. Typically, the silylated polymer, calcium carbonate fillers, titanium dioxide, thixotropic agent, and plasticizer were mixed at 30 rpm for 120 minutes at 80°C (176°F) under full vacuum. After cooling to 50°C (122°F), the silane adhesion promoter ([Aminoethyl]-gamma-aminopropyltrimethoxysilane, Silquest A-1120 silane), the silane dehydrating agent (Vinyltrimethoxysilane, Silquest A-171 silane), and dibutyltin dilaurate catalyst (Fomrez SUL 4 catalyst) were added and the mixture was stirred for an additional 30 minutes under vacuum. Representative starting sealant formulations are discussed in the paper.

Property and Performance Testing

The silylated polymer precursors, the silylated polyurethane based sealant formulations, and the commercially available sealants were drawn down to compatible thickness. The sealants were fully cured under controlled conditions, 3 days at 23°C (73°F)/50% relative humidity (RH) followed 4 days at 50°C (122°F) oven before testing.

The physical properties were evaluated using standard ASTM and/or ISO test procedures: Tensile strength, percent elongation, modulus (ASTM D 412, ISO 37, Type 2), tear resistance (ASTM D 624, ISO 34, Die C), Shore A hardness (ASTM C 661, ISO 868), Adhesion-in-peel (ASTM C 794), and weatherability (ASTM G-53-88).

Results and Discussion

(1) General SPUR+* Prepolymer-based Film Properties
The physical properties of several cured SPUR+ prepolymers are summarized in Table 3.

Table 3: Properties of the SPUR+ Prepolymer-based Films

Silane Endcapper	Silquest* A-Link* 15 Silane	Silane Endcapper 2	Silquest A-1170 Silane	Silquest Y-9669 Silane	Silane Endcapper 5
Viscosity (cps)	89,200	108,800	90,800	89,700	95,000
Tensile Strength (psi)	106	114	130	100	90
Young's Modulus (psi)	113	79	158	120	81
100% Modulus (psi)	81	64	119	81	62
Elongation (%)	148	249	113	132	188
Tear Resistance (Ibs/in)	15	19	12	17	18
Hardness Shore A	36	30	46	34	25

The experimental data show that the new silane, Silquest A-Link 15 silane gives the prepolymer mechanical properties essentially the same as Silquest Y-9669 silane. Due to the high crosslink density generated through the Silquest A-1170 silane, the resultant prepolymer exhibits higher modulus and less flexibility than the other prepolymers. The endcappers 2 and 5 are difunctional alkoxysilanes that provide the system lower modulus and higher elongation than the trifunctional silanes. However, the difunctional silanes cure slowly, requiring additional catalyst to achieve a cure rate comparable to their trifunctional counterparts. With the same catalyst level, as well for the trifunctional systems, the two samples with difunctional silane in this study required more than 3 weeks to cure.

Based on the results of Table 3, current SPUR+ prepolymer technology with amino-silane terminated silylated prepolymers is suitable for medium-to-high modulus sealants for transportation, industrial and automotive applications. The new silane, Silquest A-link 15 silane, has been designed to not only provide good mechanical properties, as well as to meet these needs in a cost effective manner.

Results and Discussion (continued)

Table 4: Color Stability of SPUR+* Prepolymers with Various Endcappers

Silane Endcapper	Initial			After Aging[1]			Δb
	L	a	b	L	a	b	
Silquest* A-Link* 15 Silane	97.58	-0.29	1.99	96.56	-1.21	6.00	4.01
Silane Endcapper 2	98.67	-0.89	4.49	97.98	-2.15	13.83	9.34
Silquest Y-9669 Silane	97.96	-0.27	2.38	82.55	3.64	72.48	70.10
Silane Endcapper 5	57.00	-0.94	4.78	57.13	-2.86	54.20	49.42

(1) 80°C oven for 7 days.

(2) Enhanced Color Stability

Color stability has been an important factor for sealants in many applications. Table 4 summarizes the color stability of cured SPUR+ prepolymer-based films. The cured films were stored in an oven at 80°C (176°F) for 7 days. Color changes were measured before and after heat treatment using a Minolta Chroma Meter CR-221.

Table 4 clearly demonstrates that the new generation of secondary amino silane endcappers, Silquest A-Link 15 silane, provides a dramatic increase in color stability, represented by Δb (in the last column). This improvement is attributed to the substitution on the secondary aminosilane. When the alkyl amino group of Silquest A-Link 15 silane and endcapper 2 replaces the phenyl amino group of Silquest Y-9669 silane or silane endcapper 5, the urea structure in the resultant SPUR+ prepolymer becomes much more color stable. Notice that all of the SPUR+ prepolymers tested were made with MDI. Use of an aliphatic diisocyanate in combination with the new silane endcappers is expected to further enhance the color stability of prepolymers prepared with SPUR+ prepolymer technology.

(3) Improved Weatherability and UV Stability

Polyurethane sealants have historically struggled with UV-through-glass performance. The isocyanate crosslink mechanism employed by most urethane sealant systems limits the breadth of UV stabilizers available, and can limit the formulated UV stability results.

Freedom from reactive isocyanate groups enables systems using SPUR+ prepolymers to be formulated with a variety of additives to meet demands for superior weatherability. The weathering characteristics of MDI-based silylated polyurethane based model sealants, stabilized with various antioxidants, UV and hindered amine light stabilizers (HALS), were tested in a QUV weatherometer.[5] The stabilizers were used at levels of one part per hundred resin. Table 5 gives a comparative summary of the accumulated accelerated artificial weathering results after 8000 hours.

The combination of a conventional UV light stabilizer and a HALS appears to offer the most promising results. Even after 8000 hours exposure, the color and the surface structure of the sealant remain nearly unchanged. The sealant still shows good flexibility. This study was based on a SPUR+ prepolymer capped with first generation silane Silquest Y-9669 silane. There are many reasons to believe that the weatherability can be further enhanced with second generation silane endcappers (such as Silquest A-Link 15 silane).

Table 5: Weatherability of SPUR+ Prepolymer-based Sealant

	(Total Exposure: 8000 hours)
Stabilizer(s)[a]	Observations/Comments
1) None	Dark brown, surface cracking & flaking, hardening.
2) Standard UV Inhibitor + HALS	No color change, minor surface cracking, still flexible.

(a) Stabilizers are typically used at addition levels of 1 phr.

Results and Discussion (continued)

Table 6: Accelerated UV Stability of SPUR+* Prepolymer-based Sealants Change in Wet Peel Strength

Silane Endcapper	Initial	After Exposure	Remained Strength (%)
Silquest* A-Link* 15 Silane	14	12	86%
Silquest A-Link 15 Silane(1)	9	13	144%
Silane Endcapper 2	36	36	100%
Silquest Y-9669 Silane	14	5	36%

(1) IPDI was used instead of MDI in this prepolymer.

Adhesion of SPUR+ prepolymer-based sealants to glass under accelerated weathering conditions was also evaluated. In this study, the cured sealant species were placed in a QUV at 60°C (140°F) under high humidity with the glass side facing the UV light source for 2 weeks (350 hours). The change in peel strength before and after provides a rapid means of assessing the impact of UV exposure at the sealant-to-glass interface.

After 350 hours exposure, the SPUR+ sealants with the N-alkyl amino silane endcappers (Silquest A-Link 15 silane and endcapper 2), exhibit little change in peel strength, while the sealant with Silquest Y-9669 silane lost 60% of its adhesion. The increase in peel strength observed in Silquest A-Link 15 silane may be related to slow initial cure. The sealant probably reached final cure during the exposure.

(4) Economic Benefits:
Silylated urethanes are more expensive to produce than urethanes. They require an extra process step (prepolymer endcapping with silane), and use of a silane intermediate. Silanes are not inexpensive materials. As such, silylated urethanes deliver enhanced performance over traditional urethane to support this higher cost technology. Usually, however, any possible cost reductions are sought.

An endcapping reaction study indicates that Silquest A-Link 15 silane can endcap an isocyanate terminated prepolymer 50% faster than Silquest Y-9669 silane. This is credited to the reduction in steric hindrance of the secondary amine that can significantly reduce the kettle time during silylation. Under the reaction conditions used in this study, the silylation time fell from 4 - 5 hours for the endcapper 4 to 1 - 2 hours for the Silquest A-Link 15 silane.

Additionally, use level efficiencies are attainable. One of the key elements in selecting an endcapper candidate becomes crosslink equivalent weight. During the synthesis of a silylated urethane prepolymer, the amount of silane endcapper required is calculated stoichiometrically. Therefore, the lower molecular weight of the silane endcapper, the less the amount required to complete the same reaction.

Silquest A-Link 15 silane offers a 13% reduction in molecular weight in comparison to first generation Silquest Y-9669 silane, translating to a 13% endcapper efficiency gain.

Thus, Silquest A-Link 15 silane offers improved UV and color stability, and comparable physical properties, with a substantial improvement in endcapping efficiency.

Conclusions

Silylated polyurethane (SPUR+ prepolymer) technology is an extension of conventional urethane polymer technology. Recent developments in silylated polyurethane endcapping structures provide improved UV and color. SPUR+ prepolymer technology provides for the formulation of one part room temperature moisture cure sealant systems with performance benefits over unmodified urethanes including: superior adhesion performance,(6) UV stability/weatherability and chemical resistance.(7)

This second generation silane endcapper (Silquest A-Link 15 silane) is favored for greater usage efficiency, faster processing cycles, and enhanced UV performance versus previous endcapping technology.

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