

Swelling of Filler-Reinforced Vulcanizates

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I. INTRODUCTION

Extensive use has been made of the kinetic theory of rubber elasticity and the Flory-Rehner¹ network theory of swelling to estimate the degree of crosslinking in vulcanized elastomers. In general, these relations allow one to calculate the number of elastically effective network chains, which in turn may be analyzed further to obtain the numbers of crosslinks, entanglements, and network defects. The success of these techniques with gum vulcanizates makes their extension to the technologically important filler-reinforced rubbers highly desirable. Unfortunately, the introduction of rigid filler particles into the network leads to some serious theoretical and practical complications. The most basic of these is the inability of the network to undergo deformations which are affine with the sample dimensions. In previous extensions of network theories to filled rubbers this has been neglected. Thus, A. M. Bueche assumed that the equilibrium modulus and equilibrium volume swelling of a filled network in a solvent may be analyzed by the relationships applicable to unfilled vulcanizates and ascribed the apparent increase in the number of network branches to rubber-filler linkages.² Kraus,³ as well as Dannenberg and Boonstra,⁴ used the same assumption in showing that apparent network chain densities calculated from swelling equilibria on filled vulcanizates contained contributions from filler aggregate structure and from changes in crosslink yield. Although these procedures can not be justified on theoretical ground they are capable of giving useful information, because at constant loading (ϕ) of a given filler the *apparent* number of network chains in a filled vulcanizate (ν) is approximately a constant multiple of the number of chains in the unfilled vulcanizate (ν_0), independent of ν_0 . Hence, a relative measure of (physical) crosslinking can be obtained from swelling data on filled stocks in this manner. Bevilacqua⁵ introduced a Guth and Gold⁶ type correction ($1 + 2.5\phi + 14.1\phi^2$) to network chain densities on filled rubbers. Again the implicit assumption was made that the filled network follows ordinary network theory.

Recently Lorenz and Parks⁷ investigated the swelling of a number of carbon black-reinforced sulfur vulcanizates. They found that the ratio of the swelling of the filled stock to that of the unfilled vulcanizate was constant—in substantial agreement with the results of Kraus³—and

interpreted this result as meaning that swelling in the filled vulcanizate is normal except for a shell of rubber around each particle. In this shell the number of crosslinks might be larger, possibly due to surface effects on the vulcanization reaction. The same sort of argument can, however, be based on attachments of polymer molecules at the surface. If the rubber adheres, swelling must obviously be restricted in the region around the filler particle, but will become normal a sufficient distance away from the surface. The important point is that the bulk of the rubber is crosslinked to the same extent as the gum vulcanizate and hence swells to the same extent, i.e., furnace blacks have no profound effect on the vulcanization stoichiometry (although they may affect the rate). The present report examines the consequences of the Lorenz and Parks model. We shall calculate quantitatively the effect on swelling of particles either completely unbonded, or completely and permanently bonded to the polymer. We shall show that the assumption of complete bonding leads to agreement with a very large volume of experimental data and that the swelling of the rubber matrix may in many cases be identified with that of the unfilled vulcanizate. Even when this is not the case, the theoretical expression derived allows calculation of corrected swelling ratios which are free of the filler effects and suitable for further analysis by network theory.

II. EFFECT OF NON-ADHERING FILLER ON SWELLING

If the linear swelling coefficient of the rubber is q_0 and the volume fraction of filler is ϕ , the final volume of swollen rubber will be $(1 - \phi)q_0^3$. In addition, as the rubber swells it forms a vacuole around each particle which will fill with solvent. This volume of solvent is obviously $\phi(q_0^3 - 1)$ and has to be added to the volume of the swollen rubber. The volume swelling ratio Q is then

$$Q = v_r^{-1} = (q_0^3 - \phi)(1 - \phi) = (v_{r_0}^{-1} - \phi)/(1 - \phi) \quad (1)$$

where v_r is the *apparent* volume fraction of rubber in the swollen gel and v_{r_0} is its true value, equal to the inverse swelling ratio of the analogous gum vulcanizate.

Equation (1) shows that total lack of filler-polymer adhesion will produce a considerable *increase* in the apparent swelling of the rubber. Examples of incomplete adhesion will be given in a later section of this report.

III. RESTRICTION OF SWELLING BY ADHERING FILLER

Consider a filler particle of radius R embedded in a matrix of rubber. If the rubber is swelled, but the bond between the particle and the rubber remains intact, swelling is obviously restricted completely at the surface. A distance r ($>R$) away from the center of the particle swelling is still partially restricted, and as r approaches infinity swelling becomes normal.

We next consider an element of volume in the unswelled rubber: $dr, r d\theta, r \sin \theta d\psi$. After swelling the dimensions of this element will be $q_r dr, q_t r d\theta$ and $q_r \sin \theta d\psi$, where the q 's will be functions of r . Conservation of solid angle requires that q_r (radial) be different from q_t (tangential). To find the relation between them we first find the distance (r') by which the element is removed from the center of the particle after swelling. This is

$$r' = \int_R^r q_r dr + R \quad (2)$$

The requirement that

$$r' d\theta = q_t r d\theta \quad (3)$$

leads to

$$q_r r - R = \int_R^r q_t dr \quad (4)$$

It follows from eq. (4) that

$$q_r = q_t + r(dq_t/dr) \quad (5)$$

We can now calculate the swelling deficiency (Δv) due to the particle for a shell of rubber bounded by R and any arbitrary r by considering the difference between the swelling of this shell and the extent to which it would have swelled in the absence of the constraint:

$$\Delta v = \int \int \int (q_r q_t^2 - q_0^3) r^2 \sin \theta dr d\theta d\psi \quad (6)$$

Here q_0 is the "normal" linear swelling coefficient. Substituting for q_r from eq. (4) and integrating:

$$\begin{aligned} \Delta v &= 4\pi \int_R^r \left[r^2 q_t^2 \left(q_t + r \frac{dq_t}{dr} \right) - r^2 q_0^3 \right] dr \\ &= (4\pi/3) [r^3 q_t^3(r) - R^3 - q_0^3(r^3 - R^3)] \end{aligned} \quad (7)$$

In evaluating the integral, use was made of the identity

$$r^2 q_t^3 + r^3 q_t^2 (dq_t/dr) = 1/3 [d(r^3 q_t^3)/dr]$$

and the fact that q_t must be unity at the lower limit (no swelling at the surface).

It is convenient at this point to replace the function q_t by the following expression

$$q_t = q_0 - (q_0 - 1) f(r) \quad (8)$$

where $f(\infty) = 0$ and $f(R) = 1$. Factoring out $R^3 q_0^3$ from eq. (7) and rearranging we find

$$\Delta v = (4\pi/3) R^3 q_0^3 \{ 1 - q_0^{-3} + r^3 R^{-3} [q_0^{-3} q_t^3(r) - 1] \} \quad (9)$$

and passing to the limit:

$$\Delta v = (4\pi/3)R^3q_0^3\{1 - q_0^{-3} + R^{-3}\lim_{r \rightarrow \infty} r^3[q_i^3q_c^{-3} - 1]\} \quad (10)$$

Making use of eq. (8) we find

$$\lim_{r \rightarrow \infty} r^3[q_i^3q_0^{-3} - 1] = \lim_{r \rightarrow \infty} \left\{ r^3 \left[-3 \frac{q_0 - 1}{q_0} f(r) + 3 \left(\frac{q_0 - 1}{q_0} \right)^2 f^2(r) - \left(\frac{q_0 - 1}{q_0} \right)^3 f^3(r) \right] \right\} \quad (11)$$

It is easily shown that if the first term converges, the second and third terms will converge to zero; hence

$$\lim_{r \rightarrow \infty} r^3[q_i^3q_0^{-3} - 1] = -3(1 - q_0^{-1}) \lim_{r \rightarrow \infty} r^3f(r) \quad (12)$$

Substitution into eq. (10) leads to

$$\Delta v = (4\pi/3)R^3q_0^3[1 - q_0^{-3} - 3c(1 - q_0^{-1})] \quad (13)$$

where

$$c = R^{-3} \lim_{r \rightarrow \infty} r^3f(r) \quad (14)$$

It is now possible to write the swelling deficiency for N particles (in unit volume of rubber) provided the particles are far enough apart so as not to interact. If ϕ is the volume fraction of filler

$$N = 3\phi/4\pi R^3(1 - \phi)$$

and

$$\Delta V (\text{all particles}) = q_0^3[1 - q_0^{-3} - 3c(1 - q_0^{-1})]\phi/(1 - \phi) \quad (15)$$

The ratio of the volume swelling ratios (Q) of the filled rubber to the unfilled rubber is obviously

$$\begin{aligned} Q/Q_0 &= (q_0^3 + \Delta V)/q_0^3 \\ &= 1 + [1 - q_0^{-3} - 3c(1 - q_0^{-1})]\phi/(1 - \phi) \end{aligned} \quad (16)$$

It is usual to denote the reciprocal swelling ratios as v_r ; these are equal to the volume fraction of rubber in the swollen gel. Noting that

$$q_0^{-3} = v_{r0}$$

we find

$$\begin{aligned} v_{r0}/v_r &= 1 - [3c(1 - v_{r0}^{1/3}) + v_{r0} - 1]\phi/(1 - \phi) \\ &= 1 - m\phi/(1 - \phi) \end{aligned} \quad (17)$$

The theory thus predicts that v_{r_0}/v_r should vary linearly with $\phi/(1-\phi)$, the slope (m) being a function of v_{r_0} . To check the agreement with experiment and to evaluate the constant c we write

$$m - v_{r_0} = (3c - 1) - 3cv_{r_0}^{1/2} \quad (18)$$

which is in a form suitable for plotting.

IV. AGREEMENT WITH EXPERIMENT

To subject the theory to an experimental test we need a system in which the yield of crosslinks will be unaffected by the presence of the filler so that v_{r_0} may be identified with v_r of the unfilled vulcanizate. This can not be guaranteed *a priori*, but there is some evidence that sulfur vulcanizates containing furnace black come reasonably close to fulfilling this condition.⁷ The carbon black also fulfills the requirement of spherical particle shape. It must be realized, however, that carbon blacks are seldom, if ever, ultimately dispersed in the polymer.

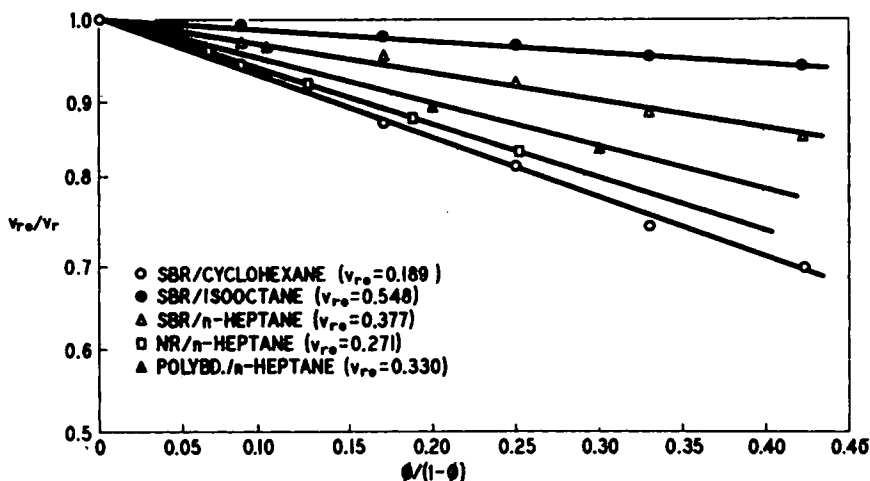


Fig. 1. Typical plots illustrating dependence of swelling on filler loading (HAF black).

In the absence of a better model we shall assume that aggregates may be considered simply as particles of increased size. Furthermore, the nature of the calculation suggests that even nonspherical particles may obey an equation of the form of eq. (17), so that it does not appear unreasonable to assume that the shape and aggregation effects can be lumped into the constant c . Finally, we assume c to be independent of q_0 , which will be true if $f(r)$ in eq. (8) is independent of q_0 . If these assumptions are realistic and if carbon black exhibits adhesion strong enough to withstand the stresses developed at the interface due to swelling or desorption by the

solvent, eq. (17) should be valid for any particular black up to moderate loadings, regardless of the polymer, the solvent used to swell the rubber, the degree of crosslinking, or the vulcanization system (as long as the latter is not interfered with by the filler).

The dependence of v_{ro}/v_r on loading is illustrated in Figure 1 for HAF carbon black. The required linear dependence on $\phi/(1 - \phi)$ is found. Few, if any, significant deviations from this relationship have been observed. To test the dependence of the slope on q_0 (or v_{ro}) a large number of these slopes has been plotted according to eq. (18) in Figure 2. These data

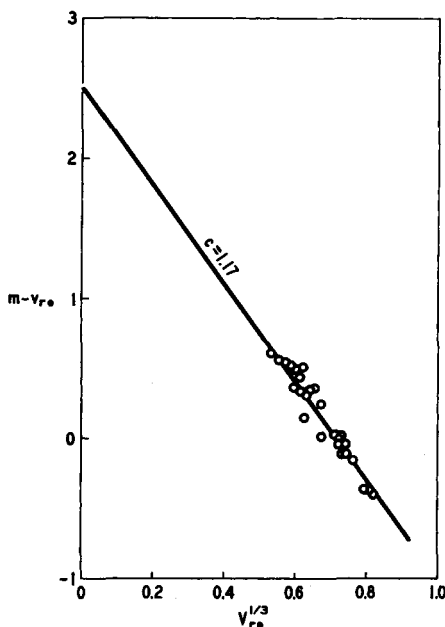


Fig 2. Determination of parameter c for HAF black.

cover four rubbers (SBR, natural rubber, polybutadiene, and butyl rubber), five solvents (benzene, cyclohexane, dibromoethane, n -heptane, and iso-octane) and various curing systems (sulfur-sulfenamide, thiuram, and a typical butyl recipe), the first two at several levels of crosslinking. Considering the great variety of the sample material the agreement is quite good, particularly for a single parameter fit. The constant c evaluated from the plot has the value 1.17.

Table I lists values of c for several carbon blacks. Each is based on at least two rubbers and two solvents. It is apparent that these are not strongly dependent on surface area or particle size. This is not necessarily at variance with eq. (14), since there is no reason to suppose that the limit $\lim_{r \rightarrow \infty} [r^3 f(r)]$ will not itself be a function of R . There appears to be some

dependence on the carbon black aggregate structure which is lowest for FT (oil absorption = 0.6 cc./g.) and highest for acetylene black (2.4 cc./g.).

Regardless of the precise physical significance of the parameter c , it is clear that eq. (17) provides a fairly close approximation to a considerable volume of experimental data. The agreement is even more remarkable

TABLE I
Values of c for Various Carbon Blacks

	Surface area, ^a m. ² /g.	Number of determina- tions ^b	Range of v_r covered	c
FT (P-33)	13.7	13	0.16-0.39	0.92
SRF (Gastex)	27.6	13	0.16-0.39	1.15
HAF (Philblack O)	75.1	107	0.15-0.55	1.17
SAF (Philblack E)	142.6	17	0.16-0.39	1.27
EPC (Wyex)	114.2	9	0.16-0.39	1.26
Acetylene (Shawinigan)	58.0	13	0.16-0.39	1.35

^a BET nitrogen adsorption method.

^b Individual v_r determinations.

when one considers that under rather typical conditions a 5% change in crosslink yield can easily change the value of v_r by some 3%—based on Flory-Rehner theory calculation. On the other hand, at 50 parts black loading a 25% error in m (say 0.3 vs. 0.4) would cause v_r to be in error by only 2%. Since small variations in degree of crosslinking, even between identical formulations, can never be ruled out, it is concluded that the theory fits the data essentially within experimental error.

V. APPLICATIONS TO PROBLEMS OF REINFORCEMENT AND VULCANIZATION

The conformance of the data with the theoretically predicted eq. (17) indicates that (1) carbon black is firmly bonded to the rubber matrix with adhesion strong enough to withstand desorption by the best solvents investigated, and (2) the crosslink yield in sulfur-sulfenamide vulcanization is in general not strongly influenced by the carbon black. This suggests two possible applications. Having once established the value of the parameter c under the above conditions, lack of adhesion of a filler will be apparent in swelling in excess of that predicted by eq. (17). Conversely, an abnormally low value of c may be taken as evidence of lack of adhesion, particularly if c decreases with increasing swelling. Effects of fillers on vulcanization stoichiometry may also be detected by the deviations caused by them. We shall illustrate these applications by a few actual examples.

Graphitized carbon black (Graphon) in butyl rubber gave the following inverse swelling ratios at level cure (identical recipe):

Solvent	ϕ	v_r	m	c
<i>n</i> -Heptane	0	0.282	≈ 0.08	0.77
	0.111	0.284		
	0.207	0.284		

The extremely low value of c compared with all the other blacks suggests that adhesion is not complete, though not entirely absent. If the latter were true, vacuole formation would lead to an actual decrease in v_r .

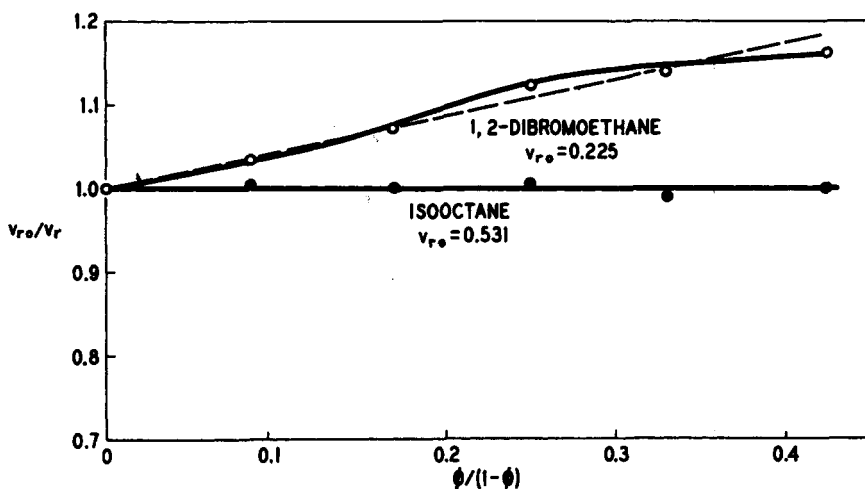


Fig. 3. Evidence for incomplete adhesion in SBR-1500/clay vulcanizates.

A similar example is that of clay-filled rubbers. Figure 3 shows swelling data in two solvents for SBR-1500 containing clay (kaolin), cured in a sulfur-sulfenamide recipe. In isooctane, a poor solvent, v_{r0}/v_r is independent of ϕ , much as in the above example with Graphon. The value calculated for c is 0.82. Up to this point one might explain these data by a repressing effect of increasing filler loadings on vulcanization, i.e., a decrease of v_{r0} with loading. That this can not be the only reason becomes clear from the swelling data on the identical vulcanizates in 1,2-dibromoethane, a good solvent. Swelling increases corresponding to a c (based on the dashed line) of only 0.14. The inapplicability of the theory indicates lack of adhesion which, as expected, becomes more pronounced under the influence of the better solvent. Similar results have been obtained with benzene and cyclohexane.

To illustrate an application involving an effect of carbon black on vulcanization, we consider the vulcanization of polybutadiene with sulfur and *N*-oxydiethylenebenzothiazole-2-sulfenamide (NOBS Special). This accelerator is known to require furnace black for "activation." Figure 4 shows swelling data in *n*-heptane for three different cure times. At level cure good agreement with eq. (17) is obtained: m (calc) = 0.31, m (obs.) =

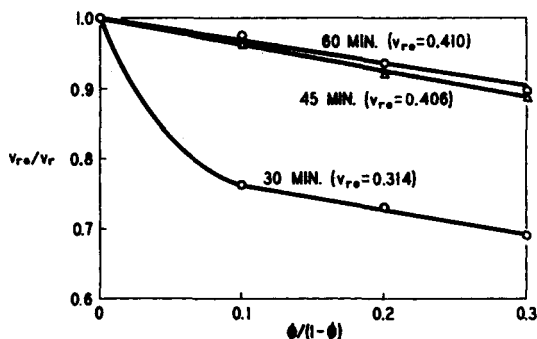


Fig. 4. Activation of vulcanization by HAF black in polybutadiene/sulfur/NOBS Special system.

0.32. The 30-min. cures diverge widely from the predicted trend. However, these vulcanizates should likewise obey eq. (17); only v_{r0} can no longer be identified with the swelling of the unfilled stock. We, therefore, calculate v_{r0} from each experimental point:

Black loading phr	$\phi/(1 - \phi)$	v_{r0}	
		30 min. cure	60 min. cure
0	0	0.314	0.410
20	0.10	0.397	0.406
40	0.20	0.403	0.412
60	0.30	0.418	0.420

Since the calculated v_{r0} are now representative of the degree of crosslinking of the rubber matrix, the accelerating effect of carbon black on the vulcanization becomes quite clear. The corrected v_r are suitable for further analysis by the Flory-Rehner theory, if desired. This procedure should prove generally useful in vulcanization studies on filled elastomers, whenever normal bonding between filler and rubber can be expected, but where the filler interacts with the vulcanization reaction. Another example of such a system is the peroxide vulcanization of carbon black reinforced elastomers as discussed by Lorenz and Parks.⁷

VI. EXPERIMENTAL

All swelling determinations were made gravimetrically, using the procedure described previously.³ In all cases the results were calculated as the volume fraction of rubber in the swollen rubber phase, assuming zero swelling for the filler. Solvents used were either Phillips pure grade hydrocarbons or Merck Analytical Reagent grade. Polymers were commercial products (No. 1 Smoked Sheet, SBR-1500, Enjay Butyl 215),

except for polybutadiene which was a *n*-butyllithium polymerized rubber of inherent viscosity (in toluene) 2.14.

Vulcanization recipes were conventional sulfur-sulfenamides, thiuram, or butyl rubber formulations. The use of processing oils or plasticizers was limited to five parts on the rubber or less to avoid possible complications in interpretation of the results. For each compound a complete vulcanization curve (swelling vs. cure time) was run, and only the data at level or maximum cure were used in correlations with theory.

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Synopsis

A theory is developed to account for the restricted swelling in solvents of crosslinked elastomers containing reinforcing fillers. Assuming swelling to be completely restricted at the filler-rubber interface due to adhesion, the following relation is obtained:

$$v_{r0}/v_r = 1 - [3c(1 - v_{r0}^{1/2}) + v_{r0} - 1]\phi/(1 - \phi),$$

where v_r is the volume fraction of rubber in the swollen rubber phase, v_{r0} is the same quantity referred to on otherwise analogous, unfilled vulcanizate, ϕ is the volume fraction of filler, and c a parameter depending on the filler, but independent of ϕ and v_{r0} . This equation is shown to hold for a large volume of experimental data on carbon blacks, involving four rubbers, several sulfur vulcanizing systems, five solvents, and a wide range of crosslinking. Conformance with the theory indicates that carbon blacks are firmly bonded to the rubber and that, in the sulfur crosslinking systems investigated, they have no significant effect on the stoichiometry of vulcanization (although they may affect the rate of vulcanization). Illustrative examples of applications of the theory to problems in filler reinforcement and vulcanization are shown.

Résumé

Une théorie est développée pour rendre compte du gonflement limité dans les solvants pour des élastomères pontés contenant des charges de renforcement. Tenant compte que le gonflement est complètement réduit à l'interface charge-caoutchouc par suite de l'adhésion. On obtient la relation suivante:

$$v_{r0}/v_r = 1 - [3c(1 - v_{r0}^{1/2}) + v_{r0} - 1]\phi/(1 - \phi)$$

où v_r est la fonction de volume du caoutchouc dans la phase de caoutchouc gonflé, v_{r0} est la même quantité rapportée à un vulcanisat analogue on renforcé, ϕ est la fonction de volume de la charge et c un paramètre dépendant de cette dernière, mais indépendant de ϕ et v_{r0} . On montre que cette équation est valable pour un grand nombre d'expériences dans le cas du noir de carbone comprenant 4 caoutchoucs, différents systèmes vulcanisés au soufre, 5 solvants et une grande gamme de degré de pontage. L'accord avec la théorie indique que le noir de carbone est fortement lié au caoutchouc et que dans les systèmes

vulcanisés au soufre et étudiés, ils n'ont pas d'effet significatif sur la stœchiométrie, de la vulcanisation (bien qu'il puisse affecter la vitesse de vulcanisation). On donne des exemples illustrant les applications de cette théorie du renforcement par des charges et par la vulcanisation.

Zusammenfassung

Eine Theorie zur Erklärung der beschränkten Quellbarkeit vernetzter Elastomerer, die verstärkende Füllstoffe enthalten, in Lösungsmitteln wird entwickelt. Unter der Annahme, dass die Quellung an der Füllstoff-Kautschukgrenzfläche wegen Adhäsion völlig zurückgedrängt ist, wird folgende Beziehung erhalten:

$$v_{r0}/v_r = 1 - [3c(1 - v_{r0}^{1/c}) + v_{r0} - 1] \phi / (1 - \phi),$$

wo v_r der Volumbruch des Kautschuks in der Quellungsphase, v_{r0} die gleiche Grösse für ein sonst analoges, ungefülltes Vulkanisat, ϕ der Volumbruch des Füllstoffes und c ein vom Füllstoff abhängiger, aber von ϕ und v_{r0} unabhängiger Parameter ist. Diese Gleichung gilt für eine grosse Zahl von Versuchsdaten an Russen, mit vier Kautschukarten, mehreren Schwefel-Vulkanisationssystemen, fünf Lösungsmitteln und einem grossen Vernetzungsbereich. Die Übereinstimmung mit der Theorie lässt erkennen, dass die Russen fest an den Kautschuk gebunden sind und dass sie bei untersuchten Systemen mit Schwefelvernetzung keinen wesentlichen Einfluss auf die Stœchiometrie der Vulkanisation besitzen (obgleich sie möglicherweise die Vulkanisationsgeschwindigkeit beeinflussen). Anwendungsbeispiele für die Theorie auf Probleme der Füllstoffverstärkung und der Vulkanisation werden gegeben.

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