Determination of network density of composites containing inert fillers from stress—strain measurements in the swollen state*

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Methods of estimating the concentration of effective network chains from the stress–strain behaviour of elastomers both dry and swollen in solvents are discussed. It is pointed out that while measurements in uniaxial extension are more difficult to carry out experimentally than measurements in uniaxial compression, they are preferred because they can provide more information about the behaviour of the elastomer. An equation is presented for relating the stress–strain behaviour of swollen composites containing inert fillers to the behaviour of a gum having the same degree of crosslinking; experimental data on SBR–glass bead composites are presented which indicate that the equation is applicable.

INTRODUCTION

The concentration of effective network chains per unit volume of whole rubber (υ_e/V) is a fundamental parameter in any description of the stress–strain properties[1,2], including the values of the stress at break, σ_b, and the strain at break, ϵ_b[3,4] of an unfilled gum elastomer. Recent work has indicated that the same description is applicable to composites containing an inert filler, and perhaps even true for composites containing active or reinforcing fillers, such as carbon black[5]. However, one of the major difficulties in attempting to relate stress–strain properties to (υ_e/V) is obtaining reliable estimates for this parameter. For the unfilled gum elastomer, methods such as the measurement of the 'equilibrium' stress–strain response in both the dry and swollen states have been employed in conjunction with the kinetic theory of rubber elasticity or modifications thereof; the procedures to be used and the preferred data reduction techniques have been described for experiments carried out in both uniaxial extension[6] and uniaxial compression[7].

For the composites, on the other hand, the situation is more complex, a central problem being to eliminate, or reduce, the effect of filler on the stress–strain behaviour so that the response due to the binder itself can be isolated from the total response of the composite. A method of reducing the effect of filler on the response is to swell the composite in a suitable liquid and measure the stress–strain response of the swollen gel. This is the method of choice in most instances. Measurements on swollen composites in both uniaxial tension and uniaxial compression have been reported in the literature[8–11] and several equations, not mutually consistent, have been used to relate the observed response to (υ_e/V).

The purpose of this report is two-fold: (1) to discuss the problems inherent in interpreting the results of the stress–strain behaviour of both gum and filled elastomers in both the dry and the swollen state; (2) to present newly derived equations which relate observed stress–strain response to (υ_e/V), and further to assess the validity of these equations by comparing their predictions with experimental data. In order to accomplish these aims, it will be convenient first to discuss briefly the stress–strain response of gum elastomers and then proceed to a corresponding discussion of composites.

EXPERIMENTAL

Styrene–butadiene rubber (Shell 1500) was used throughout this study as the base elastomer. The curing agent was dicumyl peroxide (Hercules Di Cup R). Glass beads (Superlite) were obtained from Minnesota Mining and Manufacturing Company. The reported number-average diameter of the essentially spherical filler particles was 29 μm. Direct measurement showed that the filler–size distribution could be described by the normal distribution function with a most probable value of the diameter equal to 34 μm. The compositions of the samples by wt are as shown in *Table 1*.

The compositions were mixed on a 2-roll rubber mill using normal mixing techniques. Care was taken to maintain the stocks at a reasonable temperature during incorporation of the glass filler. The temperature tended to increase during mixing, especially with the compositions having high filler loadings. Vulcanization was accomplished in an ASTM mould under pressure at 163°C for 60 min.

Densities of the composites were determined at 25°C by means of pycnometers, using water as the confining fluid.

Equilibrium swelling in the various solvents was carried out at room temperature. Small specimens, dried to constant weight, were allowed to swell in the dark in sealed bottles until no further swelling occurred. This required about one week during which the solvent was changed at least four times. After the specimens had reached maximum swelling as determined by wt, they were dried to constant

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Table 1 Composition of filled SBR samples (parts by weight)

Designation	CA	3A	4A	5A	6A	7A	8A	9A	10A
SBR (Shell 1500)	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
Glass	0	26.2	39.3	52.4	65.4	78.8	92.2	105	132
Density (g/cm^3)	0.943	1.086	1.128	1.182	1.240	1.273	1.329	1.369	1.439

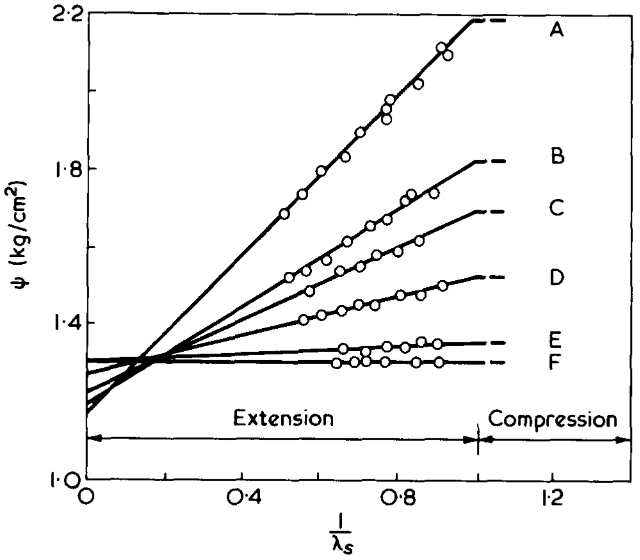

Figure 1 Behaviour of a natural rubber vulcanizate swollen to various extents in benzene in both extension and compression (hypothetical). Data of ref 3. A, ν_2 = 1.0; B, 0.74; C, 0.55; D, 0.40; E, 0.29; F, 0.20

weight. The difference in the initial dry weight before swelling and the final dry weight after swelling was taken as the weight of soluble rubber.

For the compressive stress–strain measurements, discs about 1.88 cm (0.74 in) in diameter and about 0.203 cm (0.080 in) thick were allowed to swell to equilibrium. The swollen specimens were then subjected to uniaxial compression, in the presence of excess swelling agent, using a special jig attached to the testing machine. The crosshead speed was 0.508 cm/min (0.02 in/min) and the test was terminated after the specimens had undergone strains of about 15%. Under these conditions the test is considered to be rapid enough to prevent any change in ν_2 with strain.

BEHAVIOUR OF UNFILLED ELASTOMERS

For crosslinked gum elastomers in the swollen state, the kinetic theory of rubber elasticity predicts that the uniaxial stress–strain response under equilibrium conditions can be described by[12]:

$$\sigma \equiv \frac{f}{A} = RT\frac{v_e}{V}\left(\frac{g}{\nu_2}\right)^{1/3}\left(\lambda_s - \frac{1}{\lambda_s^2}\right) \qquad (1)$$

where σ is the stress, f is the load, A is the original undeformed area of the unswollen rubber, R is the gas constant, T is the absolute temperature, (v_e/V) is the concentration of network chains per unit volume of rubber, ν_2 is the volume fraction of rubber at swelling equilibrium, g is the gel fraction and λ_s is the extension ratio based on the undeformed but swollen length.

It will be convenient to rearrange equation (1) into the following form:

$$\frac{\sigma\nu_2^{1/3}}{2g^{1/3}\left(\lambda_s - \dfrac{1}{\lambda_s^2}\right)} = \frac{v_e RT}{2V} \equiv \Psi \qquad (2)$$

If equation (2) is valid, a plot of $\sigma\nu_2^{1/3}/2g^{1/3}(\lambda_s - \lambda_s^{-2})$ against any function of λ_s, say λ_s^{-1}, should yield a linear relationship with zero slope. In what follows the applicability of equation (2) to uniaxial extension and uniaxial compression will be discussed separately.

Uniaxial extension.

In *Figure 1* (left-hand side) are shown some typical data obtained for a natural vulcanizate swollen to various extents in benzene[13], plotted in the form Ψ *versus* λ_s^{-1}. Were equation (2) valid, the data would reduce to a *single linear relation with zero slope.* It is apparent that, although linear relations are obtained for small values of λ_s, the slopes are not zero; furthermore, they vary with ν_2, the trend being a decrease in the slope with a decrease in ν_2. Although these data do not conform to equation (2), they can be represented by an equation of the type proposed by Gumbrell, Mullins and Rivlin[13] valid for small λ_s:

$$\frac{\sigma\nu_2^{1/3}}{2g^{1/3}\left(\lambda_s - \dfrac{1}{\lambda_s^2}\right)} = C_1 + \frac{C_2}{\lambda_s} \equiv \Psi \qquad (3)$$

where C_1 and C_2 are constants.

Since C_1 was found to be relatively unaffected by variations in ν_2, this parameter was set equal to the kinetic theory term[13], $(v_e/V)RT/2$. The parameter C_2 was considered to be related to departure from kinetic theory. Although the precise nature of C_2 is not at present clearly understood, its existence has been variously attributed to effects such as the failure to obtain true equilibrium stress–strain data, and to the motion of mobile chain entanglements which kinetic theory does not take into account. On the other hand, C_2 has been given the status of a material constant by Thomas[14] who derived a stress–strain law which contains a C_2 term. Furthermore, he was able to predict the variation of C_2 with ν_2 and proposed, using the data of Gumbrell[13] to evaluate a constant of the theory, that C_2 should vary as $\nu_2^{4/3}$, i.e. $C_2 = C_2''\nu_2^{4/3}$, where C_2'' is a value of C_2 when ν_2 = 1. This form of dependence of C_2 on ν_2 has been confirmed by Mullins[6] for swollen natural rubber vulcanizates with ν_2 in the range $1 \geqslant \nu_2 \geqslant 0.407$.

Using this result, equation (3) can be written as:

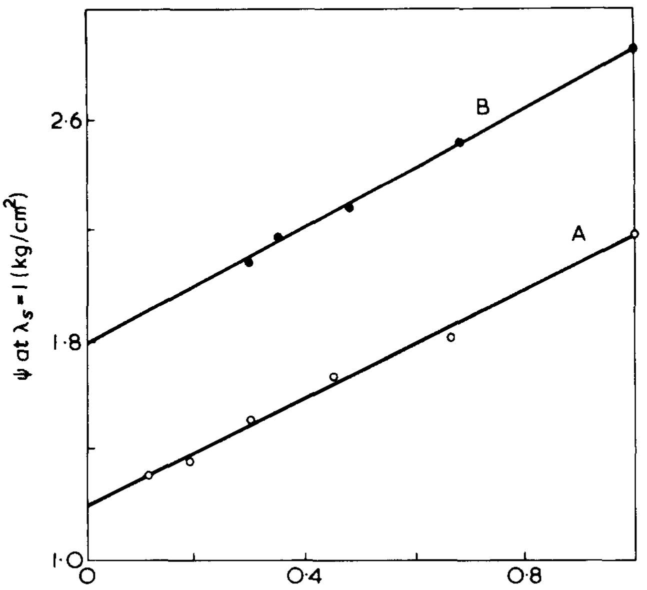

Figure 2 Variation of Ψ as a function of $v_2^{4/3}$ for data of Mullins (ref 6) and of Gumbrell (ref 13) obtained in extension. A, Data of Mullins: C_2(dry) 1.02; $C_2'' = 1.06$; B, data of Gumbrell, C_2(dry) = 1.03; $C_2'' = 1.00$

$$\Psi = \frac{RT\upsilon_e}{2V} + C_2'' \frac{v_2^{4/3}}{\lambda_s} \tag{4}$$

Thus, a plot of Ψ against $v_2^{4/3}/\lambda_s$ for a series of swollen elastomers should provide a linear plot with slope C_2'' and intercept at $v_2 = 0$ equal to $(\upsilon_e/V)RT/2$.

In order to assess the usefulness of equation (4), available data[6,13] on the stress–strain response of a gum elastomer are plotted in *Figure 2* in the form Ψ (at $\lambda_s = 1$) *versus* $v_2^{4/3}$. These data, obtained for natural rubber, were reported by Mullins[6] and by Gumbrell[13]. It is evident from the Figure that the relations are indeed linear, and further, the slopes, equal to C_2'', are in excellent agreement with the values of C_2(dry) determined for the dry elastomers. Equation (4), in general, predicts that a plot of Ψ *versus* $(v_2^{4/3}/\lambda_s)$ will superpose data of swollen vulcanizates to the stress–strain response of the dry vulcanizate. Mullins[6] has shown that this is indeed true for his natural rubber data. It can also be shown that this is true for the data of Gumbrell.

The validity of equation (4) implies that the preferred method of estimating (υ_e/V) is to perform stress–strain measurement on the dry elastomer; for in this case only, $v_2 = 1$, $C_2'' = C_2$ (dry), and thus $(\upsilon_e/V)\,RT/2$ is obtained directly[6]. On the other hand, if gum elastomers swollen to various extents are employed, then values of (υ_e/V) cannot be obtained directly, but rather Ψ must be measured as a function of v_2 and these data treated in accordance with equation (4). The implication here is that if, for example, the effects of the presence of a filler in a composite can be eliminated or reduced by measuring the behaviour in the swollen state, then Ψ must be determined as a function of v_2, i.e. measurement of Ψ at a single value of v_2 will not in general be sufficient to allow a unique value of (υ_e/V) to be directly obtained.

Uniaxial compression.

Experimentally it turns out that it is usually much more convenient to measure the stress–strain behaviour of swollen specimens in compression rather than in extension, and whereas in extension, strains of the order of a few hundred percent are employed, in compression strains of the order of only a few percent are required to obtain sufficient data for analysis. Very little study has been devoted to determining the stress–strain behaviour for an elastomer in compression. A notable example is the work of Wolf who measured the stress–strain behaviour of a rubber sample under small uniaxial extension and compression in one experiment[15]. Treloar[2] gave data which would indicate that for small strains the Ψ *versus* λ^{-1} relationship in compression for a dry elastomer can be taken as linear *with zero slope*. The behaviour in both extension and compression for small strains near $\lambda_s = 1$ is not entirely clear, due to the inherent experimental difficulties involved in measuring small strains. However, for $\lambda_s^{-1} < 0.95$ at least, Ψ extension is linear with λ_s^{-1}. In treating the results of compression experiments, it will be convenient to assume that the linear Ψ *versus* λ_s^{-1} relationship in extension and compression for small strains near $\lambda_s = 1$. Hence, since stress–strain data obtained in compression must yield the same value of Ψ as obtained in extension when $\lambda_s^{-1} = 1$, the variation of Ψ with v_2 in a compression experiment is thus related to the behaviour of the system in extension. In *Figure 1* the broken lines on the right-hand side represent the hypothetical stress–strain relationship in compression for strains up to 10%, at the indicated v_2 values.

Thus, on the assumption that Ψ in compression is independent of λ^{-1} for small strains at least, the dependence of Ψ on v_2 can be taken as:

$$\Psi = \frac{\sigma v_2^{1/3}}{2g^{1/3}\left(\lambda_s - \dfrac{1}{\lambda_s^2}\right)} = C_1 + C_2'' v_2^{4/3} \tag{5}$$

where C_1 and C_2'' have the same meanings as before. Equation (5) points out the fundamental disadvantage of compression measurements: whereas in extension, a unique value of C_1 can be obtained either from measurements on the dry elastomer or by determining Ψ as a function of v_2, in compression a unique value of C_1 can only be obtained, in general, from measurements of the variation of Ψ with v_2.

Since compression measurements involve small strains, it is permissible in most instances to expand terms in equation (5) involving the extension ratios. When this is done, we obtain:

$$\Psi = \frac{mh}{6A} = C_1 + C_2'' v_2^{4/3} \tag{6}$$

where m is the slope of the load–deflection curve and h and A are the height and the area, respectively, of the original undeformed unswollen specimen.

Support for equation (5) can be provided by the compression data of Loan[16] which show a variation of Ψ with v_2. Although he represented his data as Ψ *versus* v_2, the data can equally well be represented as Ψ *versus* $v_2^{4/3}$ and plots of this type are shown in *Figure 3* for vulcanizates of natural rubber, SBR and a polyurethane elastomer. The slopes C_2'' should be equal to the values of C_2(dry) obtained for the dry elastomer in extension, and the intercept at $v_2 = 1$ should equal the values of $C_1 + C_2$ obtained from extension tests on the dry elastomer. The values of these quantities are listed in the Figure, and considering the relatively large scatter of the data points, these results can be taken to be in accord with the predictions of equation (5).

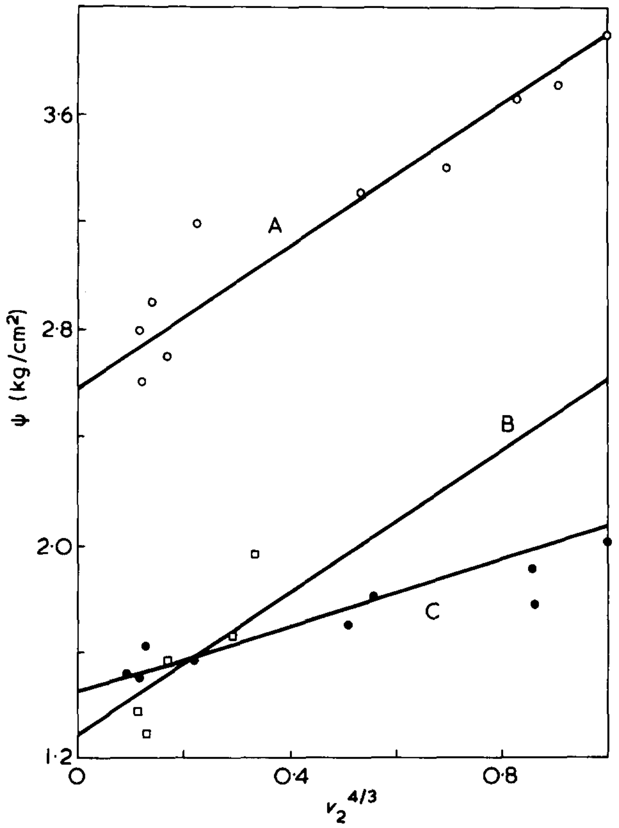

Figure 3 Variation of Ψ as a function of $\nu_2^{4/3}$ for several elastomers. Data obtained in uniaxial compression (ref 15). A, Polyurethane; B, SBR; C, natural rubber

Symbol	Elastomer	C_2''	C_2(dry)	Ψ	$C_1 + C_2$
○	Polyurethane	1.32	1.78	3.90	4.13
□	SBR	1.35	1.10	2.63	2.73
●	Natural rubber	0.60	0.69	2.25	2.14

BEHAVIOUR OF FILLED ELASTOMERS

Although the use of the technique of the measurement of stress–strain behaviour of swollen specimens can be taken as having been established under the restrictions mentioned above and related to the effect of ν_2 on the apparent value of (υ_e/V), its suitability or applicability in describing the behaviour of composites is not as well established. Consequently, various equations have been proposed at one time or another which attempt to take into account the effect of filler on the stress–strain behaviour of a swollen composite[8–11].

In the following, a new relationship, which is believed to be more correct, will be presented and compared to experimental data obtained for well-characterized composites of SBR rubber filled with glass beads and vulcanized by means of dicumyl peroxide. In order to discuss the effect of filler on the stress–strain behaviour of a composite it is necessary to distinguish between inert and active fillers. This has not always been done in the past and has thus led to the application of stress–strain relations to situations of doubtful validity.

Inert filler.

By an inert filler we mean a filler which does not interact chemically with the binder and, further, any interaction of a physical nature such as wetting of the filler by the binder is small and easily disrupted by swelling. In the dry composite, the filler will make a marked contribution to the form of the stress–strain curve due to the occurrence of the same type of hydrodynamic interaction between filler and binder which leads to the Einstein viscosity relationship. In addition to this, another effect will be dewetting, i.e. a partial separation of the binder from the filler surface, which is produced by the presence of high local strains about the filler particles when the composite is taken to moderate strains. Both of these effects will thus markedly affect the stress–strain behaviour of a composite.

When a composite containing an inert filler is allowed to swell, however, the swollen gel will consist of the swollen elastomer matrix having spherical cells which contain the filler particles totally immersed in solvent. In this situation, both the hydrodynamic and dewetting effect will have been eliminated, since the binder now no longer interacts directly with the particle. If the surface energy of the cells can be neglected, which will be true when the particles are large and the filler fraction small, then the stress–strain behaviour of the composite should mimic the behaviour of a gum vulcanizate having the same degree of crosslinking and ν_2 value. This will be true, to a first approximation at least, because the presence of inert filler should not appreicably affect the statistical distribution of chain end-to-end distances, and hence the configurational entropy of a network chain in the composite should be the same as in the gum elastomer[17]. On this basis, it is possible to relate the stress–strain response of the swollen composite to the stress–strain response of the corresponding gum elastomer having the same degree of crosslinking.

Bills[18] has shown that the volume fraction of rubber in a swollen composite containing inert filler is equal to the volume fraction of composite, ν_2^*, provided that the filler particles are far enough apart so that the swelling about each particle is independent of the presence of neighbouring particles, thus:

$$\nu_2 = \nu_2^* = \frac{V_{\text{composite}} - V_{\text{sol}}}{V_{\text{composite}} - V_{\text{sol}} + V_{\text{solvent}}} \tag{7}$$

Where $V_{\text{composite}}$ is the volume of the composite in the dry state, V_{sol} is the volume of material extracted by the solvent, and V_{solvent} is the volume of solvent in the swollen composite at equilibrium.

In addition, the dilation factor $\langle\alpha\rangle$ can be written as:

$$\langle\alpha\rangle^3 = \frac{V_s}{V} \tag{8}$$

where V_s is the total volume of the swollen *rubber phase* in the swollen gel and V is the volume of the rubber phase when the network was formed. Using this definition, it can be shown that:

$$\langle\alpha\rangle^3 = \frac{g}{\nu_2^*} \tag{9}$$

Hence, the stress–strain response of the swollen composite can be written as:

$$\sigma = \frac{RT\upsilon_e g^{2/3}}{V_c[1 - s(1 - \phi)]^{1/3}\nu_2^{*1/3}}\left(\lambda_{sc} - \frac{1}{\lambda_{sc}^2}\right) \tag{10}$$

Table 2 Properties of SBR–glass bead composites

Sample	ϕ	Solvent														
		Carbon tetrachloride			Benzene			Cyclohexane			Heptane			Iso-octane		
		g	v_2	Ψ^a	g	v_2	Ψ^a	g	v_2	Ψ^a	g	v_2	Ψ^a	g	v_2	Ψ^a
CA	0	0.875	0.118	59.1	0.874	0.132	97.3	0.875	0.168	118	0.880	0.340	138	0.885	0.420	155
3A	0.0922	0.898	0.122	70.7	0.914	0.144	98.0	0.912	0.184	126	0.904	0.370	164	0.906	0.446	178
4A	0.132	0.920	0.124	60.0	0.917	0.143	100	0.920	0.182	126	0.914	0.372	159	0.912	0.448	161
5A	0.169	0.922	0.128	70.0	0.922	0.148	110	0.925	0.186	122	0.920	0.370	150	0.915	0.455	170
6A	0.204	0.929	0.133	85.1	0.926	0.155	109	0.927	0.196	131	0.920	0.380	161	0.918	0.460	180
7A	0.234	0.925	0.125	64.1	0.926	0.148	101	0.927	0.187	119	0.922	0.374	150	0.920	0.460	178
8A	0.270	0.930	0.132	72.2	0.930	0.158	104	0.931	0.197	123	0.925	0.380	156	0.922	0.463	168
9A	0.289	0.931	0.138	58.9	0.930	0.158	102	0.932	0.205	125	0.927	0.387	164	0.922	0.472	176
10A	0.339	0.927	0.138	67.8	0.930	0.163	105	0.932	0.204	122	0.927	0.394	154	0.925	0.480	166

[a] In moles/cm^3 x 10^4

Here, V_c is the unextracted volume of the undeformed, unswollen composite; λ_{sc} is the extension ratio based on the swollen but undeformed length of the specimen; s is the sol fraction ($s = 1 - g$), and ϕ is the volume fraction of filler in the composite. If the deformations are small, the term involving λ_{sc} can be expanded in terms of the strain. This leads to:

$$\left(\lambda_{sc}-\frac{1}{\lambda_{sc}^2}\right)=\frac{3\Delta h_{sc}}{h_{sc}}=\frac{3\Delta h_{sc}v_2^{*1/3}}{h_c[1-s(1-\phi)]^{1/3}} \qquad (11)$$

where h_c is the length (or height) of the unextracted, undeformed and unswollen specimen and Δh_{sc} is the change in length under deformation. Substitution of equation (11) in equation (10) yields:

$$\sigma=\frac{3RT\nu_e}{V}\;\frac{(1-\phi)g^{2/3}\Delta h_{sc}}{[1-s(1-\phi)]^{2/3}h_c} \qquad (12)$$

where V is now the volume of unextracted, undeformed and unswollen rubber phase which was obtained using the relationship $V = V_c(1-\phi)$. This transformation yields (ν_e/V) values independent of the filler fraction.

The expression for Ψ in extension can be written as:

$$\Psi=\frac{\sigma[1-s(1-\phi)]^{1/3}v_2^{*1/3}}{2(1-s)^{2/3}(1-\phi)\left(\lambda_{sc}-\dfrac{1}{\lambda_{sc}}\right)}=C_1+C_2''\frac{v_2^{*4/3}}{\lambda_{sc}} \qquad (13)$$

and for compression:

$$\Psi=\frac{mh_c[1-s(1-\phi)]^{2/3}}{6A_c(1-s)^{2/3}(1-\phi)}=C_1+C_2''v_2^{*4/3} \qquad (14)$$

These equations reduce to the corresponding equations for the unfilled gum elastomers when ϕ is set equal to zero. To the extent that the derivations leading to equations (13) and (14) are valid, C_1 and C_2'' will be independent of ϕ.

In order to check the applicability of equation (14), stress–strain measurements in compression were carried out on SBR–glass bead composites cured by means of dicumyl peroxide and swollen in various solvents to provide a range of v_2^* values. The composites were designed to have approximately a constant (ν_e/V) value independent of the ϕ value. The data obtained are listed in *Table 2* along with the corresponding ϕ values. The data show that Ψ for a given solvent (given v_2^* value) is indeed independent of ϕ, and this is true for all the solvents used which covered a v_2^* range of about 0.1 to 0.5. It is also apparent from inspection of the Table that Ψ varies with v_2^*. The data are shown plotted in *Figure 4* as Ψ *versus* $v_2^{*4/3}$. The data seem to define two regions, i.e. an apparently linear region at relatively large

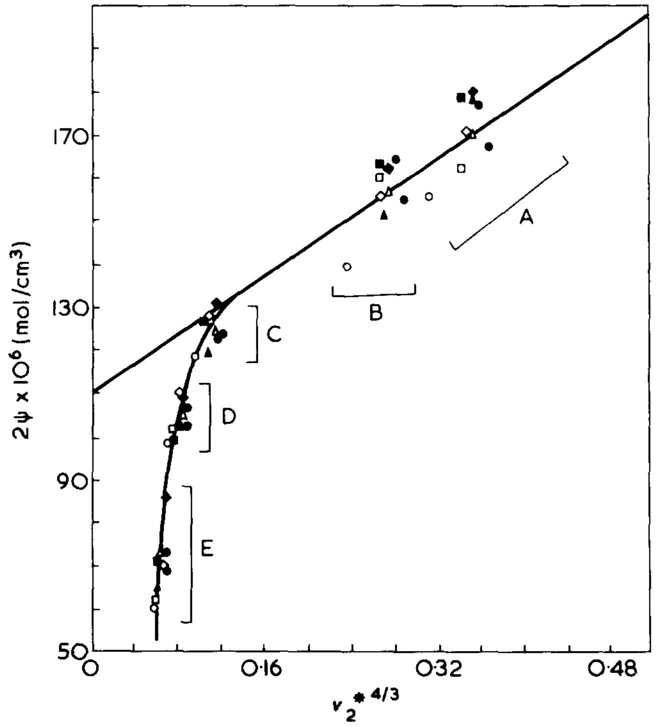

Figure 4 Variation of Ψ with $v_2^{*4/3}$ for SBR–glass bead composites. Data obtained in uniaxial compression

Symbol	Sample	ϕ	Solvent
○	CA	0	A Iso-octane
■	3A	0.0922	B Heptane
□	4A	0.132	C Cyclohexane
◇	5A	0.169	D Benzene
◆	6A	0.204	E Carbon tetrachloride
▲	7A	0.234	
△	8A	0.270	
⊕	9A	0.289	
●	10A	0.339	

ν_2^* value and a region of rapid decrease in Ψ with decreasing ν_2^*. This rapid decrease of Ψ was totally unexpected, and this constitutes the first report of such an effect. At the present time no explanation is offered for its existence, but further study is planned. The data in the linear region can reasonably be represented by equation (14). The measured slope is 165 x 10^{-6} mol/cm^3 while the predicted value based on C_2(dry) of the unfilled gum obtained in extension is 150 x 10^{-6} mol/cm^3. The intercept at $\nu_2^* = 1$ is 240 x 10^{-6} mol/cm^3 while the value calculated from $(C_1 + C_2)$ of the dry gum measured in extension is 215 x 10^{-6} mol/cm^3. Here again the agreement is reasonable. From the intercept at $\nu_2^* = 0$, the average values for (ν_e/V) of these composites is 110 x 10^{-6} mol/cm^3 which is identical to the value obtained for this parameter from superposition of failure envelopes[19].

CONCLUSIONS

The method of determining the concentration of effective network chains from the stress–strain behaviour of elastomers in both uniaxial extension and uniaxial compression has been discussed. It was pointed out that while extension measurements are more difficult to perform from the experimental standpoint than compression measurements, they are preferred because they can provide more information about the behaviour of the elastomer. It was also pointed out that it is necessary to distinguish between composites containing inert and active filler, because these are expected to differ in their response.

An equation was developed for relating the stress–strain behaviour of swollen composites containing inert fillers to the behaviour of a gum having the same degree of crosslinking, and experimental data on SBR–glass bead composites were presented which indicated that the equation was applicable.

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