

## Relationships between Chemical Structure and Properties of Polyether Urethane Sealants

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### Synopsis

Stress relaxation and swelling measurements were carried out and the data used for determination of the effective crosslink densities of one- and two-component urethane sealants. These crosslink densities were compared with calculated values. The results were correlated with the structure of the urethane sealants. Two sealant structures were evaluated: one based on mixtures of triol prepolymers and diol adducts, and the other on triol adducts. Both one- and two-component sealants were investigated. The two-component sealants had a tendency to be undercured even when quite effective catalysts were used. The one-component sealants, because of moisture cure and of biuret or allophanate formation, produced in most cases a higher crosslink density than the calculated triol crosslink density. It was also observed that curing efficiencies of the two-component sealants decreased with increasing molecular weight per crosslink. Deviations from these correlations were noted when a short poly(oxypropylene)glycol of 400 molecular weight was used for curing purposes. These anomalies were detected by stress relaxation and by swelling techniques as well as by measurement of torsional modulus. Stress relaxation studies were carried out to determine the influence of temperature, catalysts, and strain on stress decay. The results again indicated that the two-component sealants did not cure completely, and that the type of catalyst had a significant influence on degradation of urethane sealants at elevated temperatures.

### INTRODUCTION

The applications and commercial importance of urethane sealants are rapidly expanding and are showing promise of continued growth.<sup>1</sup> Both one-component and two-component urethane sealants are being used by a growing number of industries, such as highway, construction, marine, pipe, etc., because of a combination of desirable properties, i.e., good strength, excellent wear resistance, and environmental properties such as weathering, moisture, and chemical resistance.

The preparation and design of urethane sealants has been described by a number of investigators, notably Heiss,<sup>2</sup> Damusis et al.,<sup>3</sup> Bylsma et al.,<sup>4,5</sup> and Saunders and Frisch,<sup>6</sup> and some relationships between chemical structure and physical properties have been established.

The evaluation of raw materials for sealants based on idealized structures is obviously not adequate due to incomplete curing reactions. Thus, in most cases, the predicted structures differ appreciably from the actual

structures, particularly as far as crosslink density is concerned. Correlation of the idealized or predicted chemical structures with physical properties of the resulting sealants is therefore at best only qualitative in nature. Since sealants generally are characterized by low crosslink density and are thus susceptible to failure upon relatively slight degradation, it was deemed of interest to determine (1) the actual crosslink densities of typical one- and two-component urethane sealants by two different methods, (2) the curing efficiency of two-component sealants as a function of the equivalent weight of the curing diol and the type of catalysts employed in the curing process, and (3) the degradation of the sealants at elevated temperatures and the factors affecting degradation.

The determination of the crosslink density was carried out by means of the equilibrium swelling method described by Flory<sup>12</sup> and modified by Cluff et al.<sup>7</sup> and by means of stress relaxation data.<sup>8</sup>

A modified formula of the kinetic theory of rubber elasticity was applied for determining the curing efficiency of two-component sealants by use of a homologous series of polyether diols for the curing reaction.<sup>9</sup> The curing efficiencies were correlated with shear modulus-temperature data obtained by the Clash-Berg method.

Degradation of the sealants at elevated temperatures was studied by means of stress relaxation measurements. Crosslinked polyurethanes undergo flow or stress relaxation in a manner similar to polysulfide and silicone elastomers. This phenomenon, which is due to breaking and reforming of bonds, has also been termed "chemical stress relaxation" and was first investigated by Offenbach and Tobolsky<sup>10</sup> and Colodny and Tobolsky.<sup>11</sup> These studies revealed that stress relaxation in crosslinked polyurethanes occurs primarily due to scission of "weak" linkages such as biuret and disubstituted urea groups. In the present investigation the influence of polyether chain length and catalysts on the stress decay of urethane sealants was determined.

## EXPERIMENTAL

### Materials

The polyether diols and triols and catalysts used in the preparation of the sealants are shown in Table I. An 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate (TDI) was employed.

### Methods of Preparation

**Preparation of One-Component Sealants.** One-component sealants based on trifunctional isocyanate-terminated polymers suspended in TDI adducts of polyether diols are shown in Figure 1. The preparations were carried out as follows. At pigment:polyol weight ratios of 40:60, blends of pigments, consisting of 45% by volume TiO<sub>2</sub>, 5% ZnO, and 50% talc, were dispersed in poly(oxypropylene)glycols on a three-roll mill. After

TABLE I  
Polyols and Catalysts Evaluated in Urethane Sealants

	Molecular weight	Hydroxyl number	Supplier
<b>Polyols</b>			
Poly(oxypropylene) derivatives of 1,1,1-tris(hydroxymethyl)propane <sup>a</sup>			
Triol 300	306	550.1	Wyandotte Chemicals Corp.
Triol 1500	1509	111.5	" " "
Triol 2500	2607	64.5	" " "
Triol 4000	4145	40.6	" " "
Poly(oxypropylene)glycols <sup>b</sup>			
Diol 400	410	273.6	Wyandotte Chemicals Corp.
Diol 700	775	144.8	" " "
Diol 1000	1052	106.4	" " "
Diol 1300	1285	87.4	" " "
Diol 2000	1980	56.6	" " "
Diol 3000	2800	40.1	" " "
<b>Catalysts</b>			
Dibutyltin dilaurate, T-12			M. & T. Chemicals, Inc.
Stannous octoate, T-9			" " "
1,2,4-Trimethylpiperazine			Wyandotte Chemicals Corp.
1,4-Diaza(2,2,2)bicyclooctane, Dabco			Houdry Process & Chemical Co.
Lead naphthenate			Witco Chemical Co.
Chelated tin, Nuocure 29S			Nuodex Product Division, Heyden Newport Chemical Co.

<sup>a</sup> Pluracol TP series, Wyandotte Chemicals Corp.

<sup>b</sup> Pluracol P series, Wyandotte Chemicals Corp.

dispersion the pigmented base was dried by heating under reduced pressure at 110°C. or by an azeotropic distillation with benzene (or toluene). The dried pigmented base was cooled to 50–60°C. and TDI added. Stirring of the reactants at 70°C. for 2 hr. under a nitrogen blanket resulted in the formation of diol adducts.

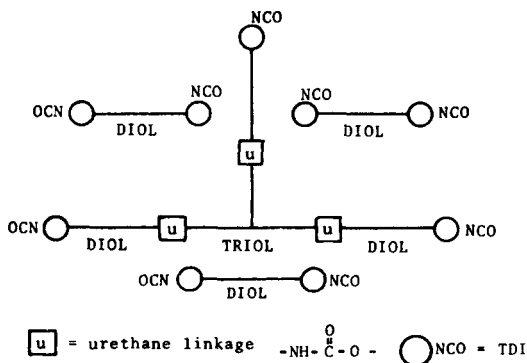


Fig. 1. Schematic structure of one-component urethane sealants. Composition: 6 moles diols, 1 mole triol, 12 moles TDI.

A partial crosslinking of the diol adducts was accomplished by the addition of triols in sufficient amounts to assure reaction with one-half of the diol adduct, resulting in the formation of isocyanate-terminated polymers. The residual unreacted diol adduct served as a suspending medium for the polymer. The crosslinking was conducted by heating at 80–90°C. for 2 hr. Stannous octoate catalyst (0.02% on solids basis) was incorporated.

**Preparation of Two-Component Sealants.** Two-component sealants composed of an adduct (polyether triol and TDI) were cured with various polyether diols (NCO/OH ratio of 1.05). They are represented schematically in Figure 2.

The polyols were dried at 110°C. at 10 mm. Hg pressure to assure a moisture content below 0.02%. TDI was added to the triol, maintaining a temperature of 70°C. for 2 hr. NCO/OH ratios of 2.0 were used in the preparation of the adducts.

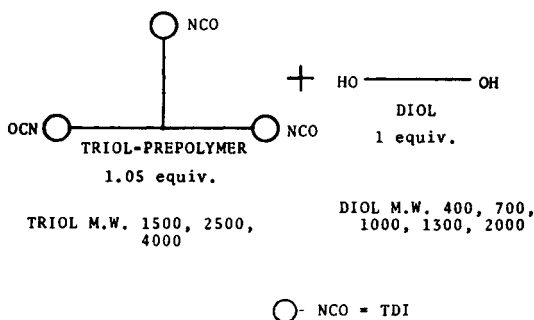


Fig. 2. Schematic structure of two-component urethane sealants.

The second component consisted of poly(oxypropylene)glycols into which pigments, antioxidants, and catalysts were incorporated. The pigments were dispersed in the poly(oxypropylene)glycol on a three-roll mill and were dried for 1 hr. at 110°C. at pressures of less than 10 mm. Hg.

The isocyanate adducts and the pigmented poly(oxypropylene)glycol bases were hand-mixed and deaerated for 3 min.

Another type of two-component sealants was prepared by blending the one-component sealants, described in Figure 1, with poly(oxypropylene)glycols having molecular weights of 400, 700, and 1300.

**Curing of Sealants.** Testing slabs of 0.25 in. thickness were molded. After 24 hr. of curing at room temperature the slabs were removed from the molds and post-cured at 25°C. and 50% R.H. for 2 weeks prior to testing.

### Test Methods

The crosslink densities of the cured sealants were determined by two methods: (1) swelling in toluene, and (2) stress relaxation.

**Crosslink Density by Swelling.** The crosslink densities  $c_s$  and number-average molecular weights of the network chains per unit volume ( $\bar{M}_{c,s}$ ) were determined by the swelling method.

The theory of swelling of crosslinked polymers was applied as suggested by Flory.<sup>12</sup>

A three-dimensional network polymer can absorb large quantities of a liquid which is a solvent for its linear segments. This causes swelling of the polymer network, and the linear segments between the crosslinks assume an elongated configuration. In a swelling sealant, an elastic retractive force develops which opposes the swelling process. The sealants immersed in toluene swell until the swelling forces, tending to dissolve the polymer, come to an equilibrium with the elastic retractive forces. This stage of equilibrium is normally reached in a few days, after which the swollen samples do not show any further increase in weight. According to the theory of elasticity<sup>13</sup> the molecular weight of the polymer between crosslinks is inversely proportional to the elastic forces at equilibrium.

The crosslink densities of the sealants were determined with the aid of cylindrical pellets (height = 0.5 in., diameter = 1.25 in.) which were allowed to swell to equilibrium in toluene. From the weight of the toluene absorbed the volume increase was calculated. The moduli of the swollen sealants obtained by compression-deflection measurements were used for the calculation of the crosslink densities.<sup>7</sup> By expressing compression-deflection data graphically, a slope  $S$ , in the range of linear proportionality, was determined which was applied to eq. (1)

$$\nu_e/V = h_0 S / 3A_0 R T = d / \bar{M}_{c,s} = 3/2 c_s \quad (1)$$

where  $\nu_e/V$  is the number of effective network chains per unit volume;  $A_0$  is the cross-sectional area of the pellet = 1.22 in.<sup>2</sup> = 7.87 cm.<sup>2</sup>;  $h_0$  is the height of the undeformed, unswollen pellet = 0.5 in. or 1.27 cm.;  $R$  is the gas constant = 82,057 cm.-g./degree-mole;  $T$  is the absolute temperature;  $S$  is the slope, graphically determined compression-deflection ratio;  $d$  is the density of polymer;  $\bar{M}_{c,s}$  is the number-average molecular weight of the network chains as determined by swelling, and  $c_s$  is the crosslink density or moles of effective crosslinks per cubic centimeter as determined by swelling.

**Crosslink Density by Stress Relaxation.** The stress at a given strain in a polymeric system, such as a cured urethane sealant, is proportional to the number of chains per unit volume. The network chains are characterized by the value  $\bar{M}_c$  which is the number-average molecular weight between crosslinks. Any changes in the number of these chains affect the stress-strain characteristics of the polymer. When a constant strain is applied to a polymeric material containing a continuous network, the stress decreases with time. This phenomenon is termed stress relaxation. The decrease of stress is caused by the stretching of chain entanglements, breaking of physical bonds, scission of the network along the chain or at crosslinks, and chemical degradation.

The most notable decrease of stress is observed at the beginning of the test, which is caused by stretching of entanglements and breaking of physical bonds. This process of relaxation reaches a plateau. The stress-strain characteristics are dependent at that plateau on the number-average molecular weight between crosslinks  $\bar{M}_{c,r}$  of the sealant. This relation is expressed as shown in eq. (2):

$$(d/\bar{M}_{c,r}) RT = f/[\alpha - (1/\alpha^2)] = 3/2 c_r RT \quad (2)$$

where  $\bar{M}_{c,r}$  is the number-average molecular weight of network chains by stress relaxation;  $d$  is the density of the polymer;  $R$  is the gas constant =  $8.313 \times 10^7$  ergs/degree-mole;  $T$  is the absolute temperature;  $f$  is the force per unit area of original cross section in dynes/square centimeter;  $\alpha$  is the extension ratio,  $l/l_0$ ,  $l$  being the stretched length and  $l_0$  the original length, and  $c_r$  is crosslink density or moles of effective crosslinks per cubic centimeter as determined by stress relaxation. Thus, inserting values for  $f$  and elongation in eq. (2),  $\bar{M}_{c,r}$  was calculated.

For the determination of crosslink densities, slabs of the cured sealants (6.0 in.  $\times$  0.5 in.  $\times$  0.125 in.) were maintained at a constant strain (usually 50–100% elongation), and the stress was continuously recorded on an Instron Universal Tester. The plateau was usually reached after 60–120 min. extension. The determination of the crosslink densities was carried out at room temperature, rather than elevated temperatures, to avoid scission of the networks.

When studying polymer degradation, the stress relaxation tests were conducted at 100°C. An increase in stress decay was noted at this temperature.

The relation between the theoretical crosslink density  $c_t$  and number-average molecular weight of network chains  $\bar{M}_{c,t}$  for these sealants was calculated on the basis of an idealized network structure. A triol at a concentration of  $c$  moles/cc. was employed as a crosslinking agent. Since each network chain would belong to two crosslinks, there would be  $3/2 c$  moles of network chains per cubic centimeter. For trifunctional crosslinks,

$$v_e/V = d/\bar{M}_{c,t} = 3/2 c_t \quad (3)$$

**Curing Efficiency.** The kinetic theory of elasticity indicates a straight-line proportionality between the stress-strain ratio and the crosslink density of the polymer. When evaluating poly(oxypropylene)glycols and triols in urethane sealants some deviation from that proportionality was noted. Three groups of sealants based on isocyanate-terminated adducts from triols of 1500, 2500, and 4000 molecular weight and cured with a homologous series of five poly(oxypropylene)glycols, of 400, 700, 1000, 1300, and 2000 molecular weight, were investigated. The pigmented and unpigmented sealants were subjected to stress relaxation tests at room temperature. For determination of curing efficiencies the stress relaxa-

tions were run at 100% elongation. A modified expression of the kinetic theory of elasticity was applied:

$$f/[(\alpha - 1)/\alpha^2] = \phi E_c d RT / \bar{M}_{c,t} = 3/2 \phi E_c c_t RT \quad (4)$$

$$\phi E_c = 2f/3[(\alpha - 1)/\alpha^2] RT c_t \quad (5)$$

where  $\phi$  is a structural coefficient;  $E_c$  is the coefficient of curing efficiency; and  $c_t$  is the theoretical crosslink density or moles of triol per cubic centimeter.

$\phi E_c$  was plotted as a function of the theoretical triol crosslink density. In the case of a complete cure the product  $\phi E_c$  should be equal to 1.0.

**Torsional Modulus.** A Clash-Berg apparatus was used for the determination of torsional modulus  $G$  according to ASTM method D1043-61T. The samples were immersed in a Dewar flask containing the heat transfer medium (isooctane). The tests were run at  $-60^\circ\text{C}$ . to  $+20^\circ\text{C}$ . The torsional modulus was calculated for each temperature by eq. (6)

$$G = 917 Tl/ab^3u\theta \quad (6)$$

where  $G$  is the torsional modulus in pounds per square inch;  $T$  is applied torque in inch-pounds;  $l$  is specimen length (span) = 1.53 in.;  $a$  is specimen width = 0.25 in.;  $b$  is specimen thickness = 0.1-0.2 in.;  $u$  is Poisson's ratio; and  $\theta$  is the angle of deflection of the torque pulley in degrees.

## RESULTS AND DISCUSSION

### Crosslink Densities

Table II and Figure 3 show the effect of polyether chain length on the crosslink densities of pigmented two-component urethane sealants. The composition of these sealants is described in Table II. In Figure 3 the ratio of crosslink density, as determined by stress relaxation, to the theoretical crosslink density ( $c_r/c_t \times 100$ ) is related to the theoretical molecular weight per triol crosslink ( $\bar{M}_{c,t} \times 1.5$ ). The higher the molecular weight per triol crosslink, the greater the tendency of  $c_r$  to deviate from  $c_t$ . Thus the sealants derived from triol of 1500 molecular weight exhibited better conformance to the theoretical crosslink density than the sealants derived from triols of 2500 and 4000 molecular weight. The chain length of the hydroxyl component had, as expected, a pronounced effect on the crosslink density, generally decreasing with increasing poly(oxypropylene)glycol chain length. Lower crosslink densities than would have been predicted were obtained with sealants prepared from starting materials of 400 molecular weight. This could have been to a large extent due to reactions reducing appreciably the size of the network structures.

The effect of catalysts and the crosslink densities by stress relaxation  $c_r$  for several two-component sealants are seen in Table III. It was found that, without catalyst,  $c_r$  constituted only 17-26% of the theoretical crosslink density  $c_t$ . Catalysts had varying influences on sealant curing, and

TABLE II  
Effect of Polyether Chain Length on the  
Crosslink Densities of Pigmented Sealants by Stress Relaxation<sup>a</sup>

Designation of sealant	M.W. of triol for NCO component <sup>b</sup>	M.W. of PPG for OH component <sup>c</sup>	$c_r \times 10^4$ , mole/cc.	$c_t \times 10^4$ , mole/cc.	$c_r/c_t \times 100$
I-1	1500	400	3.5	3.84	91.2
I-2	1500	700	2.91	3.28	88.7
I-3	1500	1000	2.51	2.94	85.5
I-4	1500	1300	1.81	2.70	67.1
I-5	1500	2000	1.12	2.18	51.4
II-1	2500	400	1.87	2.91	64.2
II-2	2500	700	2.08	2.56	81.2
II-3	2500	1000	1.74	2.36	73.7
II-4	2500	1300	1.25	2.14	58.5
II-5	2500	2000	0.846	1.75	48.3
III-1	4000	400	0.58	2.18	26.6
III-2	4000	700	1.17	2.02	58.0
III-3	4000	1000	0.93	1.86	50.0
III-4	4000	1300	0.65	1.68	38.7
III-5	4000	2000	0.46	1.48	31.1

<sup>a</sup> 10% PVC-pigment (45% TiO<sub>2</sub> rutile, 5% ZnO, 50% talc).

<sup>b</sup> NCO component = 1 mole of oxypropylene derivative of trimethylolpropane (molecular weight as specified) + 3 moles of TDI.

<sup>c</sup> OH component = poly(oxypropylene)glycol (PPG) of molecular weight as specified.

$c_r$  was found to increase up to 63% of  $c_t$ . These improvements were an indication that an effective catalyst is a necessity in two-component sealants.

Crosslink densities by stress relaxation  $c_r$  were also obtained with one-component sealants (see Table IV). In most cases  $c_r$  exceeded the theoretical crosslink densities  $c_t$  by several times. Moisture curing introduced biuret crosslinks in addition to those derived from triols. Both dibutyltin

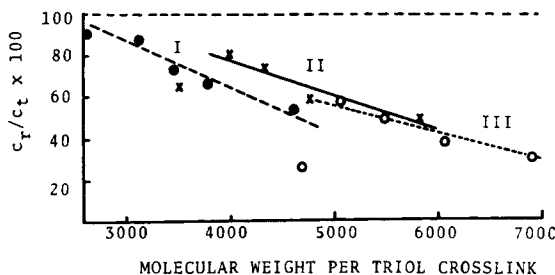


Fig. 3. Relation of molecular weight per triol crosslink to  $c_r/c_t$ : (I) NCO component: triol 1500 M.W. + 3 TDI, OH components: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000; (II) NCO component: triol 2500 M.W. + 3 TDI, OH components: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000; (III) NCO component: triol 4000 M.W. + 3 TDI, OH components: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000.



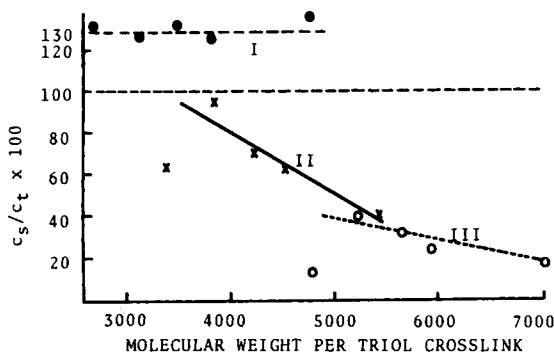


Fig. 4. Relation of molecular weight per triol crosslink to  $c_s/c_t$ : (I) NCO component: triol 1500 M.W. + 3 TDI, OH components: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000; (II) NCO component: triol 2500 M.W. + 3 TDI, OH components: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000; (III) NCO component: triol 4000 M.W. + 3 TDI, OH component: poly(oxypropylene)glycols 400, 700, 1000, 1300, 2000.

dilaurate and trimethylpiperazine were found to be efficient catalysts. They also exhibited good container stability. It is also apparent from Table IV that the crosslink densities  $c_r$ , as expected, decrease with increasing polyol molecular weight.

Table V and Figure 4 show the crosslink densities, of the same two-component sealants as described in Table II, as measured by the swelling method. In Figure 4 the ratios of crosslink densities by swelling to the theoretical crosslink densities ( $c_s/c_t \times 100$ ) are plotted as a function of the molecular weights per triol crosslinks ( $\bar{M}_c \times 1.5$ ). The experimental values of the sealants  $c_s$  with the NCO component consisting of a triol adduct of 1500 molecular weight (group I) were found to be well above the theoretical crosslink density  $c_t$ . This was due to the relatively high degree of crosslinking of these polymers, which caused a lower degree of swelling than normally required for the proper application of this method. The other two homologous series of sealants based on triol adducts of 2500 and 4000 molecular weight followed a pattern similar to that obtained by stress relaxation measurements. The same anomalous behavior was encountered with sealants cured with diol of 400 molecular weight.

The relationship between the molecular weight per crosslink, found by swelling ( $\bar{M}_{c,s} \times 1.5$ ) and by stress relaxation ( $\bar{M}_{c,r} \times 1.5$ ) is shown for pigmented sealants in Figure 5 and for the corresponding unpigmented sealants in Figure 6. Good correlations were obtained between the two methods. In Figure 5 the slope  $S$  for the series based on triol of 1500 molecular weight (group I) was 0.3; that for the series based on triol of 2500 molecular weight (group II) was 1.1; and that for the series based on triol of 4000 molecular weight (group III) was 1.3. In Figure 6 the slope for the series based on triol of 1500 molecular weight (group A) was 0.4; that for the series based on triol of 2500 molecular weight (group B) was 0.8; and that for the series based on triol of 4000 molecular weight

TABLE III  
Effect of Catalysts on Crosslink Densities of Two-Component Sealants

Designation of sealant	NCO component	OH component	Catalyst	$\bar{M}_{c,r}$	$c_r \times 10^4$ , mole/cc.	$\bar{M}_{c,t}$	$c_t \times 10^4$ , mole/cc.	$c_r/c_t \times 100$
E-1	Triol 2500, 1 mole; TDI, 3 moles; 1.05 eq.	PPG 2000, 1.0 eq.	Dibutyltin dilaurate, 1.0%	6,435	1.065	4,044	1.68	63.4
E-4	"	"	Chelated tin, 1.0%	7,750	0.880	4,044	1.68	52.3
E-5	"	"	None	23,300	0.292	4,044	1.68	17.4
E-6	"	PPG 700	None	10,656	0.640	2,780	2.45	26.1
G-1	PPG 2000, 6 moles; Triol 2500, 1 mole; TDI, 12 moles	PPG 400, 4 moles	Dibutyltin dilaurate, 0.5%	30,520	0.225	10,872	0.624	36.0
G-3	"	PPG 1300, 4 moles	Dibutyltin dilaurate, 0.5%	41,600	0.167	12,418	0.547	30.5

TABLE IV  
Effect of Catalysts and Polyether Chain Length on Crosslink Densities of One-Component Sealants

Designation of sealant	Composition of sealant	Catalyst	$\bar{M}_{c,r}$	$c_r \times 10^4$ , mole/cc.	$\bar{M}_{c,t}$	$c_t \times 10^4$ , mole/cc.	$c_r/c_t \times 100$
F-1	PPG 700, 6 moles; Triol 300, 1 mole; TDI, 12 moles	Dibutyltin dilaurate, 0.1%	980	6.93	4,710	1.44	480
F-2	PPG 2000, 6 moles; Triol 300, 1 mole; TDI, 12 moles	Dibutyltin dilaurate, 0.1%	4,076	1.67	9,525	0.715	234
F-3	PPG 2000, 6 moles; Triol 2500, 1 mole; TDI, 12 moles	Dibutyltin dilaurate, 0.1%	5,040	1.35	11,260	0.615	219
F-4	PPG 3000, 6 moles; Triol 2500, 1 mole; TDI, 12 moles	Chelated tin, 0.5%	14,670	0.464	14,220	0.477	97.2
F-5	" " "	Trimethylpiperazine, 0.5%	9,750	0.696	14,220	0.477	146
F-6	PPG 2000, 8 moles; Triol 2500, 1 mole; TDI, 16 moles	None	21,290	0.31	14,460	0.470	66

TABLE V  
Effect of Polyether Chain Length on the  
Crosslink Densities of Pigmented Sealants by Swelling<sup>a</sup>

Designation of sealant	M.W. of triol for NCO component <sup>b</sup>	M.W. of PPG for OH component <sup>c</sup>	Swelling in toluene, %	$c_s \times 10^4$ , mole/cc.	$c_t \times 10^4$ , mole/cc.	$c_s/c_t \times$ 100
I-1	1500	400	130	4.95	3.8	130
I-2	1500	700	142	4.11	3.25	126
I-3	1500	1000	164	3.82	2.92	131
I-4	1500	1300	208	3.32	2.67	125
I-5	1500	2000	236	2.98	2.14	139
II-1	2500	400	209	1.9	3.0	63.4
II-2	2500	700	188	2.5	2.66	94.1
II-3	2500	1000	249	1.56	2.42	64.5
II-4	2500	1300	273	1.41	2.25	62.7
II-5	2500	2000	349	0.74	1.87	39.6
III-1	4000	400	436	0.265	2.13	12.5
III-2	4000	700	336	0.77	1.95	39.5
III-3	4000	1000	378	0.57	1.81	31.5
III-4	4000	1300	463	0.42	1.72	24.4
III-5	4000	2000	578	0.256	1.43	17.2

<sup>a</sup> 10% PVC-pigment (45% TiO<sub>2</sub> rutile, 5% ZnO, 50% talc).

<sup>b</sup> NCO component = 1 mole of oxypropylene derivative of trimethylolpropane (molecular weight as specified) + 3 moles of TDI.

<sup>c</sup> OH component = poly(oxypropylene)glycol (PPG) of molecular weight as specified.

(group C) was 1.3. A reference line having a slope  $S$  of 1.0, representing the ideal correlation between  $\bar{M}_{c,r}$  and  $\bar{M}_{c,s}$ , is included in Figures 5 and 6. It may be concluded from the above values that the best correlation was obtained for sealants which exhibited 300% swelling or more in toluene,

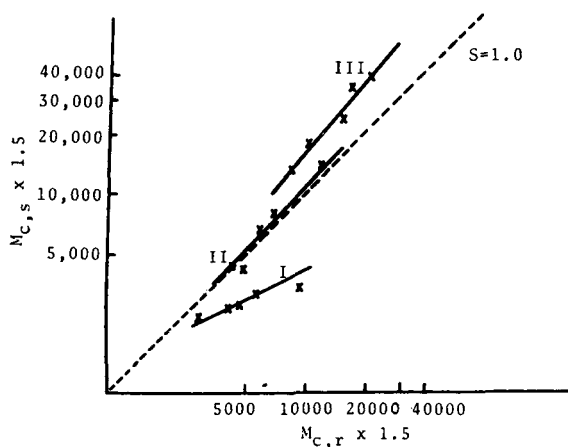


Fig. 5. Relation between molecular weights per crosslink by swelling and stress relaxation for pigmented urethane sealants.

TABLE VI  
Relative Curing Efficiency of Pigmented Sealants<sup>a</sup>

Designation of sealant	M.W. of triol for NCO component <sup>b</sup>	M.W. of PPG for OH component	$c_t \times 10^{-4}$ , mole/cc.	$1/c_t \times 10^{-4}$	$f$ , force per unit area at 100% elongation, psi	Structural curing efficiency $\phi E_c$	Relative curing efficiency $E_c$
I-1	1500	400	3.84	0.266	333	0.918	1.020
I-2	1500	700	3.28	0.304	278	0.900	1.000
I-3	1500	1000	2.94	0.340	240	0.865	0.960
I-4	1500	1300	2.70	0.371	168	0.660	0.735
I-5	1500	2000	2.18	0.460	107	0.520	0.580
II-1	2500	400	2.91	0.344	179	0.652	0.790
II-2	2500	700	2.56	0.390	199	0.825	1.00
II-3	2500	1000	2.36	0.423	166	0.745	0.904
II-4	2500	1300	2.14	0.467	120	0.595	0.722
II-5	2500	2000	1.75	0.571	81	0.490	0.595
III-1	4000	400	2.18	0.458	55.3	0.268	0.464
III-2	4000	700	2.02	0.495	111.0	0.580	1.0
III-3	4000	1000	1.86	0.537	89.0	0.507	0.875
III-4	4000	1300	1.68	0.595	62.0	0.391	0.674
III-5	4000	2000	1.48	0.675	44.0	0.315	0.545

<sup>a</sup> 10% PVC-pigment (45% TiO<sub>2</sub> rutile, 5% ZnO, 50% talc).

<sup>b</sup> NCO component = 1 mole of oxypropylene derivative of trimethylolpropane (molecular weight as specified) + 3 moles of TDI.

<sup>c</sup> OH component = poly(oxypropylene)glycol (PPG) of molecular weight as specified.

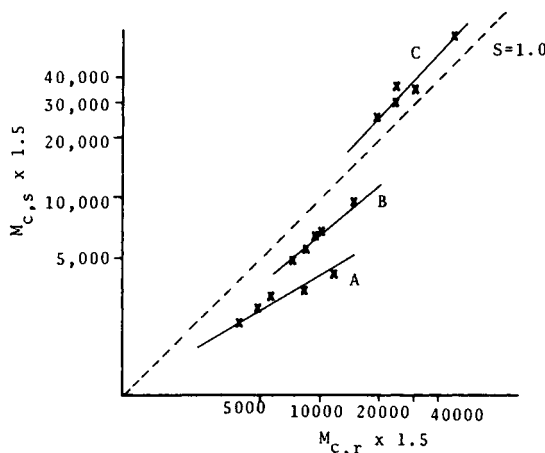


Fig. 6. Relation between molecular weights per crosslink by swelling and stress relaxation for unpigmented urethane sealants.

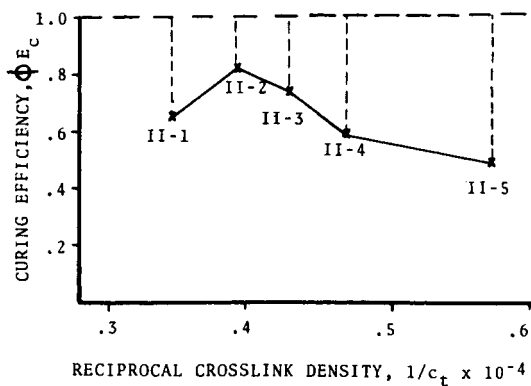


Fig. 7. Relative curing efficiency of pigmented urethane sealants with PVC = 10%; NCO component, triol 2500 M.W. + 3 TDI; OH components, poly(oxypropylene)-glycols: (II-1) 400 M.W., (II-2) 700 M.W., (II-3) 1000 M.W., (II-4) 1300 M.W., (II-5) 2000 M.W.

which usually is considered a criterion for applicability of the swelling method.<sup>7</sup>

### Curing Efficiencies

The curing efficiency of pigmented two-component sealants is presented in Table VI. The structural curing efficiency  $\phi E_c$  was derived from the modified formula of the kinetic theory of elasticity as shown in eq. (4). In the ideal case, where curing is carried to completion, the efficiency  $\phi E_c$  should be equal to 1.0. Where structural factors inhibit the completeness of cure, values of  $\phi E_c$  will deviate from 1.0. In most of the cases the highest  $\phi E_c$  value was obtained for the sealant containing 700 molecular weight diol.

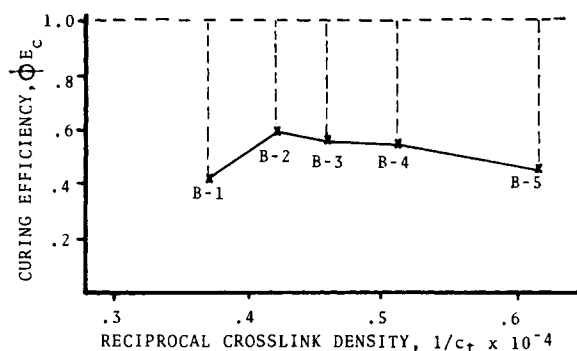


Fig. 8. Relative curing efficiency of unpigmented urethane sealants with NCO component, triol 2500 M.W. + 3 TDI; OH components, poly(oxypropylene)glycols: (B-1) 400 M.W., (B-2) 700 M.W., (B-3) 1000 M.W., (B-4) 1300 M.W., (B-5) 2000 M.W.

In Figures 7 and 8 the structural curing efficiencies  $\phi E_c$  are plotted as a function of the reciprocal crosslink densities ( $1/c_t$ ) for pigmented and the corresponding unpigmented sealants, respectively. The dependence of the structural curing efficiency on the length of the poly(oxypropylene)-glycol chain in the hydroxyl component is apparent. Deviation from this trend is clearly demonstrated again by the sealants cured with the diol of 400 molecular weight.

Whether this phenomenon is due to the formation of cyclic structures or the occurrence of other side reactions is at present still subject to speculation.

### Stress Decay Studies

The influence of three factors on degradation of the sealants was evaluated: temperature, catalysts, and strain.

The stress relaxation behavior of two-component urethane sealants at 100°C. and 50% elongation is shown in Figure 9. The relaxation time  $\tau$

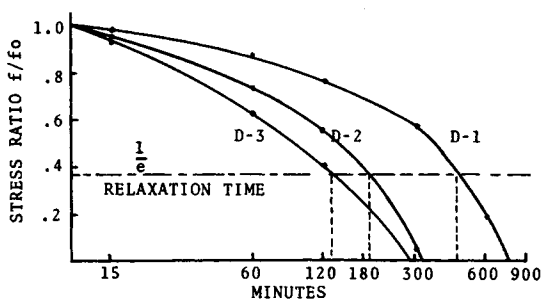


Fig. 9. Effect of polyether chain length on stress decay of two-component sealants at 100°C. and 50% elongation, with NCO component, 6 moles poly(oxypropylene)glycol 2000 M.W., 12 moles TDI, 1 mole triol 2500 M.W.; OH components 4 moles poly(oxypropylene)glycols: (D-1) 400 M.W., (D-2) 700 M.W., (D-3) 1300 M.W.; catalyst dibutyltin dilaurate, 0.5% on solids basis.

at a specific temperature is defined as the time required for the stress to decay to  $1/e$  or 36.8% of its reference value. As can be readily seen from Figure 9, the relaxation times for the three sealants D-1, D-2, and D-3 decreased with increasing chain length of the curing diol. These results correlate well with the data obtained for the experimental crosslink densities by stress relaxation (Fig. 3) and with the relative curing efficiencies (Fig. 7 and 8). Lower crosslink density and curing efficiency would result in greater stress decay.

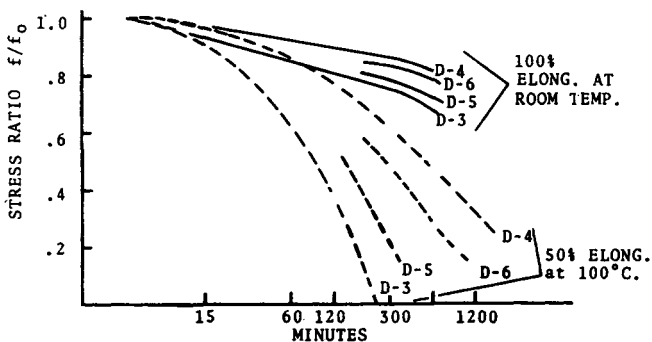


Fig. 10. Effect of catalysts on stress decay of two-component sealants, with NCO component, 6 moles poly(oxypropylene)glycol 2000 M.W., 12 moles TDI, 1 mole triol 2500 M.W.; OH component, 4 moles poly(oxypropylene)glycol 1300 M.W.; catalyst (0.5% on solids basis): (D-3) dibutyltin dilaurate, (D-4) chelated tin, (D-5) triethylenediamine (Dabco), (D-6) lead naphthenate.

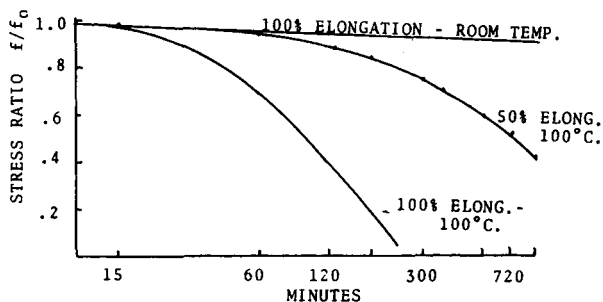


Fig. 11. Influence of strain and temperature on stress decay of one-component sealant. Sealant composition: 6 moles PPG 2000 M.W., 12 moles TDI, 1 mole triol 300 M.W.

The influence of catalysts on the stress decay of two-component sealants is illustrated in Figure 10. Stress relaxation data are shown for two sets of experimental conditions: 100% elongation at room temperature and 50% elongation at 100°C. The resistance to stress decay was greatest with D-4 (chelated tin), followed by D-6 (lead naphthenate), D-5 (Dabco), and D-3 (dibutyltin dilaurate). The order of stress decay for the above sealants was the same under both experimental conditions. Hence, it can be concluded that dibutyltin dilaurate caused the most severe deg-



radation at elevated temperature, a finding which has previously been observed with other polyurethane compositions.<sup>14</sup>

The influence of strain and temperature on the stress decay of a one-component urethane sealant is demonstrated in Figure 11. It is apparent from this figure that strain as well as temperature affect considerably the stress decay of these sealants.

### Torsional Modulus

The glass transition temperature  $T_g$  depends upon several energetic and structural parameters. Among these are the internal mobility of linear segments such as polyoxypropylene, the presence of chain stiffening agents such as aromatic rings and bulky side branches, the continuity of the polymer network, and the degree of interchain forces caused by hydrogen

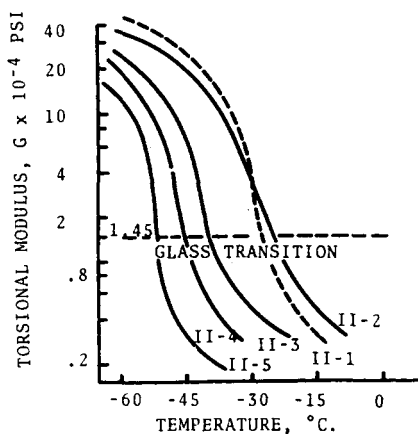


Fig. 12. Torsional modulus of two-component urethane sealants with NCO component, triol 2500 M.W. + 3 TDI; OH components, poly(oxypropylene) glycols: (II-1) 400 M.W., (II-2) 700 M.W., (II-3) 1000 M.W., (II-4) 1300 M.W., (II-5) 2000 M.W.

bonding and Van der Waal's forces. The internal mobility in the case of polyether urethane sealants is affected greatly by the oxypropylene segments and the concentration of urethane groups and aromatic rings. It could be assumed that a shorter chain length of oxypropylene segments together with a corresponding increase in the concentration of urethane and aromatic groups would result in lower internal mobility and, hence, in a higher glass transition temperature. Other factors influencing the  $T_g$  of these polymers are the crosslink density, and any reactions leading to terminations of the growing network.

Figure 12 illustrates the torsional modulus of two-component sealants (II-2 to II-5) as determined by the Clash-Berg method. The sealants cured with diols of molecular weights of 700 and greater exhibited the expected trend for the glass transition temperatures, decreasing with in-

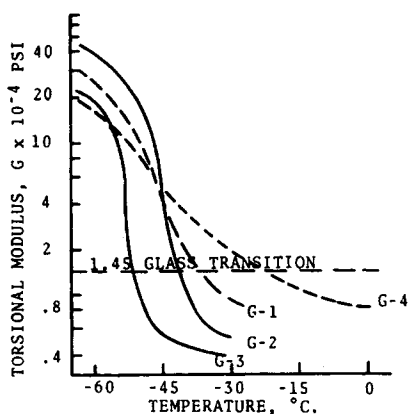


Fig. 13. Torsional modulus of urethane sealants with NCO component, 6 moles poly(oxypropylene)glycol 2000 M.W., 12 moles TDI, 1 mole triol 300 M.W.; OH components, poly(oxypropylene)glycols: (G-1) 400 M.W., (G-2) 700 M.W., (G-3) 1300 M.W.; (G-4) one-component sealant consisting of the above-described NCO component.

creasing oxypropylene chain length. However, the sealants cured with the diol of 400 molecular weight (II-1) showed a definite anomaly, exhibiting a  $T_g$  lower than that of the sealant derived from the diol of 700 molecular weight (II-2). These results may indicate a greater degree of network chain termination such as could occur by chain-terminating side reactions. These results are also in agreement with the experimental data obtained for the crosslink density by swelling (Fig. 4) and stress relaxation (Fig. 3) as well as the findings for the curing efficiencies (Figs. 7 and 8).

Torsional moduli were obtained for another series of two-component sealants (G-1, G-2, and G-3) as shown in Figure 13. A one-component sealant (G-4) is included for comparison. The latter exhibited a significantly higher  $T_g$  than the corresponding two-component sealants. This is probably due to the moisture curing process which results in the formation of urea groups and biuret crosslinks.

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### Résumé

Des mesures de relaxation de tension et de gonflement ont été effectuées et les résultats ont été employés pour déterminer les densités réelles de pontage des ciments d'uréthane à un et deux composants. Ces densités de pontage ont été comparées avec les valeurs calculées. Les résultats ont été reliés à la structure des ciments d'uréthane. Deux structures de ciment ont été évaluées; l'une basée sur des mélanges de prépolymères de triol et d'additifs diol, et l'autre sur des additifs triols. On a étudié les ciments à un et deux composants. Les ciments à deux composants avaient une tendance à être insuffisamment pris même lorsqu'on utilise les catalyseurs adéquats. Les ciments à un composant, à cause du traitement humide et de la formation de biuret ou d'allophanate, produisent dans la plupart des cas une densité de pontage plus élevée que la densité de pontage calculée avec le triol. On a également observé que les efficacités du traitement à chaud des ciments à deux composants diminuent avec une augmentation du poids moléculaire par pont. On a relevé des déviations à partir de ces relations lorsqu'on utilise un polyoxypropylène-glycol de poids moléculaire 400 pour le traitement à chaud. Ces anomalies ont été détectées par les techniques de gonflement ainsi que par mesure du module de torsion. Des études de relaxation de tension ont été effectuées pour déterminer l'influence de la température, des catalyseurs et de la déformation sur la dégradation de la tension. Les résultats montrent de nouveau que les ciments à deux composants ne sont pas complètement pris et que le type de catalyseur a une influence prépondérante sur la dégradation des ciments d'uréthane aux températures élevées.

### Zusammenfassung

Spannungsrelaxations- und Quellungsmessungen wurden ausgeführt und die Ergebnisse zur Bestimmung der effektiven Vernetzungsdichte von ein- und zweikomponentigen Urethandichtungsmassen benützt. Diese Vernetzungsdichten wurden mit berechneten Werten verglichen. Die Ergebnisse wurden zur Struktur der Urethandichtungsmassen in Beziehung gesetzt. Zwei Dichtungsmassestrukturen wurden ermittelt; eine auf Grundlage von Mischungen von Triolpräpolymeren und Dioladdukten, andre auf derjenigen von Trioladdukten. Sowohl ein als auch zweikomponentige Dichtungsmassen wurden untersucht. Die zweikomponentigen Dichtungsmassen wiesen sogar bei Anwendung sehr wirksamer Katalysatoren eine Tendenz zur unvollständigen Härtung auf. Die einkomponentigen Dichtungsmassen bildeten wegen der Feuchtigkeitshärtung und der Biuret- oder Allophanatbildung in den meisten Fällen eine höhere als die berechnete Triolvernetzungsdichte aus. Weiters wurde beobachtet, dass die Härtungsfähigkeit der zweikomponentigen Dichtungsmassen mit steigendem Molekulargewicht pro Vernetzung abnahm. Abweichungen von diesen Korrelationen traten bei Verwendung eines kurzen Poly(oxypropylen)glycols mit M.G. 400 zur Härtung auf. Diese Anomalien konnten durch Spannungsrelaxations und Quellungsverfahren sowie auch durch Messung des Torsionsmoduls erkannt werden. Spannungsrelaxationsuntersuchungen wurden zur Bestimmung des Einflusses der Temperatur, der Katalysatoren und der Verformung auf den Spannungsabfall ausgeführt. Die Ergebnisse zeigten wieder dass die zweikomponentigen Dichtungsmassen nicht vollständig aushärten und dass der Katalysatortyp wesentlichen Einfluss auf den Abbau von Urethandichtungsmassen bei erhöhter Temperatur besass.

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