Network Characterization of Silicone Rubber Vulcanizates. Part I. Solvent, Temperature, and Specimen Shape Effects on Effective Crosslink Density Determinations

R. D. SEELEY,* Sandia Laboratory, Sandia Corporation, Albuquerque, New Mexico

Synopsis

The effective crosslink densities were determined for four silica-filled silicone rubber vulcanizates which represent different degrees of crosslinking. The determinations were made from compression-deflection measurements of rubber specimens at an equilibrium swelling condition. Nine solvents representing a wide range of dilatant strengths were investigated at four equilibrium temperatures (8, 23, 41, and 60°C.) for their effect on the crosslinking determinations. Specimen shape effects were also investigated. Explicit equations of state were derived empirically and were found to be similar to the well-known Mooney-Rivlin equation in which two independent parameters are required for the definition of a dilated rubber network.

INTRODUCTION

A structural definition of an elastomeric network will be especially useful to the rubber technologist if this definitive property can be translated into meaningful property characteristics in some quantitative fashion. A method most commonly used to relate structure to behavior involves stressstrain measurements on a solvent-swollen rubber specimen after equilibrium swelling has been attained. This method is based on a Gaussian statistical network theory of elasticity as proposed by Flory and Rehner¹ and represented by the equation

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

where ν_e/V_τ is the number of moles of polymer chain segments between effective crosslinks per unit volume of an unswollen rubber, τ is the tensile (or compressive) force per unit area of a swollen rubber specimen at an extension (or compression) ratio α , ϕ_τ is the volume fraction of the swollen rubber, R is the gas constant, and T is the absolute temperature. This same method has been related to a non-Gaussian statistical theory of elasticity as proposed by Mooney^{2a,3} and Rivlin⁴ and expressed by the equation

$$2C_1 + 2C_2/\alpha = \tau \phi_{\tau}^{1/2}/(\alpha - \alpha^{-2})$$
(2)

* Present address: Department of Chemistry, Central Missouri State College, Warrensburg, Missouri.

where C_1 and C_2 are independent parameters. C_1 has been defined as the Gaussian term $(C_1 = 1/2 \nu_e/V_r RT)$, and C_2 defines the internal energy of the rubber contributed by non-Gaussian characteristics. It can be readily seen that, if the rubber behaves as a Gaussian region, eq. (2) reduces to eq. (1) as C_2 , supposedly, approaches zero.

Both equations would be appropriate for unswollen rubber, if there are no anomalous interacting forces in effect. Because this condition is improbable, the use of an "appropriate" solvent reduces the elastomeric system to an effectively crosslinked matrix whose physical response is directly associated with the basic structural elements. Essentially Flory's equation depends upon one independent parameter, while Mooney's equation depends upon two independent parameters to satisfy their respective theories. In practice these theories have not completely agreed with experimental results, and other investigators have derived more complex equations to better define an elastic matrix by using the inverse Langevin function,^{2b} for example.

Considering for the moment the nonlinear characteristics of all stressstrain curves for rubbery materials, one realizes that linearity probably exists only within the limits of experimental error even for small deformations. This fact could account for many of the inconsistencies found between experimental stress-strain data and theory (another possible experimental error involves the volume fraction of swollen rubber which will be discussed in a subsequent paper). Because the stress-strain and compression-deflection curves are likely to be continuous for all rubbers, as has been reported for sulfur-vulcanized natural rubber,²⁰ compression-deflection measurements are valid for the same theoretical arguments. Compression-deflection curves generally show considerably less deviation from linearity over a greater applied force range than the corresponding stressstrain curves; thus one would expect more quantitative data from the compression-deflection measurements.

A revision of eq. (1) by Cluff, Gladding, and Pariser,⁵ was used:

$$\nu_e/V_r = (h_0 S/3A_0 RT) \ [\phi_0(\phi_r + \phi_s)]^{-1/s}$$
(3)

where h_0 is the height of the unswollen rubber specimen, A_0 is the area of the unswollen specimen, ϕ_0 is the volume fraction of rubber in the unswollen specimen, S is the slope of the compression-deflection curve, ϕ_τ is the volume fraction of the rubber in the swollen specimen, and ϕ_s is the volume fraction of solvent in the swollen specimen. Actually either eq. (1) or (2) may be used for compression data by using negative τ values, since ($\alpha - \alpha^{-2}$) is negative. However, eq. (3) is especially attractive because the actual height of a highly swollen specimen (consequently α) is difficult to determine.

EXPERIMENTAL

Right-cylindrical test specimens were die-cut from vulcanized rubber sheets. This shape was considered to be less prone to dimensional measurement errors, and the round cross-section would tend to minimize any anom-

alous swelling effects that might occur at or near the surfaces. The four rubber formulations used in this investigation, shown in Table I, were compounded, and vulcanized with conventional rubber-processing techniques and equipment. Three homologous series of solvents (A.R. grade in most cases) were selected to give a wide range of swelling characteristics: benzene, xylene and toluene; acetone, methyl ethyl ketone (MEK). and methyl propyl ketone (MPK); methanol (MeOH), n-propanol (n-PrOH), and n-hexanol (n-HexOH). Equilibrium swelling was established (approximately 14 days) at temperatures of 8, 23, 41, and 60°C. The techniques for specimen measurements and weight determinations have been described previously.⁶ The compression-deflection measurements were made at a rate of 0.05 in./min. on a Model TTB Instron tester with an environmental chamber attachment. A temperature control of ± 0.5 °C. was maintained during the swelling times to equilibrium, and the temperature varied no more than 3°C. during the short testing interval at the higher temperatures; the variation was less at the lower temperatures.

Silicone Rubber Formulary ^a							
Ingredients	Parts by weight						
	Compound 12	Compound 13	Compound 14	Compound 15			
Silicone rubber master batch ^b Cadox TS-50°	142 1.42	142 4.26	142 5.68	142 7.10			

TABLE I

^a Cure cycle: press vulcanization was 15 min. at 113°C. (3500 psi); circulating air oven cure was 16 hr. at 250 °C.

^b Supplied by Union Carbide Corporation with 42 parts silica filler per 100 parts rubber. This is a phenyl, methyl, vinyl siloxane terpolymer.

• A 50/50 mixture of 2,4-dichlorobenzoyl peroxide and silicone fluid supplied by the Cadet Chemical Corporation.

RESULTS AND DISCUSSION

Temperature Effects

The effective crosslink density values obtained by using eq. (3) are illustrated in Figures 1-4. The curves for MPK were omitted, since the crosslink data very nearly coincided with the MEK data. The slopes S of the compression-deflection curves were determined by the least-squares method. Volume fraction calculations were corrected for the sol fraction of the rubber by assuming that half (weight) the fraction was low weight silicone polymer and that the other half was unbound silica filler. This assumption seemed reasonable because of the high silica density and because a quantitative determination of the two fractional constituents would only be slightly (if at all) more reliable. The soluble extracts varied by weight from 5% for compound 12 swollen in toluene at 60°C. to less than 0.3% for compound 15 swollen in methanol at 8°C. The sol fraction was determined for each swollen rubber specimen. Actually the highest fraction obtainable for each rubber formulation would be more appropriate if one assumes that any extractable material is noncontributory to the effective matrix structure, regardless of the solvent. However, there is evidence that this argument is not valid at 88°C. This will be discussed under solvent effects.

The variation of ν_e/V , with temperature is not linear over the entire temperature range for any of the rubber-solvent system as is shown by comparing corresponding points between isotherms in Figures 1, 2, 3, and 4. Throughout this paper all compression data have been conveniently selected at 5% deflection which represents an extrapolated value in some



Fig. 1. Variation of compression force with effective crosslink density for benzene and methanol.

cases where the specimen was not or only slightly dilated. All the systems show a ν_e/V_r minimum at some intermediate temperature near 23°C., with a slight linear increase as the equilibrium temperature is increased for the highly swollen, loosely crosslinked systems. This is illustrated in Figures 2 and 3 by the dotted lines. This condition is more in agreement with theory, and suggests that, for the silica-filled silicone rubber used in this work, a volume swelling ratio near 4.5:1 is necessary for such agreement. A possible limiting volume swelling ratio will be considered in greater detail in work now in preparation. Let it suffice to say that this ratio may have a minimum limiting value useful in establishing the "appropriateness" of a solvent at a given temperature for crosslink density calculations from eq. (1), (2), or (3).



Fig. 2. Variation of compression force with effective crosslink density for xylene and n-hexanol.



Fig. 3. Variation of compression force with effective crosslink density for toluene and acetone.



Fig. 4. Variation of compression force with effective crosslink density for MEK $(O, \bullet 0, 0)$ and *n*-Propanol $(\Delta, \blacktriangle, \Delta, \Delta)$.

Solvent Effects

The nine solvents selected for this investigation represent a wide range of dilatant strengths, as well as three homologous series of varying dipole moments, and molecular configurations. Comparing the ν_e/V_τ values for each solvent series and corresponding rubber formulations, one will note that the crosslink values generally decrease as the solvent polarity increases for the most loosely crosslinked rubber (compound 12). (For example, compare the corresponding isotherm data for MeOH, Fig. 1; n-PrOH, Fig. 4; and *n*-HexOH, Fig. 2.) This coincides with increasing volume swell ratio as shown in Figure 5, where appropriate points on the compound 12 curve are compared. These relationships become less pronounced for the more highly crosslinked rubber (formulations 13, 14, and 15). No consistency was evident between the dipole moments of the three solvent series and crosslink densities. The ketones have the highest dipole moments and the aromatics have the lowest, but the crosslinking values are highest for the alcohols and lowest for the aromatic series. A correlation between ν_e/V_r and the moles of solvent sorbed was not found for the three solvent series. Because molecular configurations are not consistent with the crosslink data for the aromatics and alcohols, any correlative ar-



Fig. 5. Relationship of effective crosslink density to volume swell ratio at 23°C.

gument is precluded. Finally, a consideration of solvent energies would lead to inconsistencies, because toluene would probably be expected to possess solvent behavior intermediate to benzene and xylene, and the two higher molecular weight alcohols would be expected to behave quite differently. This was not found for either case. With the possible exception of solvent polarity correlating with ν_e/V_{τ} in the more loosely crosslinked rubber, there appears to be little likelihood that a solvent argument can be deduced solely on the basis of the physical characteristics of the solvent.

Unswollen specimens were evaluated at 23°C. in the same fashion as the swollen specimens. The ν_e/V_τ values calculated to be 89.53, 129.68, 150.65, and 163.89 $\times 10^{-5}$ mole/cm.³ for compounds 12, 13, 14, and 15, respectively. These values are about $3^{1}/_{2}$ times greater than those obtained for the weakest solvent (methanol) swollen rubber where the equilibrium swelling was only 1.06 times the original specimen dimensions. This large decrease in ν_e/V_τ as associated with only a very small degree of solvent swelling shows that only a small amount of dilatant energy is required to overcome the secondary structural forces in the filler-reinforced rubber matrix. Perhaps, one might argue that such small quantities of solvent

would be more appropriately associated with energies of wetting. However, in view of the fact that v_e/V_r does not change thereafter by more than 6%, even with a twofold increase in volume swell, it seems more reasonable that spatial, rather than surface wetting, phenomena are responsible for the large initial decrease in ν_e/V_r . Thus, the plots of the swollen to unswollen volume ratio, V_s/V_0 , versus ν_e/V_r for the four rubber vulcanizates in Figure 5 illustrate that practically all secondary structural forces are eliminated by a very slight dilation; upon further dilation the changes in the effective crosslink density are primarily associated with phenomena related to the basic structure of the network. Semilog plots were used only to bring the high crosslink values in closer proximity to the low values, and at the same time slightly exaggerate the differences between the low values to avoid a conflict between points. The upswing in the curves at high dilation for the more highly crosslinked vulcanizates might be attributed to osmotic effects which would less likely occur in the more loosely crosslinked networks as is shown to be the case by the compound 12 curve. The crosslink values obtained at 8°C. show that secondary forces are present which could be affected to some extent by the presence of low molecular weight unbound polymer. For this reason, the sol fraction determined for each solvent-rubber system was used for rubber volume fractional calculations, rather than the highest sol fraction obtainable as with a strong solvent like toluene.

Assuming the peroxide curative reacts completely to form chemical crosslinks, the chemical crosslink densities for compounds 12, 13, 14, and 15 calculate to be 3.62, 12.22, 16.54, and 20.86 $\times 10^{-5}$ mole/cm.³, respectively. These values incorporate the noncontributory chain correction if one assumes a polymer molecular weight value of 3.5×10^{5} . From these data one can establish linear order with the corresponding effective cross-link densities at 23°C. for toluene, the three alcohols, and the unswollen rubber of compounds 12, 13, and 14. The values for compound 15 are somewhat anomalous. If the chemical ν_e/V_r values are representative of real crosslinks in the rubber matrix, then about 60% of the calculated effective crosslink density can be attributed to chain entanglements (quasi-crosslinks).

Taking the crosslink density values obtained for the unswollen rubber to represent the summation of all the forces acting in the rubber matrix, it is

Compound number	$\nu_{e}/V_{r} \times 10^{5}$, mole/cm. ³					
	Chemical	Quasi	Secondary	Total		
12	3.62	11.58	74.33	89.53		
13	12.22	16.31	101.15	129.68		
14	16.54	18.70	115.41	150.65		
15	20.86	21.08	121.95	163.89		

TABLE II Structural Contributions to Crosslink Density

then possible to deduce these individual force contributions (Table II). In view of the consistent correlative nature of the toluene-swollen rubber data at 23°C., the calculated ν_e/V_r values could be considered as most likely values representative of the total chemical (real) and chain entanglement (quasi) crosslinks of the rubber. Also, the difference in the calculated ν_e/V_r values for toluene and the corresponding ν_e/V_r values for unswollen rubber differ only by the contributions of secondary forces. From the foregoing statements, the quasi-crosslinking was found to contribute about 13% of the total forces; while secondary forces (most probably filler reinforcement along with polymer-polymer interaction) constitute about 78% of the total forces acting within the unswollen silicone rubber matrix. Actually, as shown in Table II, the quasi-crosslink values are nearly proportionately constant to the total values, but the secondary force values vary from 83% for the loosely crosslinked rubber (compound 12) to 74%for the highest crosslinked rubber.

Specimen Shape Effects

Right-cylindrical specimens from vulcanizates 13 and 15 and having different heights and cross-sectional areas were swollen in benzene, toluene, and MEK at 23°C. The ν_e/V_r data are tabulated in Table III. As was the case with the previous ν_e/V_r versus τ_r plots, the same linearity was observed with the curves intersecting the abscissa identical to benzene, toluene, and MEK curves in Figures 1, 3, and 4. Thus, the area and height of the specimens do not restrict the use of eq. (3) for calculating effective crosslink densities, at least for the reasonable dimensions considered here (Table III). Obviously, specimens with heights great enough to allow skewing under compression would yield unrealistic compression-deflection data. Actually this occurred with several specimens during this investigation.

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Compound			$\nu_e/V_r \times 10^5$, mole/cm. ³			
number	$A_0^{\mathbf{a}}$	$h_0{}^{\mathbf{a}}$	Benzene	Toluene	MEK	
13	2.91	0.66	36.82	36.67	33.40	
13	11.18	0.66	34.09	34.69	31.01	
13	20.05	0.66	35.48	35.00	14.52	
13	6.43	0.23	30.31	32.87	34.16	
13	11.37	0.23		27.51	29.52	
13	20.27	0.23		28.85	12.08	
15	2.91	0.65	48.49	46.97	42.65	
15	11.23	0.65	42.56	43.65	41.15	
15	20.06	0.66	44.19	45.53	18.71	
15	6.41	0.28	41.27	45.48	43.98	
15	11.37	0.29		37.78	35.95	
15	20.26	0.29		38.31	17.59	

TABLE III Effective Crosslink Densities for Varying Specimen Sizes

^a These values represent an average of six specimens in most cases and are not the specific values used for the ν_e/V_r calculations.

Explicit Equations and Mooney Parameters

Using the least-squares method, explicit equations of state were derived for each solvent-rubber system. These equations may be expressed in general form as

$$\nu_e/V_r = A(h_0S/A_0RT) [\phi_0(\phi_r + \phi_s)]^{-1/2} - B$$

where A and B are parameters peculiar to each solvent. After discarding some deviant points, the equations were refined by recalculation, by using minimum deviations from successive approximation to establish the most precise parameters as shown in Table IV. By rearrangement, equations similar in form to the Mooney equation or the equation recently proposed by Loan⁷ are obtained, where the Mooney parameters, C_1 and C_2 , are equivalent to $\nu_e/V_r RT/6A$, and $\alpha BRT/6A$, respectively. Assuming the foregoing relationships are real, the values of C_1 and C_2 have been calculated (Table V).

The C_2 terms, which reportedly represent a stored energy function of the rubber network as related to non-Gaussian characteristics, show their dependency on the solvent strength and equilibrium temperature. These terms are independent of the rubber formulation. C_1 , on the other hand, shows little correlation between solvent systems, even

Solvent	A	$B \times 10^5$, mole/cm. ³
Benzene	0.375	3.72
Xylene	0.376	3.72
Toluene	0.375	3.70
Acetone	0.347	1.10
MEK	0.375	3.25
MPK	0.374	3.24
MeOH	0.340	0.58
<i>n</i> -PrOH	0.342	0.83
n-HexOH	0.340	0.57

TABLE IV Parameters for the Explicit Equations of State

TABLE VA Mooney-Rivlin Parameter C_2

	C_{2} , kg./cm. ²				
	8°C.	23°C.	41°C.	60°C.	
Benzene	0.375	0.395	0.419	0.444	
Xylene	0.375	0.394	0.418	0.443	
Toluene	0.373	0.393	0.416	0.441	
Acetone	0.120	0.126	0.134	0.142	
MEK	0.324	0.345	0.366	0.388	
MPK	0.327	0.345	0.365	0.388	
MeOH	0.064	0.068	0.072	0.076	
n-PrOH	0.092	0.097	0.102	0.109	
n-HexOH	0.063	0.067	0.071	0.075	

		C1, kg./cm. ²								
Temp., °C.	Com- pound no.	Ben- zene	Xyl- ene	Tol- uene	Ace- tone	MEK	MPK	МеОН	n- PrOH	n- HexOH
8	12	1.96	2.08	1.90	2.64	1.84	2.08	4.18	3.24	3.25
	13	3.29	3.74	3.62	3.67	3.41	3.40	5.55	4.04	4.41
	15	4.32	4.86	4.75	4.27	4.32	4.56	6.31	4.51	4.59
23	12	1.73	1.77	1.70	2.08	1.70	1.42	3.75	2.50	2.63
	13	3.31	3.24	3.19	3.25	2.89	2.89	4.76	3.44	3.38
	14	4.00	3.92	3.94	3.71	2.97	3.49	5.28	4.15	3.79
	15	4.21	4.06	4.03	3.77	3.35	3.64	5.10	3.88	3.88
41	12	2.40	1.95	1.88	2.30	1.65	1.61	4.16	2.22	2.19
	13	3.63	3.61	3.32	3.89	3.27	3.37	5.57	3.57	3.69
	15	4.50	4.67	4.50	4.65	4.07	4.06	5.96	4.28	4 . 2 8
60	12	2.27	2.35	2.21		2.00		_	2.00	2.35
	13	4.37	4.00	4.02		4.15	<u> </u>		4.30	4.56
	15	5.32	5.15	5.22		4.71			5.18	5,27

TABLE VBMooney-Rivlin Parameter C

within a homologous series; and there appears to be little consistency between temperatures of 8, 23, and 41°C. There does appear to be an interrelation between C_1 values for a given solvent and different rubber formulations at each equilibrium temperature, especially for a strong solvent like toluene. At 60°C., the C_1 values approach a common value for each rubber formulation with the six solvents investigated at this temperature. The common values for C_1 at 60°C. are 2.20, 4.23, and 5.14 for compounds 12, 13, and 15, respectively.

CONCLUSION

Although the compression-deflection data from solvent-swollen silicone rubber vulcanizates relate compatibly with a Gaussian statistical theory, a non-Gaussian statistical approach as proposed by Mooney for high strains accommodates the data more explicity. The explicit equations of state derived for each solvent system are of the Mooney type, involving two independent parameters. Assuming the empirical equations are related to the theoretical Mooney equation, values for the C_1 and C_2 Mooney parameters were determined. The C_1 parameter was found to vary with rubber formulation, solvent action, and equilibrium temperature. However, at 60° C. the temperature dependence became negligible. The C_2 parameter varied with solvent and equilibrium temperature.

Good evidence was found that a limiting minimum swelling ratio of about 4.5:1 exists, below which temperature effects are characteristically nonlinear when related to force-structure considerations. This ratio is now being investigated more fully and will be reported at a later date. Perhaps the empirical equations derived in this work would reduce to one complex equation of state involving the inverse Langevin function, and preclude the usefulness of this ratio; but a consideration of this possibility is beyond the scope of this investigation. Secondary structural elements within the silicone rubber matrix were found to account for about 80% of the matrix structure of an unswollen rubber. The reinforcing potential of these elements is almost completely eliminated by a very slight dilation of the matrix. High dilation (but with $V_s/V_0 < 4.5$) demonstrates that the rubber becomes more incompressible than at lower dilations.

The shape variations investigated here, with respect to height and crosssectional area, of the right-cylindrical specimens did not create anomalous compression-deflection responses for the three solvents evaluated.

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Résumé

Les densités réelles de pontage ont été déterminées pour quatre vulcanisats de caoutchouc de silicone chargés de silice et présentant différents degrés de pontage. Les déterminations ont été faites au moyen des mesures de compression-déflection de spécimens de caoutchouc, dans des conditions de gonflement à l'équilibre. Neuf solvants, englobant un large domaine de dilatation, ont été essayés à quatre températures d'équilibre (8, 23, 41, et 60°C) afin de déceler leur effet sur la détermination du pontage. Les influences de la forme du spécimen ont également été étudiées. Empiriquement on en a déduit des équations d'état explicites; celles-ci sont similaires à l'équation bien connue de Mooney-Rivlin, dans laquelle deux paramètres indépendants sont nécessaires pour la définition d'un réseau dilaté de caoutchouc.

Zusammenfassung

Die effektive Vernetzungsdichte wurde an vier kieselsäuregefüllten Silikonkautschukvulkanisaten mit verschiedenem Vernetzungsgrad bestimmt. Die Bestimmungen wurden durch Kompressions-Ablenkungsmessungen an Kautschukproben bei Gleichgewichtsquellung ausgeführt. Neun Lösungsmittel mit einem weiten Bereich an Quellfähigkeit wurden bei vier Gleichgewichtstemperaturen (8, 23, 41, und 60°C) auf ihren Einfluss auf die Vernetzungsbestimmung untersucht. Weiters wurde der Einfluss der Probengestalt ermittelt. Zustandsgleichungen wurden in expliziter Form empirisch abgeleitet und erweisen sich als ähnlich der wohlbekannten Mooney-Rivlin-Gleichung, in welcher zwei unabhängige Parameter zur Definition eines dilatierten Kautschuknetzwerks erforderlich sind.

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