New Liquid Polysulfide Polymer Terminated with Silyl Group

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ABSTRACT: The terminal SH of liquid polysulfide polymer was capped with a silyl group. This polymer was hydrolyzed immediately by moisture at ambient temperature and returned to the original polymer. The compounds of this new polymer and the various curing agents of the conventional polysulfide polymer became moisture curable and of use as one-component sealants and adhesives. The curing speed of these compounds is very fast compared with that of not only conventional one-component polysulfide sealants, by more than three times, but also of other one-component sealants at 20°C under 30% humidity. Their storage stability is good. Their cured products showed physical properties comparable to those of the two-component polysulfide compounds. In particular, the compound of this polymer and isocyanate prepolymer showed good elasticity and good weatherability. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2642–2649, 2004

Key words: polysulfides; curing of polymers; one-component sealants; silyl group; compounding

INTRODUCTION

The liquid polysulfide polymer (LP), which was produced industrially through the efforts of Patrick[1] and others in the 1940s, has disulfide linkages in the polymeric main chain, SH terminal groups, and is liquid at room temperature. LP has found a wide range of applications by mixing it with a suitable curing agent (e.g., sealants, coating material, and adhesives in the construction and building fields) by use of the reactive terminal SH groups.[2]

This article introduces a new liquid polysulfide polymer in which the SH group is converted to a silyl group and is possible to return to the original polysulfide polymer quickly upon exposure to moisture. This new type of moisture-sensitive liquid polysulfide polymer can be used as a one-component system, but is also expected to be applied to the new vulcanization system, or to improve the properties of rubber, and the new rubber materials having a polycatenane structure.[3]

Sealants are classified into two types, one-component and two-component, resulting in different methods of application. Two-component systems are structured according to the principle that the first component contains a main polymer, such as a polysulfide polymer together with a number of important and necessary additional materials. However, it does not contain any curing agents, such as oxidizing agents in the case of polysulfide polymer, which is in the second component. The two components are manufactured and packaged separately, and they may be mixed together with suitable mixing equipment, immediately before use.

Unlike the two-component systems that require the mixing of the curing paste and the base for use, the one-component systems, which are cured by external factors such as moisture in air when it is removed from the container, offer the convenience of being ready for use without mixing. For this reason, the one-component sealants are now favored.

Whereas sealants require deep and fast curing, light and oxygen penetrate with greater difficulty than water, causing a slow curing speed.[4] Consequently, one-component sealants are invariably the water-curable type. In this instance, however, the curing speed and storage stability are important trade-offs in determining the product value of the merchandise.

Although various one-component compounds using polysulfide polymers have been tried, they all basically use a method whereby the curing agents themselves are activated by water, or a method that uses latent curing catalysts that are activated by water.[1,5]

However, the slow curing speeds of these two methods has posed a limit to their popular acceptance.

Polysulfide polymer, with its disulfide linkage in the polymer backbone, exhibits excellent resistance to oil, water, weather, and stains, and good adhesion and high impermeability to gases. With a fast curing rate,

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TABLE I
Physical Properties of LP3, LP2, and LP70

Grade[a]	Crosslinking (mol %)	Viscosity at 25°C (Pas^{-1})	Molar mass (g/mol)	SH content (wt %)
LP3	2.0	1.2	1000	6.0
LP2	2.0	45.0	4000	1.7
LP70	40.0	1.2	1200	14.5

[a] LP: $H(SCH_2CH_2OCH_2OCH_2OCH_2CH_2S)$ nH

the one-component type sealant that incorporates all of these superior qualities would make a superior merchandise. A product patented by Dow Corning[6] has a silyl group at the polysulfide polymer terminal, which is an O—Si—C linkage. It is a water-curable type that uses the properties of polysulfide rubber, although the cured product is hard and brittle.
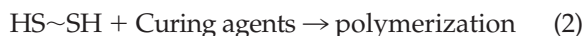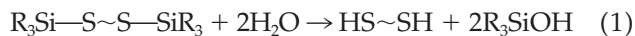
The base polymers used in elastic sealants have included isocyanate prepolymers, silicone polymers, modified silicone polymers, or polysulfide polymers.[7,8] The terminal group of the first three types of polymers all have the functional group that readily reacts to moisture and makes them fast curing, thus facilitating the design of both the one-component and two-component type sealants. By contrast, the polysulfide polymer suitable for this application has an SH as the terminal group, rendering it stable with water, that is mostly used for two-component sealants.

The alkoxy–silane-type silicone polymer and the modified silicone polymer[8] both have $\sim SiOCH_3$ as terminals, which are converted to $\sim SiOH$ with moisture. This is followed by a chain-extending reaction. Their curing speed is high.

A one-component type polysulfide polymer is produced by linking a water-sensitive protective group to the SH group. It should be expected that the addition of an SiR_3 group to the SH group in the polysulfide polymer ($HS\sim SH$) would produce a S—Si linkage that is sensitive to water, as is the case with a O—Si linkage, which is similar to the S—Si linkage.

$$R_3SiS\sim SSiR_3$$

That is, the following curing reaction system [eqs. (1)–(2)] is established:

$$R_3Si—S\sim S—SiR_3 + 2H_2O \rightarrow HS\sim SH + 2R_3SiOH \quad (1)$$

$$HS\sim SH + \text{Curing agents} \rightarrow \text{polymerization} \quad (2)$$

If this new system is applied to the liquid polysulfide polymer, a fast one-component system should conceivably be produced. Further, the retention of the performance of the two-component type polysulfide polymer also should be expected through a combination with curing agents of the conventional polysulfide polymer.[9–12]

EXPERIMENTAL

Materials

The materials used in this experiment were polysulfide polymers LP3, LP2, and LP70 (Toray Thiokol Co., Ichihara City, Japan). Table I shows their representative physical properties.

A-1, made by Nihonkagakusangyo Co. Ltd. (Tokyo, Japan), was used for lead dioxide. The manganese dioxide was from Riedel-de Haën Co. (Seelze, Germany).

Urethane prepolymer (NCO prepolymer) was synthesized in a nitrogen atmosphere by adding a diisocyanate (e.g., toluene diisocyanate) to polyether polyols (diol and triol polypropylene glycol), using a small amount of dibutyl tin dilaurate as a catalyst.

The epoxy resin used was Epon 828 (Yuka Shell Co., Ltd., Bangkok, Thailand), having 180 to 200 epoxy equivalent weight.

Silyl polysulfide polymer

Polysulfide polymer terminated with a silyl group, called silyl polysulfide polymer or silyl LP, was synthesized as follows[9,13,14]: 1000 g (0.25 mol) of polysulfide polymer (LP2 molar mass 4000 g/mol), 250 mL of benzene, and 0.5 mol (equivalent to the SH in the raw material) of triethylamine were placed and stirred in a 2-L agitator glass container at room temperature. Trimethylchlorosilane [54.3 g (0.5 mol)], equivalent to the SH mole in the raw material, was added to the mixture by drops in a nitrogen atmosphere, and was stirred for an additional 30 min. The reactant mixture was then filtered to remove the triethylamine hydrochloride, and the filtrate was heated to remove the solvent under vacuum, to yield the moisture-sensitive polysulfide polymer.

HS~SH

$$+ 2(CH_3)_3SiCl \xrightarrow{N(C_2H_5)_3} (CH_3)_3SiS{\sim}SSi(CH_3)_3$$

$$+ HClN(C_2H_5)_3 \downarrow \quad (3)$$
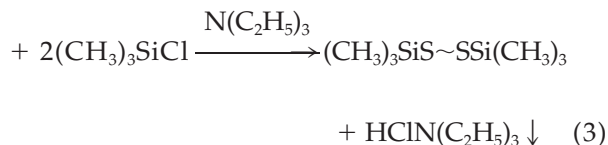
Preparing one-component composition

Fillers such as calcium carbonate, plasticizer, and inorganic oxidant (lead dioxide or manganese dioxide) were placed in a 5-L planetary mixer, and dehydrated by stirring for 2 h under vacuum at 500 Pa or less and between 100 and 120°C. The mixture was then cooled to room temperature and a specified amount of silyl polysulfide polymer and isocyanate prepolymer (in certain cases if no inorganic oxidant was used) were added. After the mixture was stirred in a vacuum for 30 min, it was transferred to a sealed container.

Preparing a sample for measuring physical properties

Two wooden spacers ($12 \times 12 \times 60$ mm), with releasing compound applied to the surface, were fitted between two aluminum plates ($80 \times 80 \times 2$ mm) having a 12-mm space in the center between the two to make an H-shaped form, in accordance with JIS (Japanese Industrial Standard) A 5758. The bottom was sealed with cellophane tape. The one-component compound was then poured into the top and cured at the specified temperature and humidity. After the specified time had elapsed (completely cured), the wooden spacers and cellophane tape were removed to test the physical properties of the cured sealant.

Method of measurement

The presence of the SH group in materials was detected using an infrared absorption spectrometer from Hitachi Co. (Tokyo, Japan). The wavenumber of the peak absorption of SH was 2560 cm^{-1}.

The stress–strain measurements were conducted at 20°C under 55% humidity, and a stretching speed of 500 mm/min, using a tensile tester by Orientec Co. (Tokyo, Japan).

The dynamic viscoelasticity of the cured sample was measured at 10 Hz between -100 and 150°C, using an RSA-II apparatus (Rheometric Scientific, Piscataway, NJ). The DSC was obtained with an increasing temperature of 10°C/min in N_2 atmosphere using an SC-30 instrument manufactured by Mettler Co., Ltd. (Zurich, Switzerland).

The sample for curing speed was prepared by pouring the one-component composition into a frame made of foam polyethylene pieces that had been erected on a polyethylene plate, and the top surface
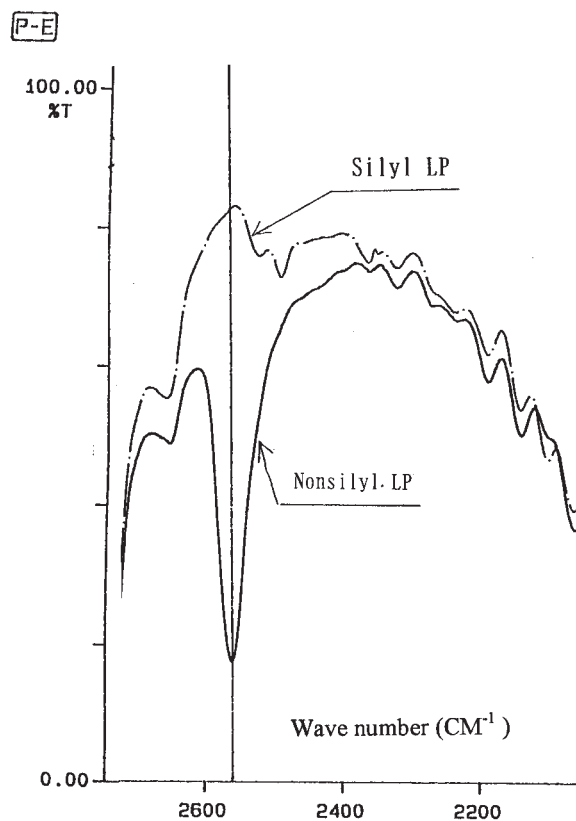

Figure 1   IR spectra of silyl LP3 and nonsilyl LP3.

was flattened out. The sample was then cured at the specified temperature and humidity. To measure curing speed, upon reaching the specified curing time, a part of the sample was sliced out, together with the frame, using a knife. After removing the uncured portions, the cured depth from the top surface was measured with a magnifying glass.

RESULTS AND DISCUSSION

Characterization of silyl polysulfide polymer and its compounds

Figure 1 shows the SH absorption peaks of the raw material (which is called nonsilyl LP) and that of the product (silyl LP). The SH peak (at wavenumber 2560 cm^{-1}) of the raw material had completely disappeared in the product material. The conversion of the SH to silyl was more than 93%. The synthesized silyl polysulfide polymer was poured into a cup and allowed to stand under the conditions of 80% humidity at 35°C. Silyl LP was completely restored to LP in less than 10 h, which was measured from the IR spectrum of the –SH band on the polymer surface. Reaction (1) had obviously occurred.

The stability of the silyl polysulfide polymer was determined by storing it in a sealed container at 90°C
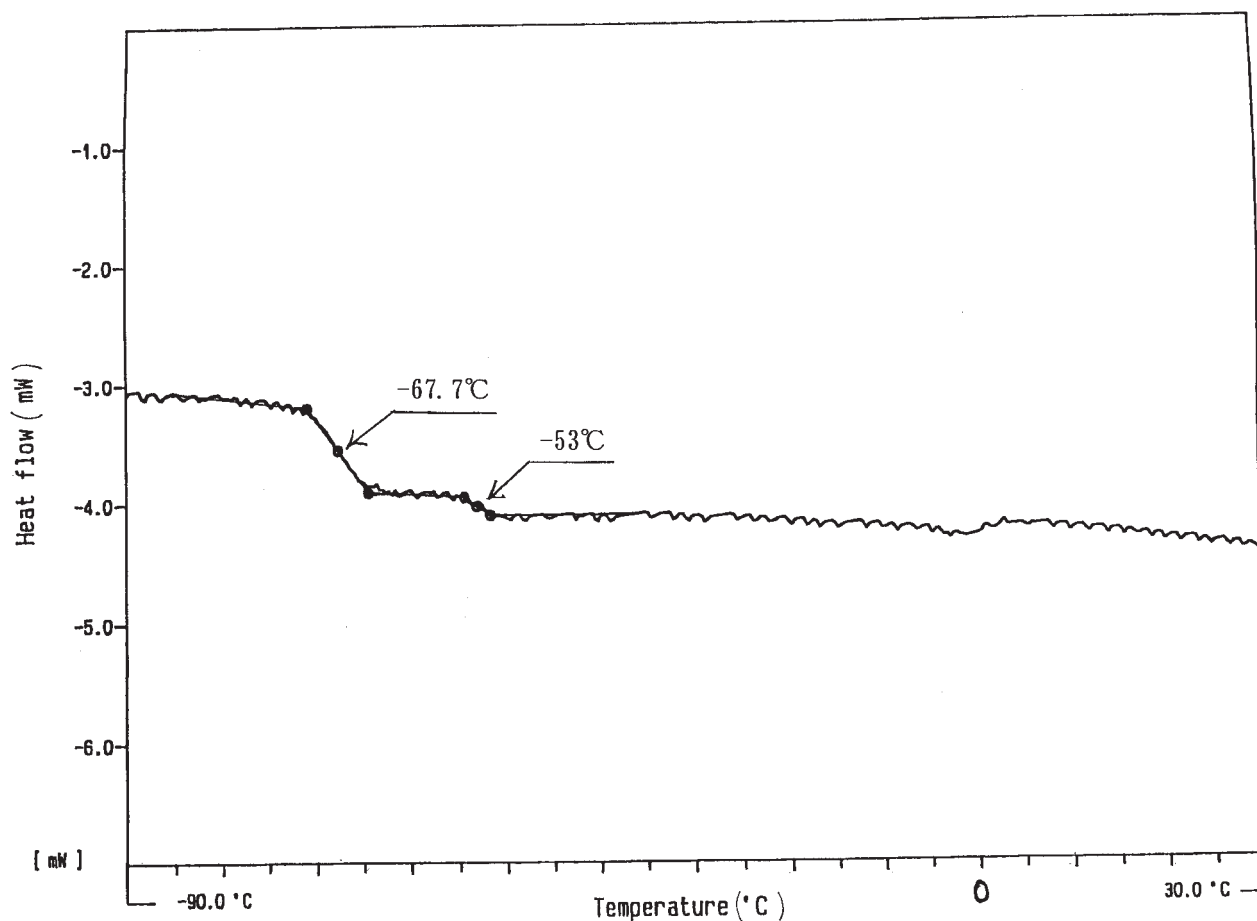
Figure 2 DSC chart of silyl LP compound (silyl LP and NCO prepolymer).

for 1 month. No change in chemical structure was observed in the IR spectrum.

A typical DSC chart and dynamic properties of the compounds made from silyl LP are shown in Figures 2 and 3, respectively. Two glass-transition temperatures are seen at −50 and −70°C. (This will be explained later in the section on combination with isocyanate prepolymer.)

Figure 3 Temperature dispersion of dynamic properties of silyl LP sealant measured at 10 Hz.

Combination with oxidant

Lead dioxide is often used as the curing agent for the polysulfide polymer in a sealant for buildings and various constructions, whereas manganese dioxide is likewise often used for polysulfide curing agent for insulating glass sealant[1,2]:
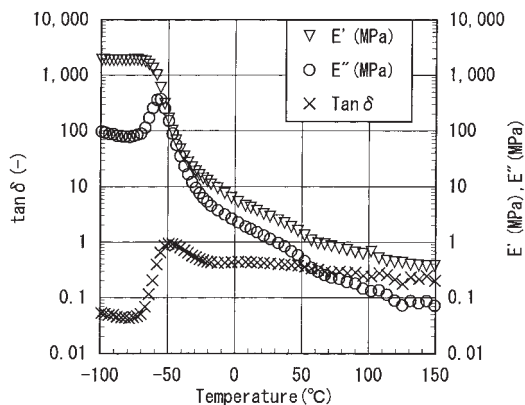
$$HS\sim SH + MO_2 \rightarrow \sim SS\sim + H_2O + MO \quad (4)$$

In eq. (4) M is either lead or manganese. These oxidants may be used in combination with silyl polysulfide polymer to produce a one-component sealant.

Calcium dioxide and sodium perborate, on the other hand, used conventionally as a curing agent in one-component type polysulfide polymer, are activated by water. The combination of silyl polysulfide polymer would yield a one-component sealant but the curing speed would not be fast. Equation (1) progresses very rapidly even if moisture is low, but eq. (4) with these curing agents progresses very slowly. (These results are explained later, as shown in Table III.)

TABLE II
Compounds of One-Component Polysulfide Polymer[a]

Compound	Parts by weight
1	
Silyl LP2	100
Lead dioxide	7
Calcium carbonate	120
Chlorinated paraffin	97
2	
Silyl LP2	100
Maganese dioxide	15
Calcium carbonate	120
Chlorinated paraffin	45
Butyl benzyl phthalate	45
3	
Silyl LP2	100
Sodium perborate and lead dioxide	Variable
Filler	120
Plasticizer	80
Molecular sieve	2
Others	3.9
4	
Silyl LP70	100
Epon 828	140
Ketimine (H_3 made by Yuka Shell)	20
5	
Silyl LP3	38
NCO prepolymer	125
Calcium carbonate	145
Dioctyl phthalate	80
Butyl benzyl phthalate	45
Triethyl amine	0.16

Compound **1** in Table II shows the composition prepared as a one-component system with lead dioxide. The shelf life of compound **1** in a sealed container at room temperatures was a half year, and when its compound was extruded from the cartridge in air, it cured to a 3-mm depth in 3 days at 20°C under 55% humidity. The reactions according to eqs. (1) and (4) had obviously occurred. After extrusion 3 h were required to achieve a tack-free surface under the same conditions. The physical properties of the cured products of this one-component compound **1** are shown in Table III, where curing conditions were 35°C under 80% humidity for 1 week (initial). In this table also the physical properties of these products after curing at 90°C for an additional week (aged) are shown. As seen in this table, the cured one-component products exhibited the same excellent rubber elasticity as that of two-component products. Effects of the byproduct generated by the hydrolysis of silyl polysulfide polymer, shown in eq. (1), were investigated. Silanol and siloxane were individually added to the composition shown in an equivalent amount of generation. Silanol had a degrading effect on the adhesion, but siloxane had no effects on the adhesion and physical properties.[15] Silanol, generated in the hydrolysis of silyl LP,

has a low boiling point and consequently evaporates or reacts to become siloxane and immediately disappears.

$$2(CH_3)_3SiOH \rightarrow (CH_3)_3SiOSi(CH_3)_3 + H_2O \quad (5)$$
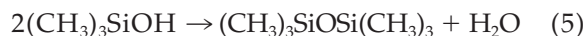
For these reasons, no attention would be required for these particular byproducts.

Compound **2** in Table II shows the one-component composition with manganese dioxide. The shelf life of compound **2** in the sealed container at room temperatures was a half year, and when its compound was extruded from the cartridge in air, it cured to a 2.2 mm depth in 3 days at 20°C under 55% humidity. Apparently, reactions eqs. (1) and (4) had occurred. After extrusion 3 h were required to achieve a tack-free surface under the same conditions. The physical properties of the cured products of this one-component compound **2** are shown in Table III, where curing conditions were 35°C under 80% humidity for 1 week. As seen in this table, the cured one-component products exhibited the same excellent rubber elasticity as that of two-component products.

Compound **3** in Table II shows the one-component composition with sodium perborate and PbO_2 type. The physical properties of the cured products of this one-component compound **3** are shown in Table III, where curing conditions were 35°C under 80% humidity for 1 week. The cure speed and shelf life are also shown in this table. As PbO_2 was replaced by sodium perborate, the physical properties of this one-component cured product were retained, although the curing rate was diminished. The reason for this was, as explained previously, that sodium perborate is activated by water.

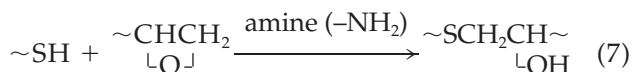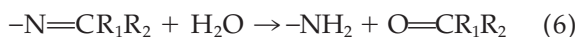## Combination with epoxy resins

If polysulfide polymer is cured by epoxy resins, the adhesion to wet surfaces is improved. Conventional one-component–type epoxy–resin adhesives are cured above room temperature. For instance, amine compounds as curing catalyst or agents of one-component type epoxy–resin remain in a solid state at room temperature and this compound does not cure. As the temperature is increased, amine compounds melt and this epoxy compounds cures. When the new system is used with an epoxy resin, a room-temperature–type one-component adhesive is produced. The basic catalyst (e.g., tertiary amine), which is used for the reaction between thiol and epoxy groups, cannot be used in this instance because the catalyst is effective for the epoxy group alone. A latent-type catalyst (e.g., ketimine type) may be used.

TABLE III
Physical Properties of Compounds of One-Component Polysulfide Polymer

Compound **1**
  Initial (cured for 7 days at 35°C, RH[a] 80%)

		Aged (for 7 days at 90°C after initial)	
50% modulus	0.12 MPa	50% modulus	0.1 MPa
150%	0.18 MPa	150% modulus	0.17 MPa
Tensile	0.26 MPa	Tensile	0.26 MPa
Elongation	400%	Elongation	270%

Compound **2**
  Initial (Cured for 7 days at 35°C, RH 80%)

50% modulus	0.15 MPa
100%	0.20 MPa
Tensile	0.285 MPa
Elongation	312%

Compound **3**

$PbO_2 : NaBO_3 \cdot 2H_2O$ (parts by weight)	Cure speed (10°C × 7 days) RH 40%	Shelf life (20°C)	Curing condition (for 7 days at 35°C, RH 80%)			
			50% modulus (MPa)	150% modulus (MPa)	Tensile (MPa)	Elongation (%)
4.0 : 0	3.0 mm	1 month	0.1	0.13	0.29	700
2.0 : 5.0	0.8	1 month	0.13	0.15	0.24	470
1.0 : 5.0	tack free	1 month	0.12	0.15	0.27	500

Compound **5**
  Initial (cured for 7 days at 35°C, RH 80%)

|		Aged (for 7 days at 90°C)	
100% modulus	0.46 MPa	100% modulus	0.44 MPa
300% modulus	0.61 MPa	300% modulus	0.78 MPa
Tensile	1.04 MPa	Tensile	1.47 MPa
Elongation	550%	Elongation	720%

[a] RH, relative humidity.

Compound **4** in Table II shows the mixture of this composition. The compound remained uncured in a container for 1 month at room temperature, but once removed from the container it moisture-cured to become tack free in 10 h at 55% humidity and 20°C.

$$-N=CR_1R_2 + H_2O \rightarrow -NH_2 + O=CR_1R_2 \quad (6)$$

$$\sim SH + {}^{\sim CHCH_2}_{\quad \lfloor O \rfloor} \xrightarrow{\text{amine (–NH}_2)} {}^{\sim SCH_2CH\sim}_{\quad\quad \lfloor OH} \quad (7)$$

The adhesion strength between two 40 × 40 × 30-mm concrete blocks was 1.7 MPa, as tested by JIS A 6024.

Combination with isocyanate prepolymer

Because the NCO group reacts with the thiol group, the presented new system, in combination with isocyanate prepolymer, produces a one-component composition. The reaction rate r_1 is defined as the production rate of thiourethane linkage.

$$R_3Si—S\sim S—SiR_3 + 2H_2O \rightarrow HS\sim SH + 2R_3SiOH \quad (1)$$

$$\sim SH + \sim NCO \xrightarrow{r_1} \sim NHCOS\sim \quad (8)$$
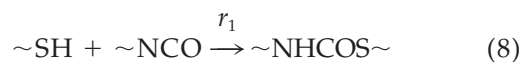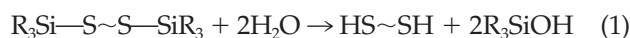
Tertiary amine is used as the catalyst here. As explained below, this new system has less foaming, rendering it more desirable than a system of isocyanate alone. The reaction rate r_2 is defined as the production rate of CO_2.

$$\sim NCO + H_2O \xrightarrow{r_2} \sim NH_2 + CO_2 \quad (9)$$

If a tertiary amine is used as the catalyst, the condition $r_1 > r_2$ holds,[16] which results in less foaming because of the presence of CO_2.

Figure 4 shows the effect of the SH/NCO ratio on the modulus of the cured product. The modulus increased with a decrease in the SH/NCO ratio. At a ratio ≤ 0.5, the modulus of the cured sealant was constant and the foaming [eq. (9)[rsqb] started. Urea, rather than thiourethane, linkage seems to be produced. At 1.0 or more, the modulus showed a steep decrease and portions of the product remained uncured; thereafter the SH/NCO ratio for the experiment was set at 0.8.

Compound **5** in Table II shows the constituent of a representative composition. The shelf life of com-
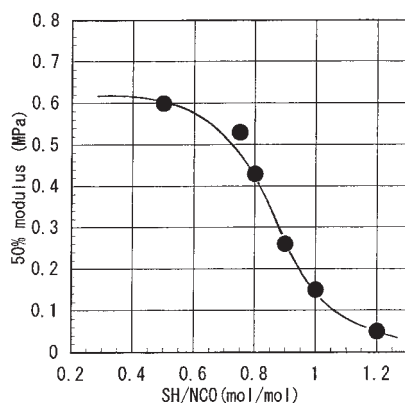
Figure 4 Influence of SH/NCO on 50% modulus of silyl LP sealant (cure conditions: 35°C × 5 days, RH 80%).

Figure 6 Tensile stress–strain curve of silyl LP sealant.

pound **5** in a sealed container at room temperatures was half a year, and when its compound was extruded from the cartridge in air, it cured to a depth of 3.0 mm in 3 days at 20°C under 55% humidity. Apparently, reactions (1) and (8) had been allowed to occur. After extrusion 3 h were required to achieve a tack-free surface under the same conditions.

Figure 2 shows the DSC chart for the cured product. Two inflection points occurred, indicating the glass-transition temperatures: one was at −53°C, indicating the polysulfide polymer framework; and the other was at −68°C, showing the polypropylene glycol framework. The DSC properties showed the properties of polysulfide polymer and polypropylene glycol, which was the NCO prepolymer. Even the dynamic elasticity showed properties, likewise similar to those of DSC, which are close to polysulfide polymer properties.

Figure 5 shows the curing rate of compound **5** in Table II under conditions of 20°C and 30% humidity. Most of the conventional-type polysulfide sealants (PS) were not cured under this low humidity. How-
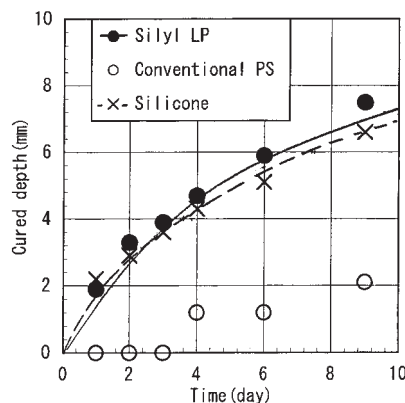
ever, polysulfide sealant (improved by the manner explained herein) exhibited a curing rate that is equivalent to or better than that of the silicone sealant. Even after a curing time of 9 days, the cured depth of silyl LP is three times more than that of conventional PS and 10% more than that of silicone. The solid line and dotted line in Figure 5 show the calculation curve of these sealants.[17]

Compound **5** in Table III shows the properties of the cured product. The cured sealant demonstrated a good elastic rubber performance and its thermal resistance was good. Figure 6 shows the stress–strain curve of this sealant, which was pulled until 600% elongation and was lost at room temperature. After one cycle, the residual elongation of reversion at 0 stress was 100%. Hysteresis loss seems to be substantial, but it does not matter because the modulus of its compounds for building sealant is small and the cycle for its change is long or 1 day.

Figure 3 shows the dynamic elastic properties of the cured product. E' increased with decreasing temperature to −73°C, and below that remained constant. On the other hand, E'' reached its maximum at −55°C, decreasing thereafter until −78°C, at which point it increased somewhat. Tan δ was approximately constant from 150 to −20°C, peaking at −55°C and decreasing to its minimum at −78°C.

The product also was a rubber with a good rate of recovery from compression (at 20°C, when 30% compressed for 1 week, the recovery rate after release was >50%).

Sealants are often painted to match the color of the building. The polysulfide sealant has a plasticizer with a polarity of solubility parameter (SP) value ≥ 9.0, which often causes the plasticizer to move into and soften an acrylic paint that is applied over it. The adoption of isocyanate prepolymer in this new system allows the use of a plasticizer of a polarity of SP value ≤ 9.0, thus preventing its movement, as is the case with urethane sealants, into the paints.

Figure 5 Relationship between cure time and cured depth (20°C, RH 30%).
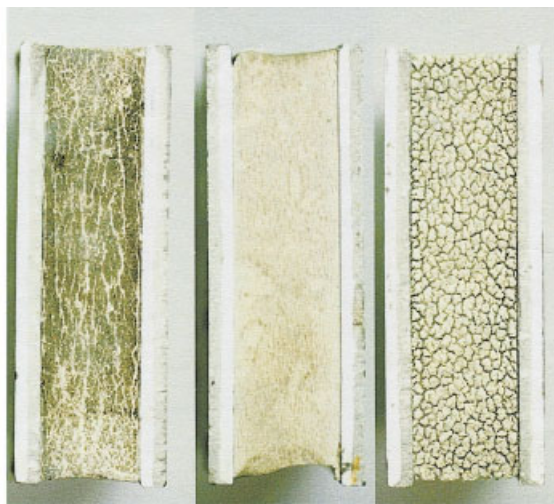
Modified Silicone   Silyl LP compound   Urethane

Figure 7 Sealants after outdoor exposure for 4 years.

The sealant in outdoor applications is exposed to direct sunlight, rain, and other elements, and is consequently required to be resistant to weather. Although the polysulfide sealant meets the required performance standards, choosing an isocyanate prepolymer with a better resistance to weather, such as xylene diisocyanate, would further improve the performance. Selection of a metallic oxidant in the conventional polysulfide sealant would cause a metallic mercaptide to be formed in the framework and degrade the recovery rate of the cured rubber product. The presented new system has eliminated such a concern and obtained a good rubber elasticity, comparable to that of the urethane sealant.

Figure 7 shows a comparison between this new sealant (silyl LP compound) and other sealants that were exposed to outdoor conditions for 4 years. The silyl LP sealant was weatherproof and clean but the urethane sealant was damaged by weather and the modified silicone sealant was stained on the surface.

CONCLUSION

One reason that has prevented popular use of the polysulfide sealant, in spite of its outstanding performance, was the slower curing speed of the conventional moisture-curable one-component sealant compared to that of other type sealants. We developed a new liquid polysulfide polymer terminated with a silyl group. It is easy to synthesize and can produce a variety of moisture-sensitive, one-component compounds using the conventional polysulfide polymer curing agents. All of the resulting compounds exhibited a fast curing rate and good storage stability, together with the uniquely excellent weather resistance and adhesion of polysulfide that is comparable to those of the conventional two-component composition. In particular, a combination with NCO prepolymer offered a fast-curing, one-component sealant, giving the polysulfide performance and outstanding dynamic elasticity and paintability.

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