

# **Analysis of Swelling of Crosslinked Rubber Gel with Occlusions**

H. J. KARAM and L. TIEN, *The Dow Chemical Company, Styrene Molding Polymers R&D, Midland, Michigan 48640*

## **Synopsis**

The contribution of the occluded polystyrene in the crosslinked rubber gel to the overall swelling has been determined theoretically and experimentally. Theoretical calculation consists of modification of the Flory-Rehner equation. The equation describes the swelling of a crosslinked polymer network in the presence of a solvent. Calculation procedures are discussed which enable one to determine the crosslink density (molecular weight between crosslinks) of the rubber network from experimentally determined swelling index and % gel measurements. The inverse calculation procedure is also described. That is, knowing the crosslink density and the amount of occlusions as determined from kinetic considerations, one can calculate the swelling index. Theoretically and experimentally determined swelling index are in excellent agreement.

## **INTRODUCTION**

The rubber gel in rubber modified styrenic polymers is characterized by the swelling index. The purpose of this study is to show quantitatively how the various factors, occlusions, type of rubber, extent of crosslinking of the rubber, solubility of the rubber, rigid phase, and solvent are related to the swelling index. Experimental work to check the validity of the analysis is discussed.

## **DESCRIPTION OF GEL AND SWELLING INDEX TEST FOR PARTIAL POLYMERS**

The authors are proposing a modification of the standard chemical gel test to measure swelling of rubber gel in rubber modified styrenic polymers. The proposed test is especially suitable for partial polymer. The standard chemical gel test gives inaccurate results for partial polymer.

The proposed test consists of dissolving 1 g of polymer based on solids level in 20 g of toluene. In case of rubber-modified styrene-maleic anhydride polymer, a 50-50 mixture of toluene and methyl ethyl ketone is used as solvent. The solution is placed in graduated glass centrifuge tubes. The graduated glass centrifuge tubes are used because one can easily note after centrifugation the volume amount of swollen gel. When using the metal centrifuge tube, there is danger of disposing of all or part of the swollen gel when one decants the supernate. This is especially true of a swollen gel of a loosely crosslinked network which is characteristic of a gel of partial polymer. The sample is centrifuged until the supernate is clear, i.e., not turbid. The current test centrifuges the sample for approximately 50 min. Experience has shown that 50 min is insufficient time to separate the gel

from solution of a highly swollen network (swelling index  $< 16$ ). One disadvantage of the glass centrifuge tube is one cannot use the high speed, 20,000- $g$  force centrifuge. The glass will shatter at such a high  $g$  force. All the results described in this report and subsequent reports on crosslinking were obtained using bench top clinical centrifuge. The use of the lower  $g$  centrifuge necessitates a longer time to separate the gel. Figure 1 shows a typical glass tube that was used in the test. Note the gel in the bottom of the tube. Upon completion of the centrifugation step volume and concentration of the upper and lower phase are determined. The concentration of the upper phase is important, as will be discussed later, if we wish to accurately determine the degree of crosslinking of the gel. The definition of gel and swelling index are the same as currently being used to describe the swollen crosslinked grafted rubber. They are

$$\text{swelling index} = \frac{\text{wet gel weight}}{\text{dry gel weight}}, \quad \% \text{ gel} = 100 \times \frac{\text{dry weight}}{\text{sample weight}}$$

The sample weight is determined from the concentration of the solution.

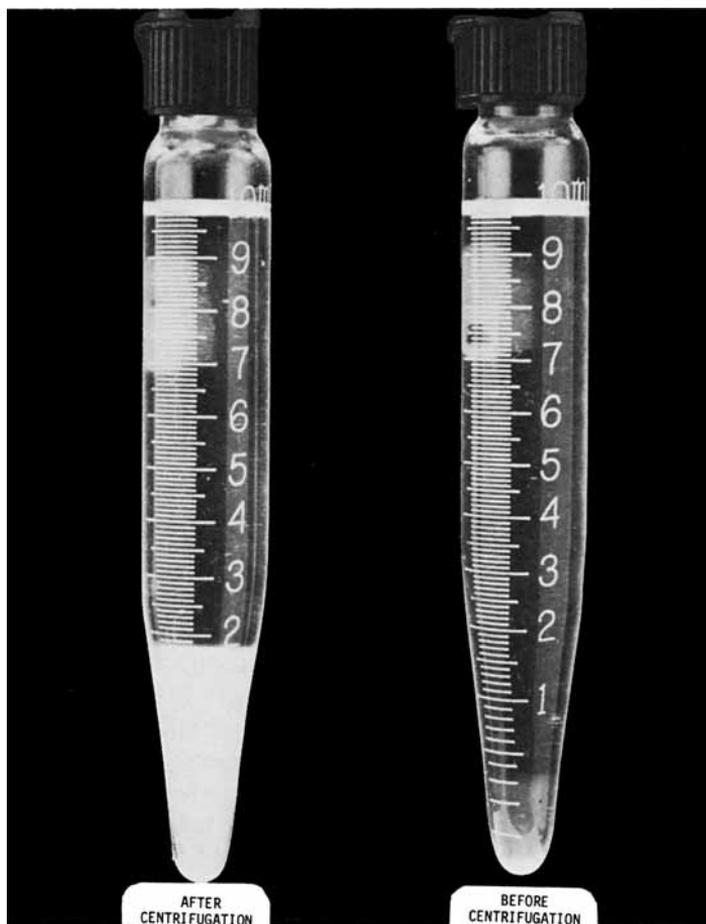


Fig. 1. Centrifugation of gel.

## THEORY OF SWELLING

## Assumptions

The procedure for calculating the swelling index of a rubber gel of a rubber-modified styrenic polymer is based on a modification of the theory of swelling crosslinked rubber proposed by Flory and Rehner.<sup>1,2</sup> The theory is discussed in detail by Treloar<sup>3,4</sup> and elsewhere.<sup>5</sup> The basic assumptions of the proposed theory are:

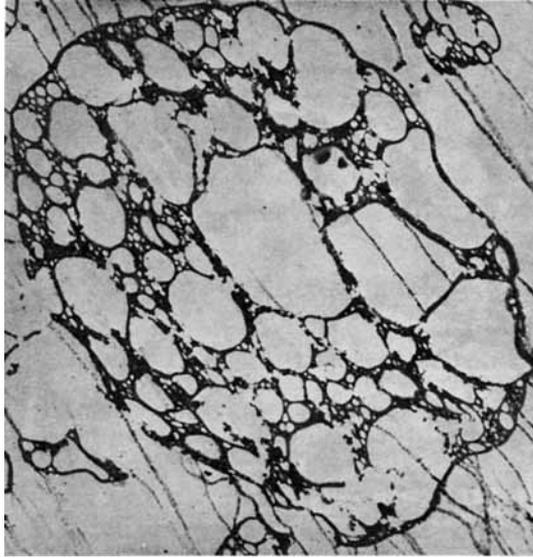
(1) Equilibrium is attained between the swollen gel and solvent. The solvent that is in equilibrium with the gel is not infinitely diluted, i.e., the polymer is dissolved in the supernate. The polymer that is dissolved in the supernate are the continuous rigid phase, and probably free and grafted rubber. The condition of infinitely diluted supernate can be attained experimentally by carefully decanting the upper phase and reswelling the network with fresh solvent. There is a possibility of rupturing the lightly crosslinked network and dissolving the occlusion in decanting the supernate. Experimentally we have observed that reswelling of the network by fresh solvent can increase the swelling index of the gel as much as a factor of 2. This assumes we don't rupture the network.

(2) The swollen gel is a distorted sphere; however, it can be represented approximately as a concentric sphere. Electron micrographs substantiate this. The continuous phase of the droplet is crosslinked ungrafted or grafted rubber. Occluded in the rubber matrix are pools of free and probably grafted continuous phase polymer. The droplets are dispersed in a continuous phase of rigid polymer. The rigid phase can be polystyrene, styrene acrylonitrile, or styrene-maleic anhydride depending on the product. It has been speculated that the rigid phase has free rubber that is soluble with it. At best this could be restricted to a very low molecular weight fraction of the rubber. In the calculations discussed in this report complete immiscibility is assumed between the two phases.

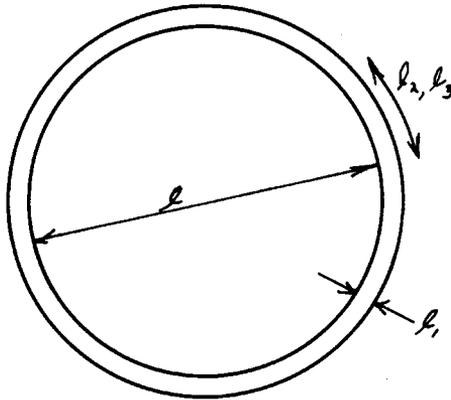
The actual configuration of the gel is replaced by an equivalent gel. Figure 2 is a schematic of the actual gel and the equivalent gel. There are two osmotic pressures developed by the swollen composite gel. They are the osmotic pressure developed by the swollen crosslinked grafted or ungrafted rubber membrane and the osmotic pressure developed by the swollen occlusion. At equilibrium, the radial stress developed by the swollen rubber membrane is offset by the external pressure as a result of dissolved polymer in the supernate.

The osmotic pressure developed by swollen occlusion results in a circumferential stress to be developed in the swollen crosslinked rubber membrane surrounding it. Without the swollen crosslinked rubber membrane, the rigid phase occlusions will swell to infinite volume, i.e., polymer will dissolve in the solvent. At equilibrium the circumferential stress is equal to the hoop stress developed by the difference of the osmotic pressure of the swollen rigid phase occlusion, and the external pressure as a result of dissolved polymer in the supernate.

The balance of forces at equilibrium can be represented by the following equations:



ACTUAL



EQUIVALENT

Fig. 2. Equivalent gel model.

$$\Sigma \tau_R = 0 \quad \text{radial stresses}$$

$$\Sigma \tau_c = 0 \quad \text{circumferential stresses}$$

(3) The simpler form of the strain energy function will be used in the derivation of the equation on the effect of occlusions on swelling. Flory has recently proposed a more involved expression. To quote Treloar<sup>3</sup> on the relative merits of the two expressions: "It is difficult to assess the validity of the revised formulae, since the respective merits of the various methods of calculating the entropy are still subject to discussion. It should be noted, however, that in most practical cases the effect of the modification of the

strain energy expression is likely to be rather small." The authors concur with the above comment.

(4) The contribution of interfacial tension forces to the overall free energy of the system is considered to be nearly zero. The assumption is valid primarily because interfacial tension between gel and solvent is nearly zero<sup>6</sup> ( $\sim 0.05$  dyn  $\cdot$  cm). The gel diameter is quite large ( $0.5\text{--}10$   $\mu\text{m}$ ). Both of these factors result in interfacial tension forces to be insignificant to the overall free energy contribution in the system. The assumption is not valid for a rubber latex particle swelling in a solvent. The interfacial tension between latex particle solvent is high ( $\sim 14$  dyn  $\cdot$  cm) and the particle diameter is small ( $\sim 1000$   $\text{\AA}$ ). Both of these factors result in a substantial contribution of interfacial tension to the overall free energy of the system.<sup>7</sup>

### Derivation of Modified Flory–Rehner Equations

Assuming the equivalent gel model is a good approximation of the actual gel, then applying the arguments advanced by Treloar,<sup>3,4</sup> we can derive the following equations. Before swelling of the gel by the solvent, we assume the dimension of the rubber membrane to be  $l_1$ ,  $l_2$ ,  $l_3$  and the occlusion to be  $l$  (See Fig. 2).  $l_1$  is dimension of the rubber membrane in the radial direction and  $l_2$  and  $l_3$  are the dimensions of the gel in circumferential direction.  $l$  is the diameter of the occlusion. Assuming a spherical gel,  $l_2 = l_3$ . The product of  $l_1 l_2 l_3 = l_1 l_2^2 = 1$  and  $l^3 = 1$ . After swelling of the gel by the solvent then the extension ratios are

$$\lambda_1 = \frac{l'_1}{l_1}, \quad \lambda_2 = \frac{l'_2}{l_2}, \quad \lambda_3 = \frac{l'_3}{l_3}, \quad \lambda = \frac{l'}{l},$$

where  $l'_1$ ,  $l'_2$ ,  $l'_3$ ,  $l'$  are the dimensions of the swollen gel. The volume fraction of rubber in the swollen rubber membrane is

$$v_R = \frac{1}{\lambda_1 \lambda_2^2} \quad (1)$$

The volume fraction of polystyrene in the swollen occlusion is

$$v_P = \frac{1}{\lambda^3}$$

but

$$\lambda_2 = \frac{l'_2}{l_2} \cong \frac{2\pi l'}{2\pi l} \simeq \lambda$$

$$v_P = \frac{1}{\lambda_2^3} \quad (2)$$

For convenience we assume

$$K = \frac{v_R}{v_P} \quad (3)$$

It therefore follows

$$\lambda_2 = K\lambda_1 \quad (4)$$

The radial stress is equal to

$$t_R = \frac{RT}{V_1} \left[ \ln(1 - v_R) + v_R + \mu v_R^2 + \frac{\rho_R V_1 v_R \lambda_1^2}{M_c} \right]$$

(Treloar,<sup>4</sup> eq. 7.34, p. 145). Condition for equilibrium swelling is the summation of the stresses in the radial direction must be equal to zero.

$$\Sigma \tau_R = 0$$

$$t_R - \Pi' = 0$$

$$\Pi' = \frac{RT}{V_1} \ln a$$

$$\frac{RT}{V_1} \left[ \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1 v_R \lambda_1^2}{M_c} \right]$$

$$- \frac{RT}{V_1} \ln a = 0 \quad (5)$$

The term  $(RT/V_1) \ln a$  is the external osmotic pressure. The term is not included in the Treloar<sup>4</sup> expression (eq. 7.34, p. 145) since he assumes the supernate is infinitely diluted, i.e., no polymer dissolved in the supernate. In our case the supernate has dissolved free polystyrene, and probably some grafted and free rubber. The concentration of polymer in the supernate can be measured. The solvent in the supernate is toluene for 100% polymer, however for partial polymer the solvent is a mixture of styrene, ethyl benzene, and toluene. The activity of the supernate can be calculated by the Flory-Huggins equation.

$$\ln a = \ln(1 - v_0) + v_0 + \mu_P v_0^2 \quad (6)$$

$v_0$  is the volume fraction of the dissolved polymer in the supernate. It can be calculated from the concentration.  $\mu_P$  is the polystyrene-solvent interaction factor and is equal to

$$\mu_P = 0.34 + \frac{V_1(\delta_P - \bar{\delta}_s)^2}{RT} \quad (7)$$

$\bar{\delta}_s$  is the mean solubility parameter of the mixed solvents in the supernate.

It is equal to

$$\bar{\delta}_s = \phi_S \delta_s + \phi_{EB} \delta_{EB} + \phi_T \delta_T \quad (8)$$

where  $\phi_S$ ,  $\phi_{EB}$ , and  $\phi_T$  are the volume fractions of the solvent components. For partial polymer the average molar volume of the solvent is equal to

$$V_1 = \frac{1}{\frac{V_T}{\phi_T} + \frac{V_S}{\phi_S} + \frac{V_{EB}}{\phi_{EB}}} \quad (9)$$

For 100% polymer

$$V_1 = V_T \quad (\text{molar volume of toluene})$$

The term  $\mu_R$  in eq. (5) is the solvent rubber interaction factor. It is equal to

$$\mu_R = 0.34 + V_1 \frac{(\bar{\delta}_s - \delta_R)^2}{RT} \quad (10)$$

$\delta_R$  is equal to the solubility parameter of the rubber. The other terms in the expression have been defined previously. Both quantities,  $\mu_R$  and  $\mu_P$  can be determined experimentally.

The term  $\lambda_1$  in eq. (5) is equal to

$$\lambda_1^2 = \frac{\lambda_2^2}{K^2}$$

via eq. (4), but

$$\lambda_2 = \frac{1}{v_P^{1/3}} = \frac{K^{1/3}}{v_R^{1/3}}$$

[via eqs. (2) and (3)] Therefore,

$$\lambda_1^2 = \frac{1}{v_R^{2/3} K^{4/3}} \quad (11)$$

Substituting the expression for  $\lambda_1$  in Eq. 5 and simplifying, we obtain

$$\left( \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1 v_R^{1/3}}{M_c K^{4/3}} \right) - \left[ \ln(1 - v_0) + v_0 + \mu_P v_0^2 \right] = 0 \quad (12)$$

The circumferential hoop stress in the swollen rubber membrane is equal to

$$t_c = \frac{1}{V_1} \left( \frac{\partial \Delta G}{\partial n_1} \right)_{l_2} = \frac{1}{V_1} \left[ \frac{\partial \Delta G_m}{\partial n} + \frac{\partial \Delta G_e}{\partial n} \right]_{l_2} \quad (13)$$

(Treloar,<sup>4</sup> eq. 7.30). The free energy term,  $\Delta G$  is the total change in free energy of the system (polymer + solvent) in passing from the unstrained state to the swollen strained state.  $\Delta G_m$  and  $\Delta G_e$  are the terms representing the corresponding free energies of mixing and network extension. For the  $(\partial \Delta G_m / \partial n)_{l_2}$  term we assume the Flory-Huggins expression:

$$\left(\frac{\partial \Delta G_m}{\partial n}\right)_{l_2} = RT \left( \ln(1 - v_R) + v_R + \mu_R v_R^2 \right) \quad (14)$$

The second term in eq. (13) is determined in the following manner:

$$\left(\frac{\partial \Delta G_e}{\partial n}\right)_{l_2} = \left(\frac{\partial \Delta G_e}{\partial \lambda_2}\right) \left(\frac{\partial \lambda_2}{\partial n}\right)_{l_2} \quad (15)$$

$\Delta G_e$  is equal to the strain energy function of the swollen rubber

$$\Delta G_e = W = \frac{G}{2} \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \quad (16)$$

As noted earlier, this is the simplified form of the strain energy function.  $G$ , the modulus of elasticity of the rubber, is equal to

$$G = \frac{\rho_R RT}{M_c}$$

The equation for the modulus elasticity of the rubber is derived from the Guth-James theory<sup>4</sup> regarding rubber elasticity. Substituting eq. (16) into (15) and the values of  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$  we obtain the following expression:

$$\Delta G_e = \frac{\rho_R RT}{2M_c} \left( \frac{\lambda_2^2}{K^2} + 2\lambda_2^2 - 3 \right)$$

$$\left(\frac{\partial \Delta G_e}{\partial \lambda_2}\right)_{l_2} = \frac{\rho_R RT}{2M_c} \left( \frac{2\lambda_2}{K^2} + 4\lambda_2 \right)$$

Simplifying, we obtain

$$\left(\frac{\partial \Delta G_e}{\partial \lambda_2}\right)_{l_2} = \frac{\rho_R RT \lambda_2}{K^2 M_c} (1 + 2K^2)$$

The second factor in eq. 15 reduces to the following expression:

$$\lambda_1 \lambda_2^2 = \frac{\lambda_2^3}{K} = 1 + n V_1 \quad (17)$$

(Treloar,<sup>4</sup> eq. 7.24, p. 143),

$$\frac{\partial \lambda}{\partial n} = \frac{3\lambda_2^2}{K} \frac{\partial \lambda_2}{\partial n} = V_1$$

Therefore,

$$\left(\frac{\partial \lambda_2}{\partial n}\right)_{t_2} = \frac{KV_1}{3\lambda_2^2} \quad (18)$$

Substituting eqs. (16) and (18) into eq. (15), we obtain

$$\begin{aligned} \left(\frac{\partial \Delta G_e}{\partial n}\right)_{t_2} &= \frac{\rho_R RT \lambda_2}{M_c K^2} (1 + 2K^2) \frac{V_1 K}{3\lambda_2^2} \\ \left(\frac{\partial \Delta G_e}{\partial n}\right)_{t_2} &= \frac{\rho_R RT V_1}{3K \lambda_2 M_c} (1 + 2K^2) \end{aligned} \quad (19)$$

$$\frac{1}{K \lambda_2} = \frac{v_R^{1/3}}{K} = \frac{v_R^{1/3}}{K^{4/3}} \quad (2 \text{ and } 3)$$

The circumferential stress in the swollen rubber membrane is equal to [via eqs. (2) and (3)]

$$t_c = \frac{RT}{V_1} \left[ \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R v_R^{1/3} V_1 (1 + 2K^2)}{3M_c K^{4/3}} \right]$$

Assuming equilibrium swelling, the circumferential or hoop stress in the membrane must be equal to the hoop stress as a result of the difference in osmotic pressure generated by the swollen occlusion and the external pressure as a result of polymer dissolved in the supernate. The osmotic pressure as a result of the swollen occlusion is approximately equal to

$$\Pi_p = -\frac{RT}{V_1} \ln a' \quad (20)$$

$a'$  is the activity of the swollen occlusion.  $\ln a'$  is given by the Flory-Huggins expression

$$\ln a' = \ln(1 - v_p) + v_p + \mu_p v_p^2$$

$\mu_p$  is the polystyrene-solvent interaction factor and is determined by the following expression:

$$\mu_p = 0.34 + \frac{V_1(\delta_p - \delta_s)^2}{RT} \quad (21)$$

For a thick membrane the circumferential or hoop stress as a result of

internal osmotic pressure and external pressure on the membrane is equal to

$$t_H = \frac{(\Pi' - \Pi_P)}{2} \left( \frac{b^3 + 2a^3}{b^3 - a^3} \right) \quad (22)$$

(the equation was obtained from Ref. 8).

The expression for  $\Pi'$  [eq. (6)] was discussed previously.  $b$  and  $a$  are the radii of the swollen rubber droplet and swollen occluded polymer, respectively. From geometric considerations (see Fig. 2).

$$\begin{aligned} b &= \lambda l + \lambda_1 l_1 \\ a &= \lambda l \\ \lambda_2 &= K\lambda, \quad l_1 \sim l \text{ and } l^3 = 1 \\ t_H &= \frac{\Pi' - \Pi_P}{2} \left( \frac{(\lambda + \lambda_1)^3 + 2\lambda^3}{(\lambda + \lambda_1)^3 - \lambda^3} \right) \end{aligned} \quad (23)$$

but previously it was shown that

$$\begin{aligned} \lambda &= \frac{1}{v_P^{1/3}}, \quad v_P = \frac{v_R}{K} \\ \lambda_1 &= \frac{1}{K^{2/3} v_R^{1/3}} \end{aligned}$$

Substituting the above expressions in eq. (23) and simplifying, we obtain

$$t_H = \frac{(\Pi' - \Pi_P)}{2} \left( \frac{(K+1)^3 + 2K^3}{(K+1)^3 - K^3} \right)$$

At equilibrium swelling, the sum of the circumferential stresses must equal to zero:

$$\begin{aligned} \Sigma \tau_c &= 0 \\ t_c - t_H &= 0 \end{aligned}$$

$$\begin{aligned} \frac{RT}{V_1} \left[ \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R v_R^{1/3} V_1 (1 + 2K^2)}{3M_c K^{4/3}} \right] \\ + \frac{\Pi_P - \Pi'}{2} \left[ \frac{(K+1)^3 + 2K^3}{(K+1)^3 - K^3} \right] = 0 \end{aligned} \quad (24)$$

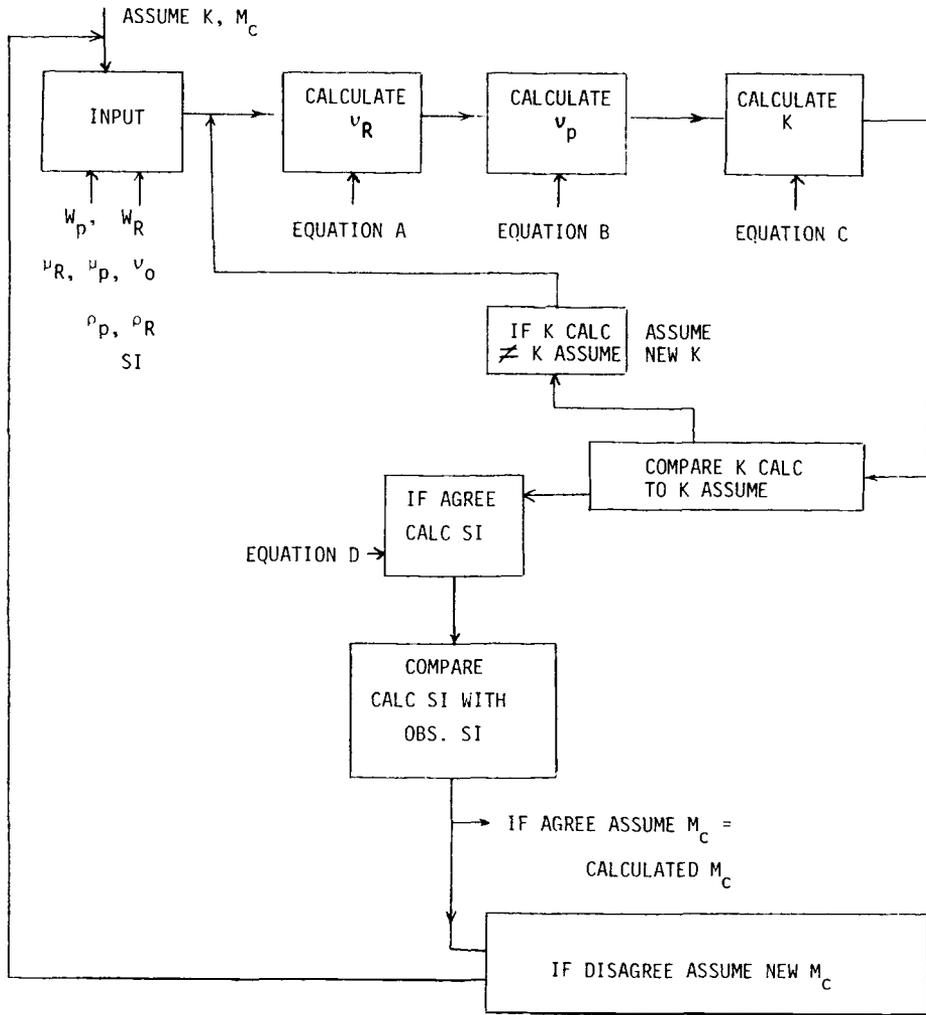


Fig. 3. Schematic of the procedure to solve eqs. (A)-(D).

Substituting the expressions for  $\Pi_p$  and  $\Pi'$  [eqs. (20) and (6)], we obtain

$$\ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1^{1/3} V_1 (1 + 2K^2)}{3 M_c K^{4/3}} + \frac{(K + 1)^3 + 2K^3}{2((K + 1)^3 - K^3)} \left\{ \ln(1 - v_P) + v_P + \mu_P v_P^2 - [\ln(1 - v_0) + v_0 + \mu_P v_0^2] \right\} = 0 \quad (25)$$

### Derivation of Swelling Index Equation

Equations (12) and (25) calculate the volume fraction of rubber in the rubber phase ( $v_R$ ) and the volume fraction of occluded rigid phase ( $v_P$ ). The volume fraction in each phase is related to the swelling index in the following manner:

$$\text{swelling Index} = \text{SI} = \frac{\text{wet gel wt}}{\text{dry gel wt}}$$

$$\text{SI} = \frac{\text{dry gel wt} + \text{wt of solvent in rubber} + \text{wt of solvent in occlusion}}{\text{dry gel wt}}$$

$$\text{SI} = 1 + \frac{\text{wt of solvent in each phase}}{\text{dry gel wt}}$$

Assume 1 g of polymer is dissolved in 20 g of solvent; then

$$\text{SI} = 1 + \frac{w_s + w'_s}{w_R + w_P}$$

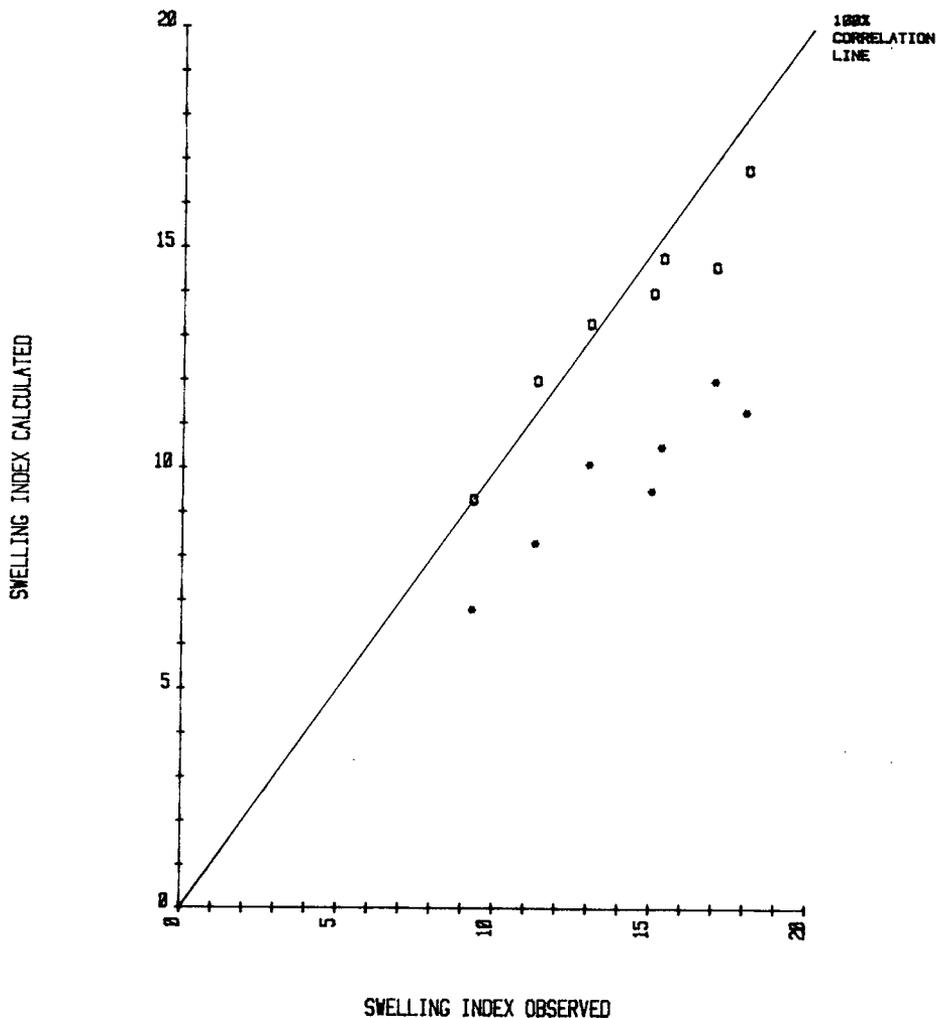


Fig. 4. Comparison of swelling index calculation. Initial composition: 7.8% ethyl benzene, 5.8% low *cis*-polybutadiene rubber, 20% polystyrene, 463 PPM initiator. Polymerization schedule indicated in test. (O) swelling index calculated with occlusions; (\*) swelling index calculated without occlusions

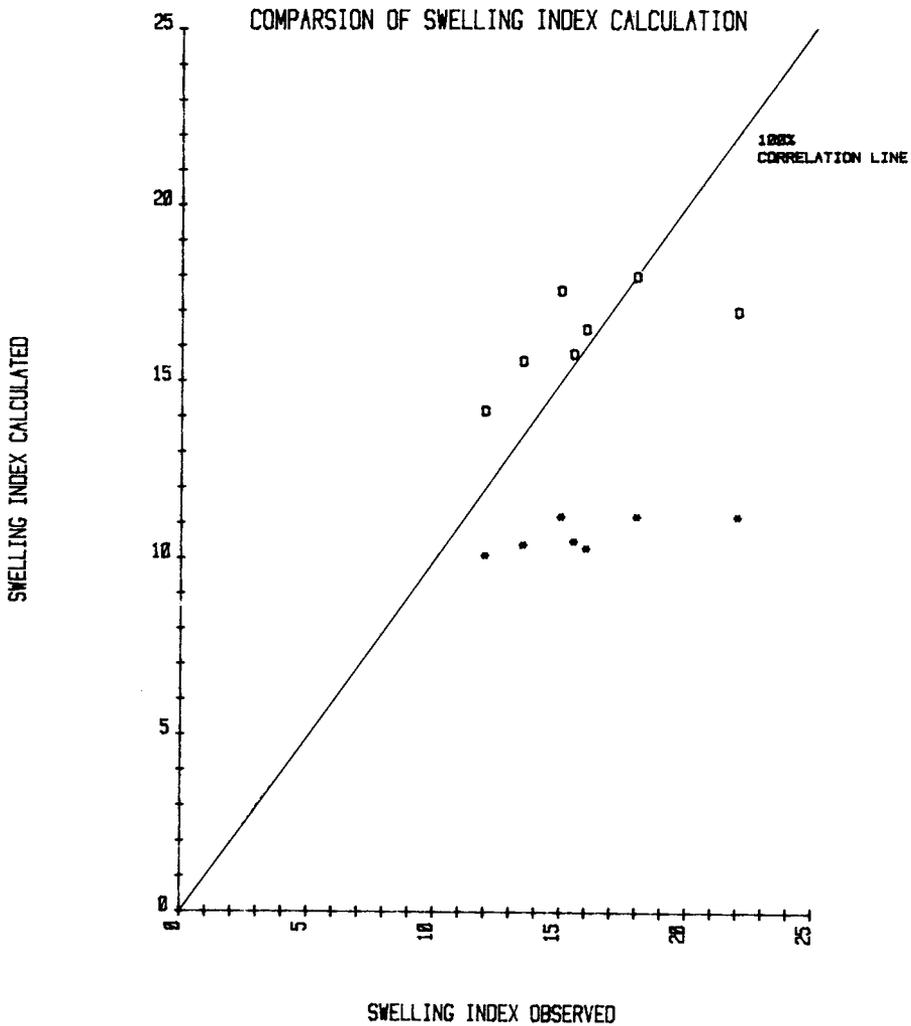


Fig. 5. Comparison of swelling index calculation. Initial composition: 7.8% ethyl benzene, 5.8% high *cis*-polybutadiene rubber, 20% polystyrene, 463 ppm initiator. Polymerization schedule indicated in test. (O) Swelling index calculated with occlusions; (\*) swelling index calculated without occlusions.

where  $w_R$  = wt of rubber fraction in gel and  $w_P$  equals wt fraction of occluded rigid phase in gel by definition

$$\text{total gel} = w_R + w_P$$

The total gel is a measured quantity.  $v_P$  the volume fraction of the occluded rigid phase is equal to by definition

$$v_P = \frac{w_P/\rho_P}{w_P/\rho_P + w_s/\rho_s}$$

$w_s$ , the weight fraction of solvent in the rigid occluded phase is equal to

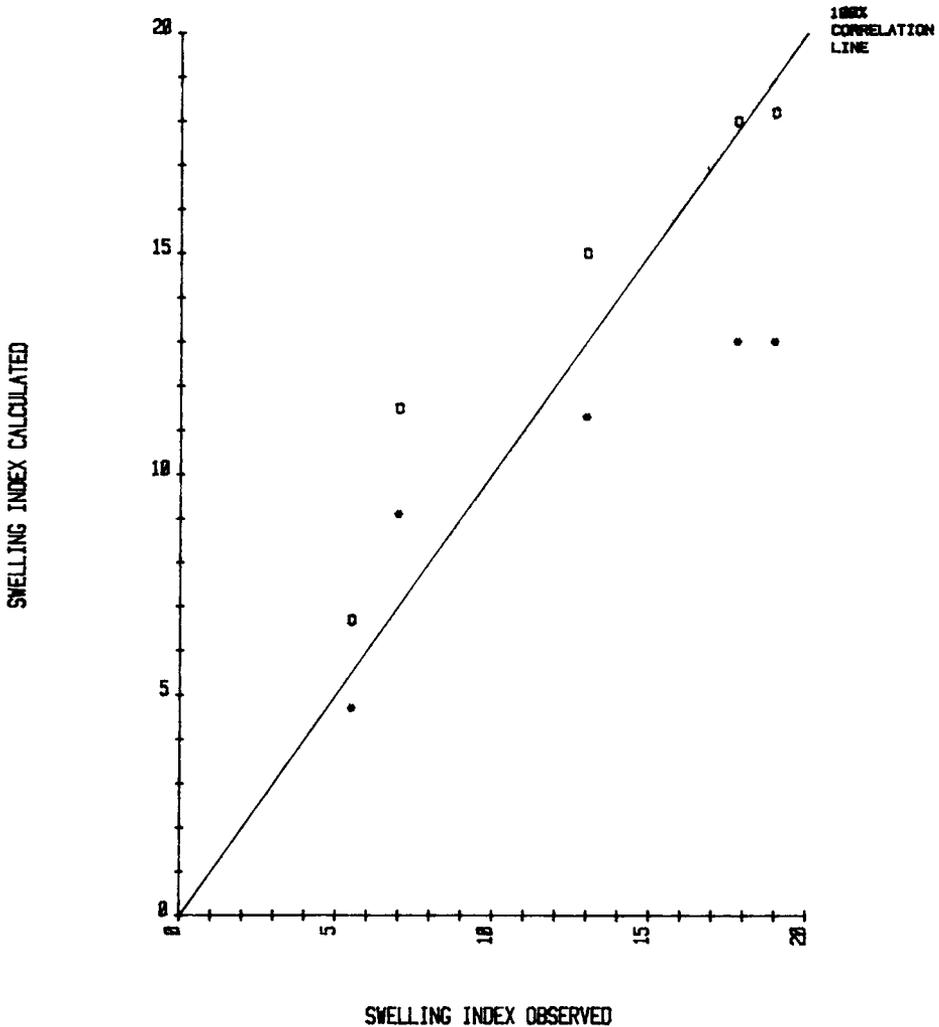


Fig. 6. Comparison of swelling index calculation. Initial composition: 90% high *cis*-polybutadiene rubber, 10% styrene, no initiator. (O) Swelling index calculated with occlusions; (\*) swelling index calculated without occlusions.

$$w_s = \frac{\rho_s}{\rho_P} w_P \left( \frac{1}{v_P} - 1 \right)$$

Similarly,  $w_s$  weight fraction of solvent in the crosslinked rubber network is

$$w'_s = \frac{\rho_s}{\rho_R} w_R \left( \frac{1}{v_R} - 1 \right)$$

$$SI = 1 + \left[ \frac{\rho_s}{\rho_R} w_R \left( \frac{1}{v_R} - 1 \right) + \frac{\rho_s}{\rho_P} w_P \left( \frac{1}{v_P} - 1 \right) \right] / (w_R + w_P)$$

**Application of the Equations**

In summary the equations that relate the swelling index to crosslink density  $M_c$  are as follows:

$$(A) \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1 v_R^{1/3}}{M_c K^{4/3}} - [\ln(1 - v_0) + v_0 + \mu_P v_0^2] = 0 \quad (12)$$

$$(B) \ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R v_R^{1/3} V_1 (1 + 2K^2)}{3M_c K^{4/3}} + \frac{(K + 1)^3 + 2K^3}{2[(K + 1)^3 - K^3]} \left\{ \ln(1 - v_P) + v_P + \mu_P v_P^2 - [\ln(1 - v_0) + v_0 + \mu_P v_0^2] \right\} \quad (25)$$

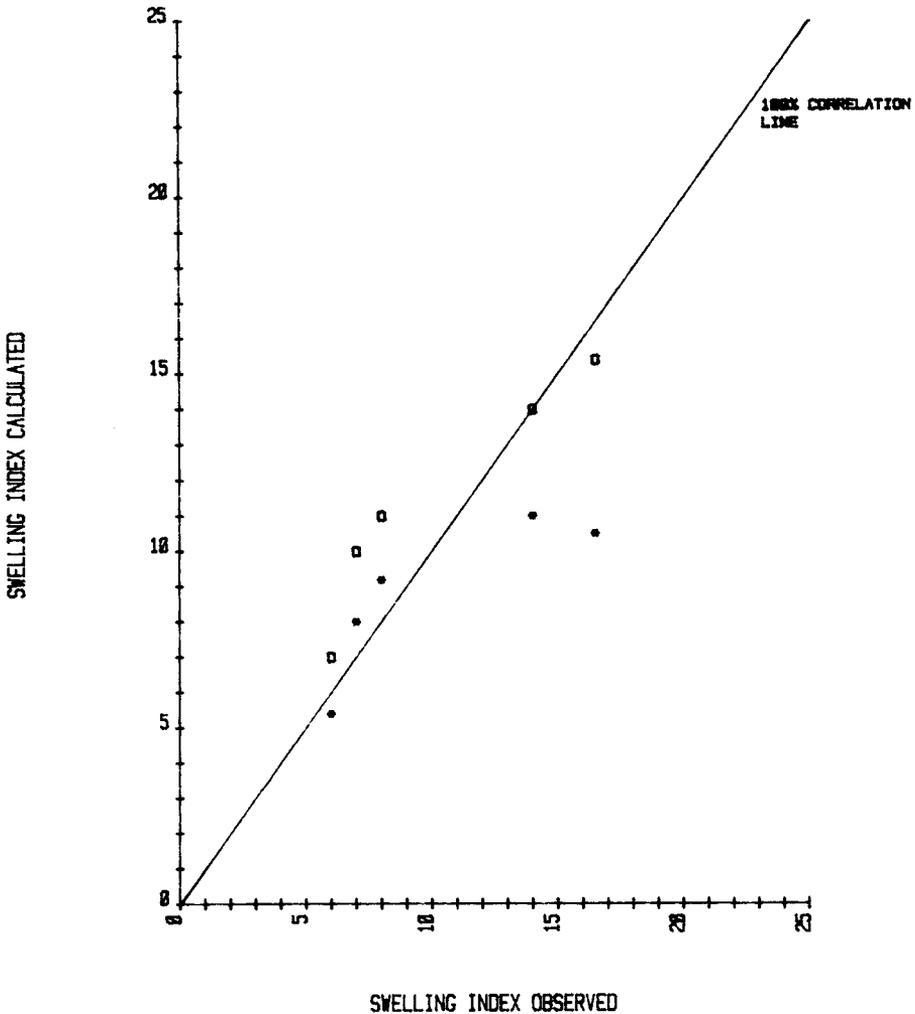


Fig. 7. Comparison of swelling index calculation. Initial composition: 90% low *cis*-polybutadiene rubber, 10% styrene, no initiator. (O) Swelling index calculated with occlusions; (\*) swelling index calculated without occlusions.

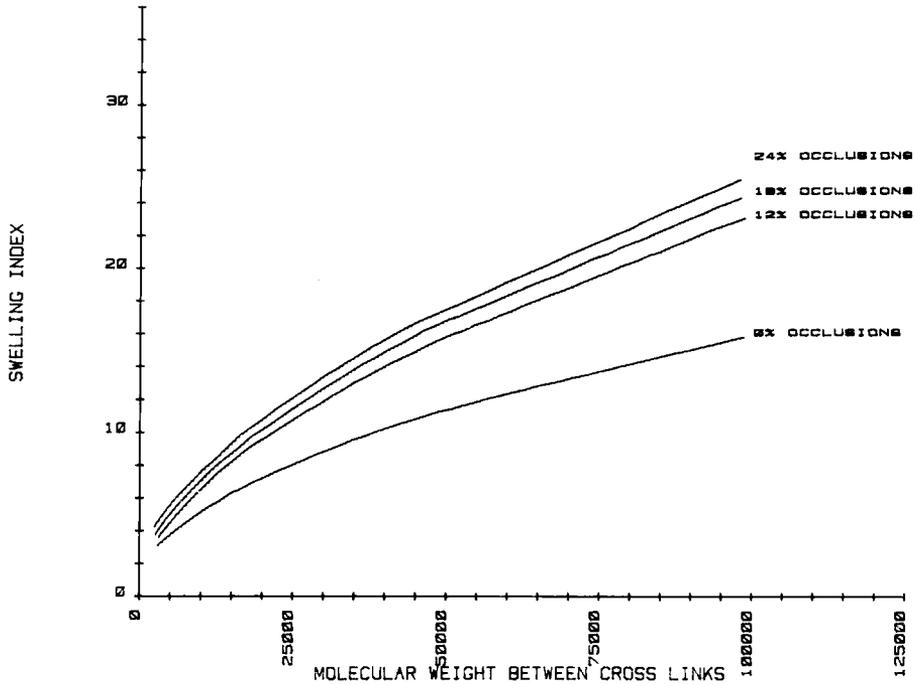


Fig. 8. Swelling index vs. cross link density. Initial composition: 7.1% polybutadiene rubber low *cis*, weight average molecular weight 282,000, number average molecular weight 100,000, 30% optical gel, solvent rubber interaction parameter 0.39, solvent polymer interaction parameter 0.34.

$$(C) \frac{v_R}{v_P} = K \quad (3)$$

$$(D) SI = 1 + \left[ \frac{\rho_s w_R \left( \frac{1}{v_R} - 1 \right) + \frac{\rho_s w_P \left( \frac{1}{v_P} - 1 \right)}{\rho_P} \right] / (w_R + w_P) \quad (26)$$

By definition the total gel fraction is defined as

$$\text{Total gel} = w_P + w_R$$

The % gel is defined as  $\frac{(\text{total gel})}{(\text{original wt of sample})} \times 100$ . In addition to these equations, the mass balance consideration must be satisfied. The total amount of solvent which is known must be equal to measured amount in the supernate plus the amount in the gel. The mass balance consideration is more important when we calculate the swelling index from kinetic considerations.

Equations (A) and (B) were derived in the preceding section. Equations (C) and (D) are based on definitions. The four nonlinear equations have four unknowns: They are  $M_c$ , the crosslink density;  $v_P$  and  $v_R$  the volume fractions of the swollen occluded polystyrene, and crosslinked rubber network, respectively;  $K$ , the ratio of  $v_R/v_P$ . The quantities  $w_P$  and  $w_R$ , the weight

fraction of occluded polystyrene and grafted and ungrafted crosslinked rubber, respectively, can be determined from electron microscopy photographs in conjunction with the image analyzer. The sum of  $W_p + W_r$  represents the total gel fraction. For swelling index less than  $\sim 18$ , the total gel can be determined by the chemical gel test previously described. For higher swelling index  $> \sim 18$ , part of the occluded polystyrene is lost in the dissolving and centrifugation step of the test. The amount lost can be determined by comparing the observed "optical gel" with the measured "chemical gel." "Optical gel" is determined from electron microscopy photographs. It is the ratio of gel area to total area of photograph. "Chemical gel" is obtained from the test previously described. The physical parameters,  $\mu_p$  and  $\mu_r$ , polymer-solvent interaction parameters can be calculated as discussed in the Derivation subsection or determined experimentally.  $\rho_s$ ,  $\rho_p$  and  $\rho_r$  density of the solvent, polymer and rubber is available in handbooks. The quantities SI, the swelling index, and  $V_o$ , the volume fraction of polymer in the supernate, are measured quantities.

Figure 3 is a flow diagram on how eqs. (A)–(D) are solved, to determine  $M_c$  for a measured swelling index. The solution proceeds as follows. Assume a value of  $M_c$  and  $K$  and solve eq. (A) for  $v_r$ . Using the calculated value of  $v_r$  and the assumed values of  $K$  and  $M_c$ , solve eq. (B) for  $v_p$ . Solve eq. (C) for  $K$ . Compare the calculated value of  $K$  with assumed value of  $K$ . If the two values agree within a certain tolerance, solve eq. (D) for swelling index.

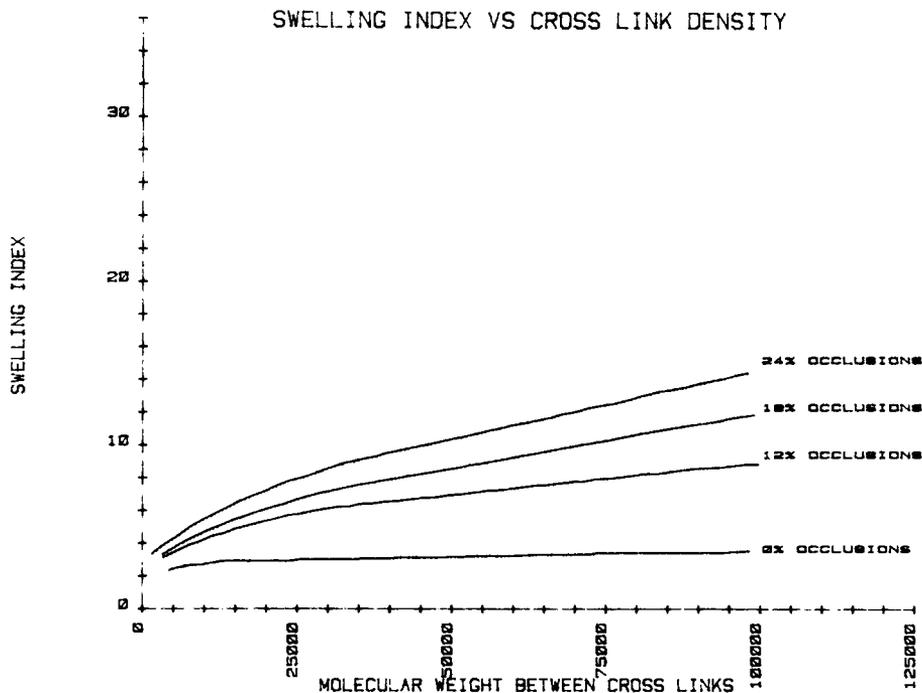


Fig. 9. Swelling index vs. cross link density. Initial composition: 7.1% polybutadiene rubber, low *cis*, weight average molecular weight 282,000, number average molecular weight 100,000, 30% optical gel, solvent rubber interaction parameter 0.60, solvent polymer interaction parameter 0.34.

If the two values of  $K$  do not agree, repeat the procedure with the calculated value of  $K$ . The calculated value of swelling index, once  $K$  converges, must agree to a certain tolerance with the measured value of swelling index. If they agree, then the assumed value of  $M_c$  is consistent with the measured swelling index. If the two values of swelling index are not in agreement, then the calculation is repeated with a new assumed value of  $M_c$ .

The swelling index calculation enables one to check the validity of the model regarding the copolymerization of styrene and polybutadiene rubber. The kinetic model calculates  $M_c$ ,  $w_R$ ,  $w_P$ , and conversion. The details of the kinetic model will be discussed in a future report. Equations (A)–(C) are solved in the manner previously discussed. The only modification is  $v_0$ ; the volume fraction of polymer in the supernate is assumed based on the conversion. This value is only approximate. The final calculation of the swelling index is made when both the material balance and the calculated and assumed value of  $K$  agree to a certain acceptable tolerance.

### EXPERIMENTAL VERIFICATION

A series of experiments were conducted to check the validity of the theory. Samples of partial polymer of approximately 25% solids were made in a laboratory polymerizer. The composition of the feed was as follows: 5.8% polybutadiene rubber (Taktene 1202, Diene 55, Diene 35 or UBE); 7.66% ethyl benzene; 463 ppm of initiator; 0.2% Irganox; 0.24% mineral oil. Samples were polymerized for 0.5 h at 25–100°C, average temperature 50°C, and 1.5 h at 115°C. At the end of the time the temperature of the jacket was lowered to 80°C. Samples of the partial polymer were drawn off into 0.25 in. ID glass ampules. The ampules were degassed by successively freezing and thawing. A vacuum was drawn on the sample when frozen to remove any dissolved gases. Previous experience has shown that this procedure can reduce dissolved oxygen to approximately 5 ppm. The ampules were sealed when frozen and under vacuum. The sealed ampules were then heated in an oil bath for various times and temperatures. The samples removed from the bath were then quenched. The % gel, swelling index, and solids were determined by the procedure described earlier. The temperature range for these experiments was from 140°C to 225°C.

A second set of experiments consisted of placing strips of rubber in a dessicator which is saturated with styrene vapor. When the samples acquired 10% by weight of styrene, they were removed and placed in glass ampules. The ampules were then sealed by the procedure described previously. The samples were then stored in a refrigerator to enable the styrene to uniformly diffuse in the sample. The glass ampules were heated for six hours at temperatures from 130°C to 225°C. The percent gel and swelling index were determined by the standard wet chemical test.

Figures 4–7 summarize part of the results obtained from the experiment. Future reports which will discuss the cross linking of polybutadiene in the presence of styrene will include all the data obtained in the study. The swelling index is calculated by two methods. The one method considers the contribution of the occlusion to the overall swelling as discussed in this report. The second method considers the swelling of the rubber membrane

as if there are not any occlusions, i.e., application of the Flory–Rehner equation with correction of the concentration of polymer in the supernate. Both calculations assume the  $M_c$  as calculated by the kinetics is correct. The details of this calculation, as stated earlier, will be a subject of a future report. Note from the figures the contribution of the occlusions to the overall swelling. The effect of the occlusion to the overall swelling cannot be ignored. The agreement between theory and experimental results is excellent.

Figures 8 and 9 calculated curves of swelling index with and without occlusions vs. molecular weight between crosslinks for different solvent polymer interaction factors. Figure 8 is for a good solvent for rubber and polystyrene and Figure 9 is for a good solvent for polystyrene and a poor solvent for rubber. Note for both cases the contribution of the occlusion to the over-all swelling decreases as the crosslinking density increases (lower value of  $M_c$ ). In our normal swelling index range of our impact polymer (9 - 15) contribution of the occlusions to the overall swelling is significant.

### CONCLUSION

(1) Flory-Rehner Equation which correlates the swelling behavior of cross-linked polymer network to the various interacting variables has been modified to include the effect of occlusions and polymer dissolved in the supernate.

(2) Excellent agreement has been obtained with calculated results obtained from the modified Flory-Rehner Equation and experimental observations. The contribution of the occluded rigid phase in the rubber gel are substantial and cannot be ignored.

(3) The equations derived enables on to determine  $M_c$ , the molecular weight between crosslink from experimentally determined swelling index and % gel measurements. The computational procedure to do this calculation is discussed.

(4) The theory of swelling which is discussed in this report enables on to check the validity of a kinetic model that describe crosslinking behavior of polybutadiene rubber and styrene.

(5) A computer program has been written and documented which facilitates the calculation procedure for  $M_c$  from given swelling index and % gel data.

### APPENDIX: NOMENCLATURE

$\Pi_R$	osmotic pressure of the swollen rubber phase (dyn/cm <sup>2</sup> )
$\Pi_P$	osmotic pressure of the swollen occluded polystyrene in the rubber gel (dyn/cm <sup>2</sup> )
$\Pi'$	osmotic pressure of the supernate (dynes/cm <sup>2</sup> )
$V$	molar volume of the mixed solvent (styrene, ethyl benzene, and toluene) (cc/g · mol)
$a$	activity of the supernate
$a'$	activity of the occluded rigid phase
$G$	modulus of rubber elasticity
$\Delta G$	change in Gibbs free energy of the system (polymer + solvent) in passing from the unstrained unswollen state to the swollen strained state (cal/mol)
$\Delta G_m$	free energy of mixing
$\Delta G_e$	free energy of the swollen extended rubber network
Gel	gel fraction

$K$	ratio of $v_R/v_P$
$l$	diameter of the unswollen occlusion (cm)
$l'$	diameter of the swollen occlusion (cm)
$l_1, l_2, l_3$	dimensions of the unstrained, unswollen rubber network (cm) (see Fig. 2)
$l'_1, l'_2, l'_3$	dimension of the strained swollen rubber network (cm) (see Fig. 2)
$M_c$	molecular weight between cross links
$n$	total moles of solvent
$R$	gas constant (cal/mol · K)
SI	swelling index
$T$	temperature (K)
$T_{\text{GEL}}$	total gel (cross linked grafted or free rubber plus occlusion)
$t_R$	radial stress (dyn/cm <sup>2</sup> )
$t_c$	circumferential or hoop stress (dyn/cm <sup>2</sup> )
$V_T$	molar volume of toluene (cm <sup>3</sup> /mol)
$V_S$	molar volume of styrene (cm <sup>3</sup> /mol)
$V_{\text{EB}}$	molar volume of ethyl benzene (cm <sup>3</sup> /mol)
$v_R$	volume fraction of rubber in the swollen rubber network
$v_P$	volume fraction of polystyrene in the swollen occluded polystyrene
$v_0$	volume fraction of dissolved polymer in the supernate
$W$	stored energy function
$w_s$	weight fraction of solvent in the rigid occluded phase
$w'_s$	weight fraction of solvent in the crosslinked rubber phase
$w_P$	weight fraction of occluded polystyrene in gel
$w_R$	weight fraction of grafted or ungrafted crosslinked rubber in the gel
$\delta_R$	solubility parameter of the rubber (cal/cm <sup>3</sup> ) <sup>1/2</sup>
$\delta_P$	solubility parameter of the polystyrene phase (cal/cm <sup>3</sup> ) <sup>1/2</sup>
$\delta_s$	average solubility parameter of the mixed solvent system (styrene, ethyl benzene, and toluene) (cal/cm <sup>3</sup> ) <sup>1/2</sup>
$\lambda_1, \lambda_2, \lambda_3$	extension ratio
$\mu_R$	rubber-solvent interaction factor
$\mu_s$	polystyrene-solvent interaction factor
$\rho_R$	density of the grafted rubber (g/cc)
$\rho_T$	density of the toluene (g/cc)
$\rho_P$	density of the polystyrene (g/cc)
$\tau_R$	summation of radial stresses (dyn/cm <sup>2</sup> )
$\tau_c$	summation of circumferential or hoop stresses (dyn/cm <sup>2</sup> )
$\phi_T, \phi_S, \phi_{\text{EB}}$	Volume fractions of ethyl benzene, toluene, styrene, respectively, assuming no polymer present.

The authors wish to acknowledge the many suggestions made by the late T. Alfrey, Jr. which greatly improved the quality of this manuscript. The authors wish to acknowledge The Dow Chemical Company which supported the work described and allowed the paper to be published.

## References

1. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11** (11), 512 (1943).
2. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11** (11), 521 (1943).
3. L. R. G. Treloar, *Proc. Roy. Soc.*, **A200**, 176 (1950).
4. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford Clarendon, London, (1958).
5. G. Gee, *Trans. Faraday Soc.*, **42**, 33 (1946).
6. H. J. Karam, unpublished data.
7. M. Norton, S. Karzerman, and M. W. Altier, *J. Colloid Sci.*, **9**, 300 (1969).
8. J. Faupel, *Engineering Design*, Wiley, New York, 1956.

Received September 12, 1983

Accepted September 14, 1984

Corrected proofs received February 17, 1985