

Crosslink Density and Solvent Swelling of Filled and Unfilled Stocks

DAVID M. FRENCH, *Energetic Materials Division, Characterization Branch, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910*

Synopsis

The network segment density (γ_g) by solvent-swollen compression modulus of gum stocks and of stocks containing nonreinforcing fillers was calculated to be $6.6093 \times 10^{-9} h_0 S \ell / \phi_B d^2$ in mmole/m³ of gel at 25°C, where h_0 is the height of the unswollen sample in cm, S is the slope of the height versus applied weight curve in g per mil (0.001 in.), ϕ_B is the volume fraction of binder, d is the diameter of the initial sample in cm, and ℓ is a factor equal to $(1 - \phi_s/\phi_B)^{1/3}/(1 - \phi_s)^{2/3}$, where ϕ_s is the volume fraction of extract. The volume fraction of crosslinked polymer containing nonreinforcing fillers at equilibrium in a solvent (V_2) was determined for the cases where the filler is insoluble and partially adheres to the binder, where the filler is partially soluble and there is no binder–filler adhesion, and where the filler is completely soluble in the swelling solvent. The relations were tested and found to hold for polyester–polyurethane stocks containing plasticizer and soluble and insoluble fillers. Log V_2 fell on single straight-line curves with respect to log γ_g for gum stocks and filled stocks both when V_2 was measured in solvents which dissolved none or dissolved part of the fillers.

INTRODUCTION

Crosslink densities of elastomeric gum stocks have been measured by methods which depend on the equation of state.¹ That is, the equilibrium stress in either tension, shear, or compression is measured at a low strain and equated to a function of crosslink density. Equilibrium is attained either by swelling in a solvent or by carrying out the pull, shear, or compression repeatedly to a degree short of failure until successive values of stress at a given strain do not change. The first method is the more accurate. Chemical means have also been used. A known concentration of copolymerizable divinyl monomer may be employed. Reactions may be carried out with known numbers of functional groups on polymers or a product resulting from a crosslinking reaction may be measured or the amount of crosslinker reacting may be determined. These chemical methods all have the defect that they assume complete reaction or neglect chain extension and dangling ends. Recently crosslink density has been calculated from telechelic stock formulations with some assumptions as to extent of reaction and from sol–gel measurements.² The latter method required calibration against crosslink density from the equation of state.

In general, the methods are applicable to gum stocks and if one regards bonds between rubber and filler as part of the crosslinking system they are applicable when reinforcing fillers such as carbon black and silica are present. If non-reinforcing fillers are used, however, either solvent swelling or application of a stress breaks the rubber–filler bonds, leaving a cavity, and interpretation of results becomes difficult. The sol–gel method is not subject to this ambiguity but is inaccurate if high proportions of plasticizer are present.

In this work a relation is presented between network segment density and solvent-swollen compression modulus which is applicable to both gum stocks and stocks containing nonreinforcing fillers such as clay, talc, ammonium perchlorate, etc. Expressions are given for equilibrium solvent swelling of filled stocks under various conditions. Solvent swelling is related to network segment density, and filled and unfilled stocks are shown to lie on the same curve.

TEST METHODS

Crosslink Density

Crosslink density, or rather network segment density, was determined by the solvent-swollen compression modulus technique introduced by Cluff, Gladding, and Pariser.³ Their relation between network segment density of gum stocks and the slope of the sample height-versus-applied-weight curve was given without a complete derivation. A derivation that has been directed to stocks containing nonreinforcing fillers is given here in Appendix A. The resulting equation is applicable to these stocks and to gum stocks but not to stocks containing reinforcing fillers. The procedure used in the experimental work was as follows:

The test specimens were cut with a No. 8 cork borer and were 6–10 mm thick. The height and diameter of the specimens were measured in cm with vernier calipers to three significant figures. The samples were swollen for one week at a temperature of 24 to 26°C in containers with ground-glass tops in 35 ml tetrahydrofuran which was saturated with the fillers in the sample. Solvent was changed twice during the week of swelling, on the third and fifth days. After seven days, the sample was removed and placed in a dish. The dish was filled with the solvent, covering the sample completely, and placed on the platform of a micrometer gauge support.

The micrometer gauge was graduated in half-mil divisions with adjustable zero point and fitted with 1.5-in.-diameter aluminum plates at the top and bottom of the plunger. The plates were of minimum weight and the bottom plate completely covered the swollen sample. The gauge was mounted on a stand having a platform vertically adjustable by a clamp. The platform was raised, the support was lightly tapped with a rubber hammer, and the gauge dial was set to zero. Weights were added to the top plate. The increments of weight were such that five or six additions caused the dial to move from zero to a final reading of about 20 mil. After the sample had been compressed by 20 mil, the weights were removed and the procedure repeated once or twice until successive readings with a given weight gave the same deflection on the dial. The gauge support was tapped lightly after each addition of weight to prevent the needle from sticking.

The data were plotted in terms of deflection in mils of the solvent-swollen stock versus weight in grams added to the gauge platform. Readings before good contact was made between the sample and the gauge plate were discarded. The best straight line was drawn visually through the valid readings and the slope of the line in g/mil was calculated.

The network segment density,

$$\gamma_g = \frac{6.6093 \times 10^{-9} h S_g^2}{\phi_B d^2} \quad \text{mmole/m}^3 \text{ of gel} \quad (1)$$

where f is $(1 - \phi_s/\phi_B)^{1/3}/(1 - \phi_s)^{2/3}$ for stocks containing nonreinforcing fillers; h = height of original unswollen sample, in cm; d = diameter of original unswollen sample, in cm; S = slope of height versus applied weight curve, in g/mil; ϕ_B = volume fraction of binder in the stock, calculated from the formulation; ϕ_s = volume fraction of sol (extract) = $d_p/d_e \times$ wt fraction extract; d_p = density initial stock, calculated from the formulation; and d_e = density extract, calculated, or by measurement on a Soxhlet extract.

The network segment density on the binder is $\gamma_g \phi_{gB}$ and in the whole stock is

$$\gamma_g \phi_{gB} \phi_B = \gamma_g \phi_g$$

where ϕ_{gB} = volume fraction of gel in the binder = $(\phi_B + \phi_f - \phi_s)/\phi_B$; ϕ_g = volume fraction of gel in the whole stock = $\phi_B + \phi_f - \phi_s$; and ϕ_f = volume fraction of soluble filler, if any.

The crosslink density is related to the network segment density by

$$x_g = \frac{2\gamma_g}{Fd_g} \text{ mmole crosslinks/g gel}$$

where F = network functionality, taken to be 3; d_g = density gel = $(d_B \phi_B - d_e \phi_s)/(\phi_B - \phi_s)$; and d_B = density binder, calculated from formulation.

Solvent Swelling

Crosslink density by solvent-swollen compression modulus was correlated with solvent swelling values using as solvents methylene chloride, acetone, and tetrahydrofuran (THF) saturated with the fillers in the stocks. Methylene chloride and saturated THF dissolved essentially none of the filler, and acetone dissolved all of the fillers except aluminum. The procedure for solvent swelling was as follows:

Samples of the material to be tested, weighing approximately 1.0 g, were cut into at least 50 pieces so that no piece weighed more than about 25 mg. The pieces were placed in an accurately tared weighing dish with a ground-glass stopper, and weighed to 0.1 mg. Thirty-five ml of solvent was added. Solvent was changed twice during a week of swelling, on the third and fifth days. After seven days, the highly volatile solvent was decanted. The inside of the weighing dish was wiped dry with absorbant tissue taking care not to wipe the sample, and the lid was quickly replaced on the weighing dish. The swollen sample and the dish were weighed immediately to the nearest milligram. The solvent was removed under full vacuum for 4 hr in a vacuum oven at 60–65°C. After cooling to ambient temperature, the sample and dish were weighed again. Three weights were obtained: the initial weight (I), the swollen weight (S), and the final weight (F).

From the three weights, I , S , and F , the volume fraction of polymer in the solvent-swollen gel (V_2), the weight percent extract on the sample, and the volume fraction of gel in the binder (ϕ_{gB}) were calculated. The quantity V_2 was calculated from

$$V_2 = \frac{a - b \left(\frac{I - F}{I} \right)}{c + d \left(\frac{S - F}{I} \right) - e \left(\frac{I - F}{I} \right)} \quad (2)$$

where $a = s_p$ when the solvent dissolves no filler, MeCl_2 ; $a = s_p(\phi_B + \phi_f)/\phi_B$ when the solvent dissolves part of the filler, acetone; $b = s_e/\phi_B$; $c = s_p$; $d = s_s$; $e = s_e$; and s_p , s_e , and s_s are the specific volumes of the initial stock, the extract, and the solvent, respectively; s_p was calculated from the formulation while s_e was calculated or measured in a pycnometer; ϕ_B is the volume fraction of binder in the original stock, and ϕ_f is the volume fraction of filler soluble in acetone in the original stock. The derivation of this expression is discussed below and in Appendix B. Definitions of the coefficients a , b , c , d , and e under other conditions are given in Table I.

EXPERIMENTAL AND DISCUSSION

Crosslink densities were measured using the solvent-swollen compression modulus method described above on the six filled and unfilled stocks listed in Table II which were prepared at three reactant ratios. The stocks were swollen in tetrahydrofuran saturated with the fillers in the stocks. Results are given in Table III in terms of mmole of network chain segments per ml of gel (γ_g) and per ml of binder (γ_B). For comparison γ_B is shown calculated from the ratio of gel to sol in the reactive portion of the binder using relation²:

$$\gamma_B = \gamma_g \phi_{gB} = 0.0065 \frac{Fd_g}{2} \left(\frac{W_g}{1 - W_g} \right) \phi_{gB} \quad (3)$$

where F = network functionality = 3; d_g = density of gel; W_g = weight fraction gel in the reactive portion of the binder; and ϕ_{gB} = volume fraction gel in the binder phase.

Solvent swelling measurements were carried out for years in the rubber industry as a qualitative measure of vulcanization. The Flory-Huggins relation showed some decades ago that solvent swelling values were related quantitatively to crosslink density through the polymer-solvent interaction parameter. Such measurements have been employed extensively for gum stocks and for stocks containing reinforcing fillers.⁴ It was pointed out by Bills and Salcedo⁵ in 1961 that the polymer in stocks containing nonreinforcing fillers broke loose from the filler particles during solvent swelling forming cavities which filled with solvent. This extra solvent is not properly part of the binder phase, and these workers showed how to correct for it. Their derivation assumed that the filler was insoluble and did not adhere at all to the binder. Blackley and Sheikh⁶ found cases of partial adherence between filler and binder but did not correct for solvent in cavities.

Properly carried out solvent swelling results are quite precise. Measurements were carried out eight times on one sample by one operator as shown in Table IV. The average deviation from the mean value of V_2 was only 1.05% of the mean.

The term V_2 occurs in thermodynamic expressions involving polymers including the Flory-Huggins equation. It is the volume fraction at equilibrium of polymer or crosslinked polymer in a single-phase solvent-swollen system and is the reciprocal of the swelling ratio for solvent-swollen crosslinked stocks. For gum stocks the term is without ambiguity. However, the presence of filler necessitates a calculation to present the data in terms of the binder phase only.

In such a case, the filler may or may not release from the binder during solvent

TABLE I
Expressions for V_2 in Various Situations^a

| | a | b | c | d | e | f |
|--|----|--|---|--------------|-------|-------------------------------------|
| Binder stocks | | s_p | s_e | s_p | s_s | s_e |
| Filled stocks—no filler dissolves, complete binder–filler adhesion | | $\frac{\phi_B s_p}{\phi_B s_p + (1 - \phi_B)\kappa}$ | $\frac{s_e}{\phi_B + (1 - \phi_B)\kappa}$ | $\phi_B s_p$ | s_s | s_e |
| Filled stocks—no filler dissolves, some binder–filler adhesion | | s_p | $\frac{s_e}{\phi_B}$ | s_p | s_s | s_e |
| Filled stocks—no filler dissolves, no binder–filler adhesion | | $\frac{s_p(\phi_B + \phi_f)}{\phi_B}$ | $\frac{\phi_B}{(s_e - s_f)}$ | s_p | s_s | s_e |
| Filled stocks—some filler dissolves | 1. | s_p | $\frac{\phi_B}{(s_e - s_f)}$ | s_p | s_s | s_e |
| Filled stocks—all filler dissolves | 2. | $\frac{s_p}{\phi_B}$ | $\frac{\phi_B}{(s_e - s_f)}$ | s_p | s_s | s_e |
| | | | | | | $\frac{s_f(I^1 - F^1)}{\phi_B I^1}$ |

^a $V_2 = \frac{a - b(I - F)/I - f}{c + d(S - F)/I - e(I - F)/I}$, where s_p = specific volume of initial stock, s_e = specific volume of extract, s_s = specific volume of solvent, s_f = specific volume soluble filler, ϕ_B = volume fraction binder, ϕ_f = volume fract. solub filler, κ = bonding factor.

TABLE II
 Formulations Employed^a

| | I | | II | | III | |
|---|------|------|------|------|------|------|
| | A | B | A | B | A | B |
| Hydroxyl-terminated polyester + polyisocyanate | 7.8 | 26.0 | 6.6 | 26.4 | | |
| Hydroxyl-terminated polyester + N/C ^b + polyisocyanate | | | | | 9.5 | 31.5 |
| Plasticizer | 22.2 | 74.0 | 18.4 | 73.6 | 20.6 | 68.5 |
| Aluminum powder | 19.5 | | 18.0 | | 19.5 | |
| Oxidizing filler ^c | 50.5 | | 57.0 | | 50.5 | |

^a Stocks were cured at three NCO/OH ratios.

^b Nitrocellulose.

^c Partially soluble in acetone, slightly soluble in tetrahydrofuran, insoluble in methylene chloride.

swelling and some or all of the filler may or may not dissolve in the solvent. The expression for the volume fraction of polymer in the solvent-swollen polymer or binder phase will assume various forms according to the conditions actually occurring. One may distinguish six conditions which lead to different expressions for V_2 . In all of these expressions some of the binder phase is assumed to be extracted by the solvent.

Binder alone present

$$V_2 = \frac{V_0 - V_E}{V_g} \quad (4)$$

Complete binder-filler adhesion

$$V_2 = \frac{\phi_B V_0 - V_E}{V_g - \phi_0 V_0} \quad (5)$$

Partial binder-filler adhesion, filler insoluble

$$V_2 = \frac{V_0 - V_E/\phi_B}{V_g [1 + \phi_0 k/\phi_B]} \quad (6)$$

See Appendix B.

No binder-filler adhesion, filler insoluble

$$V_2 = \frac{V_0 - V_E/\phi_B}{V_g} \quad (7)$$

For derivation see ref. 5.

No binder-filler adhesion, filler partially soluble

$$V_2 = \frac{(\phi_B + \phi_s) V_0 - V_E}{\phi_B V_g} \quad (8a)$$

$$V_2 = \frac{V_0 - (V_E - \Delta V_f)/\phi_B}{V_g} \quad (8b)$$

See Appendix B.

No binder-filler adhesion, filler completely soluble

$$V_2 = \frac{V_0 - V_E}{\phi_B V_g} \quad (9)$$

TABLE III
Network Segment Density and Solvent Swelling

| Formulation | Binder or filled stock | NCO/OH | ϕ_B vol. frac. binder | $\frac{I-F}{I}$ weight extract | ϕ_s vol. fract. extract | ϕ_{gB} vol. fract. gel in binder | γ_g^a comp. mod., mmole/ml | γ_B^a comp. mod., mmole/ml | γ_B^a sol-gel, mmole/ml | V_2 | |
|-------------|------------------------|--------|----------------------------|--------------------------------|------------------------------|---------------------------------------|-----------------------------------|-----------------------------------|--------------------------------|-------------------|---------|
| | | | | | | | | | | MeCl ₂ | Acetone |
| IA | Filled | 1.15 | 0.380 | 0.2425 | 0.286 | 0.249 | 0.0170 | 0.0042 | | 0.0839 | 0.152 |
| | | 1.25 | 0.380 | 0.2385 | 0.281 | 0.261 | 0.0278 | 0.0073 | 0.0110 | 0.0941 | 0.166 |
| | | 1.35 | 0.380 | 0.2372 | 0.279 | 0.265 | 0.0373 | 0.0099 | 0.0173 | 0.0977 | 0.193 |
| IB | Binder | 1.15 | 1.0 | 0.7925 | 0.736 | 0.264 | 0.0105 | 0.0028 | | 0.0542 | 0.115 |
| | | 1.25 | 1.0 | 0.7529 | 0.699 | 0.301 | 0.0250 | 0.0075 | | 0.0833 | 0.167 |
| | | 1.35 | 1.0 | 0.7398 | 0.687 | 0.313 | 0.0286 | 0.0089 | | 0.0926 | 0.182 |
| IIA | Filled | 1.10 | 0.320 | 0.2085 | 0.243 | 0.231 | 0.0303 | 0.0070 | 0.0052 | 0.0881 | 0.171 |
| | | 1.20 | 0.320 | 0.2008 | 0.234 | 0.260 | 0.0348 | 0.0090 | 0.0089 | 0.0949 | 0.188 |
| | | 1.30 | 0.320 | 0.1957 | 0.228 | 0.279 | 0.0394 | 0.0110 | 0.015 | 0.0993 | 0.192 |
| IIB | Binder | 1.10 | 1.0 | 0.7628 | 0.704 | 0.296 | 0.0211 | 0.0063 | | 0.0768 | 0.155 |
| | | 1.20 | 1.0 | 0.7466 | 0.689 | 0.311 | 0.0265 | 0.0082 | | 0.0852 | 0.160 |
| | | 1.30 | 1.0 | 0.7438 | 0.686 | 0.314 | 0.0292 | 0.0092 | | 0.0889 | 0.170 |
| IIIA | Filled | 0.75 | 0.381 | 0.2228 | 0.259 | 0.319 | 0.0348 | 0.0111 | 0.0168 | 0.124 | 0.147 |
| | | 0.85 | 0.381 | 0.2179 | 0.254 | 0.334 | 0.0651 | 0.0218 | 0.0254 | 0.145 | 0.165 |
| | | 0.85 | 0.381 | 0.2143 | 0.249 | 0.345 | 0.0670 | 0.0231 | 0.0421 | 0.152 | 0.190 |
| IIIB | Binder | 0.95 | 1.0 | 0.2135 | 0.249 | 0.348 | 0.0867 | 0.0301 | 0.0560 | 0.171 | 0.223 |
| | | 0.75 | 1.0 | 0.8041 | 0.753 | 0.247 | 0.0120 | 0.0030 | 0.0038 | 0.058 | 0.065 |
| | | 0.85 | 1.0 | 0.7740 | 0.725 | 0.275 | 0.0245 | 0.0067 | 0.0090 | 0.085 | 0.114 |
| | | 0.95 | 1.0 | 0.7198 | 0.674 | 0.326 | 0.0451 | 0.0147 | 0.0268 | 0.112 | 0.143 |

^a γ_g = Network segment density of gel; γ_B = network segment density of binder.

^b Saturated with filler.

TABLE IV
 Precision of V_2 Values

| V_2 | Deviation from mean ^a |
|-------------|----------------------------------|
| 0.1246 | +0.0002 |
| 0.1230 | -0.0014 |
| 0.1244 | |
| 0.1222 | -0.0022 |
| 0.1286 | +0.0042 |
| 0.1245 | +0.0001 |
| 0.1231 | -0.0013 |
| 0.1251 | +0.0007 |
| Mean 0.1244 | $\pm 0.0013, \sigma = 0.00195$ |

^a The value of the coefficient of variation = 0.0157.

where V_0 = initial volume; V_E = volume of extract; V_g = volume of solvent swollen gel; ΔV_f = volume of filler dissolved; ϕ_0 = volume fraction of filler in initial stock; ϕ_B = volume fraction of binder in initial stock = $1 - \phi_0$; ϕ_s = volume fraction of soluble filler in initial stock; and k = bonding factor. Equations (6) and (8) are derived below in Appendix B, while eqs. (4), (7), and (9) follow from eq. (8). Equation (9) follows from eq. (8).

Four premises were used in deriving the relations:

(1) In the absence of external or internal pressure, a hole in a piece of cross-linked rubber will occupy the same volume fraction of the rubber regardless of whether part of the rubber dissolves or whether solvent is added to the rubber.

(2) When a filled stock is swollen to equilibrium in a solvent, if the filler particles are everywhere broken loose from the polymer, the ratio of the diameters of the swollen holes around the particles to the original particle diameters will be the same as the ratio of the swollen linear dimension to the original dimension. This statement will be true even if part of the binder or part or all of the filler dissolves.

(3) Because of the pressure of the atmosphere when a solvent-swollen filled stock is dried, the stock will collapse completely around the spaces occupied by the filler particles even if some or all of the filler has dissolved.

(4) If the solvent-swollen filled stock exhibits no binder-filler adhesion, the volume of the swollen holes including filler can be expressed by $\phi_0 V_g$. See Appendix B and ref. 5.

The volume of extract, V_E , will be the weight extracted divided by the extract density. It should be remembered that if some filler dissolves, the dissolved filler will change the extract density as will degradation of the binder during aging. Equation (8b) contains the term ΔV_f , the volume of dissolved filler. To determine this volume, a separate measurement must be made of the proportion of extract and insolubles using either a solvent known not to dissolve any filler or a solvent saturated with the filler; ΔV_f then becomes the difference in weight fraction of insolubles multiplied by the initial weight and divided by the density of the dissolved filler.

In the case of stocks in a solvent which dissolves some filler eq. (8) would apply, or if in a solvent saturated with the filler eq. (6) would apply, the value of k being unknown. However, when V_2 is to be used only to calibrate against crosslink

density, the form of the relation is immaterial. For the purpose of determining polymer-solvent interaction parameters, however, the true value of V_2 must be used.

If a stock is measured in a solvent capable of dissolving filler and also in a solvent saturated with the filler, V_2 values calculated according to eqs. (6) and (8) should be the same. Expression (6), however, is identical with expression (7), with the exception of a factor in the denominator:

$$V_2 = \text{exp. (8)} = \text{exp. (6)} = \frac{\text{exp. (7)}}{1 + \phi_0 k / \phi_B} \quad (10)$$

$$1 + \frac{k \phi_0}{\phi_B} = \frac{\text{exp. (7)}}{\text{exp. (8)}} \quad (11)$$

$$k = \frac{\phi_B}{\phi_0} \left[\frac{\text{exp. (7)}}{\text{exp. (8)}} - 1 \right] \quad (12)$$

Expressions (7) and (8) can be readily calculated from experimental data. Two stocks were swollen in THF saturated with fillers and in THF less than saturated as shown in Table V. No filler was removed by the saturated solvent, but some was removed by the unsaturated THF. The appropriate expressions (7) and (8) were used for calculation with the result that essentially the same V_2 values were obtained. That is, k , the bonding factor from eq. (12), was zero. Equation (7), therefore, yielded correct values of V_2 when THF saturated with the fillers was employed as the swelling solvent. Methylene chloride gave almost complete binder-filler release, with k being approximately 0.04.

Polyester-polyurethane stocks shown in Table II were each prepared at three NCO/OH ratios with and without filler. Part of the filler was soluble in some organic solvents and the remainder, aluminum powder, was not. A high proportion of plasticizer was present. Solvent swelling was carried out in acetone, which under the conditions of test dissolved all of the filler except aluminum, in methylene chloride in which the fillers were essentially insoluble, and for most of the stocks in tetrahydrofuran (THF). When filled stocks were used, the THF was saturated beforehand with the filler.

Results are shown in Table III. The swelling tests were carried out so that all solubles were extracted. Extract contents found for stocks IB and IIB are listed but are too low. Either the stocks were mixed incorrectly or plasticizer was lost from them before the measurements. The V_2 value in methylene chloride was calculated using expression (7) above for the filled stocks and expression (4) for the gum stocks, both modified as in eq. (1) and Table I. In acetone, expressions (8a) and (4) were used, and in THF expressions (7) and (4) were used, all in the form of eq. (1) using the coefficients in Table I.

TABLE V
Effect of Dissolving of Filler on Calculated V_2 Value

| NCO/OH | Solvent | Insolubles, % | V_2 |
|--------|-------------|---------------|--------------------|
| 0.75 | sat., THF | 78.1 | 0.102 ^a |
| | unsat., THF | 73.5 | 0.104 ^b |
| 0.85 | sat., THF | 77.3 | 0.124 ^a |
| | unsat., THF | 72.8 | 0.125 ^b |

^a Using expression (7).

^b Using expression (8).

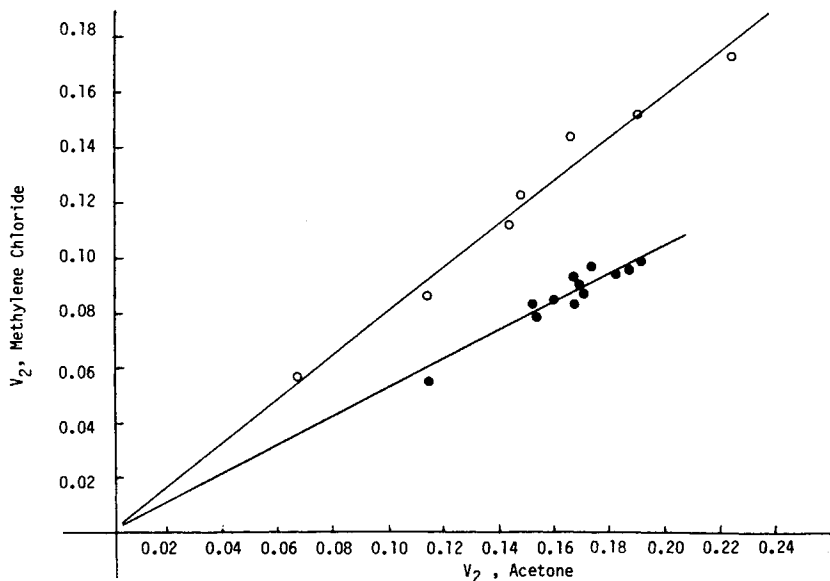


Fig. 1. Solvent swelling in methylene chloride and acetone: (●), stocks I and II, A and B; (○), stocks III, A and B.

Figure 1 compares V_2 on the various stocks swollen in methylene chloride and in acetone. The filled and unfilled stocks lie on the same curves. Stocks III, having a different composition, lie on a separate curve from stocks I and II. V_2 was correlated with crosslink density, using not the Flory-Huggins relation itself but the approximation derived from it:

$$\gamma_g = \frac{(\chi_c - \chi)V_2^n}{\bar{V}_1} \quad (13)$$

where χ = polymer-solvent interaction parameter, χ_c = polymer-solvent interaction parameter at phase separation, \bar{V}_1 = molar volume of swelling solvent, and n = approximately 5/3, so that $\log \gamma_g$ varies directly with $\log V_2$ and the curve can be characterized by the coefficient and exponent. Such curves are shown in Figures 2-4. Filled and unfilled stocks lie on the same curve showing that dividing the expression for crosslink density of the filled stocks by the volume fraction of binder as given in Appendix A is correct. It was also found that stocks III and stocks I and II gave a single curve when V_2 was measured in methylene chloride. In order for this situation to occur, the $(\chi_c - \chi)$ term in eq. (13) must be the same for all the stocks in methylene chloride.

Figure 5 compares the network segment density in the binder obtained by solvent-swollen compression modulus and by the sol-gel method of eq. (3). It is evident that the proportions of extract found from which the gel and sol contents based on reactives were calculated must be fairly correct. Agreement between the two methods is to be expected since eq. (3) was obtained using a calibration against compression modulus results.²

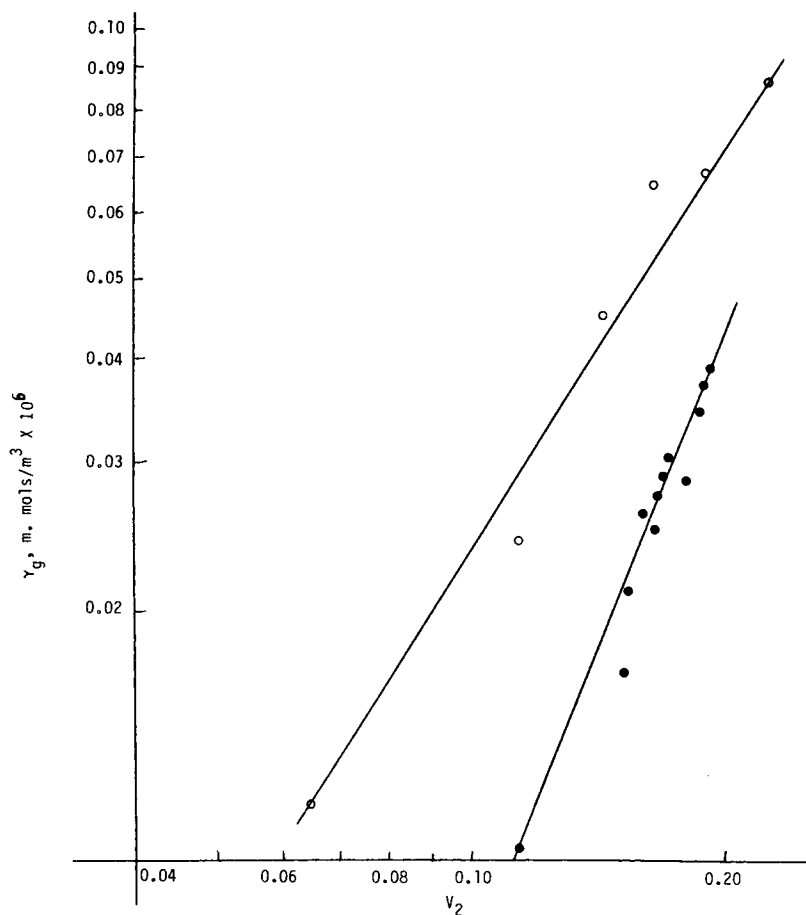


Fig. 2. Network segment density versus equilibrium swelling in acetone. For legend, see caption in Fig. 1.

CONCLUSIONS

Since $\log V_2$ of both gum stocks and filled stocks falls on single straight-line curves when plotted against $\log \gamma_g$, the values for the filled stocks are continuations of those for the gum stocks and the expressions leading to V_2 and γ_g for the filled stocks are probably correct. That is, the result of Cluff, Gladding, and Pariser³ for γ_g by solvent-swollen compression modulus must be divided by the volume fraction of binder and corrected for binder-filler release and change in dimensions during swelling as shown in Appendix A. Furthermore, the modified equations for V_2 , eqs. (6-9) give true values for V_2 for stocks containing non-reinforcing fillers under the various conditions of binder-filler adhesion and filler solubility.

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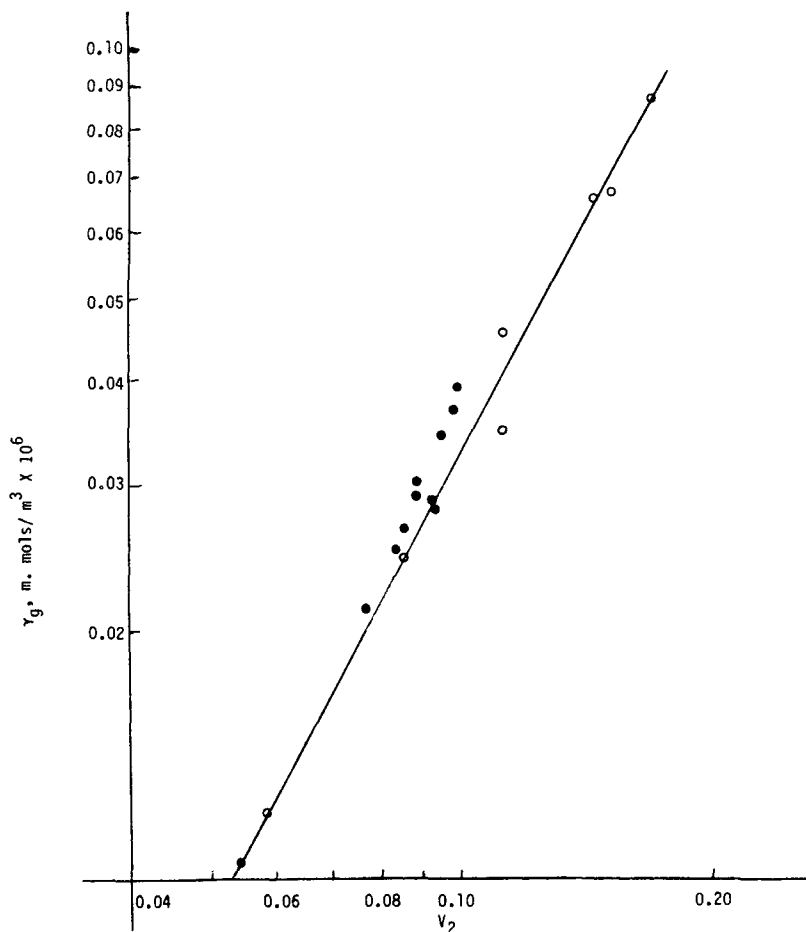


Fig. 3. Network segment density as function of equilibrium swelling in methylene chloride. For legend, see caption in Fig. 1.

APPENDIX A

Swollen Compression Modulus of Filled Stocks

Deformation of a Swollen Network

Flory,¹ p. 492, eq. (B-4), gives

$$\tau = \frac{RT\nu V_2^{-2/3}}{V_s} (\alpha - \alpha^{-2}) \quad (14)$$

where τ = force per unit area *after swelling* referred to the *swollen, unstretched* cross section; ν = network segments in a volume, V_s , of solvent-swollen stock; α = stretched length/unstretched length; and V_2 = volume fraction polymer in solvent-swollen gel. This equation was derived in terms of the dimensions of an average tetrahedral cell in the swollen state as compared to dimensions of the unswollen polymer network and the V_2 term is on the binder phase only and excludes filler. It was derived by Flory and Rehner⁷ and by James and Guth⁸ for a gum stock. The relation between the variables in eq. (14) may be determined for a filled stock by introducing into the beginning of the derivation of eq. (14) the equation of Bills and Salcedo⁵ for V_2 , the volume fraction of binder in a solvent-swollen gel in a stock containing nonreinforcing fillers. Their equation is

$$V_2 = \frac{\text{vol stock} - (\text{vol extract}/\phi_B)}{\text{vol solvent-swollen stock}}$$

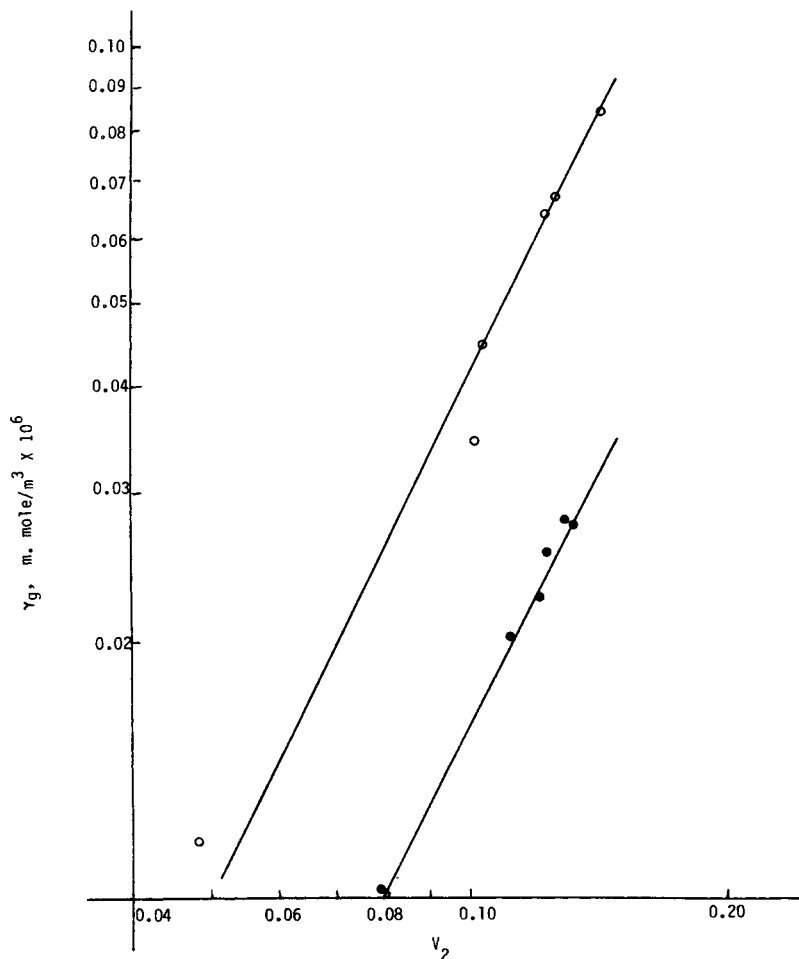


Fig. 4. Network segment density versus equilibrium swelling in tetrahydrofuran: (●), stocks IA and IIA; (O), stocks III, A and B.

In the absence of extract,

$$V_2 = \frac{\text{vol stock}}{\text{vol solvent-swollen stock}}$$

Letting α_x , α_y , and α_z represent the dimensional changes due to swelling of the filled stock,

$$\alpha_x \alpha_y \alpha_z = \frac{\text{vol solvent-swollen stock}}{\text{vol stock}} = \frac{1}{V_2}$$

which is identical to $\alpha_x \alpha_y \alpha_z$ for gum stocks. Because of this identity, further development as on page 492 of Flory's textbook¹ leads to eq. (14) so that eq. (14) is correct for filled stocks with τ , γ , and V_2 having values appropriate for these (extracted) stocks. The network segments per unit volume of swollen extracted stock are

$$\frac{\nu}{V_s} = \frac{\tau V_2^{2/3}}{RT(\alpha - \alpha^{-2})} \tag{15}$$

It should be observed that the "front factor" (8-12) was not introduced into eq. (14). This omission was deliberately made by the author, since he regards the existence of the front factor as doubtful. A possible exception would be the ratio of the mean-square end-to-end distance in the undeformed network and the free network segments.^{8,9} This ratio, however, probably has a value close to 1.

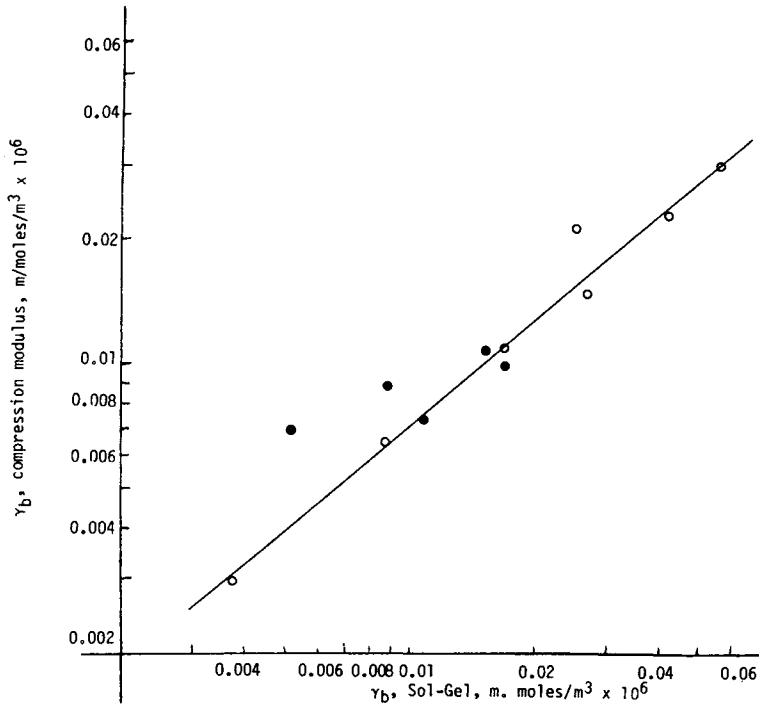


Fig. 5. Comparison of binder network segment density by compression modulus and sol-gel methods. For legend, see caption in Fig. 4.

If the sign of the denominator is reversed in eq. (15), i.e., $(\alpha^{-2} - \alpha)$ instead of $(\alpha - \alpha^{-2})$, it is also valid when α is the compression ratio, defined as h/h_s , where h is the height of the compressed swollen sample and h_s is the height of the swollen uncompressed sample. Making use of the approximation

$$\left[\left(\frac{1}{\alpha} \right)^3 - 1 \right] = 3 \left[\frac{1}{\alpha} - 1 \right] \quad (16)$$

it can be shown that

$$\alpha^{-2} - \alpha \cong \frac{3(h_s - h)}{h_s} = \frac{3\Delta h}{h_s} \quad (17)$$

or

$$\frac{v}{V_s} = \frac{\tau h_s V_s^{2/3}}{3RT \Delta h} \quad (18)$$

Approximation (16) is sufficiently exact if $1/\alpha$ is between 0.9 and 1.1, that is, for 10% compression or less. Some other workers^{13,14} have not used this approximation, but according to results of Melley and Stuckey¹⁵ more exact expressions yield results which differ negligibly from those obtained employing the approximation and which are used here and by Cluff, Gladding, and Pariser.³

τ and Δh in Terms of Compression Modulus of Extracted Stock

τ is the weight on a unit area of the swollen stock from which the extract has been removed. In terms of the dry extracted stock

$$\begin{aligned} \tau &= \tau_0^1 V_2^{2/3} \\ \tau_0^1 &= \frac{S \Delta h}{A^1} \end{aligned}$$

where τ_0^1 = weight per unit area of unswollen extracted stock; A^1 = area of sample after swelling and drying, and S = slope of the weight vs. Δh curve.

$$\tau = \frac{S\Delta h V_2^{2/3}}{A^1}$$

from which

$$\frac{\nu}{V_s} = \frac{Sh_s V_2^{4/3}}{3RTA^1} \tag{19}$$

V₂ for a Filled Stock

Up to this point with development has been for a swollen and extracted stock. The variables will now be placed in terms of an unswollen stock containing plasticizer. V_2 is the volume fraction of insoluble binder in the solvent-swollen gel exclusive of filler. The fillers are assumed to be non-reinforcing and the ideas of Bills and Salcedo⁵ would hold:

$$V_2 = \frac{\text{initial vol filled stock} - \frac{\text{vol extract}}{\text{vol fraction binder}}}{\text{vol solvent swollen stock}} \tag{20}$$

For a gum stock the volume fraction of binder is 1.0.

Let V_0 = initial vol stock, unswollen = h_0^3 ; V_0^1 = Vol dried stock after swelling = $(h_0^1)^3$; V_E = vol of sol (extract); V_f = vol of filler; V_g = vol of solvent swollen stock = h_s^3 ; h_0 = initial height of unswollen stock; h_0^1 = height of *dried* stock after swelling; h_s = height of solvent-swollen sample; ϕ_s = vol fraction sol (extract) in initial stock; ϕ_{sB} = vol fraction sol (extract) in binder; and $V_0^1 = V_0 \times$ vol fraction gel and filler in initial stock = $V_0(1 - \phi_s)$. Then

$$(h_0^1)^3 = h_0^3(1 - \phi_s) \tag{21}$$

Substituting symbols in eq. 20 for V_2 ,

$$V_2 = \frac{V_0 - (V_E/\phi_B)}{V_s} = \frac{V_0}{V_s} \left(1 - \frac{V_E}{V_0\phi_B} \right) = \frac{V_0}{V_s} (1 - \phi_{sB}) = \left(\frac{h_0}{h_s} \right)^3 (1 - \phi_{sB}) \tag{22}$$

from which

$$V_s = \frac{V_0}{V_2} (1 - \phi_{sB}) \tag{23}$$

$$h_s = \frac{h_0}{V_2^{1/3}} (1 - \phi_{sB})^{1/3} \tag{24}$$

Correction for Change in Dimensions

The area of the dry extracted sample in terms of the initial area is $A(1 - \phi_s)^{2/3}$. Making this change and substituting eqs. (23) and (24) in eq. (19) we obtain

$$\frac{\nu}{V_0(1 - \phi_{sB})} = \frac{Sh_0(1 - \phi_{sB})^{1/3}}{3RTA(1 - \phi_s)^{2/3}}$$

Now ν/V_0 is γ , the network chain density of the initial filled stock. It is equal to $\phi_B\phi_B = \phi_{gB}\phi_B\gamma_g$, where γ_B and γ_g are the network chain densities of the binder and gel and ϕ_{gB} is the volume fraction of gel in the binder, or $(1 - \phi_{sB})$.

Therefore,

$$\gamma_g = \frac{h_0S}{3RTA\phi_B} \frac{(1 - \phi_{sB})^{1/3}}{(1 - \phi_s)^{2/3}} \tag{25}$$

For convenience ϕ_{sB} may be replaced by ϕ_s/ϕ_B .

Collection of Terms

In terms of the diameter of the sample, d ,

$$\gamma_g = \frac{4h_0Sf}{3RT\pi d^2\phi_B} \quad (26)$$

$$= \frac{6.6093 \times 10^{-9}h_0Sf}{\phi_B d^2} \quad (27)$$

where γ_g = network segment density, mmole/m³ of gel; h_0 = height of original unswollen sample, cm; S = slope of height versus applied weight curve, g/ml (0.001 in.); R = 84780 g-cm/K-mole; T = 298.2 K; ϕ_B = vol fraction of binder in original stock = 1.0 for gum stocks; ϕ_s = vol fraction of sol (extract); d = diameter original unswollen sample, cm; and $f = [(1 - \phi_s/\phi_B)^{1/3}]/[(1 - \phi_s)^{2/3}]$.

APPENDIX B

Equilibrium Solvent Swelling of Filled Stocks*

A known amount of a crosslinked binder stock or filled stock containing no reinforcing filler is swollen to equilibrium in several changes of a good solvent for the noncrosslinked binder. The weight of the swollen stock is measured. The solvent is removed and the amount of dry stock remaining is determined.

Volume of Swollen Holes and Bonding Factor

Define the following quantities: l_0 = dimension of stock in dry condition, l = swollen dimension, a_0 = filler particle diameter, a = diameter of swollen hole around particle, n = number of filler particles in a unit vol, k = binder-filler bonding factor, V_0 = initial vol of stock, V_g = vol of swollen stock, V_d = vol of dried stock after swelling, V_E = vol of extract, ϕ_0 = initial vol fraction of filler, ϕ_d = vol fraction filler in dried stock after swelling, and V_2 = vol fraction of polymer in the swollen gel.

When a filled stock is swollen to equilibrium in a solvent, if the filler particles are everywhere broken loose from the polymer, the ratio of the diameters of the swollen holes around the particles to the particle diameters will be the same as the ratio of the swollen linear dimension to the original dimension, i.e.,

$$a/a_0 = l/l_0 \quad (28)$$

even if some or all of the particles dissolves. However, if some bonding of filler particles to polymer remains, the statement will not be true and a "bonding factor" will be introduced. Let

$$a/a_0 = (1 - k)^{1/3} (l/l_0) \quad (29)$$

where k may vary from zero for zero bonding to possibly as high as 0.9 but cannot reach 1 for complete bonding.

$$\text{volume of filler} = \phi_0 l_0^3 = n\pi a_0^3/6 \quad (30)$$

$$a_0/l_0 = (6\phi_0/n\pi)^{1/3} \quad (31)$$

$$\text{volume of swollen holes including filler} = n\pi a^3/6 \quad (32)$$

$$a = (1 - k)^{1/3} \frac{la_0}{l_0} = (1 - k)^{1/3} l \left(\frac{6\phi_0}{n\pi} \right)^{1/3} \quad (33)$$

$$\frac{n\pi a^3}{6} = (1 - k)\phi_0 l^3 = (1 - k)\phi_0 V_g \quad (34)$$

If part of the filler dissolves, $k = 0$ and

$$\text{volume of holes, including remaining filler,} = \phi_0 V_g \quad (35)$$

* This section owes much to a paper of K. W. Bills, Jr., and F. S. Salcedo.⁵

General Expression for V_2

initial filler volume = $\phi_0 V_0$

final filler volume = $\phi_d V_d$

volume polymer after swelling and drying = $V_0 - V_E - \phi_d V_d = (1 - \phi_d)(V_0 - V_E)$ (36)

It is assumed that the holes collapse around the filler particles on drying:

volume solvent in swollen holes = $\phi_0 V_g - \phi_d V_d = \phi_0 V_g - \phi_d (V_0 - V_E)$

volume solvent in swollen polymer = $V_g - (V_0 - V_E) - [\phi_0 V_g - \phi_d (V_0 - V_E)] = V_g - V_0 + V_E - \phi_0 V_g + \phi_d V_0 - \phi_d V_E$

$$V_2 = \frac{(1 - \phi_d)(V_0 - V_E)}{(1 - \phi_d)(V_0 - V_E) + V_g - V_0 + V_E - \phi_0 V_g + \phi_d V_0 - \phi_d V_E} = \frac{(1 - \phi_d)(V_0 - V_E)}{(1 - \phi_0)V_g} \quad (37)$$

The $(1 - \phi_d)$ must be expressed in eq. (37) in terms of the filler that dissolves. The filler that dissolves may be known accurately in cases where there is a filler or mixture of fillers, one or more of which dissolves completely in the solvent. In the general case the filler that dissolves must be determined by a separate experiment using another solvent known not to dissolve any filler.

Let ϕ_f = volume fraction of filler in initial stock which dissolves. By definition,

$$\phi_d = \frac{(\phi_0 - \phi_f)V_0}{V_0 - V_E}$$

and since $(1 - \phi_0) = \phi_B$,

$$V_2 = \frac{(\phi_B + \phi_f)V_0 - V_E}{\phi_B V_g} \quad (38)$$

Replacing Volumes by Weights

Let I = initial weight, S = equilibrium solvent swollen weight, F = final dry weight after swelling, s_p = specific vol of initial stock, s_e = specific vol of extract, and s_s = specific vol of solvent. Substituting these in eq. (38), dividing numerator and denominator by I , and noting that V_g is the actual volume of the solvent-swollen gel and is the initial volume of the sample minus the volume of extract and plus the volume of solvent in the sample, $(S - F)/d_s$, we obtain

$$V_2 = \frac{\frac{s_p(\phi_B + \phi_f)}{\phi_B} - \frac{s_e}{\phi_B} \left(\frac{I - F}{I} \right)}{s_p + s_s \left(\frac{S - F}{I} \right) - s_e \left(\frac{I - F}{I} \right)} \quad (39)$$

When the proportion of filler dissolving is not known, a separate experiment using a solvent in which the filler is insoluble would have to be carried out. In such a case $\phi_f V_0$ is the volume of filler dissolving which can be expressed as

$$\left[\left(\frac{I - F}{I} \right) - \left(\frac{I^1 - F^1}{I^1} \right) \right] I s_f$$

where s_f = specific volume of filler dissolving and the primes refer to the case where the filler is insoluble. Then eq. (38) becomes

$$V_2 = \frac{s_p - \frac{1}{\phi_B} (s_e - s_f) \left(\frac{I - F}{I} \right) - \frac{s_f}{\phi_B} \left(\frac{I^1 - F^1}{I^1} \right)}{s_p + s_s \left(\frac{S - F}{I} \right) - s_e \left(\frac{I - F}{I} \right)} \quad (40)$$

Here $(I^1 - F^1)/I^1$ will vary with the state of cure and cannot be regarded as a constant. The calculated values of V_2 from this equation are quite sensitive to the value of $(I^1 - F^1)/I^1$ used.

Partial Binder-Filler Adhesion

If none of the filler dissolves and there is some adhesion between the binder and filler in the presence of the swelling solvent, then k in eq. (34) is not zero. As a result, eq. (37) becomes

$$V_2 = \frac{(1 - \phi_d)(V_0 - V_E)}{[1 - (1 - k)\phi_0]V_g} \quad (41)$$

Making use of the relations

$$V_0 - V_E = V_d$$

and

$$\phi_d V_d = \phi_0 V_0$$

Equation (41) may be transformed to

$$V_2 = \frac{V_0 - \frac{V_E}{(1 - \phi_0)}}{\left[1 + \frac{\phi_0 k}{(1 - \phi_0)}\right]V_g} \quad (42)$$

From the general case of partial filler solution, eqs. (38) and (39), the other cases given in the text above may be derived except that for complete binder-filler adhesion.

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