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Cross-Linking of Methyl Silicone Rubbers. Part II. Analysis of Extractables from Samples Cross-Linked under Various Conditions

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Cross-Linking of Methyl Silicone Rubbers. Part II. Analysis of Extractables from Samples Cross-Linked under Various Conditions

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ABSTRACT

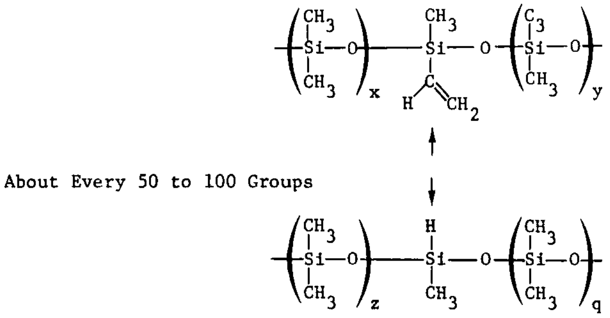
During the cross-linking under themal conditions of two pre-polymers, a variety of compounds may be formed in addition to the desired cross-linked network, i.e., branched chain, large ring, and linear chain of twice pre-polymer molecular weight. In order to evaluate these processes with as little chemical complication as possible, a series of two component methyl silicone pre-polymers (Sylgard 184, 186, and 188) have been cross-linked with vinyl silicone pre-polymer at various ratios of reactive groups and concentrations in silicone oil. These rubbers were evaluated by thermomechanical analysis (TMA) and then swollen with n-hexane. The cross-link density was evaluated from TMA and hexane swelling. The extracts were studied by gel permeation chromatography. As the "catalyst" concentration (active hydrogen containing pre-polymer) was increased from 5 to 60%, the percent and average molecular weight of the hexane-soluble fraction was found to decrease for the 186 and 188 samples. No higher molecular weight fraction was extractable from the

184 sample. For all samples the modulus and cross-link density increased until 10 to 30% catalyst was present. Above this concentration these parameters dropped off gradually. Evidence is offered to support the view that polymerization in dilute solution promotes cross-linking. The molecular weight changes noted for the extractables from the 186 and 188 sample suggests that branched chain formation predominates as a side reaction product. Little original pre-polymer is extractable in an unreacted state. Differential scanning calorimetry was employed to follow the thermodynamics of the reaction.

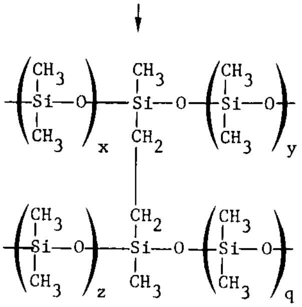
INTRODUCTION

In Part I of this study an experimental two-component silicone rubber was cross-linked at various component ratios and in the presence of compatable diluting agents [1]. These two-component poly(methylsiloxanes) condense to yield cross-links but no volatile or nonvolatile second product. This greatly simplifies calorimetric and mechanical studies. Given some understanding of the chemical principals of the reaction, the two-component methylsiloxanes should be model systems for the study of the thermodynamics of cross-linking by modern techniques of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermomechanical analysis (TMA).

This study extends the previous work with an experimental siloxane resin system to three commercially available systems: Sylgard 184, 186 and 188. The name and numerical designations are registered trade names of the Dow Corning Co. Each resin system designates a "resin" and "catalyst" pair which are actually both polymeric methylsiloxanes. One component contains a reactive hydrogen every 50 or 100 units in place of a methyl, and the other component contains a pendant vinyl group. The basic reaction is as follows:



Combined in the Presence of Heat and a Soluble Platinum Catalyst



The work with these three systems is concerned with the following:

1. Molecular weight distribution of reactants and extractable products.
2. Effect of alterations in proportions of reactive species on the heat of reaction, cross-link density, and elastic modulus (Young's) of the rubber. The cross-link density and modulus were determined by both TMA and hexane swelling. The equations for the necessary calculations have been given in detail in the previous study [1].

EXPERIMENTAL

Gel Permeation Chromatography (GPC)

Due to the relative insolubility of both the pre-polymers and the extracted polymer after cure, GPC of these materials is difficult. Chloroform is a reasonably good solvent. Solutions of 0.2% solids in chloroform were ultrafiltered and automatically injected into a Waters Associates 200 GPC in 2 ml volumes. The chromatograph was equipped with five columns covering the porosity range 1×10^6 Å (3 columns), 1×10^4 Å, and 1×10^3 Å. The mobile phase was chloroform. Data was acquired and digitized with a time share IBM 1800 computer system. Both the auto-inject and on-line data acquisition system have been described elsewhere [2]. After the acquisition the data was reduced off-line with a modified Pickett-Cantow program. The chromatograph was calibrated with the usual narrow molecular weight polystyrene fractions.

The molecular weights expressed in this paper are styrene equivalent molecular weights. If it is assumed that the hydrodynamic radii of polystyrene and poly(methylsiloxane) are equivalent, the molecular weight averages calculated will be uniformly 28.8% too high. This is based upon the ratio of monomer molecular weights, 74 for dimethylsiloxane and 104 for styrene.

This error has not been corrected in the tables and figures since relative molecular weights are of interest. Truly accurate molecular weights would require calibration with narrow fractions of poly(methylsiloxane). In addition the extracts from cross-linked samples are almost surely branched. This complication will introduce large errors in the absolute value of the GPC-determined molecular weight. It is well known that branched molecules have an effective hydrodynamic radius much smaller than a linear molecule of equivalent weight. These limitations must be held in mind when considering GPC data on the systems of interest in this paper. However, by comparing molecular weight trends and various systematic variables it is possible to extract much useful data from the GPC study.

Extraction Studies

Samples of silicone rubber were formed in aluminum foil cups. Each sample contained sufficient finished product to produce two samples for swelling and one sample for TMA. The samples for swelling were weighed dry and placed in 50 ml of spectral grade hexane and covered. This hexane contained no detectable solid residue in 500 ml of solvent. The samples were swollen for 2 days, removed from the hexane, blotted twice, and weighed. The balance atmosphere was saturated with hexane vapors. Care was exercised to lose the minimum volume of hexane in the transfer. The temperature during swelling averaged 25 ± 1°C. After the samples had swollen to constant volume, the hexane was carefully decanted into a weighted planchette, the swelling flask washed with more hexane, and the contents of the planchette evaporated to dryness at 35°C in a vacuum oven. The planchette was reweighed and the percent extractable was determined. As stated above, this residue was taken up in chloroform for the GPC study. It is necessary to exercise some care with certain silicone formulations to exclude small chips of rubber which break off during swelling. These cause an insignificant error in the swelling weights but a serious error in apparent residue weights. The swelling data were converted into cross-link density and elastic modulus using the following equations:

$$v_2 = (1/\rho_r)/[(w/\rho_h) + (1/\rho_r)] \tag{1}$$

where v_2 is the volume fraction of the polymer in the swollen state; ρ_r is the density of the rubber = 0.9926 g/cc, ρ_h is the density of hexane, and w is the grams of hexane sorbed per gram of rubber.

$$\nu_e = -[2.303 \log(1 - v_2) + v_2 + \chi_1 v_2^2]/V_1 (v_2^{1/3} - v_2/2) \tag{2}$$

where ν_e is the moles of effective network chain per cubic centimeter for tetrafunctional sites, χ_1 is the solvent/polymer interaction parameter = 0.48(4), and V_1 is the molar volume of hexane = 130.6 cc/mole.

$$\nu_e = E/3RT \tag{3}$$

where E is the elastic modulus (Youngs), R is the gas content = 8.314 × 10^7 ergs/mole °K, and T is the temperature in °K.

NMR and Titration Studies

NMR spectra were obtained on a Varian T-60 spectrometer using tetramethylsilane as a lock and carbontetrachloride as the solvent. The uncross-linked samples were brominated by the method of Uhrig and Levin [3]. The samples were titrated with a standard bromine solution in glacial acetic acid. The titration solvent was chloroform. The end point was detected by the color of excess bromine. Difficulty was experienced using more conventional potentiometric methods due to the insolubility of the silicones in the titration solvent. The results from the direct bromination are shown in Table 1. Obviously, the process is neither simple nor direct. The products of bromination were examined by NMR and IR.

Thermomechanical Analysis

The spherical indentation measurements were made with a Du Pont TMA using a probe of radius 0.1416 cm. Loads from 10 mg to 5 g were employed, the range being determined by the softness of the sample. The elastic modulus was calculated as described previously [1] with the equation

$$F = \frac{16}{9} E r^{1/2} p^{3/2} \tag{4}$$

where F is the force, r is the probe radius, and p is the penetration. In practice the load in grams was graphed versus the TMA penetration to the 3/2 power. Load was the y-axis. Thus $F/p^{3/2}$ = slope × 980. The 980 translates the force into dynes/cm^2. Given the modulus, the cross-link density can be calculated from Eq. (3).

TABLE 1. Bromination of Siloxane Resin Components

Component	Average number of monomer units between pendent vinyls
Sylgard 184 resin	4,780
Sylgard 186 resin	15,000
Sylgard 188 resin	17,700
Sylgard 184 catalyst	2.8
Sylgard 186 catalyst	15.1
Sylgard 188 catalyst	5.1

DSC Studies

The DSC technique has been described in detail previously [1]. Briefly, a Perkin-Elmer DSC 1-B was employed for all measurements of heat reaction temperature and activation energy. The heating rate was 20°C/min. Sample weights were chosen so that a substantially constant deflection was obtained at 4 mcal/sec sensitivity. The samples were heated in open aluminum planchettes. The samples were made from the same identical mixture as employed for the TMA and swelling samples. The DSC data was acquired on an IBM System 7 computer using a program developed at IBM. The kinetic data were calculated by the techniques of Barrett [4] and Rogers and Morris [5]. These are Methods I and II in the tables.

RESULTS

Chemical Composition Studies

As this study progressed it became obvious that the chemistry of these commercial silicones was somewhat more complex than had initially been supposed. This is most clearly demonstrated in the results of NMR and bromination experiments.

The bromination data shown in Table 1 for the resin systems is about as would be expected, i.e., the right order of magnitude. The vinyl content is so low as to be at the limits of detection. However, the statistics of the experiment were such that it can be stated with confidence that the 184 resin has three times the amount of unsaturation as the 186 and 188 systems. The NMR spectra of resins 184, 186, and 188 showed the expected patterns of methyl protons in the presence of silicone. The vinyl protons are far too low in concentration to be detected by conventional NMR. No other resonances were noted.

The bromination results on the catalyst systems cannot be accounted for on the basis of the expected chemistry. The results in Table 1 are several thousand times too high. Other reactions must have taken place. The NMR curves on the catalyst systems were also unusual but similar to one another. The curve for catalyst 184 is shown in Fig. 1. The expected methyl protons are present in addition to resonances at 4.65 and 5.85 ppm. The small peaks at 0.7 and 1.2 ppm are spinning side bands. The superimposed high sensitivity scan at 5.85 ppm may show pendant vinyl groups. These were not expected in the catalyst.

The 4.65 ppm resonance was examined by studying the partially brominated products (35 and 75%). The NMR spectra are shown in Figs. 2 and 3. The 4.65 ppm resonance is very sensitive to bromination. Although not shown in this example, the 5.85 ppm resonance disappeared completely early in bromination. A concurrent IR study showed that for the 35% brominated materials, the silyl groups were reduced by ~33% over the unbrominated material. This would account for the high values given by bromination as shown in Table 1. At present we are unable to account chemically for this process. Obviously,

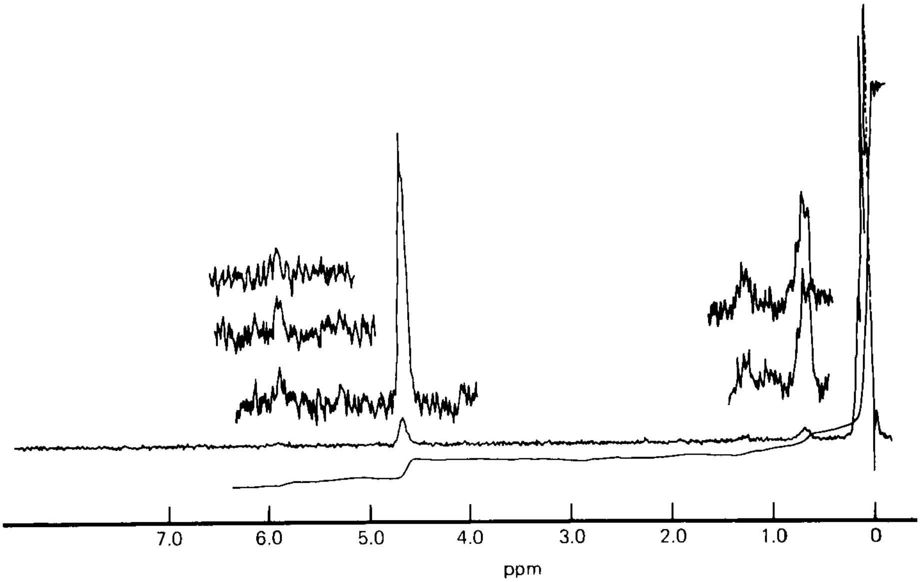


FIG. 1. NMR spectrum of Sylgard 184 catalyst showing brominatable proton resonances.

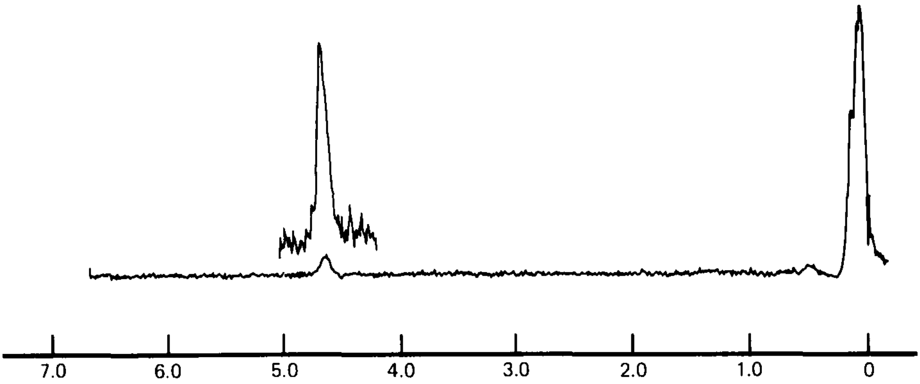


FIG. 2. NMR of 35% brominated Sylgard 184 catalyst.

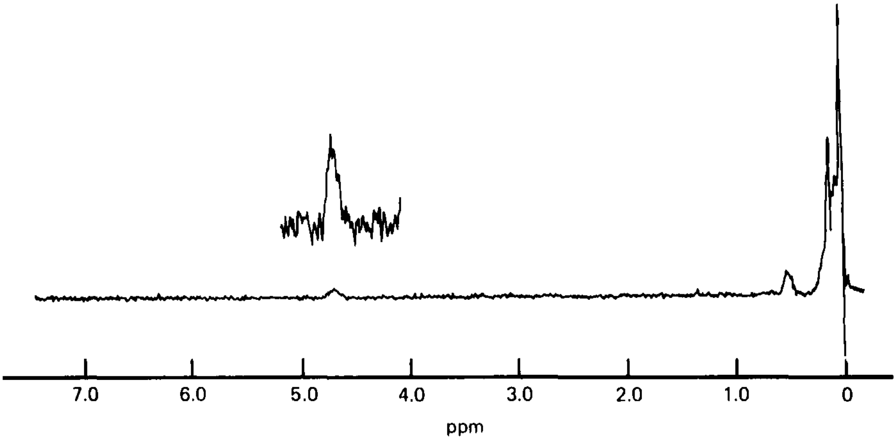


FIG. 3. NMR of 75% brominated Sylgard 184 catalyst.

bromination cannot be used to determine the labile hydrogen content in this material.

Gel Permeation Studies

The uncross-linked resins and catalysts were chromatographed and all produced bimodal molecular weight distributions. These are given in Table 2, and examples of the 184 resin and catalyst are shown in

TABLE 2. Gel Chromatographic Results on Uncross-linked Resin and Catalyst

	Mode 1			Mode 2	
Sample	Peak $\overline{M}_w$[a]	U	% Sample[b]	Peak $\overline{M}_w$[a]	Sample[b]
184 Resin	49000	1.4	85	2000	15
184 Catalyst	47000	1.3	20	1000	80
186 Resin	31000	1.6	97	700	3
186 Catalyst	55000	1.2	20	2000	80
188 Resin	57000	1.1	92	3000	8
188 Catalyst	69000	1.2	20	2000	80

[a] Weight-average molecular weight.

[b] Calculated on the basis of an equal refractive index increment for polymer and oil.

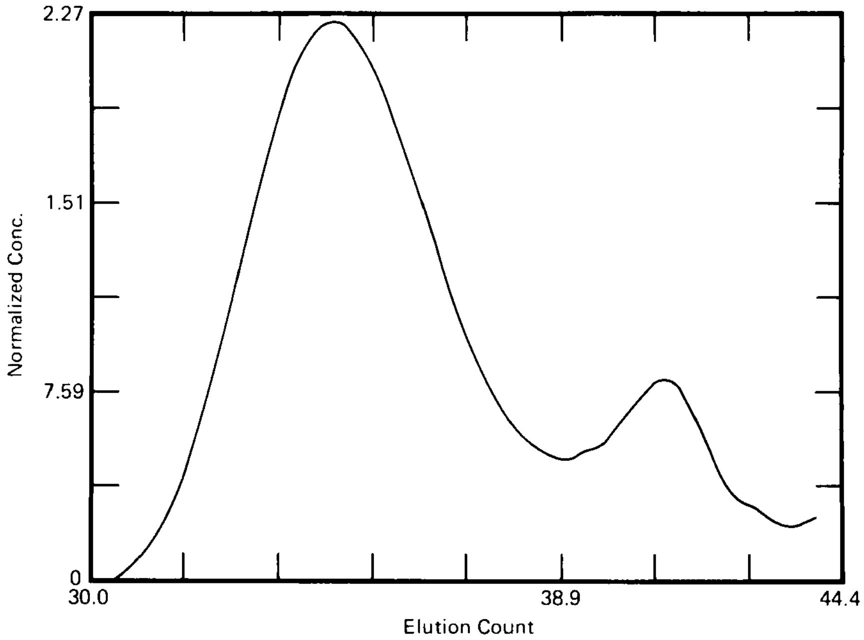


FIG. 4. Gel permeation chromatogram of Sylgard 184 resin in chloroform.

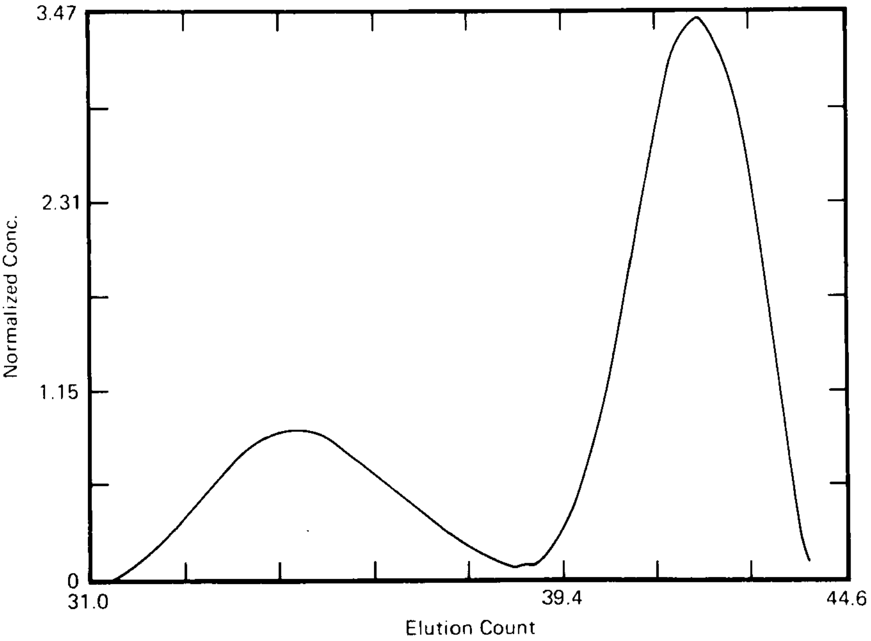


FIG. 5. Gel permeation chromatogram of Sylgard 184 curing agent in chloroform.

Figs. 4 and 5. The first peak is the high molecular weight pre-polymer, and the second peak is a low molecular weight diluting oil. NMR and IR spectral examination of the second peak indicates that it is identical to a relatively inert methyl silicone oil. The oil is probably added to adjust the viscosity of the combined resin and catalyst for various molding operations. From earlier work it may be supposed that the oil will alter the rate and completeness of cross-linking [1]. Except for the low molecular weight of the 186 resin component, there is nothing unusual about the molecular weights of the starting materials. The 186 resin is the most concentrated pre-polymer. The number of functional groups must be subject to some variation. As stated previously, we were unable to make a satisfactory direct measurement of the vinyl or active hydrogen content by several methods (NMR, IR, bromine titration). This is probably due to the low concentration of the active groups. The manufacturer indicates that one reactive group occurs per 100 monomer units. In that case the 186 catalyst should have twice as many groups as the 186 resin. The 184 and 188 resins and catalysts should be about equal. The 188 pair should present a more viscous mixture prior to

TABLE 3. Characteristics of Hexane Extractable Materials after Polymerization

Catalyst content	5	10	15	20	30	40	50	60
			Sylgard 184 System					
Total solubles, %	7.9	3.6	3.9	4.8	7.1	9.4	12.6	16.9
1st mode $\overline{M}_w$[a]	-	-	-	-	-	-	-	-
Concentration, %	-	-	-	-	-	-	-	-
2nd mode $\overline{M}_w$[a]	1948	1687	1904	1881	1896	1391	3076	3274
Concentration	100	100	100	100	100	100	100	100
			Sylgard 186 System					
Total solubles, %	35.5	6.4	5.5	6.1	6.8	7.8	8.4	9.4
1st mode $\overline{M}_w$[a]	56000	47000	27000	29000	31000	33000	33000	33000
Concentration, %	90	15	5	6	8	10	15	20
2nd mode $\overline{M}_w$[a]	1400	1400	1400	1400	1400	1200	1100	1200
Concentration %	10	85	95	95	92	90	85	80
			Sylgard 188 System					
Total solubles, %	41.0	15.0	5.6	3.8	3.8	4.7	6.5	8.5
1st mode $\overline{M}_w$[a]	37000	23000	33000	37000	33000	33000	33000	33000
Concentration, %	75	20	5	5	3	3	5	5
2nd mode $\overline{M}_w$[a]	1600	1400	1500	1400	1400	1400	1500	1500
Concentration, %	25	80	95	95	97	97	95	95

[a] Weight-average molecular weights.

polymerization than the 184 mixture, due to the higher molecular weight of the diluting oils.

The resin/catalyst mixtures of various concentrations show a wide variation in the percent and the molecular weight of the extractables (see Table 3). With the exception of the 184 system, all extracts are bimodal. The 184 system from the lowest catalyst concentration studied (5%) shows no high molecular weight extract. This indicates that a completely cross-linked network is formed from the lowest concentrations of catalyst. Even without a high molecular weight portion, the total percent extractables follows the same general trend as that of the other two systems as a function of catalyst concentration. There is a minimum in the extract percent curve near the stoichiometric point between resin and catalyst as indicated by the modulus and calorimeter studies and by the manufacturer. This minimum is shown graphically in Fig. 6. At higher concentrations there is some indication that a reaction does occur to produce low molecular weight material in the 184 system. The molecular weight sharply increases above 40% catalyst to a number significantly greater than the original low molecular weight fraction present in either resin of catalyst (see Tables 2 and 3).

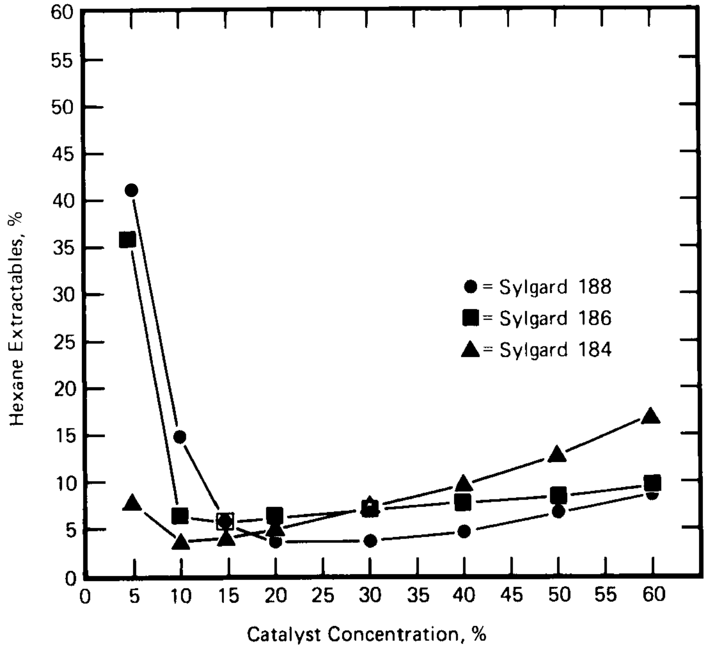


FIG. 6. Variation of extractable materials from Sylgard samples as a function of catalyst concentration.

The high molecular weight fraction predominates in the extractable portion of the 186 and 188 systems at 5% catalyst. This material is probably not related to excess resin since the molecular weight is much too high (56,000 in extract vs 31,000 in the original for the 186 resin). The extract is probably a highly branched structure with a core of excess resin molecules. The actual molecular weight could be as much as 50% higher due to branching effects in the GPC.

The percentage of high molecular weight material in the extracts drops off rapidly as the catalyst concentration is increased to the stoichiometric point. Both the measured molecular weight of the extract and the absolute amount of extract follow the same trend. This could be due to both an absolute decrease in high molecular weight material not held in a cross-linked network and to entrapment of molecules (physical) in a tightly cross-linked cage. The latter case is reinforced by the decrease in the low molecular weight fraction. In the previous study pure silicone oils were blended with the resin catalyst mixture prior to cross-linking [1]. It was not possible to extract more than 60 to 70% of these oils in hexane near the stoichiometric point.

Above the stoichiometric point the high molecular weigh portion of 186 and 188 extractables assumes a relatively constant value, ~33,000, as the resin content is increased. The low molecular weight oil predominates, but the molecular weight continues to increase. Since we have no absolute measure of branching, it is impossible to say if this apparently constant high molecular weight is absolutely constant or an artifact of increased branching.

Cross-link Density and Elastic Modulus Study

The data derived from the TMA and hexane swelling experiments are shown in Table 4. The same general trends noted previously with other systems apply to these data [1]. However, some notable exceptions are evident. The agreement between the same parameter (modulus or cross-link density) calculated from TMA and swelling is reasonably good for the 186 system. However, the cross-link density calculated by swelling is in serious error for the 184 and 188 systems.

On the basis of the physical appearance of the 20% catalyst sample of Sylgard 188, it is safe to say that the cross-link density is not 111.8×10^{-5} moles/cc. This density should be expected to produce a hard glass, which the sample surely is not. The error probably resides in the choice of the wrong value for χ_1 in Eq. (2).

The value of 0.48 had proven satisfactory for other silicone rubber systems [6] as well as the 186 system. Since the factors affecting the solvent/polymer interaction parameter are exceedingly complex, it is useless to speculate at this stage upon the reasons for the

TABLE 4. Modulus and Cross-link Density Correlation for a Series of Sylgard Rubbers

% Catalyst	Elastic modulus[a] (dynes/cm^2)		Cross-link density[b] (moles/cc)		Sample
	TMA	Swelling	TMA	Swelling	
5	5.4	1.1	7.4	15.4	Sylgard 184
10	11.8	66.3	16.2	90.7	
15	9.5	55.9	12.9	75.2	
20	5.4	38.0	7.4	52.1	
30	6.4	31.6	8.8	43.2	
40	8.7	34.7	11.7	47.5	
50	3.5	36.9	4.8	50.6	
60	3.0	30.1	4.2	41.2	
5	0.6	2.8	0.8	3.8	Sylgard 186
10	7.5	8.4	10.0	11.5	
15	9.5	7.7	13.0	10.5	
20	6.1	6.4	8.3	8.8	
30	5.1	4.8	7.0	6.5	
40	5.2	3.8	7.1	5.2	
50	5.5	2.8	7.5	3.9	
60	6.9	2.2	9.5	3.0	
5	0.5	1.3	0.7	1.8	Sylgard 188
10	2.3	6.5	3.1	8.9	
15	8.5	25.0	12.0	34.2	
20	8.8	81.8	12.2	111.8	
30	19.0	77.2	26.0	105.7	
40	9.6	53.2	13.0	72.8	
50	8.6	44.1	11.7	60.4	
60	6.3	35.7	8.7	48.9	

[a] Modulus $\times 10^{-6}$, i.e., $5.4 = 5.4 \times 10^{6}$ dynes/cm^2.

[b] Cross-link density $\times 10^{5}$, i.e., $7.4 = 7.4 \times 10^{-5}$ moles of effective cross-link/cc.

problems noted in the 184 and 188 systems. However, since this parameter is multiplicative, the values have a relative usefulness within a given system.

The variation of elastic modulus (TMA) and apparent cross-link density (swelling) with catalyst concentration are shown in Figs. 7, 8, and 9. The maximum modulus and maximum cross-link density do not always occur at the same catalyst concentration (see Figs. 8 and 9). This could be due to the contribution to the TMA modulus of entangled and/or branched chains which are not detected by hexane swelling. The secondary maximum on System 184 at 40% catalyst may be due to the same effect. System 188 appears to be very sensitive. There is some reflection of this in the data on the extracts (see Table 3).

Calorimetric Data

The heat of reaction (exothermal) is very dependent on catalyst concentration in the presence of excess resin. However, from Fig. 10 it is obvious that other reactions than that shown in the Introduction can occur. The maximum heat of reaction occurs at concentrations of

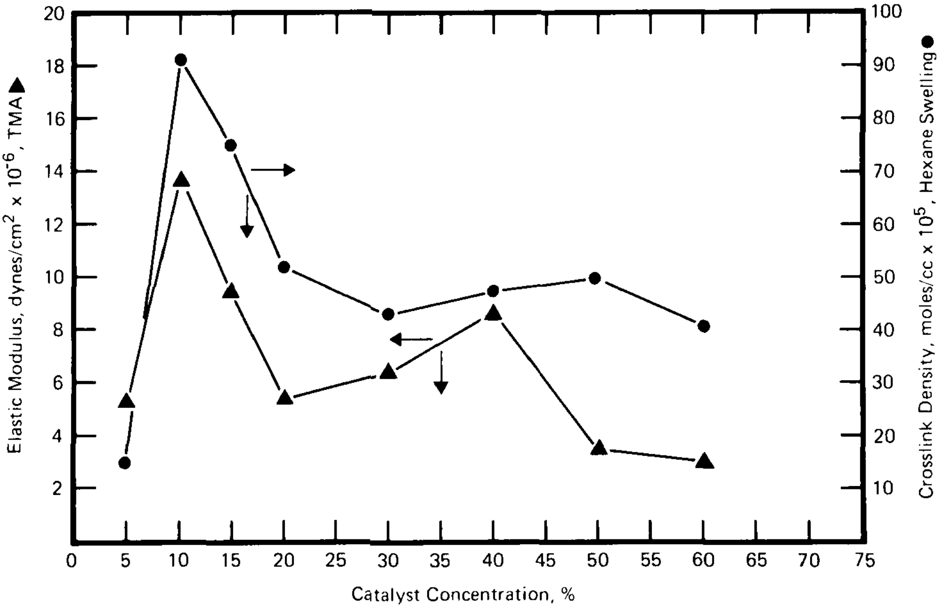


FIG. 7. Variation of elastic modulus and cross-link density with catalyst concentration Sylgard 184.

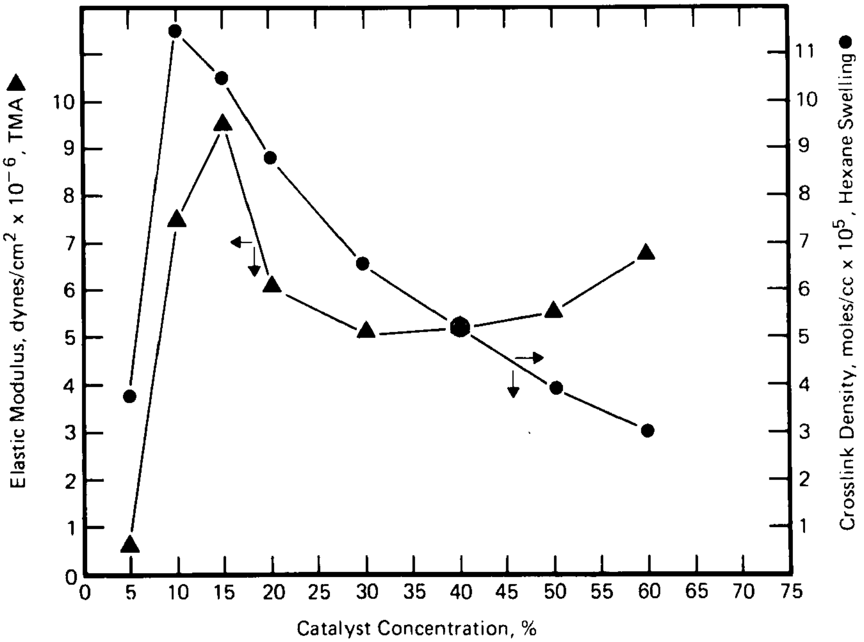


FIG. 8. Variation of elastic modulus and cross-link density with catalyst concentration Sylgard 186.

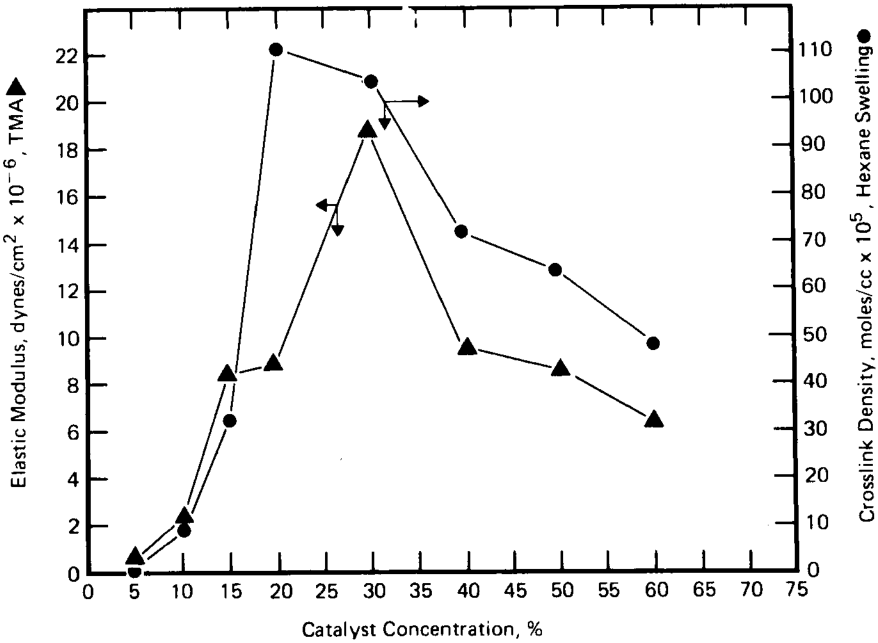


FIG. 9. Duration of elastic modulus and cross-link density with catalyst concentration Sylgard 188.

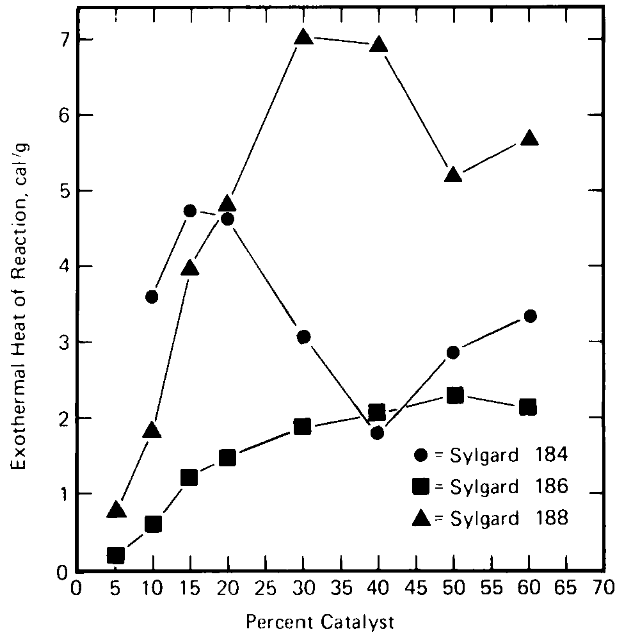


FIG. 10. Effect of catalyst concentration on the heat of reaction of three Sylgard systems.

catalyst above that required to induce the highest modulus of elasticity (compare Figs. 7 to 10). Indeed, reasonable correlation exists between maximum cross-linking and maximum heat of reactions except for the 186 system. The 186 system shows a slowly increasing reaction heat above 15% catalyst. If all of the systems had the same functionality and cross-linked to the same extent, then these results should form a system of congruent curves. This is not the case. Secondary reactions, probably involving the methyl groups, are important.

The energy of activation also shows a systematic variation with catalyst concentration (see Table 5). The activation energy was calculated by two methods as discussed previously. For this series of samples agreement between the two methods, one using partial areas and the other using rates calculated by the curve height, is reasonably good. This was not the case in the previous study [1]. A portion of the error observed in that study must be ascribed to errors encountered in the determination of the base line. The authors are unable to account for the shifts of the exothermal maximum temperature with catalyst concentration. This could be due to an alteration in the path of the

TABLE 5. Thermodynamic Data on Three Sylgard Systems

System	Catalyst concentration (%)	Heat of reaction (cal/g)	Exothermal peak temp (°C)	Energy of activation	
				Method I [4] (kcal/mole)	Method II [5] (kcal/mole)
Sylgard 184	10	3.64	97.5	46.5	42.8
	15	4.75	97.4	51.4	47.6
	20	4.65	92.9	84.3	79.4
	30	3.09	88.6	72.8	67.7
	40	1.76	91.1	69.9	63.4
	50	2.87	96.6	55.9	51.1
	60	3.34	99.3	42.8	39.6
Sylgard 186	5	0.20	103.3	40.9	31.3
	10	0.55	96.0	56.1	51.0
	15	1.24	111.4	47.8	42.9
	20	1.45	109.3	42.7	36.8
	30	1.86	110.4	43.8	38.2
	40	2.06	112.7	39.7	35.6
	50	2.30	117.0	36.5	33.0
	60	2.15	118.5	31.8	28.2
Sylgard 188	5	0.72	107.0	34.0	28.7
	10	1.80	113.8	37.9	31.6
	15	3.93	114.1	41.0	35.3
	20	4.82	113.4	36.6	32.5
	30	7.03	109.3	49.6	45.8
	40	6.95	112.0	53.1	49.1
	50	5.17	114.5	52.1	46.5
	60	5.71	115.0	45.6	42.0

TABLE 6. Gelation of a 10% Catalyst Sylgard 184 System at 25°C

Time from mixing (hr)	Heat of reaction (cal/g)
0	4.75
3	4.25
5	3.0

reaction as a function of catalyst concentration. NMR did indicate vinyl groups on the catalyst. It is very probable that intrachain cross-linking is significantly different kinetically from interchain processes.

The reaction producing a cross-linked system does occur at a finite and appreciable rate at 25°C. The results of allowing a 10% catalyst mixture of the 184 system to age show this clearly (see Table 6). The formation of an open gel at low temperature significantly alters the structure of the network formed at elevated cure temperatures on the aged samples (see Table 7). The modulus and cross-link density of samples held at 25°C for 5 hr and then cured by programmed heating generally show a decrease in most cases. However, the weight extracted by hexane and molecular weight distribution of the extracts show only small effects. It is proposed that gelation at low temperatures results in an open network. In this network many cross-linkable groups remain unreacted upon heating due to restriction by location. This behavior would place serious restrictions on the pot life of these systems for applications where the elastic properties are critical.

CONCLUSIONS

The commercial Sylgard systems, which are the subject of this study, are significantly different from the silicone rubber reported in an earlier study. In every aspect of this investigation there is good indication that secondary reactions are significant. From an applied viewpoint, significant alterations in the thermal and mechanical properties have been observed when either the ratio of components is varied 10 to 20% or the duration of the reaction is changed. The initial assumption that these systems could furnish models for the convenient study of cross-linking processes must be seriously revised. The results of the GPC study may have some application to the general theory of network formation. However, this picture is complicated by branching and secondary reactions.

This particular approach to the analysis of a reactive polymer system,

TABLE 7. Effect of 5 hr 25°C Treatment on Final Properties of Three Sylgard Systems

System	Elastic Modulus TMA × 10^{-6} cynes/cm^2	Cross-link density swelling × 10^5 (moles/cc)	% Extractable	Molecular weight of extract	
				Mode I	Mode II
184 fresh	11.8	90.7	3.6	-	1700
aged	6.9	80.7	4.0	-	1800
186 fresh	7.5	11.5	6.4	46000	1400
aged	3.8	9.3	8.7	41000	1400
188 fresh	7.5	8.9	15.0	23000	1400
aged	3.0	9.5	13.7	33000	1600

DSC, GPC, and NMR, are valuable. In an applied case the data obtained by these means should afford improved quality control and reliability.

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