

Determination of Effective Crosslink Density in Silicone Rubber*

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Synopsis

In the investigation reported here, the effective crosslink densities for solid and cellular silicone rubbers were determined from physical tests of solvent-swollen specimens, and theoretical crosslink densities were calculated from chemical analysis data. A method was developed to accurately measure the compression and the deflection of swollen rubber specimens; and empirical equations were derived which relate compression, deflection, and effective crosslink density of toluene-swollen specimens of silicone rubber. Flory-Huggins solvent interaction parameters have been calculated.

INTRODUCTION

Performance characteristics of an elastomeric material are difficult to determine in any except actual performance conditions, and this kind of testing can be costly and time consuming. Usually, the rubber technologist must resort to laboratory testing and then express his test data in terms of performance potential. Naturally, the test data developed in the laboratory are expressed as a composite of all forces acting on and within the material. But if these forces are considered as two types—dependent and independent—nearly all physical data can be used much more quantitatively by analyzing the independent force contributions.

In terms of this discussion, the basic structural elements of the material such as the polymer chains, the relative orientation of the polymer chains, and the crosslinking between chains are considered independent forces. All other forces (from fillers, plasticizers, etc.) are considered as dependent forces, and the contribution of these dependent forces in any single physical test would depend on the condition of the basic structural elements. According to Flory's¹ network-statistical theory of elasticity, the effective crosslinking in vulcanized rubber is a function of the stress-strain relationship of a solvent-swollen rubber. The general validity of this theory has been confirmed by other investigators²⁻⁵ and may be expressed by eq. (1)

$$\tau = RT \nu_e / V_r \phi_r^{-1/3} (\alpha - \alpha^{-2}) \quad (1)$$

where τ is the tensile stress, R is the gas constant, T is the absolute tem-

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perature, ν_e/V_r is the crosslink density (i.e., effective mole concentration of polymer chains between crosslinks/volume of rubber corrected for additives), ϕ_r is the volume fraction of rubber in the material, and α is the extension ratio of the specimen. Recently, this expression was modified by Cluff, Gladding, and Pariser in such a way that effective crosslink densities can be determined from compression-deflection data.⁶ This relationship may be expressed by the eq. (2):

$$\nu_e/V_r = (h_0 S / 3A_0 RT) [\phi_r (1 - \phi_a)]^{-1/3} \quad (2)$$

where ν_e/V_r is the effective crosslink density expressed as moles of polymer chains between crosslinks within a certain volume of rubber, h_0 is the unswollen specimen height, A_0 is the unswollen specimen cross-sectional area, R is the gas constant, T is the absolute temperature, S is the slope of the compression-deflection curve of the swollen specimen, ϕ_r is the volume fraction of rubber in the unswollen specimen, and ϕ_a is the volume fraction of additives in the swollen specimen.* Equation (2) was used to calculate the effective crosslink densities in this work.

A preliminary investigation made prior to the work reported here showed that crosslink density determinations of cellular rubbers made using compression-deflection data were especially useful, since the physical state of cellular rubber necessarily limits the physical properties that can be measured. Based on the foregoing discussion, a basic approach has been developed to determine the structural characteristics of both solid and cellular rubbers which is a measure of the performance potential of these rubbers.

EXPERIMENTAL PROCEDURE

Materials Preparation

The basic materials used in this investigation were cellular and solid silicone formulations with varying concentrations of crosslinking agents and cell-forming compounds (Table I). The ingredients were compounded using a differential two-roll rubber mill. The mixing technique and the milling cycle were both controlled and were thus consistent with standard practices for formulation of these rubber recipes.⁷ Optimum vulcanization and cure conditions were used for all materials.⁷

Specimen Preparation

Cylindrical specimens approximately 0.46 cm. high and 6.5 cm.² in cross section were die-cut from cured rubber slabs. These specimens were oven-dried for 2 hr. at 100°C. and then weighed on an analytical balance. Specimen height was measured on a Dice electronic micrometer; six readings were averaged to the nearest ten-thousandth of an inch. The speci-

* ϕ_a used in this report differs from previous reported data in that it reflects the total nonrubber volume of the specimen (cellular voids and additives) rather than just the additives within the rubber matrix.

TABLE I
Formulary of Solid and Cellular Silicone Rubbers
Compound No.^a

	1	2	3	4	5	6	7	8	9	10	11
Silicone rubber ^b	100	100	100	100	100	100	100	100	100	100	100
Silica filler ^c	42	42	42	42	42	42	42	42	42	42	42
Cadox TS-50 ^d	1.42	4.22	2.83	2.83	4.22	6.39	0.71	5.68	2.83	0.71	1.42
Cell-forming agent ^e	226	226	226	—	—	226	226	226	113	—	—

^a Recipes are given in parts by weight.

^b A high strength silicone rubber supplied by Union Carbide Corporation.

^c This filler of 2.23 density was masterbatched with the rubber when received.

^d A 50% mixture of 2,4-dichlorobenzoyl peroxide and a silicone fluid (49.8% by chemical analysis) supplied by Cadet Chemical Corporation.

^e A proprietary material of Union Carbide Corporation.

men area was determined using an effective diameter calculation derived from the average of two surface diameters normal to each other, less a sample undercut correction. These measurements were made with the use of a Jones and Lamson optical comparator.

The weighed, measured samples were placed in specimen jars and then immersed in selected solvents as indicated in column 2 of Table II. The samples were allowed to swell until equilibrium swelling was attained (at least 10 days). The temperature was maintained at 23°C. within $\pm 0.5^\circ\text{C}$. throughout the investigation, including the period of compression-deflection work.

Testing Procedure

In testing the specimens, a special steel platen tray was mounted on the compression cell of an Instron Tester. The tray was filled with the appropriate solvent and the instrument was calibrated. The swollen specimen was then placed in the tray and subjected to a compression loading at a rate of 0.05 in./min. The test was discontinued when the sample had been deflected approximately 10%. This test was repeated twice after a 1.5-min. recovery period for each test. The deflection cycle was recorded on an autographic recorder. After testing, the samples were weighed in a manner similar to that described by Moore and Watson,⁸ and the data obtained were used to calculate the volume of solvent in the swollen samples.

Chemical Analysis

A chemical analysis of the crosslinking agent (Cadox TS-50) showed a 49.8% concentration of the 2,4-dichlorobenzoyl peroxide.* In an attempt to analyze quantitatively the silicone rubber masterbatch for silica filler content by a centrifuge technique, a value of 27% was obtained; this value was at first considered unreliable because of apparent incomplete silicone polymer-filler separation in a dilute solvent solution. However, by using both a mathematical method of successive approximations of specimen density† and the volume data of compounds 4 and 5 from Table I, a silica filler content of 30% by weight was obtained for both compounds. This showed that the value of 27% was more accurate than was first believed.

EXPERIMENTAL RESULTS

The volume, crosslink density, and swelling data are tabulated in Tables II and III. Columns 3 and 4 of Table III show the unswollen (V_0) and swollen (V_{0s}) specimen volumes, respectively. In Table II, the column 9

* Crosslinking agent and peroxide reference used throughout this report will mean this material.

† The density of the silica filler was accepted as 2.23 g./cc. from information supplied by the Union Carbide Corp. A density of 0.97 g./cc. was used for the silicone oil in the Cadox TS-50. This latter value is not critical, since the silicone oil constitutes about 1% or less of the total material volume.

TABLE II
Crosslink Densities for Silicone Rubber at 23°C.

Compound no.	Solvent	Unswollen specimen height, h_0 , cm.	Unswollen specimen area, A_0 , cm. ²	Rubber volume, V_r	Rubber volume fraction, ϕ_r	Non-rubber volume fraction, ϕ_n	Slope, compression-curve, S , g./cm.	Crosslink density (mole/cm ³ .)	
								Effective, ^a $\nu_e/V_r \times 10^4$	Theoretical, ^b $\nu_e/V_r \times 10^6$
1	Toluene	0.460	6.477	1.132	0.3799	0.1929	19230	2.68	3.08
2	Toluene	0.466	6.478	1.106	0.3666	0.2104	37130	5.35	10.32
3	Toluene	0.466	6.482	1.115	0.3692	0.2291	31130	4.51	6.70
4	Toluene	0.485	6.389	2.582	0.8404	0.0463	168980	18.32	6.70
5	Toluene	0.486	6.389	2.552	0.8216	0.0564	218520	24.00	10.32
6	Toluene	0.458	6.453	1.033	0.3486	0.2651	57770	8.56	16.07
7	Toluene	0.433	6.453	1.108	0.3970	0.1408	11970	1.52	1.26
8	Toluene	0.438	6.442	1.034	0.3668	0.2161	52300	7.14	14.18
9	Toluene	0.469	6.453	1.475	0.4892	0.1616	82390	10.70	6.70
10	Toluene	0.476	6.363	2.564	0.8471	0.0311	56400	5.98	1.26
11	Toluene	0.478	6.368	2.568	0.8446	0.0382	100110	10.68	3.08
1	MEK	0.461	6.485	1.129	0.3777	0.2484	14230	2.04	3.08
2	MEK	0.467	6.475	1.105	0.3660	0.2859	29020	4.34	10.32
3	MEK	0.465	6.471	1.111	0.3697	0.2695	23400	3.45	6.70
4	MEK	0.484	6.397	2.573	0.8317	0.0637	143910	15.69	6.70
5	MEK	0.484	6.399	2.542	0.8251	0.0703	182470	19.99	10.32
7	MEK	0.432	6.432	1.106	0.3981	0.1981	10190	1.33	1.26
8	MEK	0.437	6.467	1.039	0.3678	0.2749	42960	5.98	14.18
9	MEK	0.469	6.410	1.471	0.4890	0.2165	67450	9.01	6.70
10	MEK	0.475	6.371	2.544	0.8417	0.0473	51930	5.52	1.26
11	MEK	0.480	6.360	2.561	0.8384	0.0561	86220	9.33	3.08

^a Determined from compression-deflection data.

^b Determined from chemical analysis data.

TABLE III
Toluene and MEK Swelling Data for Silicone Rubber at 23°C.

Compound no.	Solvent	Unswollen specimen volume, V_0 , cm. ³	Swollen specimen volume, V_{0s} , cm. ³	Swelling ratio, S_r ($= V_{0s}/V_0$)	Relative swelling ratio, $S_{r_{tol}} = S_r$ (toluene)/ S_r (MEK)
1	Toluene	2.980	9.579	3.18	1.3
2	Toluene	3.018	9.084	3.01	1.4
3	Toluene	3.019	8.314	2.75	1.2
4	Toluene	3.072	10.580	3.44	1.3
5	Toluene	3.107	9.831	3.16	1.3
6	Toluene	2.956	7.265	2.46	
7	Toluene	2.791	11.954	4.28	1.4
8	Toluene	2.819	8.262	2.93	1.3
9	Toluene	3.027	9.606	3.17	1.3
10	Toluene	3.027	14.862	4.91	1.5
11	Toluene	3.041	12.361	4.07	1.4
1	MEK	2.988	7.487	2.51	
2	MEK	3.020	6.697	2.22	
3	MEK	3.005	7.030	2.34	
4	MEK	3.094	8.172	2.64	
5	MEK	3.097	7.705	2.49	
7	MEK	2.778	8.441	3.04	
8	MEK	2.826	6.500	2.30	
9	MEK	3.008	7.101	2.36	
10	MEK	3.022	10.104	3.34	
11	MEK	3.054	8.805	2.88	

shows effective crosslink densities calculated from compression-deflection data by using eq. (2). Column 10 shows the crosslink densities calculated from chemical analysis data. The equation used to obtain these values is

$$\nu/V_r = (1/V_r)[(W_o/M_o) - (2W_p/M_p)] \quad (3)$$

where ν/V_r represents the moles of polymer chains between crosslinks per unit volume of rubber, W_o is the weight of crosslinking agent (peroxide), M_o is the molecular weight of the peroxide, W_p is the polymer (silicone rubber) weight, and M_p is the molecular weight of the polymer, which was taken to be 3.5×10^5 .⁹ These crosslink densities are theoretical values, since they were calculated assuming correct polymer weight, 100% crosslinking efficiency, and no polymer interaction, and also assuming that polymer chain ends do not contribute to crosslink efficiency.

The effective crosslink densities shown in column 9 of Table II were obtained by averaging two compression-deflection curves on each of either two or three specimens.

Table III, column 5 lists the volume swell ratio ($S_r = V_{0s}/V_0$) and the last column lists the relative volume swell ratios, S_r (toluene)/ S_r (MEK).

TABLE IV
Compression Data for Swollen Silicone Rubber at 23°C.

Compound no.	Compression, g./cm. ² at various deflections														
	Toluene-swollen specimens					MEK-swollen specimens					Unswollen specimens				
	2%	4%	6%	8%	10%	2%	4%	6%	8%	10%	2%	4%	6%	8%	10%
5 (solid)	386	958	1530	2102	2674	354	820	1285	1751	2216	896	2398	3899	5400	6903
4 (solid)	299	744	1189	1635	2080	250	597	944	1291	1638	593	1750	2906	4063	5220
11 (solid)	158	440	722	1004	1286	128	344	560	777	994	592	1855	3118	4381	5645
10 (solid)	90	260	429	599	768	88	224	361	497	633	694	1582	2513	3444	4376
9 (cellular)	163	456	749	1042	1335	125	344	564	784	1003	240	626	1013	1400	1787
6 (cellular)	125	368	610	853	1096										
8 (cellular)	129	331	533	734	936	110	262	413	565	716	194	444	694	943	1193
2 (cellular)	85	242	399	555	712	72	183	294	406	517					
3 (cellular)	65	197	329	461	593	66	156	247	337	428	128	321	514	707	899
1 (cellular)	48	132	215	298	378	45	98	154	209	264	80	231	381	532	682
7 (cellular)	15	65	115	135	214	10	48	86	124	161					

The compression data over a 10% deflection range for both toluene- and MEK-swollen samples are tabulated in Table IV. The data are arranged in descending curative level order for the solid and cellular rubber, which corresponds to descending crosslink density values.

DISCUSSION

Effects of Cell-Forming Agent Concentrations on ν_e/V_r

The effect of cell-forming agent concentration on effective crosslink density is shown in Figure 1. Note that the toluene and MEK curves are

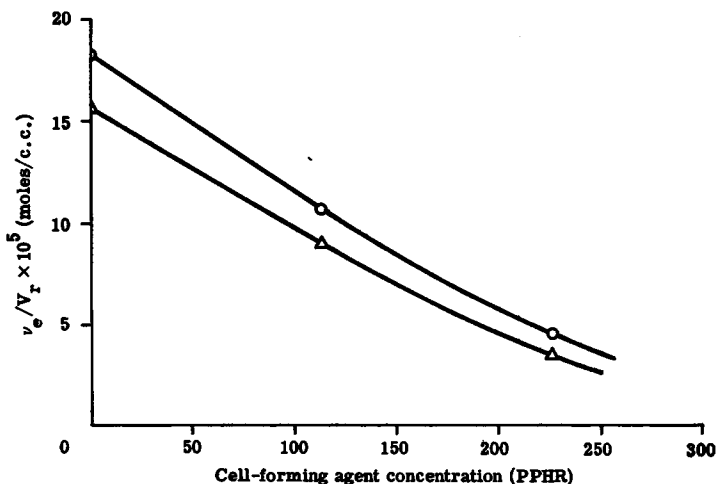


Fig. 1. Effective crosslink density vs. cell-forming agent concentration for silicone rubber swollen in (O) toluene and (Δ) MEK.

very similar with the crosslink density values decreasing with increasing cell-forming agent concentration (especially apparent in compounds 4, 9, and 3). It is not known if the decrease in crosslink density is a peroxide-inhibiting effect by the cell former and/or a structural weakening effect by the increasing number of cells. Since the toluene and MEK curves are quite similar, it is possible that a solubility parameter such as S_{rel} in column 6 of Table III could be introduced into eq. (2), thus superimposing the MEK curve on the toluene curve. An investigation of other solvents will be necessary to establish the validity of introducing such a parameter.

Effects of Crosslinking Agent Concentration on ν_e/V_r

The effect of peroxide (crosslinking agent) concentration on crosslink density for cellular and solid silicone rubber swollen in toluene and MEK is graphically illustrated in Figure 2. The rubber swollen in toluene had crosslink values greater than those of MEK-swollen rubber at corresponding peroxide concentrations.

The curves illustrate that an orderly increase in crosslinking occurs with increasing peroxide concentration for both cellular and solid silicone rubber. The toluene and MEK curves for the cellular rubber are quite similar with concentrations greater than 1.5 parts peroxide per 100 parts rubber. With solid rubber, the two curves diverge rather rapidly with increasing peroxide concentration. All four curves appear to intercept at the origin,

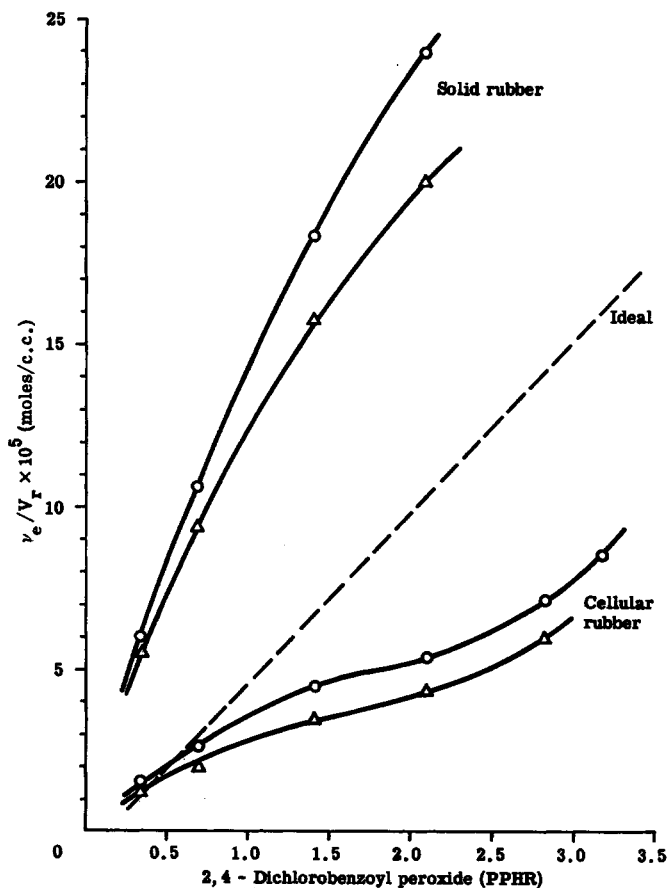


Fig. 2. Effective crosslink density vs. peroxide concentration for silicone rubber swollen in (O) toluene and (Δ) MEK at 23°C.

which would be expected even for a weak solvent such as MEK, since silicone rubber shows little effective crosslinking in the absence of a vulcanizing agent. The fact that the curves are not linear may be explained by the following: the exact peroxide efficiency is not known, the theory may not accurately define the system, and the swelling action is not ideal. However, the important consideration is that the relationship proceeds in an orderly fashion.

Relationship of τ_r Versus ν_e/V_r for Toluene-Swollen Rubber

Figures 3 and 4 show the relationship between effective crosslink density and compression over a deflection range of 10 per cent. A linear relationship could be anticipated, since toluene is a moderately strong solvent for silicone rubber; this is the case for both cellular and solid rubber. Hookean behavior was observed over the deflection range investigated. Further,

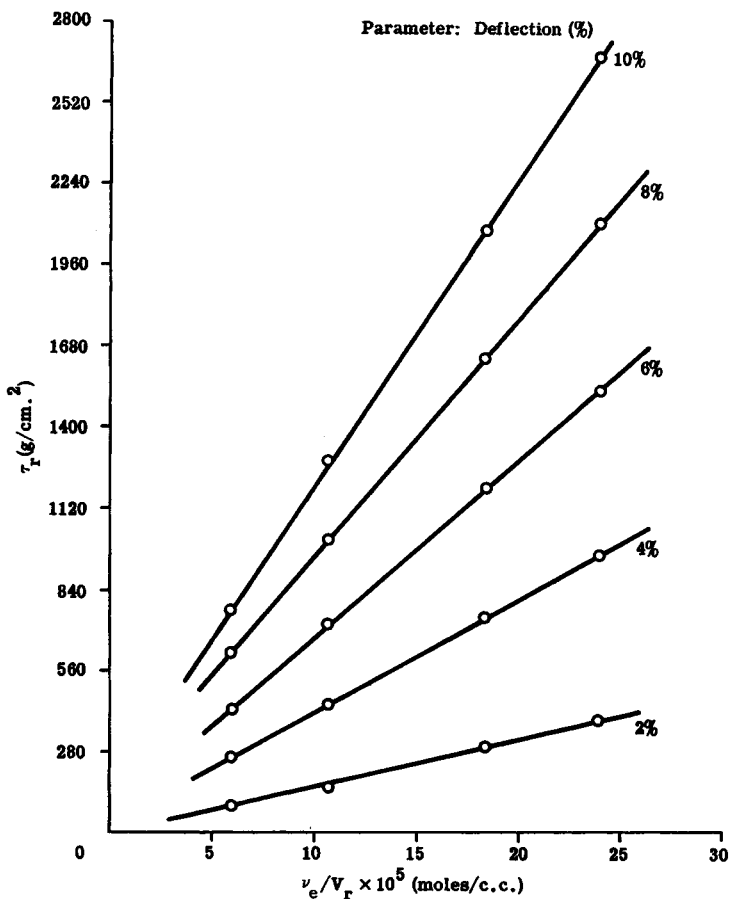


Fig. 3. Compression vs. effective crosslink density of solid silicone rubber swollen in toluene.

the curves could be expected to terminate at the origin if no interfering forces were present. The curves for cellular rubber do tend to the origin; however, the curves for solid rubber do not.

The slopes for both sets of curves change uniformly, thus allowing empirical equations to be derived relating compression, deflection, and crosslink density for the two systems. These equations are known to be valid within the limits investigated. For solid silicone rubber swollen in toluene,

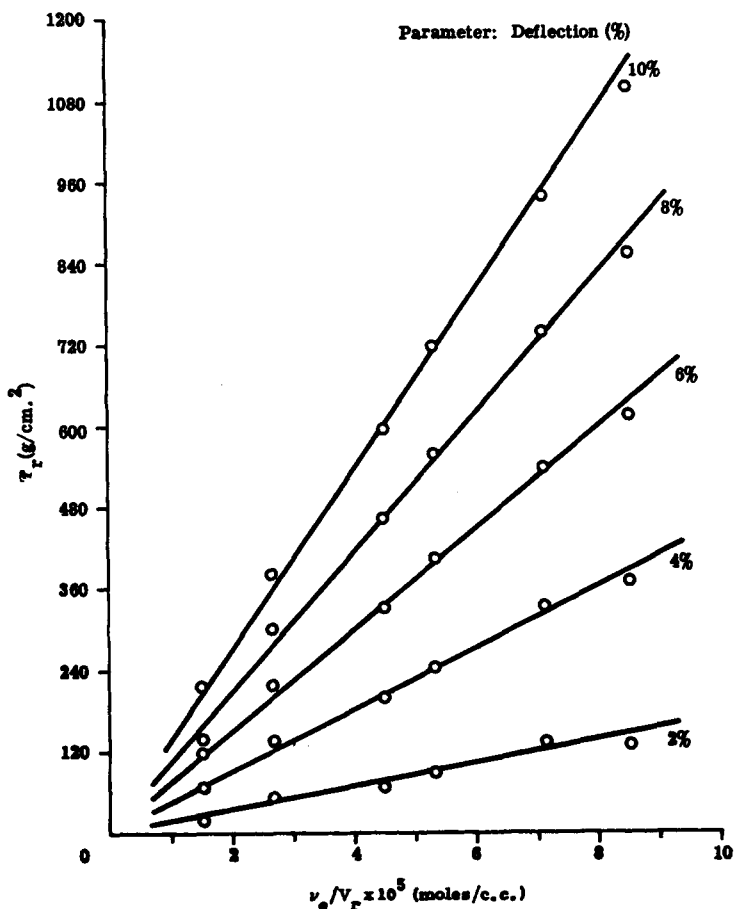


Fig. 4. Compression vs. effective crosslink density of cellular silicone rubber swollen in toluene.

the correlation of the data allows the following expression to be derived:

$$\tau_r = 6 \times 10^6 \nu_e / V_r (185d - 1) + 44(41d - 1) \quad (4)$$

where τ_r is expressed in grams (load)/square centimeters (cross-sectional area) of rubber and d is the corresponding percentage of deflection. For cellular silicone rubber, the equation is

$$\tau_r = 1 \times 10^6 \nu_e / V_r (1927d - 18) \quad (5)$$

where the term designations are the same as those for eq. (4).

Although the cellular rubber swollen in toluene represents a more ideal system, the linear relationships of both systems are quite significant. This fact is encouraging, since positive relationships are shown between the physical behavior of silicone rubber and crosslink density with toluene-swollen specimens.

Relationship of τ_r Versus ν_e/V_r for MEK-Swollen Silicone Rubber

The compression versus effective crosslink density values for MEK-swollen solid and cellular silicone rubber are shown graphically in Figures 5 and 6. For the solid rubber, the curves tend to intercept at about the same values as those shown for toluene in Figure 3. However, the MEK curves

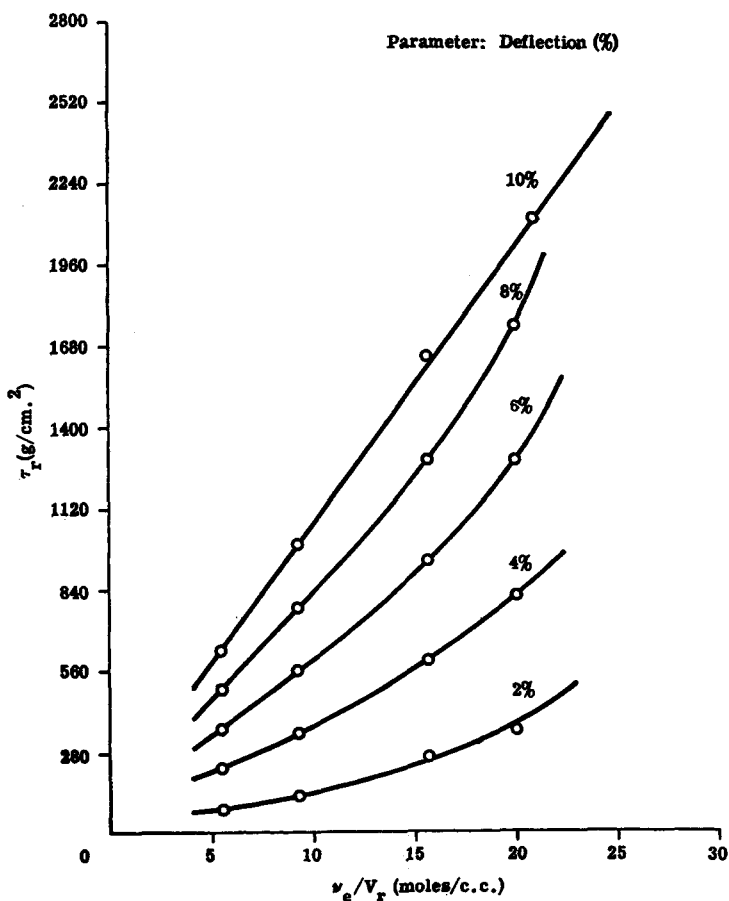


Fig. 5. Compression vs. effective crosslink density of solid silicone rubber swollen in MEK.

do not show the same linearity as the toluene curves, with the possible exception of the 10% deflection curve. This would indicate that MEK is not an effective swelling agent for this work.

The curves for the cellular rubber were sigmoid and tended to intercept at some negative compression value. This condition could be expected if the retractive forces in the rubber were strong at the time of testing. In cellular as well as solid silicone rubber swollen with MEK, it can be con-

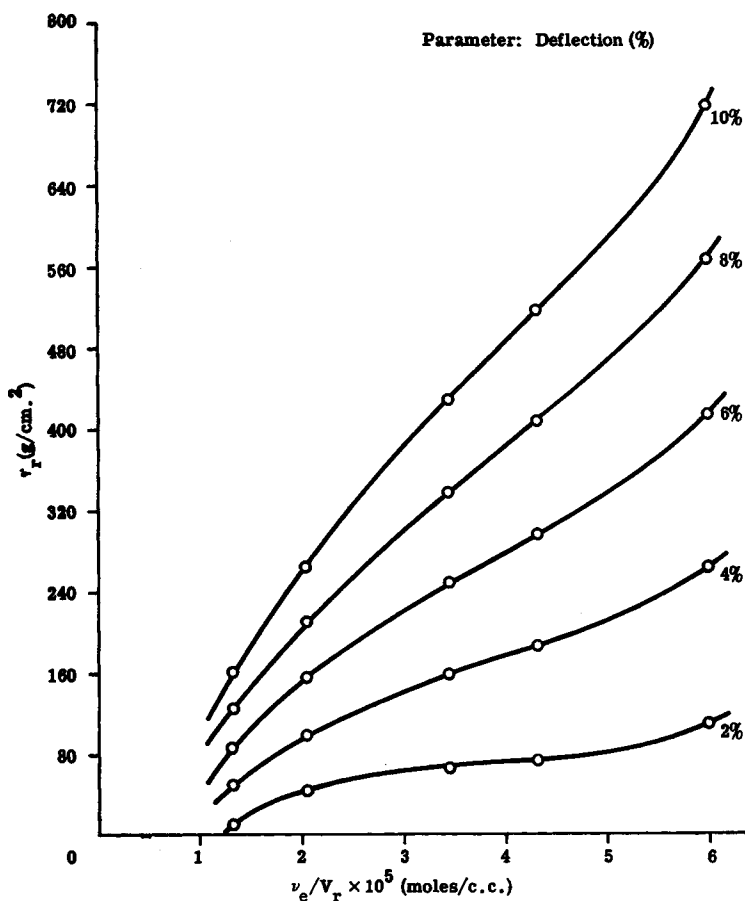


Fig. 6. Compression vs. effective crosslink density of cellular silicone rubber swollen in MEK.

cluded that the data have only potential value in ultimately defining the dependent force contributions in a rubber matrix system.

Comparison of τ_r Versus ν_e/V_r Between Toluene- and MEK-Swollen Rubber

By comparing Figures 3, 4, 5, and 6 it can be seen that swollen solid rubber exhibits the same compression characteristics for both MEK and toluene as the effective crosslinking approaches zero. Cellular rubber-toluene comes closest to being the ideal rubber-solvent system. The solid rubber-MEK and solid rubber-toluene systems exhibit tension forces, and the cellular rubber-MEK system shows a contraction force at equilibrium swelling. Note that in the solid rubber-toluene system an ideal response in τ_r versus ν_e/V_r is observed at deflections slightly greater than 2%. How-

ever, further work will be required with other solvents and different cellular silicone rubbers to substantiate this observation.

Figure 7 illustrates the relationship of crosslink densities of toluene-versus MEK-swollen rubber. The dashed line shows a curve which would apply if toluene and MEK both had the same swelling action. The solid rubber curve is linear throughout, while the cellular rubber curve appears to attain linearity at crosslink densities above 2×10^{-5} mole/cc. Both curves have been extended at the lower ends to show the positive value for MEK when the toluene value is zero. This tendency would characterize MEK as a weaker solvent because the MEK values reflect other rubber structure forces (filler effects, etc.).¹⁰

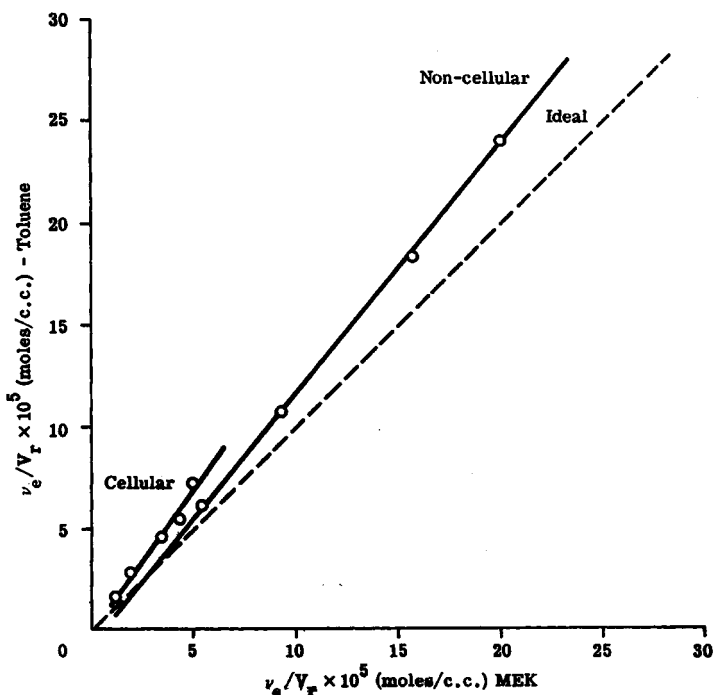


Fig. 7. Relationship of the effective crosslink density of toluene vs. MEK-swollen silicone rubber at 23°C.

Comparison of ν_e/V_r Values From Physical and Chemical Data

In Figure 8, the theoretical crosslink densities derived from chemical analysis are compared with the calculated effective crosslink densities. Since the chemical analysis values involve the assumptions that the peroxide is totally effective, that the average molecular weight of the silicone polymer is reasonably accurate, and that the ineffective chain end corrections are reasonable, these values must be considered as "ideal" crosslink densities. Therefore, the curves would not necessarily pass through the origin unless

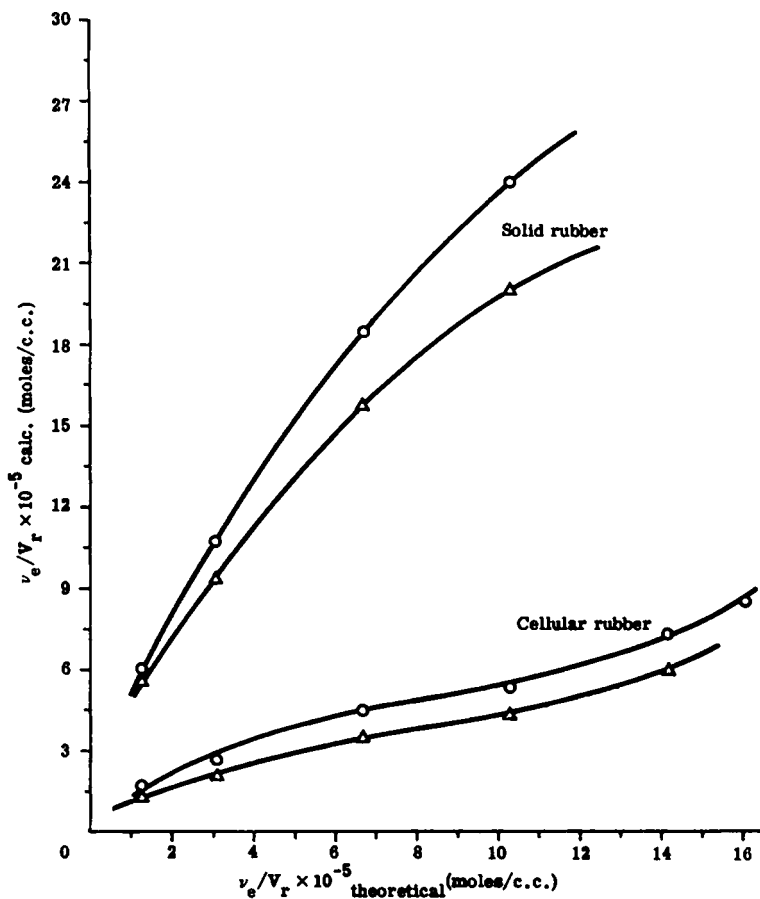


Fig. 8. Effective crosslink density from physical data vs. theoretical crosslink density from chemical analysis data from silicone rubber at 23°C. swollen in (O) toluene and (Δ) MEK.

the rubber systems were ideally crosslinked and the effective crosslink densities reflected only true crosslinks (dashed line in Fig. 7). Rather, the curves would be expected to intercept at some positive value of ν_e/V_r (calculated). This cannot be determined from the curves shown, but they do appear to substantiate this proposition.

Laboratory Physical Test Data

Tensile, elongation, modulus, and compression set values were determined for the solid silicone rubber compounds (compounds 4, 5, 10, and 11). These data are tabulated in Table V. The modulus, elongation at break, and compression set values follow a pattern consistent with crosslink density values. However, the tensile values are not consistent and show a maximum at a curative concentration of about 1.5 parts peroxide per 100 parts

TABLE V
Physical Properties of Solid Silicone Rubber

Compound no.	Modulus, kg./cm. ²			Elongation at break, %	Tensile strength, kg./cm. ²	Compression set, 70 hr. at 150°C. at 30% deflection
	100%	200%	300%			
10	5.53	10.76	19.26	608	57.37	25.4
11	8.86	22.57	44.01	445	77.48	
4	14.34	36.91	67.81	345	80.29	31.1
5	17.37	53.43		247	76.14	35.1

rubber; this inconsistency is evidenced in other work.⁴ Tensile values are obtained under extreme conditions: when molecular reorientation is occurring at a rapid rate, filler effects are at a maximum, and rubber structure breakdown is accelerating. Tensile data, therefore, cannot be related to a fundamental property of rubber without some necessary adjustment for these interfering occurrences.¹¹

Although Table V provides an insufficient basis for establishing definite relationships to effective crosslink densities, it is apparent that the modulus, elongation, and compression set values exhibit the expected pattern with crosslink values (the data are arranged in increasing crosslink values). Further investigation of these conditions will be necessary to establish quantitative relationships.

Flory-Huggins Interaction Parameter

From the experimental data, the Flory-Huggins solvent interaction parameters* μ have been determined for toluene and MEK (Table VI). The solvent interaction parameter is related to the crosslink network of rubber at equilibrium swelling by the Flory-Rehner equation:¹⁶

$$-\left[\ln(1 - \phi_s) + \phi_s + \mu\phi_s^2\right] = V_1(\nu_e/V_r)(\phi_s^{1/3} - \phi_s/2) \quad (6)$$

where ϕ_s is the volume fraction of rubber in a swollen specimen, V_1 is the solvent molar volume, and μ is the interaction parameter.

The data in Table VI show that toluene has stronger swelling action than MEK. The μ values decrease (lower cohesive energy density) with respect to the solid versus high cellular material, but for the low cellular rubber, the μ values are intermediate. The μ values decrease with increasing curative concentrations above 1.42 phr.

* Both Flory¹² and Huggins,¹³ using thermodynamic concepts, derived equations that relate the energy of dilution of a polymer-solvent system to the volume fraction of rubber in a swollen polymer. These equations involve an interaction parameter that is related to the cohesive energy density of the polymer and solvent¹⁴ or the heat of dilution.¹⁵ Although μ has not been rigorously defined, it offers a rather simple and useful means of determining crosslink density with eq. (6).^{3,4}

TABLE VI
Flory-Huggins Interaction Parameters

Compound	Curative concn., phr ^a	μ	
		Toluene	MEK
Silicone, solid	0.71	0.454	0.568
Silicone, solid	1.42	0.458	0.568
Silicone, solid	2.83	0.434	0.552
Silicone, solid	4.22	0.390	0.528
Silicone, low cellular	2.83	0.356	0.500
Silicone, high cellular	0.71	0.442	0.507
Silicone, high cellular	1.42	0.475	0.529
Silicone, high cellular	2.83	0.436	0.501
Silicone, high cellular	4.22	0.402	0.490
Silicone, high cellular	5.68	0.346	0.459
Silicone, high cellular	6.39	0.340	—

^a Cadox TS-50, parts per 100 parts silicone rubber.

SUMMARY

As a result of the investigations reported here, a simple and precise method was devised to measure the compression-deflection of solvent-swollen silicone rubber. The method was found to be reliable, and the resultant data were used to calculate effective crosslink densities of solid and cellular silicone rubber compounds. Empirical equations were derived relating compression and deflection to effective crosslinking of solid and cellular silicone rubber swollen in toluene. The weak swelling action of MEK precludes the derivation of empirical relationships between compression, deflection, and effective cross-linking of the rubber.

The investigation further showed that toluene is a better and more useful swelling agent than methyl ethyl ketone (MEK). The volume swelling ratios for toluene and MEK were determined. Toluene was found to be about 1.4 times more effective as a swelling agent than MEK. Limited laboratory physical test data show a reasonable correlation to v_e/V_r data. (More testing will be required to establish definite relationships.) This investigation also showed that the method employed here for crosslinking determinations is suitable for cellular rubber, since the data obtained from toluene-swollen specimens agrees quite well with theoretical calculations. Finally, the Flory-Huggins interaction parameters for toluene and MEK were determined.

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Résumé

On a déterminé les densités effectives de ramification pour des caoutchoucs de silicone solide et cellulaire à partir des tests physiques de spécimens gonflés dans le solvant, et les densités théoriques de pontage ont été calculées à partir des données d'analyses chimiques. On a développé une méthode pour mesurer avec précision la compression et la déflexion des échantillons de caoutchouc gonflé; et on a déduit des équations empiriques qui relient la compression, la déflexion et la densité effective de ramification des échantillons gonflés par le toluène des caoutchoucs de silicone. Les paramètres d'interaction de solvant de Flory-Huggins ont été calculés.

Zusammenfassung

Bei den hier beschriebenen Untersuchungen wurde die effektive Vernetzungsdichte in festem Silikonkautschuk und solchem mit Zellstruktur aus physikalischen Tests an gequollenen Proben bestimmt und die theoretische Vernetzungsdichte aus analytisch-chemischen Daten berechnet. Eine Methode zur exakten Messung der Kompression und Durchbiegung gequollener Kautschukproben wurde entwickelt; empirische Beziehungen zwischen Kompression, Durchbiegung und effektiver Vernetzungsdichte Toluol-gequollener Silikonkautschukproben wurden abgeleitet. Wechselwirkungsparameter mit dem Lösungsmittel nach Flory-Huggins wurden berechnet.

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