A THERMODYNAMIC STUDY OF THE CROSSLINKING OF METHYL SILICONE RUBBER

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ABSTRACT

The crosslinking reaction in a two component methyl silicone rubber has been studied by thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). The rubber was formed from two methyl silicone prepolymers; one containing reactive hydrogens every 50 to 100 groups and the other polymer containing pendant vinyl groups at the same frequency. In the presence of a platinum catalyst above 60 °C crosslinking proceeds without a loss or gain in weight. The heat of reaction, energy of activation (calculated by two methods) crosslink density and elastic modulus (Young's) were studied as a function of prepolymer concentration, dilution and swelling. A preliminary value for the heat of reaction per mole of Si–H and $SiCH=CH_2$ has been calculated. From crosslink density measurements both by hexane swelling and TMA and DSC heats of reaction a qualitative picture has been obtained of the role of entangled chains in producing effective crosslinks.

INTRODUCTION

The formation of interchain crosslinks is of primary interest to the areas of thermosetting polymers and rubbers. Effective crosslinks may result from chemical bonds, entangled chains, looped chains and interchain crystal formation. Chemical crosslinks usually occur as the result of an exothermal reaction upon heating the polymer to some predetermined temperature. Looped and entangled chains follow from multiple crosslinking as a result of normal chain configuration. Interchain crystal formation is endothermal and is a property of many moldable rubber-like materials. The hard segmented-chain urethanes are a good example[1-3].

In this paper the authors are concerned with effective crosslinks which are due to the formation of chemical bonds between two high molecular weight chains and any looped or entangled interactions. Since the thermodynamic picture of an exothermal reaction is frequently complicated by the loss of some volatile product during polymerization, we have chosen a two component silicone rubber which crosslinks predominantly via reaction between a pendant vinyl group and an active hydrogen, see Fig. 1. This reaction does not result in a weight gain or loss. Bueche has derived an almost complete picture of the solvent–polymer interaction parameters for sili-
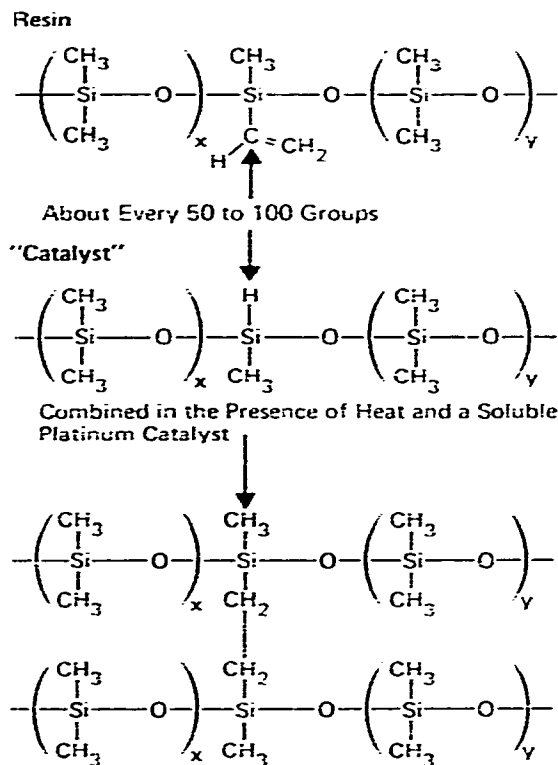
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Resin

Fig. 1.

cones[+]. This makes possible the determination of the effective crosslink density by hexane swelling techniques as well as from the elastic modulus[5].

The object of this study was to explore the effects of component ratio, inert diluents and method of calculation on the exothermal heat, temperature, and energy of activation of the crosslink reaction. In addition, a study was made of effects of the above on the crosslink density.

EXPERIMENTAL

Materials

The silicone rubber chosen for this study was Dow-Corning XR-63-493. This is a low viscosity two component methylsilicone. The components are explained in Fig. 1. The number average molecular weights of both components are nearly equal, 16,000, both having a polydisperity of 4 by gel permeation chromatography (GPC). There is some difference in viscosity between components due to the presence of the pendant vinyl group on the "polymer". The primary crosslinking reaction is between pendant vinyls and active hydrogens. These groups are distributed along their respective chains about one every 100 monomer units according to the manufacturer. At this point we say "primary" crosslinking reaction, for other reactions appear to

take place under the proper conditions. The initiator for the primary reaction was $\sim 1\%$ platinum chloride.

For the studies at various resin "catalyst" concentrations, about 10 g of components were weighed out into a plastic planchette and thoroughly mixed for ten minutes with a glass rod. Using a plunger type dropper, samples ranging from ~ 5 to ~ 50 mg were carefully weighed into Perkin–Elmer DSC-1B large planchettes. The sample size was varied depending on the reaction heat of the particular mixture. The planchettes were neither sealed nor covered, for there are no volatile products from the reaction. Since the Perkin-Elmer DSC-1B platform domes were used (as they should always be), the lid is unnecessary on a nonvolatile fluid sample. The lids are sufficient to balance the only important variable between samples, i.e., the thermal emissivity.

The silicone oil dilutions were done with Dow-Corning Fluid 200 on a weight basis. The mixing was carried out in plastic planchettes as described above. No diluted or initiated samples were held for more than 7 hours before running in the DSC-1B. Two dilutions were made in all cases: 1 to 1 and 1 to 3 silicone rubber to silicone oil. Each dilution and resin catalyst concentration were run at least three times to obtain some statistical significance. Spectral grade hexane was used in the swelling and extraction studies.

Calorimetry

A Perkin–Elmer DSC-1B differential scanning calorimeter was used for all calorimetric and temperature measurements. The instrument was calibrated in the 50 to 200 °C temperature range by melting semi-conductor grade naphthalene, indium, and tin. Temperatures were corrected as described previously[6]. Data were acquired on an IBM 1800 computer through an analog to digital converter. Areas and corrected temperatures were obtained from the digital data using on-line and off-line computer programs. A significant improvement in accuracy was noted using this digital method over the more conventional recorder trace interpretation.

The scanning calorimeter was operated at a heating rate of 20 °C/minute for all measurements. Sample sizes were adjusted so that a constant sensitivity could be employed, 4 mcal/sec. Obviously, this series of constraints resulted in the necessity of running a number of trial samples. However, with experience, these problems were minimized.

The reason for the use of a high heating rate and constant sensitivity is found in the nature of the thermodynamics of an exothermal reaction acting in a DSC-1B. The DSC-1B is able only to add power or decrease power to the filaments of the sample and reference heaters in response to heat evolution or absorption in the sample. There are no facilities for the controlled *removal* of heat in the instrument except by radiation. During an endothermal process the calorimeter control circuit simply adds heat by increasing filament power to keep both sample and reference balanced in temperature and heating at a linear rate. Should the sample, during an exothermal reaction, heat faster than the heating program for the average of the

sample and reference, the DSC-1B will simply not record the event. The resultant error is serious. Therefore, it is essential that the heating program be sufficiently rapid to prevent the thermal reaction from "running away". For our sample heat and weights 20°C/min was the lowest possible heating rate. The sensitivity was held constant to prevent response times of the system from interfering as a systematic variable in the exothermal heat measurements. As was demonstrated in an earlier publication, maximum precision is obtainable on the DSC-1B only if the differential power consumption is kept to within a multiple of 2 or 3 of the calibration conditions[6].

Crosslink measurement, indentation modulus

The crosslink density of all samples was measured using the DuPont Thermo-mechanical Analyser (TMA) equipped with a spherical indenter of radius 0.1416 cm. The indentation of the spherical foot was measured with a moveable core transformer under at least three loadings. The loadings, depending on the stiffness (elastic modulus) of the sample, ranged from 20 mg to 5 g. Adherence to theory was checked after each measurement by making a plot of probe load versus indentation (penetration) to the 3/2 power. Only linear plots passing through the origin were used for subsequent calculation of the elastic modulus and crosslink density.

TMA measurements were made at room temperature on the same sample that the heat of reaction had been determined. It was possible to use the samples popped from the DSC-1B planchettes when the load range was carefully adjusted. Only in two cases (near the ideal ratio of catalyst and resin) was it necessary to make thick samples especially for TMA. In these cases the heat of reaction is so large that small samples had to be used for calorimetry. These were too thin to produce linear pene-tration plots. Special thick samples were made in the DSC-1B from the same mixture for TMA. Heats were not calculated on these for obvious reasons.

Crosslink measurement, hexane swelling

Hexane swelling was applied only to samples which contained no silicone oil. The method is not satisfactory if a significant portion of the sample is extractable. The measurements were made after the TMA study on the same sample disk originally formed in the DSC-1B. The sample was weighed on a Mettler analytical balance, swollen in spectral grade hexane for 48 hours, blotted and reweighed. Evaporation of hexane during the weighing operation was minimized by saturating the balance atmosphere with hexane vapor from a full petri dish of hexane placed beside the balance pan. To test for extraction of material, each swollen sample was dried overnight at 50°C at 4 mm pressure of flowing nitrogen in a vacuum oven. The dried sample was then reweighed. It was found that the hexane could not be satisfactorily removed in the static atmosphere of a vacuum or drying oven. Therefore, absolute vacuum was sacrificed in favor of a low pressure but moving inert atmosphere. On a series of five samples especially made for the test, hexane removal was found to be 99.85% complete after 16 hours of the above treatment. The weight after eight days of treatment was taken as representing 100% removal. However, traces of hexane

were still noted in a mass spectrometer scan made of evolved gases at 10^{-6} torr and 180°C. The authors feel that this evidence notwithstanding, hexane removal was sufficiently complete for the purposes of the accuracy of this study.

The silicone oil-filled samples were extracted with 200 ml of hexane five times over a period of three days. The extracted samples were dried in the same way as the above bulk polymerized samples. The amount of sample extracted was obtained both from sample weight loss and by evaporation of the hexane solution. In all cases used in this study the two numbers agreed to within 3%. The higher number for the percent extracted was used in calculations.

CALCULATIONS

Heat of reaction

The heat of the exothermal reaction was calculated from the total area under the DSC curve, the weight of the sample, and by comparison with materials of known endothermal heats of fusion. This gives a heat of reaction in terms of calories per gram. By comparison of the number of crosslinks (in terms of moles of crosslink) per unit volume and knowing the density of the rubber with the specific reaction heat, the molar heat of reaction was calculated. The main source of error in the heat measurements was in determining the temperature at the onset of the reaction for the purposes of base line construction. This error is serious only at low catalyst concentrations and high dilutions.

Energy of activation

All existing methods for the calculation of the energy of activation, E, from DSC traces depend on the Arrhenius equation

$$K = Ae^{-E/RT}$$

where K = the rate of the reaction, A = the frequency factor, E = energy of activation, R = gas constant and T = the temperature. However, several distinct approaches have been applied to obtaining this information from DSC curves. Method I cited in tables and figures in this work makes use of an area/height relationship[7]

$$K = \frac{dH/dt}{A-a}$$

where A = total area under the curve, a = area to temperature T, and dH/dt = height of the curve above the base line at temperature T. A plot of log K versus $1/T$ for several values of a should yield a straight line of slope $-E/R$, if the kinetics are first order.

Method II involves only rate measurements with no areas involved[8]

$$-E = \frac{4.58 \log (d_1/d_2)}{1/T_1 - 1/T_2}$$

where d_1 and d_2 are the heights of the curve above the base line at temperatures T_1 and T_2. The values of d are in effect reaction rates at specific temperatures.

Some question may be raised as to the validity of using a kinetic equation written for a first order process to examine the silicone crosslinking reaction. Two arguments can be offered in defense of this. 1) Plots of log K versus $1/T$ were linear within a standard deviation of 10^{-3} and 2), first order kinetics have been shown to govern the crosslinking of epoxy systems—even where the kinetics are demonstratably second order by formula[9]. We may only speculate that the rate controlling step is first order or equivalent to it.

Crosslink density from swelling

The volume fraction of the swollen polymer, V_2, in hexane was calculated using the following relationship[4]

$$V_2 = \frac{1/\rho_r}{(W/\rho_n)+(1/\rho_r)}$$

where ρ_r = density of the rubber = 0.9926 g/cc (by experiment),

ρ_n = density of hexane = 0.6603 g/cc (ref. 10), and

W = grams of hexane sorbed per gram of rubber.

For tetrafunctional crosslink sites the mole of effective network crosslinks per cc, v_e, is

$$v_e = -[2.303 \log(1-V_2)+V_2+\chi_1 V_2^2][V_1(V_2^{\frac{1}{3}}-V_2/2)]^{-1}$$

where V_1 = molar volume of hexane = 130.6 cc/mole (ref. 10) and

χ_1 = solvent polymer interaction parameter for hexane/silicone rubber
= 0.40 (ref. 4).

Elastic modulus from TMA

A plot of three or more penetration values to the 3/2 power on the x-axis and load values on the y-axis was made[5]. These must lie on a straight line passing through zero, if the limits of the equation are to be satisfied. The elastic modulus, E_m, is expressed by

$$E_m = \left(\frac{F}{P^{\frac{3}{2}}}\right)\left[\frac{9}{16r^{\frac{1}{2}}}\right]$$

where $F/P^{\frac{3}{2}}$ is identical to the above slope times 980. The value 980 converts the slope to dynes/cm^2, and r is the radius of the probe, in this case 0.1416 cm.

Crosslink density from the elastic modulus

The mole of effective crosslink/cc may be calculated from the experimentally determined E_m by

$$v_e = \frac{E_m}{3RT}$$

where T = sample temperature in the TMA = 293 °K and

R = gas constant in force units = 8.314×10^7 ergs/mole °K.

The double calculation of v_z served a twofold purpose. On samples where swelling measurements could be made, i.e., no extractables, a useful check of two approaches could be made. On samples containing extractable oils only the indentation (TMA) method was applicable.

RESULTS

Effect of resin "catalyst" concentration

The number of reactive hydrogens in the crosslinking mixture has a profound effect on the shape, temperature and size of the DSC exotherm. Representative curves are shown in Fig. 2. Below 20% resin catalyst the reaction is characterized by a relatively broad exotherm with a vertex near 110°C. At 10% catalyst this vertex moves upward to 113–114 °C .Above 10% catalyst (the theoretical equilibrium mixture according to the manufacturer) the vertex temperature decreases.
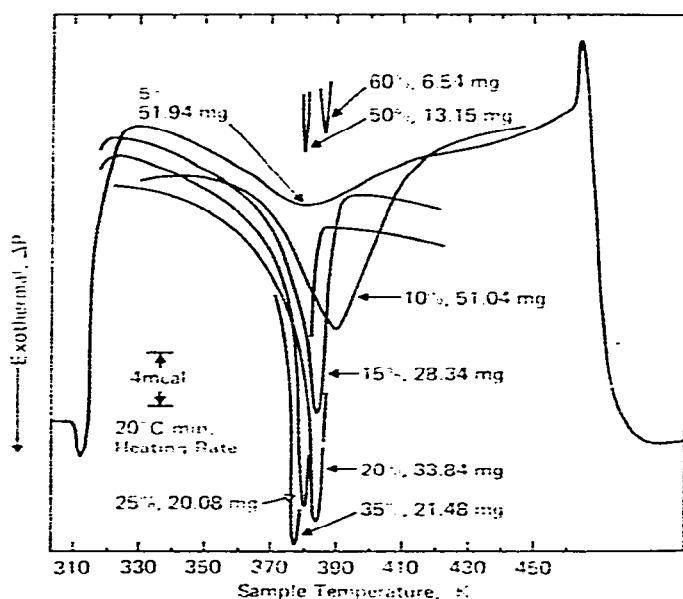

Fig. 2. Effect of catalyst concentration on the shape and location of the silicone rubber thermoset exotherm.

This shift of shape and size of the exotherm is dramatically reflected in the heat of the reaction, Fig. 3, and the energy of activation, Fig. 4. The heat of reaction is maximized between 15 and 20% catalyst. The same is clearly true of the minimization of the energy of activation calculated by method I, and less clearly by method II. On closer examination of the heat and activation curves an anomaly is observed.
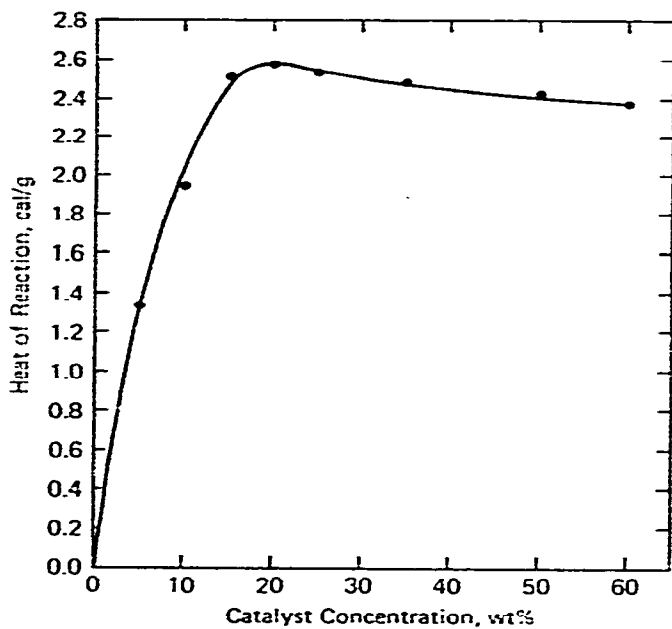
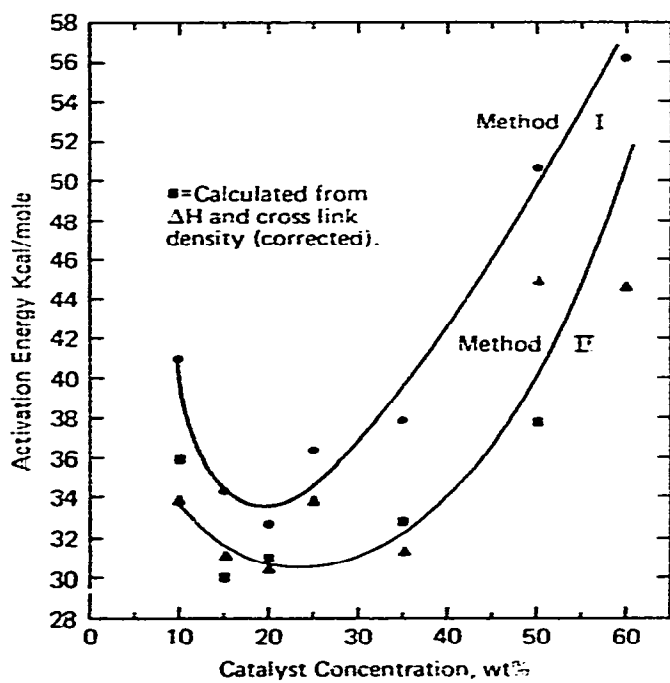Fig. 3. Effect of catalyst concentration on the exothermal heat reaction.

Fig. 4. Exothermal energy of activation as a function of catalyst concentration.

Between 5 and 20% catalyst the heat of reaction increases rapidly and the activation energy decreases sharply. Above 20% catalyst the heat of reaction remains relatively constant up to at least 60% catalyst. It would be expected to decrease at a much more rapid rate. The activation energy increases above and below the 20% catalyst concentration as would be expected if the resin concentration controlled the rate above 20% and the catalyst content controlled the rate below 20%.

The above results lead to the conclusion that a second reaction can occur in the presence of excess catalyst. The molar heat of reaction should be roughly the same but the activation energy somewhat higher.

When the crosslink density is studied as a function of catalyst concentration, Fig. 5, a picture similar to the activation energy becomes apparent. Up to 20% the molar concentration of effective crosslinks increases rapidly. Above 20% catalyst the
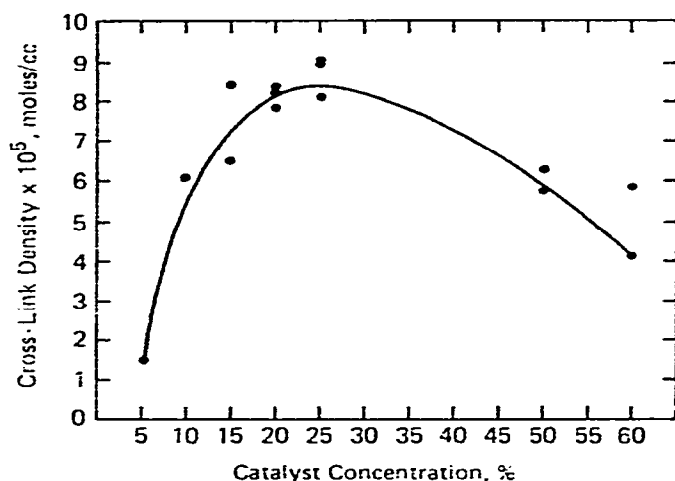

Fig. 5. Crosslink density variation with catalyst concentration.

effective crosslink density decreases at a rate which will give a value near zero at 100% catalyst. It is important to remember that swelling data and TMA data are responsive only to the mole of *effective* crosslink/cc, this is the true crosslink density. Should a molecule of resin and a molecule of catalyst react at only one site or at two widely spaced sites, an effective crosslink has not been formed. Rather, a higher molecular weight branched chain or ring molecule has been produced. Looped or tangled chains will produce effective crosslinks without liberating heat.

The formation of a bond which does not result in an effective crosslink will liberate the same amount of heat as one in a crosslink network so long as the reaction is between a reactive hydrogen and a pendant vinyl. Thus, it is not surprising that the heat of reaction, Fig. 3, remains relatively constant while the effective crosslink density decreases, Fig. 5, above 20% catalyst.

Given the effective crosslink density in moles/cc, the heat of reaction, and the density of the silicone rubber, it is possible to calculate the heat of reaction in calories/ mole of reactive species. Obviously, this calculation will have little meaning for

catalyst/resin mixtures deviating too much from the mixture which yields the maximum number of crosslinks for the reasons given above. However, in the range from 15% to 30% catalyst, the calculation should be valid. The heat of reaction was found to be ~31 kcal/mole in that range. In Fig. 4, values for ΔH are shown plotted with the activation energy. The numbers should not be compared together, since activation energy is a kinetic property and a measure of the energy barrier between the unreacted and reacted states, and the heat of reaction expresses the absolute energy content difference between the two states without consideration of path. In regions of composition where the kinetics and the reacting species are the same, values of both E and ΔH should remain relatively constant. This point is illustrated in Fig. 4. The authors cannot account for the absolute magnitude differences between E calculated by methods I and II.

In the above paragraphs we have assumed that the effective crosslinks are due only to chemical bonds whose reaction and existance are detectable thermally. As we shall see later it is possible that up to half the "effective" crosslinks per gram may be due to entangled and looped chains. Since these are non-chemical, inclusion in the denominator of the calculation of heat per bond formed from DSC and TMA data will result in a low value for the heat of reaction. Thus, it is possible that the heat of reaction of SiH with $SiCH=CH_2$ could be as high as ~62 kcal/mole. No doubt it is greater than 30 kcal/mole, but error cancellation between branched structure formation (little contribution to the crosslink network) and loop and entanglement crosslink formation (no contribution to the heat of reaction) has probably served to make the true answer lie nearer to 31 kcal/mole than to 62.

Effect of dilution on the reaction

In a crosslinking reaction it is possible that some bonds which are labile do not react because of steric effects. It is easy to envision a condition where a reactive hydrogen may not react with a pendant vinyl because of previous reactions on the same pair of chains. In addition, as the reaction progresses, the viscosity of the mixture increases. This could alter the energy of activation if there is an appreciable viscosity coefficient.

TABLE I

EFFECT OF DILUTION ON THE HEAT OF REACTION AND ACTIVATION ENERGY

% catalyst	% silicone oil	ΔH (cal/g)	Corrected ΔH* (cal/g)	E by method I (kcal/mole)	E by method II (kcal/mole)
10	0	1.95	1.95	41.3	37.8
	50	0.817	1.63	47.4	38.4
	67	0.459	1.38	34.3	34.1
20	0	2.69	2.69	32.0	29.9
	50	1.45	2.90	23.2	34.5
	67	0.239	0.717	37.3	43.8

*Corrected for dilution mass.

To test these ideas a mixture of 10% catalyst in 90% resin was diluted with silicone oil by 1/2 and 1/3. The original mixture and the two dilutions were run in the DSC. The experiments were repeated for a 20% catalyst mixture. The results are shown in Table I and Figs. 6 and 7.
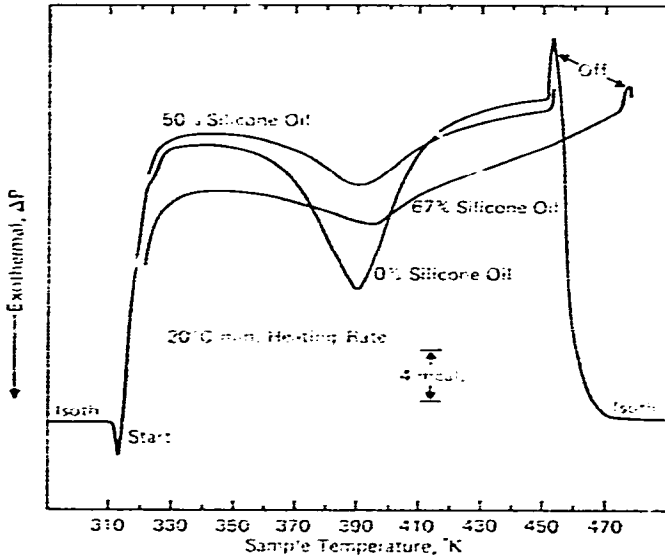

Fig. 6. DSC scans of 90% resin 10% catalyst silicone rubber thermosets.
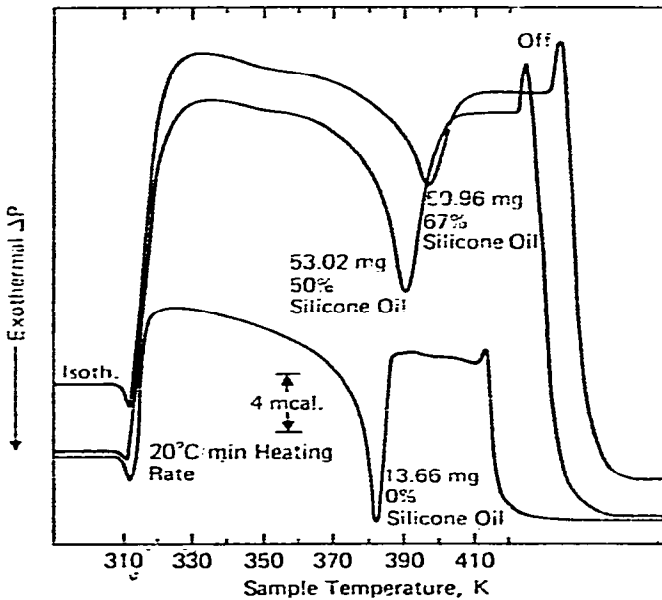

Fig. 7. DSC scans of 80% resin 20% catalyst silicone rubber thermosets.

From the general shapes of the curves in Figs. 6 and 7 it is apparent that the effects of the diluting silicone oil are somewhat different depending on catalyst content. At the 20% catalyst level (maximum heat of reaction), the addition of silicone oil sharply increases the temperature at maximum reaction rate. With no oil the maximum is near 383°K, this increases to 390°K v·⁺ ₁ 50% oil and to 398°K for 67% oil. The effect is in the same direction at the 10% catalyst level, but over a smaller temperature range. The 50% oil content rate maximum is the same as the 20% catalyst but the 0% and 67% oil are higher and lower respectively.

The above effects are probably due to kinetic changes brought about by improved molecular mobility in the solutions with silicone oil. In experiments done outside the calorimeter, a very soft gel was formed in silicone oil solutions at low temperature which persisted to temperatures well above the normal crosslinking temperatures for 0% oil mixtures. The preliminary formation of an open crosslink network could actually hinder the reaction. The natures of the branched chain molecules and other materials extractable from the thermoset rubber are now being investigated in greater detail by IR, GPC and NMR and will be reported in the future.

If dilution were a simple displacement effect, it should be possible to calculate the reaction heat of undiluted sample knowing ΔH of a diluted mixture and the concentration. This has been attempted and the results given in column four of Table I. This is obviously not possible. At 10% catalyst the back calculated ΔH values are too small by 16 to 30% compared to ΔH determined on an undiluted sample. For a 20% catalyst sample the behavior is somewhat different. The 50% dilution has a reaction heat 8% too high, but the 67% dilution is three fold too low. The activation energies should, within a catalyst concentration range, be constant irrespective of dilution. This is obviously not the case, irrespective of the method of calculation of E.

On the basis of this study, it is difficult to explain the effects of dilution on the reaction in any but general terms. Concentration of reactive groups, the formation of gels, and altered configuration of the final crosslinked network are highly interacting factors. The data in Table I do demonstrate clearly that great caution should be observed when extrapolating kinetic and thermal results made at one concentration to another concentration. The network is very sensitive.

Comparison of TMA and swelling measurements of crosslink density

Reasonably good agreement was noted between the crosslink density calculated from TMA data and hexane swelling. A consistant deviation of about 10% was observed in most cases in favor of the mechanical measurements, see Table II. This could be due to an error in the exact value of the solvent–polymer interaction parameter, χ. In this study Bueche's value of 0.40 was employed in the swelling-crosslink density calculation[4]. That value was developed for silicone rubbers crosslinked by a mechanism different from one employed in this study. Seeley, in a major study of polymer–solvent interaction parameters for silicone rubbers has noted a variation (apparently random) of ~13% between physical and swelling data[11]. Some of this

TABLE II

A COMPARISON OF CROSSLINK DENSITY DETERMINED BY MECHANICAL AND
HEXANE SWELLING ON SILICONE RUBBERS REACTED IN BULK

% catalyst	TMA		Hexane swelling	
	Elastic modulus (dynes/cm²)	Crosslink density (moles/cc)	Elastic modulus (dynes/cm²)	Crosslink density (moles/cc)
10	66.0×10^5	9.03×10^{-5}	59.4×10^5	8.06×10^{-5}
20	59.8×10^5	8.19×10^{-5}	53.8×10^5	7.30×10^{-5}
25	69.2×10^5	9.49×10^{-5}	62.0×10^5	8.60×10^{-5}
35	49.8×10^5	6.81×10^{-5}	44.1×10^5	6.22×10^{-5}
50	42.2×10^5	5.77×10^{-5}	38.3×10^5	5.23×10^{-5}
60	42.9×10^5	5.86×10^{-5}	37.1×10^5	5.37×10^{-5}

was due to variations in homogeneity between different rubber specimens created during mixing, molding and curing operations. In consideration of the differences between the silicone rubbers and possible experimental variables, a 10% to 13% variation is acceptable.

Effect of diluents on the crosslink density and elastic modulus

The formation of the crosslink network in the presence of silicone oil produces a material with a reduced elastic modulus. These results are shown in Table III and Fig. 8. The modulus decreases in a regular but non-linear manner. The general effect is predictable and well known, i.e., the presence of the oil produces an expanded
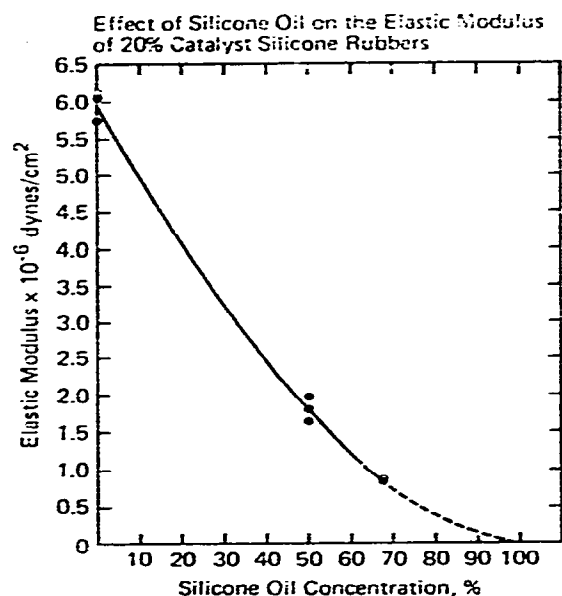

Fig. 8. Effect of silicone oil on the elastic modulus of 20% catalyst silicone rubbers.

network with a lower number of "effective" crosslinks. The rubber is in effect expanded or swollen with a non-volatile "solvent".

TABLE III

CRITICAL EFFECTS OF THE DILUTION OF SILICONE RUBBER WITH SILICONE OIL

Sample		Elastic modulus[a] (dynes/cm^2)	Crosslink density[a] (moles/cc)	% extracted in hexane
% catalyst	% oil			
5	0	11.2×10^5	1.54×10^{-5}	data lacking
extracted[a]		31.8×10^5	4.35×10^{-5}	data lacking
10	0	66.0×10^5	9.03×10^{-5}	
extracted		93.5×10^5	12.8×10^{-5}	4.17
10	50	21.1×10^5	2.89×10^{-5}	
extracted		36.6×10^5	5.01×10^{-5}	49.7
10	67	9.46×10^5	1.29×10^{-5}	
extracted		46.5×10^5	6.36×10^{-5}	62.9
20	0	59.8×10^5	8.19×10^{-5}	
extracted		87.5×10^5	12.0×10^{-5}	4.62
20	50	18.1×10^5	2.48×10^{-5}	
extracted		56.3×10^5	7.71×10^{-5}	54.9
20	67	9.3×10^5	1.28×10^{-5}	
extracted		33.7×10^5	4.61×10^{-5}	71.8
25	0	69.2×10^5	9.49×10^{-5}	
extracted		88.1×10^5	12.0×10^{-5}	4.70
35	0	49.8×10^5	6.81×10^{-5}	
extracted		93.9×10^5	12.8×10^{-5}	5.27
50	0	42.2×10^5	5.77×10^{-5}	data lacking
extracted		44.0×10^5	6.02×10^{-5}	
60	0	42.9×10^5	5.86×10^{-5}	data lacking

[a] From TMA measurements.

When the TMA measured crosslink density is examined, the picture is somewhat less consistant, see Fig. 9. On the basis of simple volume additivity, the measured effective crosslink density would be expected to be a simple linear function (the density of the oil and rubber are nearly the same and very close to 1 g/cc). Thus, if the bulk sample were forced to occupy a 50% larger volume (diluted prior to crosslinking with 50% oil) we should expect to measure 50% fewer crosslinks per unit volume. This would be $\sim 4.1 \times 10^{-5}$ moles/cc. Instead, the measured crosslink density is 2.5×10^{-5} moles/cc. Thus, a 50% dilution prior to crosslinking results in a $\sim 60\%$ reduction in the number of effective crosslinks over the bulk sample. A possible explanation for this anomaly can be found in the work of Mark and coworkers[12-14]. He postulates three types of network from his studies of poly(cis-1,4-butadiene) crosslinked in bulk and in the presence of hexane with the chains extended in equilibrium position, see Fig. 10.
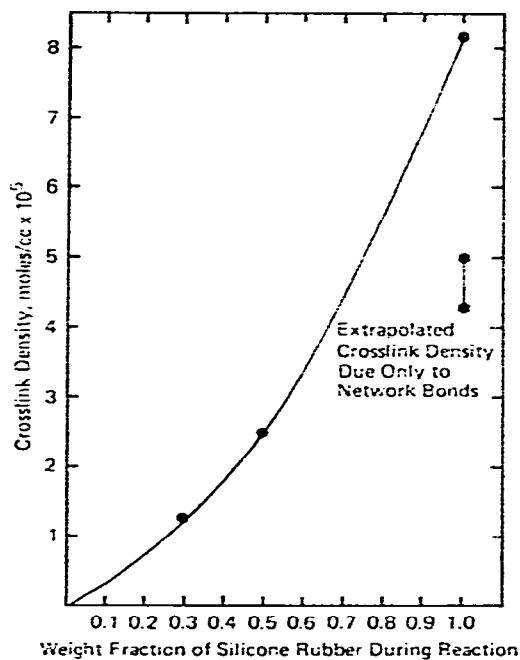
Fig. 9. Variation of TMA measured crosslink density with silicone oil dilution for 20% catalys samples.
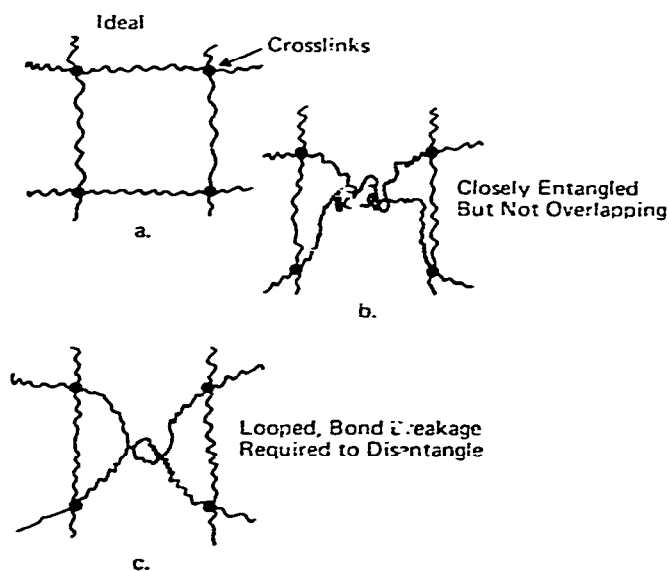

Fig. 10. Models of crosslink networks[14].

In *a* all "effective" crosslinks are chemical bonds. In *b* a percentage of the "effective" crosslinks are due to closely entangled chains. On swelling with a good solvent these chains may become untangled and more independent. There is a good chance that deswelling would not result in the same entanglement. In case *c* the

chains are looped over and would on swelling or deswelling yield an "effective" but not a chemical crosslink.

Although this study does not aspire to the completeness and rigid adherence to equilibrium conditions of Mark's studies, many points of agreement can be found. In general, it is evident the formation of a rubber in the expanded state yields crosslink anomalies not predictable from simple geometric or classical considerations[14].

It is interesting to speculate, using the data in Fig. 9, on what the actual number of chemical crosslinks may be. It is safe to say that it is somewhat lower than that indicated by TMA measurements on the bulk polymers. If we postulate a linear relationship using the origin and either the 50% or 33% dilutions, the number of chemical crosslinks would be between 4.3 and 5.0×10^{-5} moles/cc. This is between 53 and 60% of the number measured on the bulk polymer. It is conceivable that the presence of th, silicone oil may completely negate effective crosslinks of type b and c at very small indentations. At higher deformations, not covered in this study, the looped chains of type c may still be effective as crosslinks.

Extraction of the silicone oil from the dilute samples should produce materials with networks comparable to the samples prepared by Mark et $al.$ in the deswollen state[12]. In that case those workers prepared silicone rubbers by irradiative crosslinking in hexane. For the present comparison the previously made silicone rubbers polymerized in the presence of silicone oil were extracted with five washes of hexane over a period of 4 days. The modulus and crosslink density were measured by TMA. The amount of material extracted by the hexane and the TMA results are shown in Table III.

In all cases the elastic modulus and effective crosslink density increase, even in the bulk polymerized sample. In the latter case only 4 to 5% of the sample was extractable. However, the apparent crosslink density increased by 42% for the 10% catalyst, and 46% for the 20% catalyst sample. Although the magnitude of the change is not predictable, the only reasonable explanation is that some extensive modification of the network entanglement, model b, occurred on swelling and deswelling.

Formation of the crosslink network in the presence of silicone oil diluent obviously has profound effects on the deswollen network as shown in Table III and Fig. 11. On the basis of simple considerations it may be proposed that the diluted samples after removal of the silicone oil by extraction in hexane should be identical to the bulk polymerized sample after the same process. This is not the case. The dilute polymerized samples are somewhat less crosslinked than the bulk polymerized material, Fig. 11. The degree of crosslinking appears to vary in an almost linear manner with concentration. The thermal data, Table I, have indicated that diluted samples produce less heat on crosslinking than would be predicted on the basis of the bulk sample. This information makes the situation even more complex than cases a, b, and c would indicate.

Although chemical alterations may exist in the silicone oil diluted and extracted polymers, no such argument may be proposed for the undiluted bulk polymer. Since opening (and closing) of crosslinks is not likely, only a change in the degree of entan-
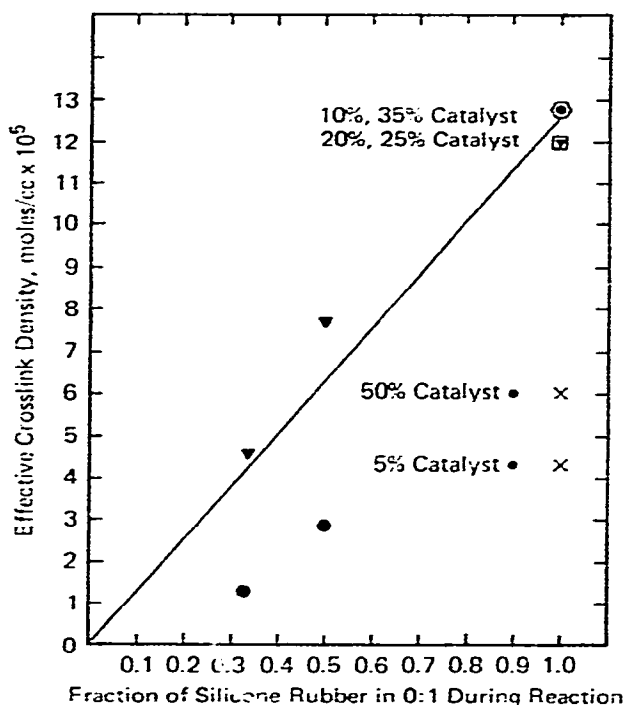
Fig. 11. Effect of reaction mixture concentration on the effective crosslink density of extracted (swollen–deswollen) samples.

gled chain "crosslinks", model *b*, can account for the increase in effective crosslink density of hexane extracted samples.

In Fig. 11 samples in the 10 to 35% catalyst range appear to become comparable when polymerized in silicone oil and extracted. Samples in the 5 and 50% catalyst range do not increase in effective crosslink density to the same degree. This may be due to open network formation in the presence of a large excess of one reactive group or the other, which are not completely extracted by hexane. Indeed, the open networks may be attached to the crosslinked network as side branches. Thermally, this should not be and is not apparent. The reaction of an Si–H with Si–CH=CH$_2$ produces the same amount of heat irrespective of network formation.

CONCLUSIONS

The thermal and mechanical behavior of a simple silicone rubber appears to be extremely complex. The sample chemical crosslink model is not sufficient to explain the mechanically measured effective crosslink density of polymers prepared in bulk and dilute solution. Additionally, hexane extraction confirms that entangled "crosslinks" of both permanent and variable nature may account for up to 50% of the effective crosslinks. The heat of the crosslinking reaction may be up to twice as large per mole of reactive material as that evaluated from simple arithmetic considerations, (heat/cc)/(moles of effective crosslink/cc).

Although the agreement between TMA and hexane swelling calculation of crosslink density is good, the TMA has been found to give results about 13% higher than hexane swelling. This may be in part due to an error in the solvent polymer interaction parameter. Entangled chains may also produce the same effect.

An examination of the variation of reaction heat with concentration has shown that the reaction path is altered with the concentration of components. Side reactions become important. Significant differences have been found between activation energies calculated from the *same* DSC traces by different mathematical approaches. This latter finding opens up to question the entire area of activation energy calculation. Additional work will be required to determine the extent of revisions necessary in present thinking.

From this small set of experiments it is difficult to draw general conclusions. However, the use of combined thermal and mechanical methods has been demonstrated to be a powerful tool for the exploration of crosslinked networks. Future efforts with the addition of NMR and GPC should provide more definitive answers to some questions arising about real networks and rubber behavior.

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