

Modification of Polysulfide Sealant with Polysulfide Polythio-urethane-urea

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ABSTRACT: With a small amount of isocyanate-terminated polysulfide (NCO-PSF-NCO) as additive, the commercial polysulfide-based sealant had significant improvement in mechanical properties. The test results showed that 5% of NCO-PSF-NCO could help to rise 50% in the tensile strength and 27% in the ultimate elongation of the polysulfide sealant. The adhesive strength to substrates such as steel, epoxy-coated or polyurethane-coated surface also increased significantly. Dynamic mechanical thermal analysis and differential scanning calorimetry analysis revealed that formed polysul-

fide polythio-urethane-urea (polysulfide-urea) contributed to a slight increase in the T_g of the polysulfide sealant. It might be due to the domains of polysulfide-urea, which had effects of physical crosslinking and chain-extending on the polysulfide sealant. However, the introduction of polysulfide-urea structures had no appreciable influence on oil resistance of the polysulfide sealant. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2599–2604, 2007

Key words: polysulfide; sealant; modification; polyurea

INTRODUCTION

The low-molecular-weight polysulfide polymers (PSF) bearing thiol end groups (Thiokols LP) have been produced since 1940. These liquid polysulfide oligomers are synthesized by the aqueous polymerization of short chain dichlorohydrocarbons with sodium polysulfide.^{1,2} Most of the curing agents are metal peroxides, which make use of the reducing property of the thiol group to cause crosslinking, the main reaction procedures were reported by early researchers.^{3,4} For instance, manganese dioxide is often used as curing agents via oxidation reaction shown in Scheme 1.

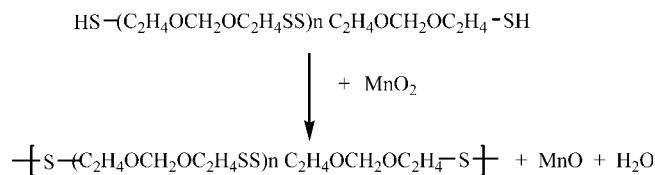
To obtain the optimum properties, the commercial polysulfide sealant should contain curing agent, curing modifier, suitable fillers, plasticizer, and adhesion additives, among which fillers increase the tensile properties, plasticizer improves the working properties of the sealant while lowering its modulus, the incorporation of adhesion additives is known to improve adhesion. Polysulfide sealants have wide applications in industries, they can adhere to glass, steel, wood, and concrete, and they have high resistance against UV radiation and environment, exhibit good low-temperature properties, low water-vapor transmission, and resist against solvents and chemicals.^{5,6} There have

been many publications on the characterization of metal peroxides-cured polysulfide,^{7–11} reporting the results of thermogravimetry analysis, dynamic mechanical analysis, tensile strength and hardness testing. Also thermal stability and photodegradation of the liquid polysulfide and cured polysulfide are studied by Mahon et al.^{12,13}

Taking the advantage of lower cost, polysulfide sealants continue to be the dominant part of the elastomeric sealants; however, they are facing strong challenges from silicone and polyurethane-based sealants. One of the reasons is their relatively poor tensile properties and weaker adhesive strength.¹⁴ This article is concerned with how to improve mechanical properties and adhesive strength of polysulfide sealant via a method of low cost and simple technique.

Thiol group in the liquid polysulfide can also react with diisocyanates.¹⁵ Using this reaction, we have studied structural and mechanical properties of polysulfide-based polyurea,¹⁶ UV-cured polysulfide thio-urethane acrylate,¹⁷ and modification of polybutadiene polyurea with polysulfide-based polyurea to produce superior resistance to oil.¹⁸ In this article, we use isocyanate-terminated polysulfide (NCO-PSF-NCO) prepolymer and diamine as reactive additives, which added to the polysulfide matrix to form a polysulfide polythio-urethane-urea (polysulfide-urea) system through copolyaddition. We found there was remarkable increase in mechanical properties and adhesive strength after conventional curing process.

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Scheme 1 Oxidation of liquid polysulfide by manganese dioxide.

EXPERIMENTAL AND CHARACTERIZATION

Liquid polysulfide (JLY121: SH% = 6.2–7.5%, $M_n = 1000 \pm 200$; JLY155: SH% = 1.0–1.4%, $M_n = 5000 \pm 400$, with 2% mol trithiol) supplied by JinXi Research Institute of Chemical Industry, China was dehydrated under vacuum at 100°C for 3 h before use. Isophorone diisocyanate (IPDI, supplied by CRENDVA Speziaichemie, Germany) was used as received. Ethacure-100 (supplied by Albemarle, USA) was used without purification.

Isocyanate-terminated polysulfide (NCO-PSF-NCO) was prepared according to the procedure done before.^{16–18} Different amount of NCO-PSF-NCO was added to the fixed commercial polysulfide sealant, and the mixture was cured at 50°C for 48 h.

Stress–strain analysis

The tensile strength and the ultimate elongation were tested using Instron4466 instrument on dumb-bell-shaped samples. The sample was 2-mm thick. The specimens with gauge length of 10 mm were tested at room temperature using a crosshead speed of 50 mm/min.

Hardness test

Hardness of the samples was measured using a Shore a Durometer according to the principles of ASTM D 2240.

Differential scanning calorimetry

Measurements of the soft segment glass transition temperature were made with PYRIS-1 DSC (produced by Perkin–Elmer, Waltham, MA), at heating rate of 20°C/min from –100°C to +100°C.

Dynamic mechanical thermal analysis

All measurements were carried out using DMTA-V (produced by Rheometric Scientific, Piscataway, NJ). The dimensions of the specimens were 7 mm × 10 mm × 0.5 mm. The fixed frequency was at 10 Hz. The temperature range was from –90°C to +150°C and the samples were heated at a nominal rate of 3°C/min.

Adhesive strength testing

The adhesive behavior was studied by the lap shear test. The used substrate was commercial stainless steel. The steel treatment consisted of three steps: (1) the surface was abraded with 100-mesh abrasive paper, (2) then the surface was cleaned by solvent wiping with acetone, and (3) the surface was dried with dry air. After surface treatment, the steel pieces (100 mm × 25 mm × 2 mm) were assembled into lap shear joints with 12.5 mm of overlap length. The prepared samples were stored at 50°C for 48 h before test. The adhesive strength was tested in a universal tensile mechanical machine at a crosshead speed of 5 mm/min. Each result was obtained by the test repetition with five samples.

Oil (and water) absorption and resistance test

The films were cut into 20 mm × 20 mm × 2 mm strips, the dry weight (W_d) of which was determined, and then immersed in pump oil at room temperature. The wet weight with different immersion time (W_t) was determined by wiping off the surface oil with paper. The absorbed oil content was then calculated from the oil content: $W(\%) = (W_t - W_d) \times 100/W_d$.

In the oil resistance test, the specimens were immersed in 50°C pump oil, and tensile strength was tested after different immersion times.

The water absorption and resistance test are following the procedure used in oil absorption and resistance test.

RESULTS AND DISCUSSION

Synthesis

The formulations of polysulfide sealants before and after modification are outlined in Tables I and II, and the reaction among polysulfide, NCO-PSF-NCO, and diamine is described in Scheme 2.

The NCO-PSF-NCO prepolymer was prepared using 2.05 equiv IPDI reacted with 1.0 equiv PSF, and then the above NCO-PSF-NCO was added into polysulfide sealant. Although the reactivity of thiol

TABLE I
Chemical Composition of Polysulfide Sealant

Samples	Polysulfide sealant (PSF0)
JLY 155	100
JLY 121	30
SRF black	40
Calcium carbonate	10
Stearic acid	1
Plasticizer	10
MnO ₂	7
Epoxy resin	4
Coupling agent	2
E100	1

TABLE II
The Composition and Properties of Polysulfide Sealants Before and After Modification with NCO-PSF-NCO

Samples	Weight composition of NCO-PSF-NCO/polysulfide sealant	Stress (MPa)	Strain (%)	Hardness Shore A
PU	100/8 ^a	11.2	214	81
PSF0	0/100	3.4	322	58
PSF03	3/100	4.1	374	62
PSF05	5/100	5.1	411	67
PSF10	10/100	4.3	501	64
PSF20	20/100	3.9	619	61

^a The curing agent is E100.

and NCO was much lower than that of amine and NCO, the concentration of thiol was evidently higher than amine in this sealant system. The NCO group not only reacted with diamine to form urea bond, but also reacted with thiol group in polysulfide as a chain extender. The urea formation and PSF chain-extending simultaneously happened in the sealant. As a result, the added NCO-PSF-NCO functioned as a chain extender, which helped to improve extensibility of polysulfide sealant, at the same time, the polyurea from IPDI and diamine served as hard segment domains in polysulfide sealant, these domains performed as physical crosslinking due to the strong urea-hydrogen bonds.

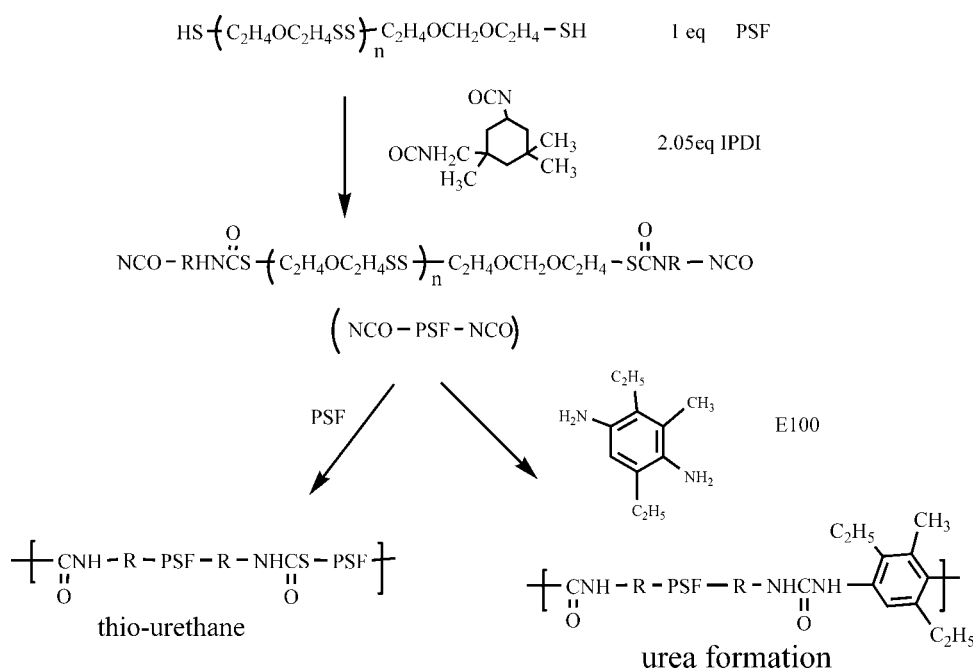
Stress-strain analysis

The results of stress-strain analysis performed on film of polysulfide sealant before and after modifica-

tion are shown in Figure 1, and summarized in Table II.

In commercial formula of polysulfide sealant, the tensile strength is mainly dependent on filler reinforcement. The fillers perform as physical crosslinking, increasing the strength, adjusting needed rheological properties, and reducing the cost of the sealant. There are no other hard segments in polysulfide sealant. In our polysulfide sealant composition, in addition to the oxidation curing by MnO₂, the thiol of liquid polysulfide could also react with the NCO group in the NCO-PSF-NCO prepolymer. The added NCO-PSF-NCO had both the effects of physical crosslinking and chain-extending on the polysulfide sealant, which can improve the tensile strength and ultimate elongation of sealant simultaneously.

Based on the stress and strain results, it can be seen that the tensile strength of modified polysulfide sealants increased with the increasing content of



Scheme 2 The reaction among polysulfide, NCO-PSF-NCO, and diamine.

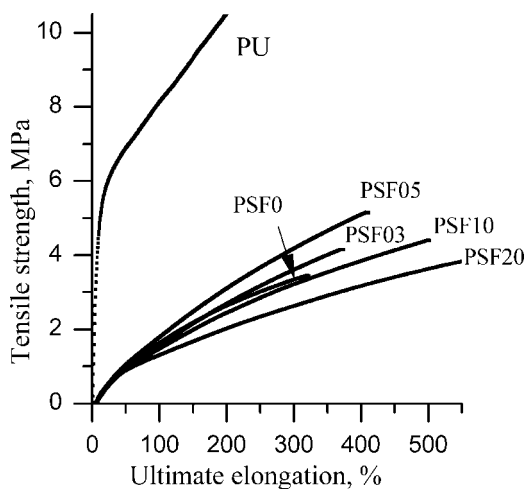


Figure 1 Stress-strain curves of polysulfide thio-polyurea, polysulfide sealant before and after modification.

NCO-PSF-NCO up to a maximum value, then decreased after more additive was added. The maximum tensile strength was obtained at a level of 5 phr NCO-PSF-NCO additive (PSF05). However, modified polysulfide sealants showed a continued increase in elongation at break from PSF03 to PSF20. The differences in behavior between the stress and strain properties of modified polysulfide sealants are due to the following reason: the NCO-PSF-NCO prepolymer served as chain extender (thio-urethane formation) and physical crosslinking point (urea formation). As more NCO-PSF-NCO prepolymer added, more PSF chain extended, more urea also formed. However, as soon as the diamine was used up, NCO-PSF-NCO prepolymer only had the effect of chain-extending. It was not surprising that 5% addition of NCO-PSF-NCO prepolymer just met the maximum value in tensile strength. This was also approved by hardness test. The hardness test gave Shore A value of 58 for PSF0, 62 for PSF03, 67 for PSF05, and 64 and 61 for the additive used at 10 and 20% (PSF10 and PSF20), respectively. These data indicated that PSF05 had the maximum degree of crosslinking.

TABLE III
Glass Transition Temperature of PU, PSF0, and PSF05

Samples	T_g ($^{\circ}\text{C}$) ^a		T_g ($^{\circ}\text{C}$) ^b
	From E''_{\max}	From $\tan \delta_{\max}$	
PU	-32.6	-10.7	-38.6
PSF0	-50.3	-34.4	-50.3
PSF05	-37.6	-28.5	-47.3

^a From DMTA (10 Hz).

^b From DSC.

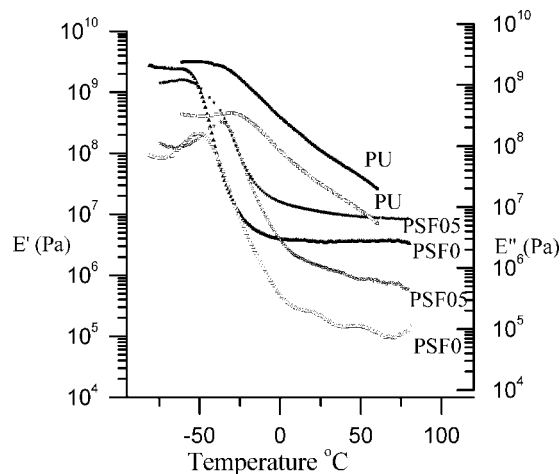


Figure 2 The temperature dependence of storage modulus of PU, PSF0, and PSF05.

DMTA and DSC analysis

Results of DMTA and DSC analysis for PU, PSF0, and PSF05 are collected in Table III. Figures 2 and 3 represent the temperature dependence of the storage (E'), loss modulus (E''), and loss tangent ($\tan \delta$) for PU, PSF0, and PSF05, respectively. DSC scans of the materials are shown in Figure 4.

In Figure 3, for PU, the broad peak of $\tan \delta$ could be accounted for intermixing by the hard segment on the soft-segment phase.¹⁶ A comparison of soft segment glass transition temperature in polysulfide sealant before and after modification indicates that PSF05 apparently exhibited higher glass transition temperature than PSF0. The same observation can be found in DSC scan. This was due to the reaction between NCO-PSF-NCO prepolymer and liquid polysulfide, as well as the good compatibility of poly-

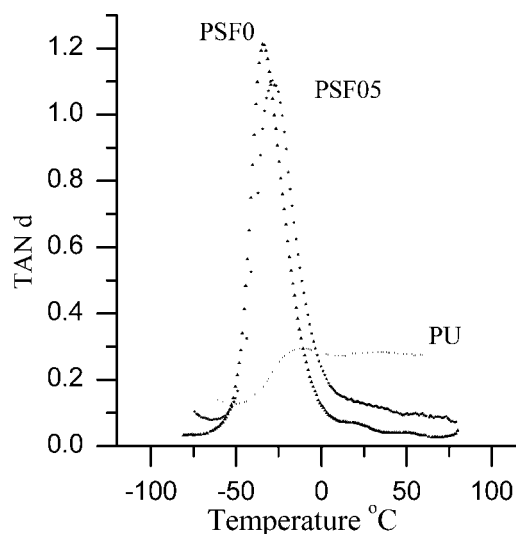


Figure 3 The temperature dependence of the loss tangent of PU, PSF0, and PSF05.

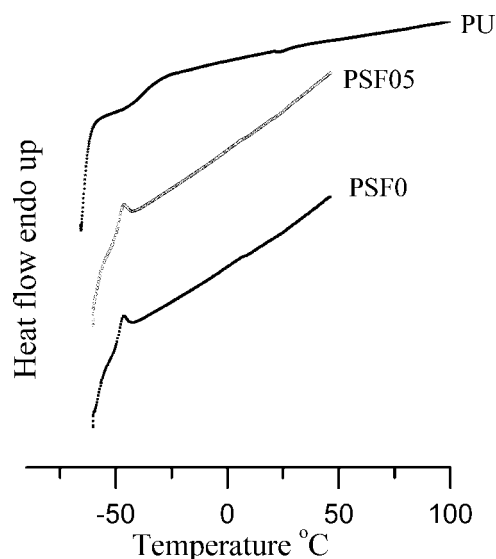


Figure 4 The DSC scans of PU, PSF0, and PSF05.

sulfide sealant and polysulfide-urea. Polysulfide-urea gave a large number of domains dispersing in the soft-segment matrix, which resulted in higher T_g (from -50.3°C moving to -37.6°C from data of E'').

Adhesive strength testing

The adhesive behavior was studied by the lap shear test. The substrate used was commercial stainless steel. After surface treatment, the steel pieces were used directly or coated by polyurethane coating or epoxy-based coating. The coating was aged at 70°C for 72 h. The adhesive strength results were listed in Table IV.

If polysulfide sealant is applied to the "aged" polyurethane-coated surface, as studied by Usmani,⁷ most of the surface isocyanate (NCO) groups have been consumed by heat/humidity in the coating. The adhesion of polysulfide sealant would be due to slight interdiffusion, dipole-dipole attraction, and van der Waals attractive force. These electronic forces will be insufficient. The breakage often occurs at the interface and the shear strength will be very low. In our case, the adhesive strength of polysulfide sealant to the polyurethane coating was 1.2 MPa, much lower than those of epoxy-based coating and steel (2.8 MPa and 2.6 MPa), because epoxy groups

TABLE IV
The Adhesive Strength of PU, PSF0, and PSF05

Substrate	Steel (MPa)	Polyurethane coating (MPa)	Epoxy-based coating (MPa)
PU	10.8	8.2	6.5
PSF0	2.6	1.2	2.8
PSF05	4.2	4.1	4.4

can increase the electronic attractive forces, which help to improve adhesion.

As shown in Table IV, PU had much higher adhesive strength than PSF. A 60% increase in the adhesive strength was observed when polysulfide sealants were modified with 5 phr NCO-PSF-NCO (PSF05). For all breakage occurred in bulk of lap shear joints, other than in the adhesive-adherend interface between the sealant and substrate, the factor responsible for adhesion was determined by bulk tensile strength of the sealant. Since polysulfide-urea reinforcement significantly increase the bulk tensile strength of polysulfide sealant, the adhesive strength of PSF05 reached to 4 MPa despite of different substrates.

Oil (and water) absorption and resistance test

As a sealant, one of the important properties is the resistance to oil (or water). Figure 5 shows curves of the percentage increase in mass of the polysulfide sealants immersed in pump oil (and water) at room temperature. The tensile strength of samples before and after oil (and water) immersion at 50°C is presented in Figure 6. From oil absorption test, it appears that both polysulfide sealants (before and after modification) absorbed little oil (less than 0.3%) after immersed in oil for 20 days. The oil resistance test shows that the polysulfide sealants were remarkably stable upon oil, and their tensile strength had no apparent change even after the samples had been immersed in oil at 50°C for 8 days. This outstanding oil resistance is due to the sulfur linkages in chain, which enhance the solubility parameter of the polymer. These results indicate that the introduction of

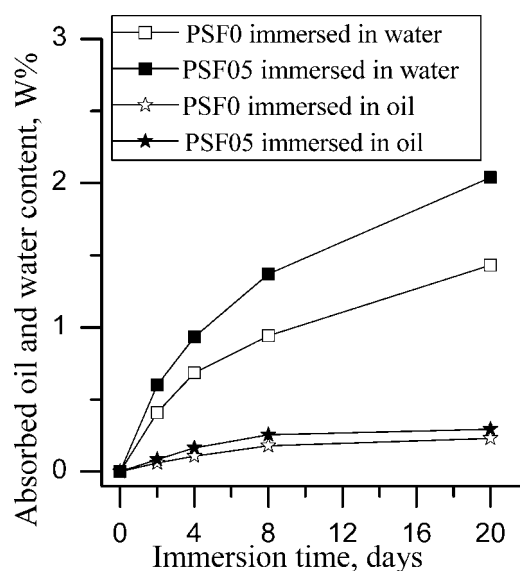


Figure 5 Oil and water absorption of PSF0 and PSF05.

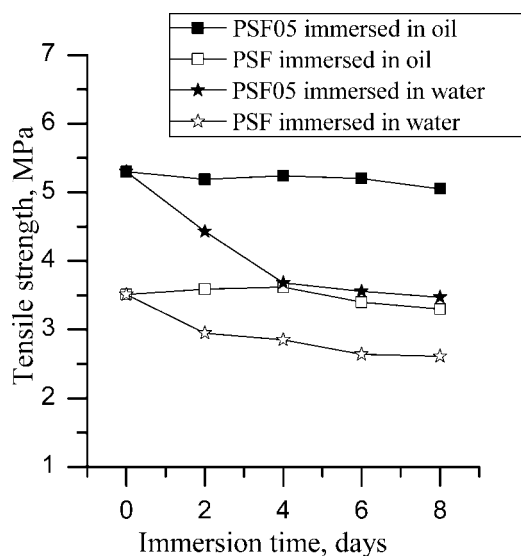


Figure 6 Effect of oil and water on tensile strength of PSF0 and PSF05 at 50°C.

the polysulfide-urea structures has no appreciable influence on oil resistance of the polysulfide sealant.

In contrast, the water absorption of samples increased with the immersion days. After 20-day immersion in water, the sealants absorbed more than 1.4% water (1.43% for PSF, 2.0% for PSF05, respectively), and the water absorption tendency was increasing. After 4 days of immersion in water at 50°C, PSF0 and PSF05 both sustained a significant reduction in tensile strength. PSF0 retained 74% of its initial value, and PSF05 retained 65% of its initial value. However, the tensile strength of PSF05 was also much higher than that of PSF after water immersion.

CONCLUSIONS

The NCO-PSF-NCO additive significantly improved the tensile strength and ultimate elongation of the polysulfide sealant. Five-phr additive resulted in

50% increase in the tensile strength and 27% increase in the ultimate elongation of the polysulfide sealant. Furthermore, there is about 60% increase in the adhesive strength for the breakage that took place in the bulk of sealant other than in the adhesive-adherend interface. The oil and water resistance of polysulfide was unaffected by the introduction of polysulfide thio-urethane-urea. Our work may extend the applications of polysulfide sealant.

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