

## Three Methods for Determining the Swelling of Silicone Rubber

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### Synopsis

A solvent swelling method is often a convenient means of characterizing the structure of a polymeric network, if the appropriate solvent-polymer interaction parameters are known. Three such methods for measuring the solvent dilative action on silica-filled, silicone rubber networks have been investigated. First, the quantity by weight of solvent sorbed by the rubber was determined by measuring the weight gain of a rubber specimen at equilibrium swelling. Second, the increase in volume of the rubber specimen was determined by optical and electronic instruments. Third, the volume of solvent taken up by the rubber specimen was measured directly by a simple apparatus which was designed by the author. The effective crosslink densities were calculated by using appropriate interaction parameters. These density values were then compared for the three techniques.

### INTRODUCTION

The Flory-Huggins equation<sup>1</sup> is potentially useful for characterizing the structure of high molecular weight polymers, because only conditions of solvent equilibrium swelling of the polymer have to be found, once an appropriate solvent-polymer interaction parameter is known. The volume of polymer in a right cylindrical specimen can be easily determined by conventional density-weight methods. Also, there are three simple techniques for determining the quantity of solvent associated with equilibrium swelling of a polymer specimen.

The experimental errors involved in several methods of determining the rubber and solvent volumes of a rubber-solvent system have been discussed by van Wijk.<sup>2</sup> However, van Wijk did not discuss possible volume errors inherent to the dilation phenomena, such as solvent sorption that does not contribute to any rubber network deformation which applies to statistical network theories. One such error was considered in this investigation which compares three methods of determining solvent swelling volumes in terms of effective crosslink densities. Because the shape and size of the rubber specimens were suitable for compression-deflection measurements, further comparisons were made with crosslink densities which were calculated from modified statistical network theory equations of state derived by the author in previous work.<sup>3</sup>

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## EXPERIMENTAL

Four silica-filled, silicone rubber vulcanizates were compounded and cured as described in an earlier investigation.<sup>3</sup> Only the vulcanizing agent, dichlorobenzoyl peroxide, was varied, the content being 0.71, 2.13, 2.84, and 3.55 parts agent per 100 parts of silicone rubber for formulations 1, 2, 3, and 4, respectively. The solvents were analytical grade in most cases. The averaged measurements of two specimens were used for each volume calculation made by methods I and II, while one specimen was used at each of the four temperatures for method III.

### Method I. Solvent Volume Determination by Weight

The rubber specimen was immersed in the solvent and allowed to swell until no further sorption was detected. The weight of the equilibrium swollen specimen was measured by using a procedure similar to that described by Moore and Watson.<sup>4</sup> The specimen was rinsed twice in fresh solvent to remove the soluble materials. The solvent was then removed from the specimen by vacuum and heat (approximately 100°C.) until constant weight was attained. The final specimen weight was taken as the true rubber specimen weight because the original unswollen specimen weight included such extraneous materials as the sol fraction of polymer and soluble impurities. The difference between the swollen specimen weight and the dried specimen weight was taken as the amount of solvent sorbed by the specimen. The corresponding solvent volume was calculated by using the solvent density data which are available in the International Critical Tables for the 8, 23, 41, 50, and 60°C. temperatures. The volume of solvent calculated to wet the surface of the silica filler in the rubber specimen was subtracted from the total solvent volume because this quantity of solvent was considered to be noncontributory to the dilation phenomenon.<sup>5</sup>

### Method II. Solvent Volume Determination by Specimen Swelling Measurements

The rubber specimen was allowed to swell to equilibrium in the same fashion as described for method I. When equilibrium swelling was attained, the specimen was measured for thickness with an electronic micrometer. The specimen was reimmersed in the solvent for a few minutes, then the specimen cross-sectional dimension was measured in two positions with an optical comparator. These measurements were used to calculate the swollen volume of the rubber specimen. The volume of the unswollen specimen was calculated in the same way for the swollen specimen. The difference between the swollen and unswollen specimen volumes was taken as the solvent volume. Also, specimen swelling was measured several times during the experiment to obtain swelling rate data.

### Method III. Solvent Volume Determination by Direct Measurement

This method utilized a sorption apparatus (Fig. 1) designed by the author. This simple instrument permits convenient measurement of the

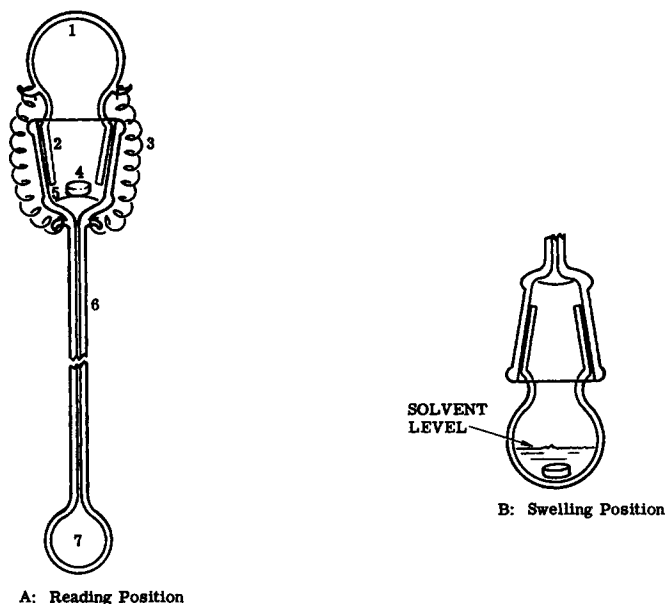


Fig. 1. Sorptometer for rubber-solvent systems: (1) swelling chamber; (2) 60/50 standard taper joint; (3) McLeod springs; (4) rubber specimen; (5) spring wire; (6) graduated column (10 ml.); (7) solvent reservoir (50 ml.).

solvent sorption rates and the solvent sorbed at equilibrium swelling. Another desirable feature of this instrument is that it can be easily installed in a temperature chamber and operated accurately over a much greater temperature range than is practical or safe with the other two methods. Unlike the first two methods, which require the specimen to be removed from the solvent environment for measurement, this direct method permits the specimen to remain in a closed system throughout the swelling period.

The instrument is operated by first filling the solvent reservoir and graduated column with solvent, and then placing the rubber specimen in the specimen chamber (see Fig. 1A). By inverting the assembly, the specimen is immersed in the solvent (Fig. 1B). To determine the amount of solvent sorbed at a given time, the assembly is returned to its original position and the solvent volume loss is read from the graduated column. The dimensions of the instrument shown in the illustration are not critical because once this device is constructed, any solvent-rubber combination can be accommodated by varying the size of specimen or the strength of the solvent.

The volume fractions of rubber at equilibrium were calculated by using the corrected solvent volumes for the first and third methods; the second method did not require this correction. The volume fraction-interaction parameter relationships established earlier<sup>5</sup> for corresponding silicone rubber formulations were used to calculate the effective crosslink density values. These values are tabulated in Table I.

## DISCUSSION

The crosslink densities shown opposite the physical test method (Table I) were calculated from empirical equations of state derived by the author<sup>3</sup> on the basis of compression-deflection data. These crosslink density values are primarily for reference because they have been derived in part from a physical response of the rubber to an external stress, and because a correlation of a polymer structural parameter to the physical properties of the polymer is paramount for this and previous work.<sup>3,5,6</sup> Comparing the effective crosslink density values calculated from the swelling data of the three methods with those by the physical test method, one will note considerable variation in some cases. However, by excluding a few highly deviant values, the average deviation from the physical test method is about 13% for the three methods. The variation in homogeneity between different rubber specimens created during the mixing, molding, and curing operations of the rubber might explain deviations of this order. The variation in the crosslinking values with temperature for the three methods is generally more uniform than found to be the case with the values obtained from compression-deflection data. With the exception of the values at 8°C., the stronger solvents yielded crosslink density values which increase with

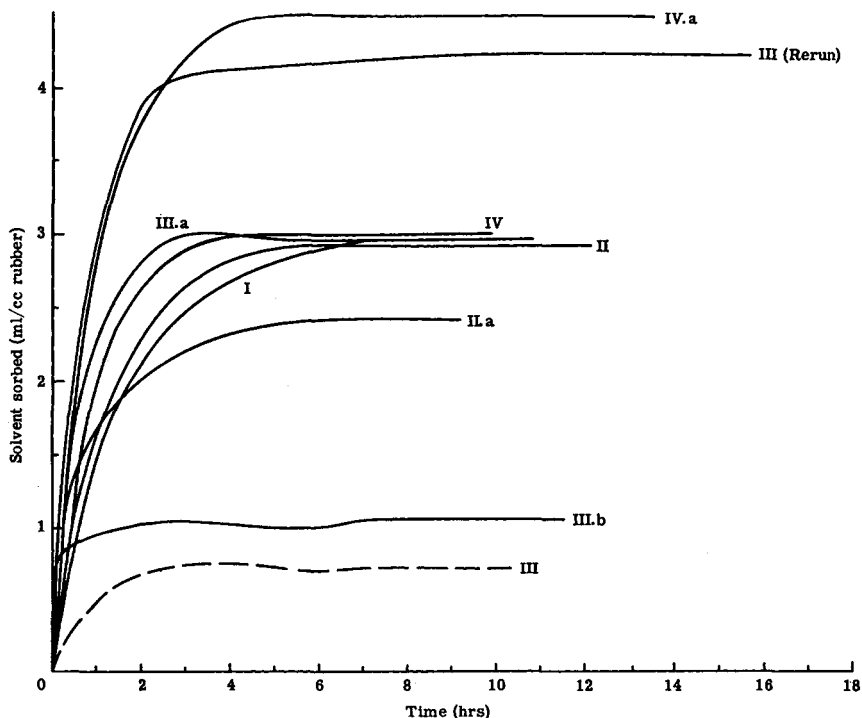


Fig. 2. Solvent sorption-time curves: (I) toluene, 8°C.; (II) toluene, 23°C.; (III) toluene, 41°C.; (IV) toluene, 50°C.; (IIa) MEK, 23°C.; (IIIa) MEK, 41°C.; (IVa) MEK, 50°C.; (IIIb) *n*-PrOH, 41°C.

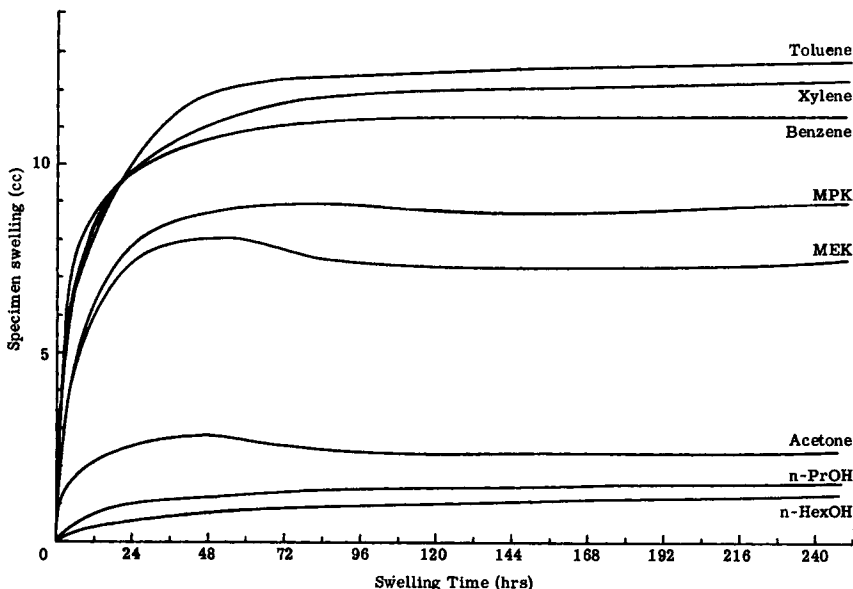


Fig. 3. Rubber specimen swelling for compound 1 at 23°C.

increasing equilibrium temperature, while the weaker solvents generally showed crosslink values which decreased with increasing equilibrium temperatures.

The effective crosslink density data derived from specimen swelling (method II) is limited because measurements were only conducted at 23°C. This method is limited because it cannot be conveniently carried out at temperatures far removed from ambient temperature with the present size and operating limitations of the electronic and optical equipment. With the exception of compound 1 swollen in toluene and xylene and some of the values for the weak solvents, overall correlation was considered quite close compared to the weight method values.

Although the data obtained by method III are limited, the data correlation appears to be as close as for the other methods. In addition, method III offers the unique advantages mentioned earlier. A pressure correction for this method was not considered because one of the objectives of this investigation was to determine the variation in the structural definition of a rubber vulcanizate achieved by using the three methods in the most direct and simple way possible. Solvent sorption with respect to time for this method is shown in Figure 2 for comparative purposes. A sorption determination for toluene at 41°C. with compound 1 yielded an unreasonable equilibrium sorption value (see dashed line, Fig. 2). A subsequent determination gave a more realistic result, and the effective crosslink density value in Table I was calculated from the rerun result. The only explanation for the abnormal sorption experienced in the first determination is that the rubber specimen surface was covered with a lyophobic substance such as a mold release applied during the curing of the rubber.

The amount of solvent volume sorbed with respect to time based on specimen volume changes is shown in Figure 3. The maxima are unique in the curves for the solvents with moderate swelling strengths after about 48 hr. The data and procedure have been thoroughly reviewed, and there appears to be no experimental error peculiar to these solvents. Therefore, if this phenomenon is true for the reported system, there is a possibility that it may be true for other rubber-solvent systems. Consequently, experiments affected by specimen size (such as stress-strain or compression-deflection measurements which are used with a statistical network theory equation of state to characterize polymer networks) may yield varying results, if equilibrium times less than approximately 72 hr. are considered when moderate swelling solvents are used. No logical explanation can be given now for this phenomenon, but its existence might account for some of the arguments in the literature concerning the validity of statistically derived equations of state which accommodate compression-deflection or stress-strain data.<sup>7-9</sup>

### CONCLUSIONS

Three techniques for determining the quantity of solvent sorbed by a silicone rubber at equilibrium have been evaluated in terms of effective crosslink densities of the rubber by using appropriate solvent-rubber interaction parameters. These crosslink density values were compared with corresponding values which were calculated from compression-deflection data and found to have an average deviation of 13% by excluding a few higher deviations. The higher deviations were more predominant for the strong (aromatics) and weak (alcohols) solvents when the interaction parameter values were most sensitive to small changes in the volume fraction of the swollen rubber.

An apparatus of simple construction has been made to directly measure the quantity of solvent taken up by the rubber at equilibrium swelling. This instrument conveniently measures the amount of solvent sorbed at any time, and it allows a greater range of experimental temperatures for rubber-solvent swelling investigations.

The relationships of solvent sorption and rubber specimen swelling with time indicate an anomalous swelling behavior for solvents of moderate swelling strengths.

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### Résumé

La méthode du gonflement par le solvant est souvent un moyen commode pour caractériser la structure d'un réseau polymérique si les paramètres d'interactions polymère-solvant correspondants sont connus. Trois de ces méthodes de mesure de l'action de dilatation du solvant sur des réseaux de caoutchouc à base de silicone, remplis de silice ont été étudiées. En premier lieu, la quantité en poids de solvant adsorbé par le caoutchouc a été déterminée par mesure du gain en poids d'un spécimen de caoutchouc en équilibre de gonflement. En second lieu, l'augmentation de volume du spécimen caoutchouteux a été déterminée à l'aide d'instruments optiques et électroniques. En troisième lieu, le volume de solvant adsorbé par le spécimen caoutchouteux a été mesuré indirectement par un simple appareillage décrit par l'auteur. Les densités de pontages réels ont été calculées en se servant des paramètres d'interaction appropriées. Ces valeurs de densités ont alors été comparées pour les trois techniques.

### Zusammenfassung

Eine Lösungsmittelquellungsmethode bietet oft ein bequemes Mittel zur Charakterisierung der Struktur eines Polymernetzwerkes, sobald die entsprechenden Lösungsmittel-Polymer-Wechselwirkungsparameter bekannt sind. Drei solche Methoden zur Messung der dilatierenden Lösungsmittelinwirkung auf kieselsäuregefüllte Silikonkautschuknetzwerke wurden untersucht. Bei der ersten wurde die Gewichtsmenge des vom Kautschuk aufgenommenen Lösungsmittels durch die Messung der Gewichtszunahme einer Kautschukprobe beim Quellungsgleichgewicht bestimmt. Bei der zweiten wurde die Volumszunahme der Kautschukprobe mit optischen und elektronischen Instrumenten bestimmt. Bei der dritten wurde das Volumen des durch die Kautschukprobe aufgenommenen Lösungsmittels direkt mit einem einfachen vom Autor entworfenen Apparat gemessen. Die effektive Vernetzungsdichte wurde mit den entsprechenden Wechselwirkungsparametern berechnet. Diese Dichtwerte wurden dann für die drei Methoden verglichen.

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