

The Deformation Behavior of Poly(dimethyl siloxane) Networks. II. Equilibrium Swelling

S. VENKATRAMAN,* A. NIXON,[†] and A. HIGHE

Corporate Technology, Raychem Corporation, Menlo Park, California 94025

SYNOPSIS

The equilibrium swelling behavior of end-linked silicone networks has been studied, using low molecular weight silicone oils as diluents. Using the phantom and affine versions of the Flory–Rehner elasticity theory, the predictability of the equilibrium swelling has been examined. It was found that a modified version of the Flory–Rehner equation can be used to predict the equilibrium swelling behavior, provided the interaction parameter is known or measured. The modification is the use of the measured elastic shear modulus of the network prior to swelling, to calculate the density of network chains needed in the equation for swelling. This implies that both entangled and chemically linked chains contribute to the swelling behavior, since the modulus itself is predicted by the use of an equation that incorporates the contribution of entanglements. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In Part I of this series,¹ we examined the applicability of the theories of polymer networks to modulus prediction, using end-linked poly(dimethyl siloxane) networks as a model system. In this article, we address the swelling deformation of the same networks.

Equilibrium swelling has been used extensively as a means of network characterization; most of these studies are summarized in review articles.^{2–4} Swelling behavior has been used to estimate cross-link density (see Ref. 2, pp. 33–51 and Ref. 5) to critically evaluate various theories of network elasticity^{6–8} and to estimate the polymer–diluent interaction parameter χ .⁹ In this article, we examine the swelling behavior of end-linked poly(dimethyl siloxane) (PDMS) networks and demonstrate the use of a modified form of the Flory–Rehner equation to predict equilibrium swelling ratios.

Most theories of equilibrium swelling assume separability of the elastic and mixing terms. Thus,

at equilibrium, the free energy of mixing equals the free energy of deformation:

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (A\nu RT/V_d)((\Phi_2)^{1/3} - B\Phi_2) \quad (1) \end{aligned}$$

where Φ_2 is the equilibrium volume fraction of polymer (or network); V_1 , the molar volume of diluent; V_d , the volume of the (dry) network; and ν , the number of network chains. The factors A and B are the source of much controversy. In the affine model of networks elasticity, $A = 1$ and $B = \frac{1}{2}$ for tetrafunctional networks. In the phantom network model, $A = \frac{1}{2}$ and $B = 0$. In addition, the quantity ν is subject to debate: From a scan of the literature, it is unclear whether trapped entanglements, in addition to chemical cross-links, contribute to ν . For small deformations, there is some agreement that trapped entanglements contribute to the measured modulus.^{1,10–12} However, for larger deformations such as those involved in swelling in good solvents, the contribution of trapped entanglements to ν is less certain.^{13,14} In our analysis of the equilibrium swelling data, we compare the predictions of the affine and phantom models and the possible contributions of trapped entanglements.

* Current address: Cygnus Therapeutic Systems, 400 Penobscot Drive, Redwood City, CA 94063.

[†] To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 52, 1619–1627 (1994)

© 1994 John Wiley & Sons, Inc.

CCC 0021-8995/94/111619-09

If some diluent is present during the cross-linking of the network, eq. (1) must be modified to

$$-(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ = (A\nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3} - B\Phi_2) \quad (2)$$

where the term $\Phi_x^{2/3}$ now accounts for the initial diluted state of the network. The network concentration, or weight fraction, during cross-linking is now Φ_x , defined as V_d/V_x , where V_x is the volume of network at cross-linking.

In this study, we cross-linked PDMS molecules in the presence of varying amounts of linear PDMS oils as diluents. Two inert PDMS oils of two different molecular weights were used. The networks were subsequently swollen in the same PDMS oil used during the cross-linking step. The swelling ratios, or the network volume fraction at equilibrium, were compared to theoretical predictions, with and without entanglement contributions to the term ν . Similar approaches have been taken by others for poly(ethylene oxide) networks,⁷ for polyurethane networks,¹⁵ and for polyethylene networks.¹⁶ The influence of trapped entanglements on ν has been inferred from the swelling behavior of PDMS networks also.¹¹

EXPERIMENTAL

End-linked PDMS networks were prepared as described elsewhere.^{1,11} Vinyl-terminated PDMS (V-PDMS) of known molecular weight was reacted with a tetrafunctional siloxane [tetrakis(dimethyl siloxy)silane, or TDSS] in the presence of a platinum catalyst. To prevent premature reaction at room temperature (during mixing), an inhibitor was added to the catalyst. The cross-linking reaction was carried out in the "dry" state (no diluent) and with varying amounts of either of two inert diluents, which were long-chain trimethyl-terminated PDMS oils. The characterization of the starting materials is given in Table I.

Preparation of Reaction Mixture

The stoichiometric maximum (the ratio of V-PDMS to TDSS that yields maximum modulus) was determined to occur at a weight ratio of 0.0023 (wt of cross-linker/wt of V-PDMS). All reactions were carried out at this ratio. A two-part system was formulated so that when mixed in equivalent amounts, the above ratio of V-PDMS to TDSS would be attained. Part A contained the V-PDMS, the inert

Table I Characterization of Network Precursors

| | Supplier | M_n | M_w |
|------------------|---------------|---------------------|----------------------|
| Precursor | | | |
| V-PDMS | Huls Petrarch | 26,300 ^a | 120,000 ^a |
| TDSS | Huls Petrarch | 329 ^b | — |
| Diluents | | | |
| PDMS oil 1 | Huls Petrarch | 4,400 ^a | 6,600 ^a |
| PDMS oil 2 | Dow-Corning | 16,000 ^a | 32,000 ^a |

^a Determined by GPC measurements in toluene, using the universal calibration assumption.¹

^b Formula molecular weight; purity estimated to be > 98% by GC.

diluent, and the catalyst/inhibitor complex. Part B contained the TDSS, the V-PDMS, and the diluent. The amount of catalyst was adjusted such that in the final reaction mixture the active platinum concentration was 15 ppm.

Measurement of Moduli

Samples with Inert Diluent at Cross-linking (G_x)

Dynamic mechanical shear moduli were measured using the following procedure: Parts A and B were mixed and degassed. The reaction mixture was poured onto the platen of a Rheometrics mechanical spectrometer (RMS-605). The top platen was then lowered, and the chamber heated to 70°C. After 15 h at 70°C, the platens were cooled to 30°C. This cross-linked sample was then analyzed by small amplitude dynamic measurements, as described in Ref. 1, and the modulus–frequency spectrum obtained. (The modulus in the low-frequency range, for these networks, was independent of frequency; we used this low-frequency modulus, or the "plateau" modulus, in the data analyses.) These moduli were designated G_x or "wet" moduli.

Samples from Which the Inert Diluent Was Extracted (G_d)

Sample networks prepared with the PDMS oil 2 were subjected to an extraction procedure (for reasons to be discussed below). A disc-shaped cross-linked sample (with varying amounts of the inert diluent) was first prepared. The sample had a diameter of 2.5 cm and thickness of approximately 0.2 cm. The disc was placed in 300 mL toluene in a closed container at ambient temperature for 24–48 h. The disc (now swollen in toluene) was floated in water overnight and exposed to the air flow in an

exhaust hood. It was then dried in a vacuum oven at 100°C for 3 h. The dried sample was weighed. The above extraction and drying treatments were repeated until constant weight was attained. The sample diameter was then measured. The disc was centered on the 2.5 cm plate of the RMS. Dynamic modulus measurements were carried out using the regular procedure, except that the actual diameter of the sample was used for all calculations rather than the plate diameter. The moduli thus measured (in the low-frequency range) were designated “dry” moduli or G_d .

Swelling Measurements

For the higher molecular weight diluent, PDMS oil 2, equilibrium swelling times at room temperature were of the order of 3 to 4 months. To accelerate the swelling measurements, all samples were exposed to oil at 100°C. Two specimens of each sample type were held by wires and floated in a beaker full of swelling oil. The beaker was covered with aluminum

foil and kept in an oven at 100°C. In all the measurements reported here, the diluent incorporated into the network at cross-linking and the swelling fluid were kept the same. Periodic weight measurements were made over about 60 days for each fluid, until the weights were constant. For calculations of the volume fractions, it was assumed that the densities of the network and the swelling fluid were identical.

RESULTS AND DISCUSSION

The rates of swelling for the various networks, swollen in the two oils, are compared in Figures 1 and 2. As expected, the lower molecular weight fluid attains equilibrium faster, but in both cases, the times to equilibrium are long.

Networks cross-linked with varying amounts of oil were swollen in the same oil to equilibrium, and the equilibrium volume fractions in each case are given in Table II. In addition, Table II also contains

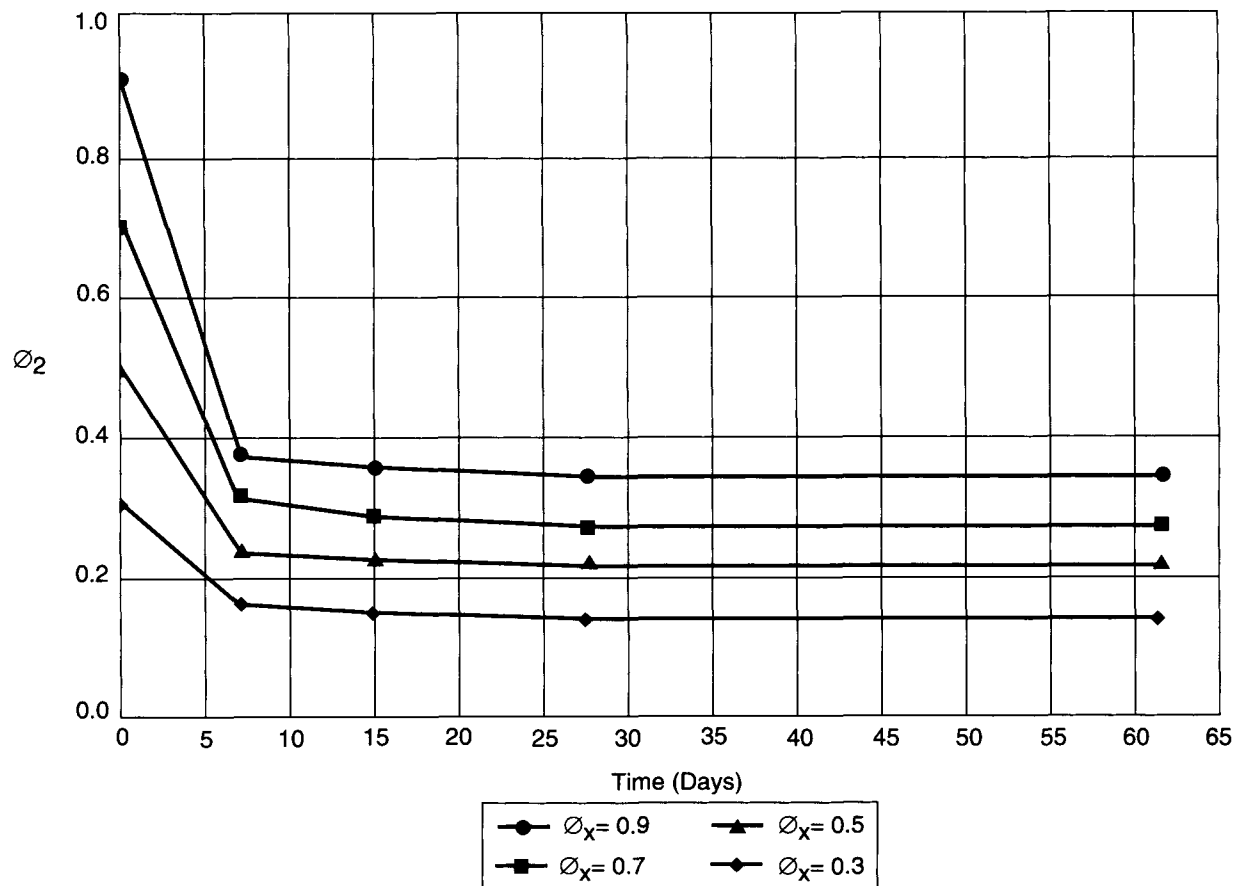


Figure 1 Rate of swelling of PDMS network in oil #1.

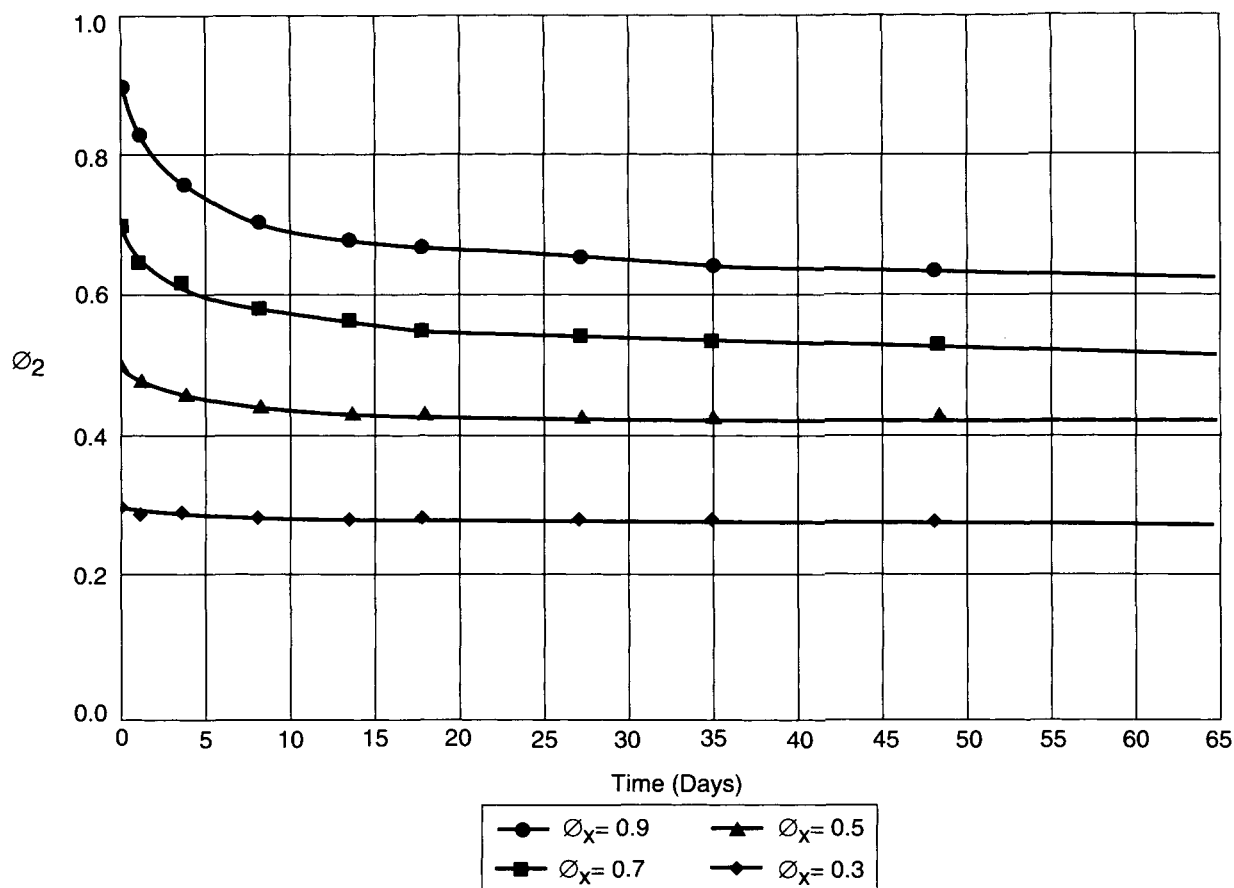


Figure 2 Rate of swelling of PDMS network in oil #2.

the measured values of the “extracted” or “dry” moduli, G_d , and the “wet” moduli (or moduli measured prior to extraction), G_x , for each sample.

In Table II, the moduli measured with inert diluent present during cross-linking (G_x) are independent of the molecular weight of the PDMS diluent.

This is to be expected, as the modulus is determined largely by eq. (3):

$$G_x = 0.5 \times (dRT/M_n) C_x + 1.45 \times 10^6 (C_x)^{2.4} \quad (3)$$

where C_x , the weight fraction of network, is equal to the Φ_x used in eqs. 1 and 2, since the densities of

Table II “Plateau” Moduli and Equilibrium Swelling for PDMS Network in Two PDMS Oils

| Φ_x | G_d (dynes/cm ²) | G_x (dynes/cm ²) | | Φ_2 (eq.) | |
|----------|-----------------------------------|-----------------------------------|-------------------|--------------------|-------|
| | | Oil 1 ^a | Oil 2 | Oil 1 ^a | Oil 2 |
| 1.00 | 2.0×10^6 | 2.0×10^5 | 2.0×10^5 | 0.400 | — |
| 0.90 | 6.8×10^5 | 5.5×10^4 | 5.8×10^4 | 0.350 | 0.621 |
| 0.70 | 6.3×10^5 | 3.85×10^4 | 3.5×10^4 | 0.280 | 0.523 |
| 0.50 | 4.0×10^5 | 1.7×10^4 | 1.7×10^4 | 0.220 | 0.414 |
| 0.30 | 2.75×10^5 | 5.3×10^3 | 5.5×10^3 | 0.140 | 0.278 |

^a Moduli were measured separately for networks prepared in oil 1 and oil 2.

^b Equilibrium Φ_2 measured for networks prepared in either oil and swollen in the same oil.

the network and the swelling oils are assumed to be identical. In eq. (3), it is clear that the chemical nature of the diluent is not significant, as long as it is inert to the cross-linking reaction.

We took two approaches to the analysis of the data in relation to theoretical predictions. In the first approach, we assumed that the affine or phantom versions of eq. (1) was valid and that the term ν/V_d represented the number of network chains per unit volume, i.e., chemically cross-linked chains. This term is equivalent to d/M_n , with d the density and M_n the number-average molecular weight of the precursor polymer. We then equated the elastic and mixing terms to obtain values of χ as a function of concentration of network:

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (A\nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3} - B\Phi_2) \quad (2) \end{aligned}$$

For an affine network, $A = 1$, $B = \frac{1}{2}$,

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (\nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3} - 0.5\Phi_2) \quad (4) \end{aligned}$$

For a phantom network, $A = 0.5$, $B = 0$,

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (0.5\nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3}) \quad (5) \end{aligned}$$

There are two unknowns: χ and ν . We used stoichiometry and the polymer molecular weight to calculate ν , assuming completeness of reaction. We then solved for χ at each concentration and obtained the values shown in Table III.

In Figure 3, the calculated values of χ (only χ values for oil #2 are shown, but the trends hold for

Table III Calculated Values of Interaction Parameter Using the Affine and Phantom Theories

| PDMS Oil | Φ_x | Φ_2 (eq.) | Calculated χ | |
|----------|----------|----------------|-------------------|--------|
| | | | Phantom | Affine |
| Oil #1 | 0.9 | 0.35 | 0.223 | 0.018 |
| | 0.7 | 0.28 | 0.083 | -0.163 |
| | 0.5 | 0.220 | -0.052 | -0.322 |
| | 0.3 | 0.140 | -0.414 | -0.80 |
| Oil #2 | 0.9 | 0.621 | 0.30 | 0.171 |
| | 0.7 | 0.523 | 0.117 | 0.004 |
| | 0.5 | 0.414 | -0.096 | -0.191 |
| | 0.3 | 0.278 | -0.486 | -0.541 |

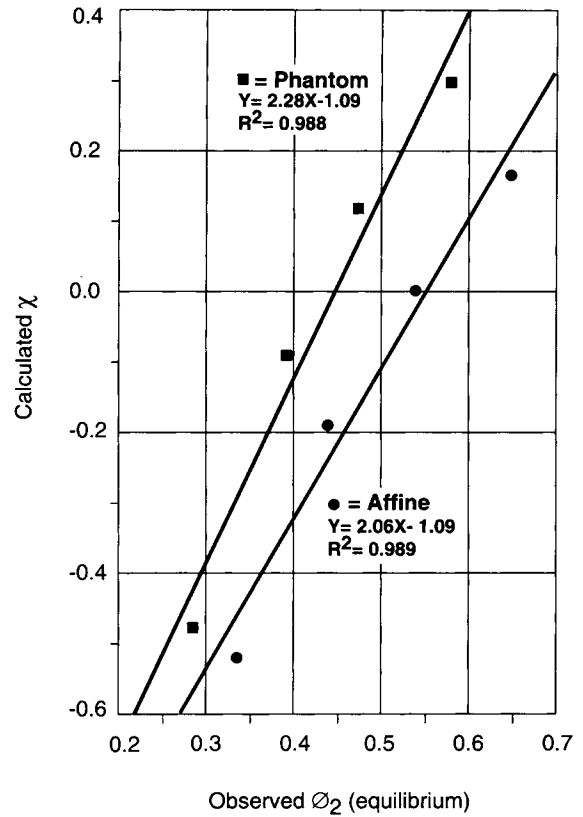


Figure 3 Concentration dependence of calculated χ values, oil #2.

oil #1 as well) are plotted against concentration of the network in the equilibrium swollen state. As can be seen, this concentration dependence is substantial and, in our view, unrealistic for a system of a network very similar in structure to the swelling medium. Previous work on the same type of network^{12,17,18} showed less substantial dependence.

The second approach was to try to predict the equilibrium Φ_2 using the experimentally measured shear modulus to estimate ν and assuming a constant χ across this concentration range. There are six equations (three each for the phantom and affine models) that can then be used to predict the equilibrium Φ_2 .

We start with the affine and phantom equations for the swelling equilibrium equations:

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (\nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3} - 0.5\Phi_2) \quad (4A) \end{aligned}$$

$$\begin{aligned} & -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ & = (0.5 \nu RT/V_d)(\Phi_x^{2/3}\Phi_2^{1/3}) \quad (5P) \end{aligned}$$

The term νRT is usually equated to the shear modulus in rubber elasticity theory (see Ref. 19, p. 470):

$$\begin{aligned} G_d &= \nu RT/V_d \text{ (affine limit);} \\ G_d &= 0.5\nu RT/V_d \text{ (phantom limit)} \end{aligned} \quad (6)$$

Thus, we can substitute the measured dry modulus, G_d , for these terms in eqs. (4A) and (5P), to obtain

$$\begin{aligned} -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ = G_d(\Phi_x^{2/3}\Phi_2^{1/3} - 0.5\Phi_2) \end{aligned} \quad (4A')$$

$$\begin{aligned} -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ = 0.5G_d(\Phi_x^{2/3}\Phi_2^{1/3}) \end{aligned} \quad (5P')$$

Or the equations can be recast such that the modulus-at-cross-linking or G_x (measured before extraction of diluent) is used, since¹⁰

$$\begin{aligned} G_d &= A(\nu RT/V_d); \quad \text{and} \quad G_x = A(\nu RT/V_x) \\ &= A(\nu RT/V_d)(V_d/V_x) = AG_d\Phi_x \end{aligned} \quad (7)$$

with $A = 1$ and 0.5 for the affine and phantom limits, respectively, and by definition, $\Phi_x = V_d/V_x$. Substitution of G_x for G_d in eqs. (4A') and (5P') gives

$$\begin{aligned} -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ = G_x[(\Phi_2/\Phi_x)^{1/3} - \Phi_2/2\Phi_x] \end{aligned} \quad (4A'')$$

$$\begin{aligned} -(RT/V_1)[\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\ = 0.5G_x(\Phi_x^{-1/3}\Phi_2^{1/3}) \end{aligned} \quad (5P'')$$

In each case, the equations were solved numerically for each oil to obtain Φ_2 . The only unknown in eqs. (4A', A'') and (5P', 5P'') is then χ ; χ is obtained by using the measured value of Φ_2 for one concentration

for oil 2 ($\chi = 0.344$, using the values for $\Phi_x = 0.50$) in eq. (4A''). This χ value was then assumed to be constant for the other concentrations. [For all the concentrations given here, χ ranges from 0.344 to 0.390 if eq. (4A'') is used, and calculations using the average of these values give results similar to the ones reported below using the value of $\chi = 0.344$.]

The same value of χ for oil 2 (0.344) was used to calculate χ for oil 1 using the following equation (Ref. 19, pp. 507-509):

$$\chi(\text{oil 1}) = \chi(\text{oil 2}) \times M_1/M_2$$

where M_2 and M_1 are the corresponding number-average molecular weights of the two oils (see Table I). This equation assumes a linear chain-length dependence for χ and gives a value of $\chi = 0.095$ for oil 1.

From Table IV it can be seen that the use of eqs. (4A') and (4A'') (for the affine model) give reasonable agreement of the calculated Φ_2 with the observed degree of swelling at all concentrations for both PDMS oils. The agreement between predicted and measured values is graphically depicted in Figures 4 and 5. With the affine model, either the G_d or G_x values may be used to predict equilibrium degrees of swelling, once χ is calculated using one observed degree of swelling value.

If the same procedure is followed to calculate Φ_2 using the phantom model [with eqs. (5P') and (5P'')], we obtain similar agreement. The values of χ obtained are 0.105 for oil #1 and 0.381 for oil #2; the calculated and experimental values are shown in Table V.

Alternatively, the measured degrees of swelling can be used to calculate an average χ value over the Φ_x range studied. Such a calculation (for the affine model) gives $\chi = 0.10$ for oil #1 and $\chi = 0.37$ for oil

Table IV Comparison of Measured and Calculated Φ_2

| PDMS Oil | Φ_x | Φ_2 (eq.) | Measured G (dynes/cm ²) | | Calculated Φ_2 Affine | |
|----------|----------|----------------|---------------------------------------|--------------------|----------------------------|---------|
| | | | G_d | G_x | w/G_x | w/G_d |
| Oil #1 | 0.9 | 0.350 | 6.81×10^5 | 5.54×10^5 | 0.317 | 0.331 |
| | 0.7 | 0.280 | 6.32×10^5 | 3.85×10^5 | 0.271 | 0.289 |
| | 0.5 | 0.220 | 4.02×10^5 | 1.74×10^5 | 0.190 | 0.203 |
| | 0.3 | 0.140 | 2.74×10^5 | 5.3×10^4 | 0.109 | 0.135 |
| Oil #2 | 0.9 | 0.621 | 6.81×10^5 | 5.83×10^5 | 0.615 | 0.624 |
| | 0.7 | 0.523 | 6.32×10^5 | 3.49×10^5 | 0.524 | 0.563 |
| | 0.5 | 0.414 | 4.02×10^5 | 1.76×10^5 | 0.414 | 0.433 |
| | 0.3 | 0.278 | 2.74×10^5 | 5.49×10^4 | 0.267 | 0.307 |

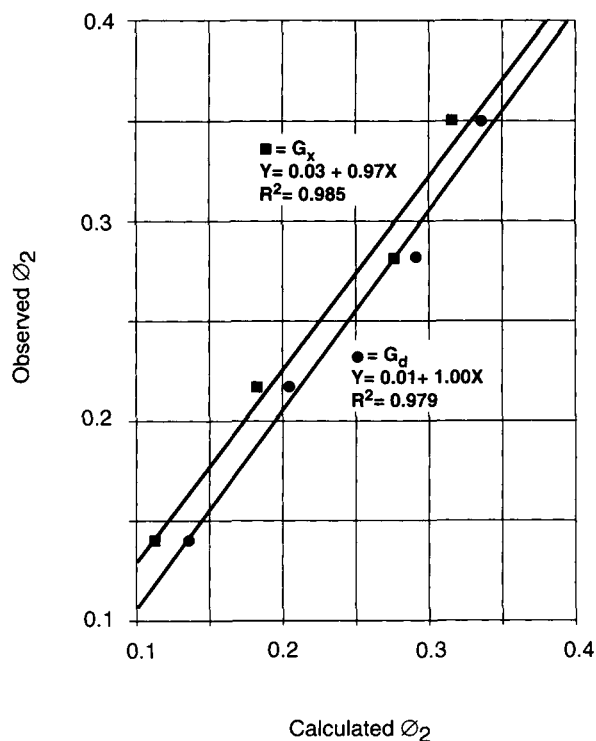


Figure 4 Observed and predicted ϕ_2 values, oil #1.

#2 [using G_x in eq. (4A'')]. If G_d is used in eq. (4A'), then we get $\chi = 0.082$ for oil #1 and $\chi = 0.30$ for oil #2.

The use of eqs. (4A') and (4A'') for prediction of swelling in these networks has other implications beyond the applicability of the affine or phantom models. Although the contribution of trapped entanglements to modulus is fairly well accepted (see Ref. 1 for a discussion), their influence on equilibrium swelling behavior is still a matter of some controversy. In our previous article,¹ we noted that the equilibrium modulus of these networks could be calculated from a summation of two contributions, the covalent cross-links and "trapped" entanglements, as with eq. (3) reproduced below:

$$G_x = 0.5 \times (dRT/M_n)C_x + 1.45 \times 10^6(C_x)^{2.4} \quad (3)$$

Here, the first term denotes the contribution from chemically cross-linked chains and the second term arises from the contribution of trapped entanglements. The shear modulus, at any network concentration, cannot be predicted by consideration of chemical cross-links alone.

In eq. (4A''), when we substitute the measured G_d and G_x for the terms $A\nu RT/V_d$ and $A\nu RT/V_x$, we are, in effect, using a network chain density that is

now a combination of chemically linked chains and trapped entanglements, i.e., the ν term is now the number of "effective" chains:

$$\nu_{\text{eff}}/RT = \nu_c/RT + \nu_e/RT = G_x \times V_x = G_d \times V_d$$

Since the substitution of the measured moduli, which contains contributions from covalent links and entanglements, helps predict the swelling behavior, it follows that trapped entanglements do contribute to the equilibrium swelling of these networks, in contradiction to observations made by some workers.^{3,20} However, other authors have noted explicitly the contribution of trapped entanglements to swelling behavior.^{7,8,21} But the substitution of measured equilibrium *shear moduli* in an equation of type (4A') has not previously been made in order to predict degrees of swelling, as we have demonstrated here, although Gnanov et al.⁷ made a substitution of the *elongational* modulus in a study of poly(ethylene oxide) networks swollen in dioxane and water. Similarly, Zang et al.⁵ found that the M_c

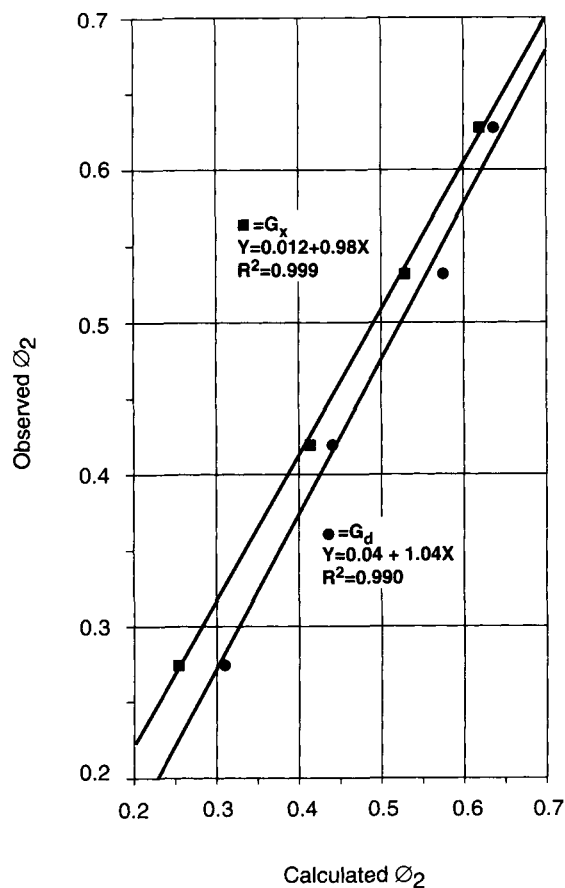


Figure 5 Observed and predicted ϕ_2 values, oil #2.

Table V Comparison of Measured and Calculated Φ_2

| PDMS Oil | Φ_x | Φ_2 (eq.) | Measured G (dynes/cm ²) | | Calculated Φ_2 Phantom | |
|----------|----------|----------------|--|--------------------|--------------------------------|---------|
| | | | G_d | G_x | w/G_x | w/G_d |
| Oil #1 | 0.9 | 0.350 | 6.81×10^5 | 5.54×10^5 | 0.260 | 0.274 |
| | 0.7 | 0.280 | 6.32×10^5 | 3.85×10^5 | 0.225 | 0.242 |
| | 0.5 | 0.220 | 4.02×10^5 | 1.74×10^5 | 0.155 | 0.168 |
| | 0.3 | 0.140 | 2.74×10^5 | 5.3×10^4 | 0.088 | 0.113 |
| Oil #2 | 0.9 | 0.621 | 6.81×10^5 | 5.83×10^5 | 0.590 | 0.599 |
| | 0.7 | 0.523 | 6.32×10^5 | 3.49×10^5 | 0.511 | 0.554 |
| | 0.5 | 0.414 | 4.02×10^5 | 1.76×10^5 | 0.414 | 0.436 |
| | 0.3 | 0.278 | 2.74×10^5 | 5.49×10^4 | 0.275 | 0.327 |

obtained from swelling (using an affine model) is identical to the M_c obtained from a modified form of the Mooney–Rivlin theory for elongational modulus. This finding is equivalent to a demonstration of the applicability of an equation similar to (4A'), with the Mooney–Rivlin modulus in place of the shear modulus. However, since there is still some question regarding the choice of the low-strain or high-strain "modulus" in elongation and the difficulties associated with the measurement of these moduli, we believe that the equilibrium shear modulus is a preferred substitute.

We favor the following procedure as a practical means to predict equilibrium degrees of swelling from measured moduli of networks:

Measure the shear moduli of networks in the diluted state, prior to swelling, at frequencies low enough that the "plateau" modulus is obtained.

Choose any one network, e.g., the "dry" network (no oil at cross-linking) and measure the equilibrium degree of swelling for the system of oil + network. Calculate χ using eq. (4A"). [Alternatively, the network with a concentration in the middle of the range studied could be used to do the swelling measurement and χ calculated using eq. (4A").] If literature values are available for the system, then, obviously, this step can be avoided.

Use eq. (4A") to predict the equilibrium degree of swelling for all other networks, assuming χ to be constant across this concentration range. For silicone networks swollen in silicone oils, this approach works over a range of initial network concentrations, from the dry to about 20% network.

CONCLUSIONS

We believe that this work demonstrates that trapped entanglements contribute to swelling behavior and that the affine or phantom models are appropriate for calculation of equilibrium degrees of swelling. Although we restrict our conclusions to PDMS networks swollen in PDMS oils, we believe that the following is applicable to any network swollen in solvents where χ is concentration-independent:

1. For end-linked PDMS networks, cross-linked in the presence of a PDMS oil and swollen in the same oil, the following equation can be used to predict the equilibrium degree of swelling:

$$\begin{aligned}
 & -(RT/V_1) [\ln(1 - \Phi_2) + \Phi_2 + \chi(\Phi_2)^2] \\
 & = G_x [(\Phi_2/\Phi_x)^{1/3} - [(2/f)\Phi_2/\Phi_x]] \quad (4A'')
 \end{aligned}$$

where f is the functionality of the network cross-link points. This equation works well for $1.0 < \Phi_x < 0.2$ and for PDMS oils of different molecular weights. These oils must, however, be inert to the cross-linking reaction.

2. The network–diluent interaction parameter, χ , is constant over the same range of Φ_x .
3. For PDMS oils of different molecular weights, the χ value needs to be measured for only one. For oils of other molecular weights, the equation

$$\chi(M_a) = \{\chi(M_1)/M_1\} \times M_a$$

yields χ .

4. The modulus of the cross-linked network can either be measured directly or estimated from the equation derived in Part I of this series:

$$G' = G_x = 0.5 \times (dRT/M_n)C_x + 1.45 \times 10^6 (C_x)^{2.4} \quad (3)$$

where G' is the "plateau" modulus, or the modulus at low frequency; M_n , the number-average molecular weight of the precursor polymer; and C_x , the network weight fraction at cross-linking.

We would like to thank Dr. Clayton Henderson for some constructive comments at several stages of the work.

REFERENCES

1. S. Venkatraman, *J. Appl. Polym. Sci.*, **48**, 1383 (1993).
2. K. Dusek and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).
3. J. P. Queslel and J. E. Mark, *Adv. Polym. Sci.*, **71**, 229 (1985).
4. S. Candau, J. Bastide, and M. Delsanti, *Adv. Polym. Sci.*, **44**, 29 (1982).
5. Y.-H. Zang, R. Muller, and D. Froelich, *Polymer*, **30**, 2060 (1989).
6. B. E. Eichinger and N. A. Neuburger, in *Biological and Synthetic Polymer Networks*, O. Kramer, Ed., Elsevier, New York, Chap. 28, 1988.
7. Y. Gnanov, G. Hild, and P. Rempp, *Macromolecules*, **20**, 1662 (1987).
8. K. A. Kirk, S. A. Bidstrup, E. W. Merrill, and K. O. Meyers, *Macromolecules*, **15**, 1123 (1982).
9. I. Bahar, Y. Erbil, B. Baysal, and B. Erman, *Macromolecules*, **20**, 1353 (1987).
10. L. M. Dossin and W. W. Graessley, *Macromolecules*, **12**, 123 (1979).
11. N. R. Langley and J. D. Ferry, *Macromolecules*, **1**, 353 (1968).
12. E. M. Valles and C. W. Macosko, *Macromolecules*, **12**, 673 (1979).
13. B. Erman and P. J. Flory, *Macromolecules*, **15**, 806 (1982).
14. M. A. Llorente and J. E. Mark, *J. Chem. Phys.*, **71**, 682 (1979).
15. M. Ilavsky, K. Bouchal, and K. Dusek, *Makromol. Chem.*, **190**, 883 (1989).
16. A. P. De Boer and A. J. Pennings, *J. Polym. Sci.*, **14**, 187 (1976).
17. J. E. Mark and Z. M. Zhang, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 1971 (1983).
18. R. W. Brotzman and B. E. Eichinger, *Macromolecules*, **16**, 1131 (1983).
19. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
20. J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
21. A. P. DeBoer and A. J. Pennings, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 187 (1976).

Received October 4, 1993

Accepted December 29, 1993