

Elasticity Theory and Crosslinking of Reinforced Rubber

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ABSTRACT: For filler fraction C , molecular weight M_c between crosslinks, and equilibrium swelling v_r , the Flory function $M_c = F(v_r)$ was corrected for a hard fraction $C_h = (1 + \beta)C$, βC being rubber occluded within the primary filler structure. However, a small effect of a Graphon filler was unjustifiably attributed to rubber stretched hard by swelling; later research wrongly attempted to estimate β from $F(v_r)/F(v_c)$ where v_c considers the hard filler as rubber. By avoiding these mistakes, and with $1/F_o(v_r)$ as unfilled crosslinking, Blanchard's constraint equations for linkage reinforcement ϕ and reinforced crosslinking $1/M_c$ are now simplified to

$$\phi = \frac{1 - C_h \frac{F_o(v_r)}{F(v_c)}}{1 + C_h \frac{F_o(v_r)}{F(v_c)}} = \frac{1 - \beta C \frac{F_o(v_r)}{F(v_r)}}{1 + \beta C \frac{F_o(v_r)}{F(v_r)}}$$

$$\frac{1}{M_c} = \frac{1 - C_h}{1 + C_h} \frac{1}{F(v_c)} = \frac{1 - \beta C}{1 + \beta C} \frac{1}{F(v_r)}$$

Alternatively, $1/M_c$ can be obtained from the theoretical modulus $G = F/(\alpha - 1/\alpha^2)$, by the stress F at extension ratio $\alpha = 2$ following two very different prestretches, $\alpha_b \gg 2$. The choice of 100% strain ($\alpha = 2$) is to minimize low-strain Mooney–Rivlin deviation from simple rubber theory and to avoid particle contact effects. The choice $\alpha_b \gg \alpha \gg 2$ is to avoid stress upturn as $\alpha \rightarrow \alpha_b$. Then, for two prestretches $\alpha_b = 3$ and $\alpha_b = 4.5$ or 5 (400%), corresponding prestresses S_1 and S_2 , moduli G_1 and G_2 , and force per linkage factors $X_1 = \alpha_b S_1 / G_1^{2/3}$ and $X_2 = \alpha_b S_2 / G_2^{2/3}$, the primary modulus G^* is

$$G^* = G_1 - G_r F(X_1) = G_2 - G_r F(X_2)$$

$$F(X) = (1 + kX^{1/2} + (k^2/2)X) \exp(-kX^{1/2})$$

Because $k = 0.276$ for all rubbers and fillers, the secondary modulus G_r is known from $(G_1 - G_2)/(F(X_1) - F(X_2))$. Hence,

$$G^* = G_2 - \frac{(G_1 - G_2)F(X_2)}{F(X_1) - F(X_2)}$$

$$\frac{1}{M_c} = (1 + V) \frac{1 - \beta C}{1 + \beta C} \frac{G^*}{\rho RT}$$

Here $(1 + V)$ allows for network dilution by filler volume V per milliliter of rubber, $C = V/(1 + V)$, and βC is rubber occluded within the particle aggregate structure of carbon blacks. The measured (effective) crosslinking $1/M_c^l$ is obtained by omitting $(1 - \beta C)/(1 + \beta C)$ from the above equations. The structure parameter β might be determined from G_r using the present test prescription and modern furnace blacks with negligible to high structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 119–129, 1998

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INTRODUCTION

The objectives of Blanchard and Parkinson's investigation of stress-strain behavior were to understand carbon black reinforcement of rubber and to obtain insights into how carbon particle reinforcement might be improved or replaced. Later work, especially the present article, extends this basic study to equilibrium swelling in solvent and considers the relation between swelling and tensile modulus. This later work is concerned mainly with how to measure the crosslinking of polymers having carbon particle reinforcement or nodules of transition constraints.

For general test evaluation, rubber technologists traditionally make much use of tensile equipment and swelling measurements and they could get more information and compatibility from their measurements. Quantitative comparisons of the degree of vulcanization of practical rubbers may be of great interest to rubber compounders. Moreover, there is a need to establish a quantitative method for comparing the differing particle aggregate structures of carbon blacks in rubber.

The quantitative theory presented here is based on inductive reasoning from experience, not deductive reasoning from *a priori* assumptions. That is to say, it emerges from experiments to discover what in practice represents both the equilibrium modulus and swelling of reinforced rubbers. The theory involves a hard fraction model, but this quantitative device is an aid to experimentally discover how the reinforced system behaves. However, the theory does assume the simplest form of the basic theory of rubber elasticity. It may be objected that low tension strains are not in practice represented by a single modulus parameter. The present article identifies the specific circumstances in which stress-strain behavior can be expressed by a single modulus G as in the basic theory of rubber elasticity.

When vulcanized rubber swells in solvent, an equilibrium is reached between swelling and the elastic restoring force. For rubber without particulate reinforcement, Flory and Rehner¹ related the equilibrium volume fraction v_r of rubber to the molecular weight M_c between crosslinks, so that in the later Flory refinement²

$$M_c = \frac{-\rho V_1 (v_r^{1/3} - v_r/2)}{\mu v_r^2 + \ln(1 - v_r) + v_r} = F(v_r) \quad (1)$$

Here V_1 is the molar volume of the solvent, ρ is the density of the rubber, μ is the rubber-solvent interaction constant, and $1/M_c$ is the measure of crosslinking. The extra term $v_r/2$ distinguishes the Flory refinement from the original Flory-Rehner equation. This refinement was adopted because $v_r/2$ is relatively large for the reduced swelling caused by carbon black reinforcement. Hence, results using the original Flory-Rehner $M_c = F(v_r)$ might not be quite as good as those obtained here. I do not feel qualified to judge controversy over the Flory refinement.

For the tension modulus of unfilled vulcanizates a theoretical equation was derived by Guth and James^{3,4} and later by Wall,⁵ who used a different method, and also by Treloar⁶ who showed that it follows from modification of Kuhn's earlier model.⁷ For stress F at low and moderate extensions, the theoretical modulus is $G = \rho RT/M_c$ in the equation

$$F = G(\alpha - 1/\alpha^2) \quad (2)$$

Here F is the force per unit area of the original cross section, α is the ratio of the extended length to the initial length, ρ is the rubber density, and RT is the product of the gas constant and absolute temperature. James and Guth showed that F is theoretically the same whether the $1/M_c$ crosslinks are free or fixed at their most probable positions.⁴

Softening by prestretching is a striking feature of reinforced rubber, and this was first studied by Mullins⁸ and Mullins and Tobin⁹ as a way of investigating reinforcement. For reinforced and prestretched rubber, Blanchard and Parkinson¹⁰ introduced a logarithmic empirical equation. In this the modulus G corresponded roughly with eq. (2), and an empirical term $\mu(\alpha - 1)^4$ represented the stress upturn at elongations approaching the prestretch. Blanchard and Parkinson used a wide range of prestresses (30–200 kg/cm²) to establish a measure of the strength of the strongest rubber-filler linkages broken by each prestretch. They argued that breaking force per linkage was proportional to the prestress S and that it must have the dimensions $(M)(L)(T^{-2})$ of force, so that for U surviving linkages per unit volume,

$$\frac{(M)(L^{-1})(T^{-2})}{(L^{-3})^\rho} = (M)(L)(T^{-2})$$

Here $(M)(L^{-1})(T^{-2})$ are the prestress dimen-

sions and (L^{-3}) is the dimension of U . Hence, $\rho = 2/3$ so that $S/U^{2/3}$ is proportional to the force per linkage. This was replaced by $S/G^{2/3}$ because U is proportional to the modulus G in the basic theory of rubber elasticity. However, only an experiment could justify the proposed measure of linkage strength. For this to be a true measure X , the filler concentration must affect the number of linkages but not their strength distribution. By taking $X = \alpha_b S/G^{2/3}$ for prestresses α_b , this condition was met, although for the fixed prestresses there was enormous variation of α_b with filler concentration.

Because α_b is dimensionless the product $\alpha_b S/G^{2/3}$ still has the dimensions necessary for a measure of force per linkage. Hence, the linkage strength distribution was obtained by graphing the measure G of linkage number versus force per linkage X . By trial and error, using tangents dG/dX , this distribution was satisfactorily represented by

$$dG = -AX^{1/2} \exp(-kX^{1/2}) dX \quad (3)$$

where dG is proportional to the number of linkages with breaking strengths between X and $X + dX$, k is the strength distribution parameter, and A is a constant of proportionality. By integration this law of prestress softening was expressed by the equations

$$G = G^* + G_r F(X) \quad (4)$$

$$F(X) = (k^3/4) \int_x^\infty X^{1/2} \exp(-kX^{1/2}) dX \quad (5)$$

Here $k^3 G_r/4$ replaces A , G^* is the residual modulus after high prestresses, and G_r is a removable (secondary) modulus. The integrated function is a γ function:

$$F(X) = (1 + kX^{1/2} + (k^2/2)X) \exp(-kX^{1/2}) \quad (6)$$

The strength distribution parameter $k = 0.276$ is independent of the filler concentration and common to secondary linkages formed by various fillers in both natural rubber (NR) and styrene-butadiene rubber (SBR).¹⁰⁻¹² Berry et al.¹³ found that milling treatment before cure reduced the labile modulus G_r in the Blanchard-Parkinson equation, but with little effect on G^* . The success of this analysis of reinforced modulus was confirmed also for butyl rubber by Skinner and colleagues¹⁴ and by Blanchard.¹⁵

Dilution by filler reduces the number of elastic

Table I Weights of Formula Ingredients

SBR 1500	100.0
Zinc oxide	3.0
Stearic acid	1.0
Santoflex IP	0.75
Santoflex AW	0.75
Carbon black	0-65
CBS accelerator	1-2.0
Sulfur	1-2.5

chains in the ratio $1 : 1 + V$, where V is the filler volume per milliliter of rubber. Hence, the corrected modulus is $(1 + V)G$ and the corrected modulus components are $(1 + V)G^*$ and $(1 + V)G_r$. The question arises how far X is affected by this correction of G . If a unit cube of the network has linear dimensions expanded by a factor $(1 + V)^{1/3}$, the force on the expanded cube is $(1 + V)^{2/3}S$ to give prestress S . Therefore, we have¹¹

$$X = \alpha_b (1 + V)^{2/3} S / (1 + V)^{2/3} G^{2/3} = \alpha_b S / G^{2/3}$$

Hence, X is independent of correction for the volume occupied by the filler. An interesting feature is that the product $\alpha_b S$ is the prestress on the stretched cross section.

The present article takes account of the aggregate structure of carbon blacks. It dispenses with the time, trouble, and costs of multiple prestresses, multipoint stress-strain curves, and the resulting graphs and calculations.

EXPERIMENTAL

For swelling measurements v_r on gum and reinforced SBR vulcanizates, the respective cross-link measures $1/F_o(v_r)$ and $1/F(v_r)$ were varied widely by varying the sulfur and accelerator contents as originally detailed.¹⁶ The chosen black fillers were High Abrasion Furnace (HAF) and Graphon; i.e., partially graphitized Medium Processing Channel (MPC). Table I shows the ingredient formulae by weight per 100 gm rubber.

The compounds were all cured for 40 min at 148°C (with 15-min rise). Equilibrium swelling in toluene was determined by the initial weight, the swollen weight, and the weight after drying out the toluene. Allowance was made for the filler volume and the small volume of sulfur and zinc oxide; it was assumed that the remaining ingredients were extracted by the toluene. Equation (1)

Table II Effective Linkage Reinforcement ϕ^l

HAF Black Volume, C	Crosslinks without Black, $10^4/F_o(v_r)$	Effective Linkage Reinforcement, $\phi^l = F_o(v_r)/F(v_r)$
0.216	0.91	1.72
	1.52	1.89
	1.88	1.90
	2.34	1.89

was calculated taking $\rho V_1 = 100.6$ and $\mu = 0.28$ for SBR-toluene.

For reinforced rubber that had not been swollen, the quoted data were obtained as previously described.^{10,11} Based on this experience, the procedure for obtaining G , G^* , and G_r is now drastically simplified by the analysis and proposals in the present study. After prestretching much of the set was incomplete elastic recovery, that is, it disappeared on heating. Because only a small part of the set was a true change in dimensions, no allowance was made for it. However, this neglect would not be justified if the state of cure was inadequate.

DISCUSSION

Theory for Swelling of Reinforced Rubber

Gee showed that swollen vulcanizates are in close agreement with rubber elasticity theory,¹⁷ in contrast to dry rubber that at low strains required the deviation parameter C_2 of Mooney¹⁸ and Rivlin et al.¹⁹ For various solvents and polymers this advantage of swelling the rubber was confirmed by Gumbrell and coworkers.²⁰ Moreover, swelling dissolves the secondary rubber linkages on reinforcing particles, and so distinguishes the primary crosslinks $1/M_c$. Equilibrium swelling also has the important feature that carbon particles do not swell in solvent. Hence, loadings of carbon black in rubber provided an experimental basis to establish a hard fraction model for elasticity theory.^{16,21-23} Some rubber also becomes hard by occlusion in primary aggregates of carbon particles. Hence, this hard fraction model provides an experimental basis to derive the effect of primary black structure on crosslink measurements $1/F(v_r)$.

By swelling measurements on reinforced SBR, Kraus^{24,25} discovered that the state of cure has little effect on the ratio of measured crosslinking $1/F(v_r)$ to that of gum rubber without reinforcement. Blanchard¹⁶ took this into account by defining effective linkage reinforcement ϕ^l as the

ratio of the effective crosslinking $1/M_c^l$ to the corresponding gum measurements $1/F_o(v_r)$.

Because $1/M_c^l = 1/F(v_r)$, we have

$$\phi^l = F_o(v_r)/F(v_r) \quad (7)$$

where $F_o(v_r)$ is the Flory function of v_r for the corresponding gum vulcanizates. The results for SBR reinforced with 50 phr HAF black are presented in Table II. These linkage reinforcements are so high they seem to reflect the presence of hard rubber occluded in the primary aggregates of HAF black particles.

If the hardened rubber is not precisely represented by ϕ^l , it may be that carbon black induces additional rigid segments Λ_r so that comparison should be with chains shortened to $F_o(v_r) - \Lambda_r$. Then eq. (7) becomes $\phi^l = (F_o(v_r) - \Lambda_r)/F(v_r)$. On transposing this, it becomes

$$F(v_r) = (1/\phi^l)F_o(v_r) - \Lambda_r/\phi^l \quad (8)$$

The application of this equation is shown by the top graphs in Figure 1, their slope being the aver-

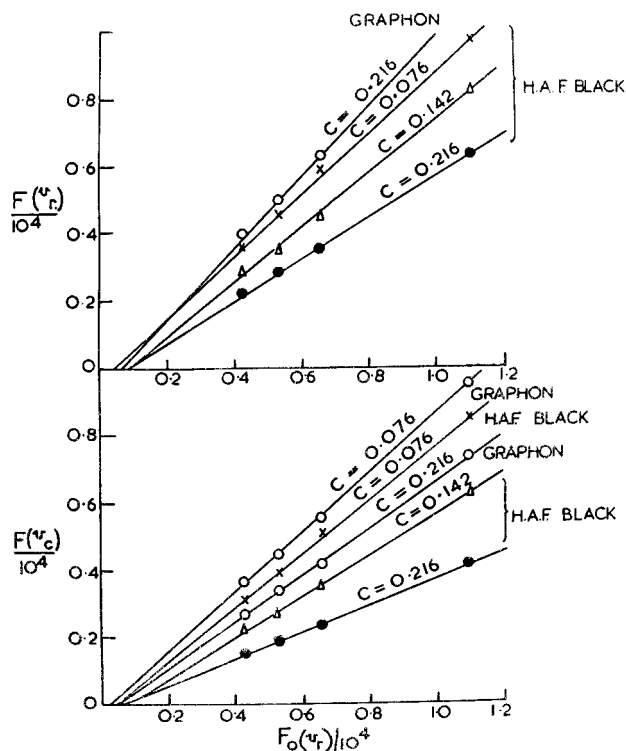


Figure 1 Experimental basis of the hard fraction model for equilibrium swelling (v_r) of reinforced SBR vulcanizates: The upper graph relates Flory function $F(v_r)$ to corresponding $F_o(v_r)$ without carbon black; the lower graph of $F(v_c)$ where v_c counts black as rubber. Adapted from Blanchard.¹⁶

Table III Experimental Basis for Model of Swelling of SBR

	Volume Fraction, C	Linkage Reinforcement ϕ^\dagger from eq. (8)	Calibration γ_c	
			From eq. (11) and Figure 1	Taking $\gamma_c = 1 + C$
HAF Black (wt %)				
15	0.076	1.09	1.06	1.076
30	0.142	1.22	1.13	1.142
50	0.216	1.61	1.22	1.216
65	0.263	2.23	1.28	1.263
Graphon Black (wt %)				
15	0.076	0.98	1.06	1.076
30	0.142	1.25	1.13	1.142
50	0.216	0.93	1.21	1.216
65	0.263	1.18	1.27	1.263

age $1/\phi^\dagger$. Their intercepts Λ_r/ϕ^\dagger are not quite negligible.

The volume of reinforcing carbon particles will be the main hard phase in a hard fraction model. To establish this model by an experiment, the equilibrium swelling v_r can be replaced by higher values v_c that count carbon particles as rubber. As a first step M_c can be taken as not much less than gum values $F_o(v_r)$. Then with M_c as a rough substitute for $F_o(v_r)$ in eq. (7), and adjustments Λ_c and Λ_r for carbon and hard rubber,

$$\phi^\dagger = (M_c - \Lambda_c - \Lambda_r)/\gamma_c F(v_c) \quad (9)$$

Here the factor γ_c is introduced to calibrate the model. On transposing $F(v_c)$ and ϕ^\dagger the equation becomes

$$F(v_c) = (1/\phi^\dagger \gamma_c)(M_c(1 - \Lambda_c/M_c) - \Lambda_r) \quad (10)$$

Because Λ_c/M_c is the hard fraction of carbon, we can substitute the carbon black fraction $C = \Lambda_c/M_c$. Therefore, taking $F_o(v_r)$ as the nearest measure for M_c ,

$$F(v_c) = \frac{(1 - C)}{\phi^\dagger \gamma_c} F_o(v_r) - \frac{\Lambda_r}{\phi^\dagger \gamma_c} \quad (11)$$

The application of this equation is shown by the lower graphs in Figure 1. Their slopes $(1 - C)/\phi^\dagger \gamma_c$ provide experimental estimates of the calibration factor γ_c for the model. This calibration is possible because ϕ^\dagger is known from applying eq. (8) to the slopes of the upper graphs in Figure 1. Table III shows that the results are substantially equivalent to $\gamma_c = 1 + C$. For this hard fraction model, success of the constraint factor $(1 - C)/(1$

+ C) is shown by the agreement between the two right-hand columns of Table IV. The table covers a very wide range of cures and carbon volume fractions from 0.076 to 0.263.

To allow for the total hard fraction of carbon and rubber, we can substitute a factor $(1 - C_h)/(1 + C_h)$ to replace $(1 - C)/\gamma_c = (1 - C)/(1 + C)$ in eq. (11). Moreover, the small refinement Λ_r can be subsumed in C_h so that the true linkage reinforcement ϕ can be obtained by rewriting eq. (11),

$$\phi = \frac{1 - C_h}{1 + C_h} \frac{F_o(v_r)}{F(v_c)} \quad (12)$$

Here $C_h = (1 + \beta)C$ where βC is hard rubber. Equation (12) was first published many years ago,¹⁶ except that I later introduced a front factor in a mistaken attempt^{22,23} to use v_c to obtain β . (Because I was not satisfied with the last of these conference articles,²³ it was not submitted for publication.) Corresponding to $(1 - C_h)/(1 + C_h)$ for $1/F(v_c)$, we have $(1 - \beta C)/(1 + \beta C)$ for $1/F(v_r)$. Therefore, measured (effective) values $1/F(v_r)$ can be corrected for hard occluded rubber βC by writing

$$\frac{1}{M_c} = \frac{1 - \beta C}{1 + \beta C} \frac{1}{F(v_r)} \quad (13)$$

$$\phi = \frac{1 - \beta C}{1 + \beta C} \frac{F_o(v_r)}{F(v_r)} \quad (14)$$

For reinforced rubber these constraint equations distinguish true crosslinking from effective values $1/M_c^\dagger$ and ϕ^\dagger . The occluded rubber parameter β must be independently evaluated, and this problem is discussed later.

Table IV Success of Mathematical Model for Equilibrium Swelling of Reinforced SBR

HAF Black Volume, C	Crosslinks without Black ($\times 10^4$)	Constraint Ratio, $\frac{F_o(v_r)}{F(v_c)}$	Effective Linkage Reinforcements ϕ^l	
			$\frac{F_o(v_r)}{F(v_r)}$	$\frac{1 - C}{1 + C} \frac{F_o(v_r)}{F(v_c)}$
0.076	0.91	1.30	1.13	1.12
	1.52	1.29	1.13	1.11
	1.88	1.36	1.19	1.17
	2.34	1.38	1.21	1.19
0.142	0.91	1.72	1.32	1.29
	1.52	1.88	1.45	1.41
	1.88	1.96	1.52	1.47
	2.34	1.90	1.47	1.43
0.216	0.91	2.64	1.72	1.70
	1.52	2.84	1.89 ^a	1.83
	1.88	2.85	1.90 ^b	1.84
	2.34	2.82	1.89	1.82
0.263	0.91	3.72	2.19	2.17
	1.52	3.37	2.01	1.97
	1.88	3.57	2.15	2.08
	2.34	3.50	2.13	2.04

^a Effective crosslinking $1/M_c^l = 2.87 \times 10^{-4}$.

^b Effective crosslinking $1/M_c^l = 3.57 \times 10^{-4}$.

Graphon is partially graphitized MPC black; it differs from HAF black in that it gives little linkage reinforcement and has no aggregate structure to occlude rubber. The results for Graphon black in SBR are shown in Table V. Even in this case the success of the hard fraction model is shown by close agreement between the two right-hand columns. This is because Graphon differs from inert fillers in bonding strongly enough to prevent swollen vacuoles from forming round the particles. For inert fillers such as calcium silicate, both $I/F(v_r)$ and $((1 - C)/(1 + C))(1/F(v_c))$ give spurious results because swollen vacuoles cause v_c to be the true v_r .

For fine carbon blacks, Tables IV and V taken together establish the hard fraction model for high and low extremes of carbon–rubber interaction and for a wide range of vulcanization and carbon black concentration. The model has not been tested for large particle blacks with little ability to reinforce.

Tension Modulus of Reinforced Rubber

Reinforced rubber must first be prestretched to apply the theory of rubber elasticity to near-equi-

librium conditions of tension modulus. In my theory rubber–filler bonds are broken by prestretching, and this view is supported by vacuole formation with coarse inorganic fillers. Except for occlusion of rubber by carbon particle aggregates, filler particles do not constitute a hard fraction at strains well below the prestretch; they add to network bonds but do not prevent chain molecule extension around the hard particles. Dannenberg,²⁶ Boonstra,²⁷ and Brennan et al.²⁸ envisioned slip relaxation and molecular rearrangement during prestretching, with elimination of short chains between carbon particles. The drastic softening by prestressing is illustrated in Figure 2 for MPC black particles having little aggregate structure to occlude the rubber. These stress–strain curves^{10,16} were obtained at 20 mL/min.

A feature of Figure 2 is the spectacular stress upturn or strain hardening at elongations approaching the prestretch ratio α_b . Extension beyond this “breaking” strain α_b of the surviving network is possible only because more network bonds are broken by higher prestresses S . This implies that the force per linkage factor $X = \alpha_b S / G^{2/3}$ is operative for rubber that is stretched hard like a plastic. Blanchard^{15,16} showed that his em-

Table V Success of Hard Fraction Model for Slight Linkage Reinforcement by Graphon in SBR

Graphon Volume Fraction, C	Crosslinks without Black ($\times 10^4$)	Linkage Reinforcement $\phi = \phi^l$	
		$\frac{F_o(v_r)}{F(v_r)}$	$\frac{1 - C F_o(v_r)}{1 + C F(v_c)}$
0.076	0.91	1.01	0.99
	1.52	1.03	1.01
	1.88	1.05	1.03
	2.34	1.03	1.01
0.142	0.91	1.15	1.13
	1.52	1.04	1.01
	1.88	1.05	1.02
	2.34	1.04	1.01
0.216	0.91	0.98	0.97
	1.52	1.04	1.01
	1.88	1.07	1.04
	2.34	1.07	1.03
0.263	0.91	1.10	1.09
	1.52	1.03	1.01
	1.88	1.02	1.00
	2.34	1.02	0.99

pirical term μ is due to non-Gaussian chain displacements at high strains and is closely related to the modulus G at moderate strains. Hence, determination of μ is unnecessary; thus we can dispense with the graphs and calculations representing the multipoint logarithmic upturn.

For small elongations, several experimental points and a second modulus parameter C_2 are needed to define the Mooney¹⁸ and Rivlin et al.¹⁹ deviation from theory. Moreover, particle contact forces contribute to modulus at the lowest elongations.¹⁵ For a range of elongations Figure 3 shows moduli G from eq. (2) for 50 phr HAF black in NR.²⁹ Accordingly, a single 100% strain ($\alpha = 2$) is now chosen to fully dispense with multipoint curves and the resulting graphs and calculations. Theoretically, this choice differs by 10% from the Blanchard–Parkinson G for the whole stress–strain curve.¹⁰ For 100–180% stretches, the modulus G from eq. (2) is constant in Figure 3 in accordance with basic elasticity theory. This was achieved by applying much greater prestretches of 150–300% to minimize short chains and temporary entanglements. Taken together with $\alpha = 2$ for the G measurement, this identifies the circumstances in which there is negligible $2C_2/\alpha$ and $2C_1 \approx G$ in the Mooney–Rivlin equation for deviation from the basic theory.

To further simplify the procedure, each test

piece should be prestretched only once and only two prestretches should be chosen. These two prestretches α_b should be very different for accurate solution of the simultaneous equations from eq. (4). The choice $\alpha_b \gg \alpha \gg 2$ is also made to avoid stress upturn for $\alpha \rightarrow \alpha_b$. Then for two prestretches $\alpha_b = 3$ and $\alpha_b = 4.5$ or 5, corresponding prestresses S_1 and S_2 , moduli G_1 and G_2 , and force per linkage factors $X_1 = \alpha_b S_1 / G_1^{2/3}$ and $X_2 = \alpha_b S_2 / G_2^{2/3}$,

$$G_1 = G^* + G_r F(X_1) \quad (15)$$

$$G_2 = G^* + G_r F(X_2) \quad (16)$$

Here G^* is the primary modulus, G_r is the removable (secondary) modulus, and $F(X)$ is given by eq. (6). Because $k = 0.276$ for all rubbers and fillers, the secondary modulus G_r is known from

$$G_r = (G_1 - G_2) / (F(X_1) - F(X_2)) \quad (17)$$

Because G_2 is the closest to removal of G_r , the effect of errors in G_r is best minimized by using G_2 rather than G_1 to calculate G^* . Hence, the residual or primary modulus is given by

$$G^* = G_2 - \frac{(G_1 - G_2)F(X_2)}{F(X_1) - F(X_2)} \quad (18)$$

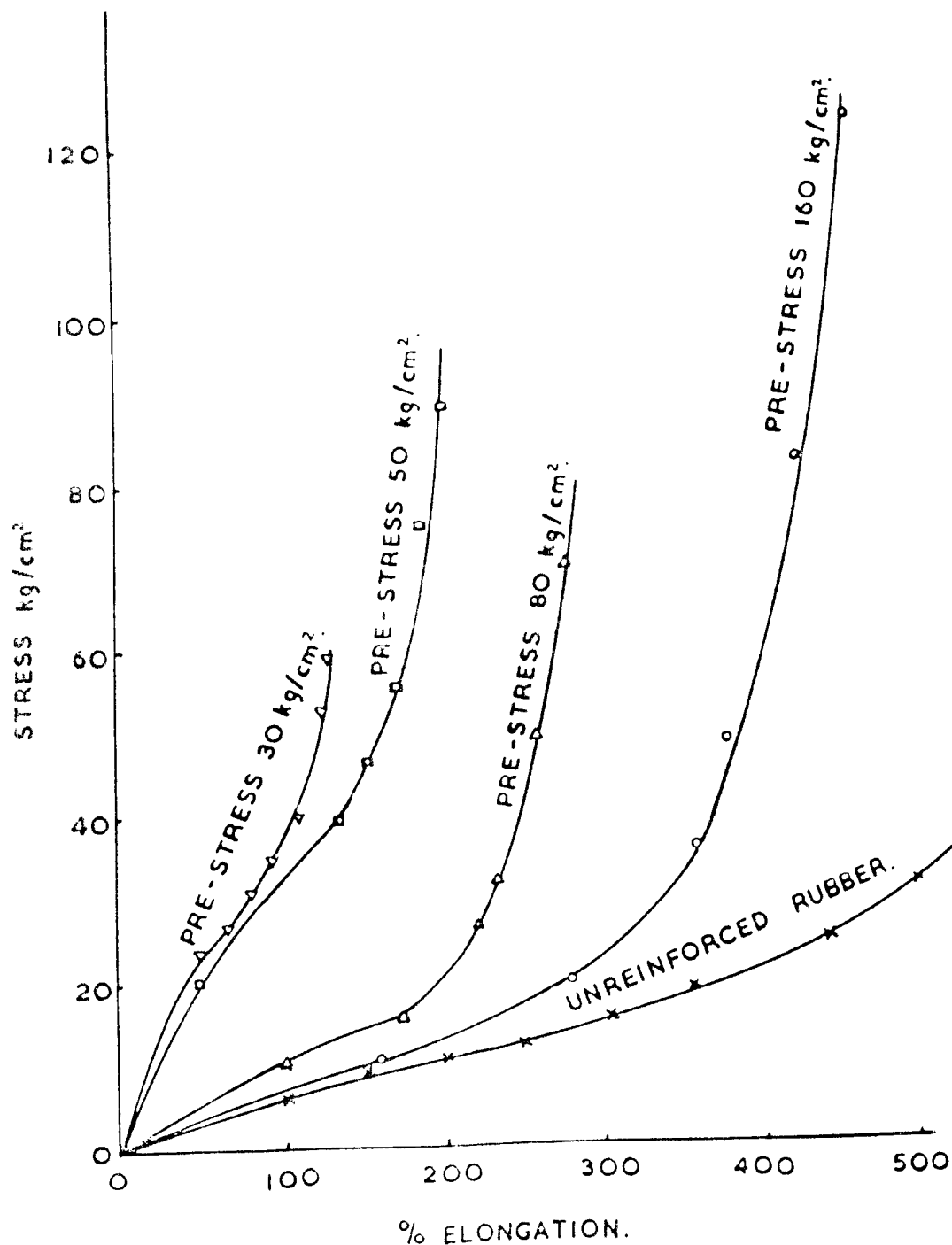


Figure 2 Stress-strain curves for prestressed natural rubber (NR) vulcanizates reinforced by 50 phr MPC black ($V = 0.26$). Adapted from Blanchard.¹⁶

For 50-phr HAF black the G^* in previous articles was 5.2 kg/cm^2 for SBR¹¹ and 5.4 kg/cm^2 for NR.¹⁰ For a corresponding prestretched gum vulcanizate, G^* was about 3.7 kg/cm^2 according to this previous work.¹² Hence, for $V = 0.26$ the measured (effective) linkage reinforcement was $(1 + V)G^*/$

3.7 (i.e., 1.77 for HAF-SBR and 1.84 for HAF-NR). This is in fair agreement with the effective linkage reinforcement $\phi^1 \approx 1.9$ from equilibrium swelling (see Table IV). This agreement shows that the primary aggregate structure of carbon black is not broken down by prestretching.

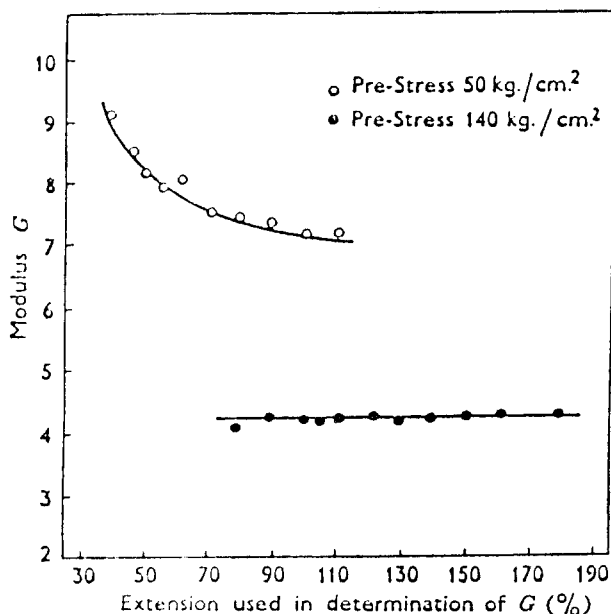


Figure 3 Constant modulus G for NR-HAF black at elongations of ca. 100% (i.e., negligible Mooney-Rivlin deviation from basic theory at $\alpha = 2.0$). Adapted from Blanchard.²⁹

Blanchard and Parkinson argued that the primary black structure had survived milling into rubber and so would not be broken by prestretching. With the factor $(1 + V)$ to allow for network dilution by carbon black, the measured (effective) crosslinking $1/M_c^l$ is given by

$$\frac{1}{M_c^l} = \frac{(1 + V)G^*}{\rho RT} \quad (19)$$

Here V is the volume of carbon black per milliliter of rubber, ρ is the rubber density, and RT is the product of the gas constant and absolute temperature. From $(1 + V)G^*$ the effective crosslinking $1/M_c^l$ is ca. 3.0×10^{-4} for $V = 0.26$ of HAF black in SBR. This compares well with between 2.87×10^{-4} and 3.57×10^{-4} from equilibrium swelling (see $C = 0.216$ and the two middle cures in Table IV).

Effect of Primary Aggregation on Effective Crosslinking

Medalia^{30,31} suggested that primary aggregates of carbon black restrict rubber deformation by occlusion of the rubber. On the basis of Medalia's conclusions, Sambrook³² suggested that rubber occluded within particle aggregates is responsible for the effects of primary structure on modulus,

etc. My hard fraction model established the effect of occluded rubber on the elastic reaction to equilibrium swelling [see eq. (13)]. In the case of a reaction to elongation, the corresponding effect of occluded rubber is to increase equilibrium moduli G by a factor $(1 + \beta C)/(1 - \beta C)$. Therefore, to relate primary modulus G^* to true crosslinking $1/M_c$, it must be corrected by $(1 - \beta C)/(1 + \beta C)$. Hence, the true crosslinking is

$$\frac{1}{M_c} = (1 + V) \frac{1 - \beta C}{1 + \beta C} \frac{G^*}{\rho RT} \quad (20)$$

where G^* is from eqs. (2) and (18). In practice the structure parameter β will include any effect of the chain configuration of the structure (i.e., aggregate shape factor). Because the primary structure may be partially broken down by shear mixing into rubber, it would be best if β could be determined from the secondary modulus G_r of the mixed rubber.

Equilibrium tension modulus depends on the carbon black loading and primary aggregate structure, not appreciably on the particle size of the black. Hence, the structure parameter β should be obtainable from the secondary modulus G_r , provided that the test prescription and vulcanization are suitably standardized.

For rubber without reinforcement the small prestress softening can be expressed crudely by eq. (17) with G_r defined as the gum value G_{r_0} . Let g be the increase in G_r per unit volume of a carbon black having negligible structure. The structure parameter β increases G_r in the ratio $(1 + \beta C)/(1 - \beta C)$. Therefore, we can write

$$\begin{aligned} (1 + V)(G_r - G_{r_0}) \\ = gV(1 + \beta C)/(1 - \beta C) \end{aligned} \quad (21)$$

As $C = V/(1 + V)$ this becomes

$$G_r = G_{r_0} + gC(1 + \beta C)/(1 - \beta C) \quad (22)$$

The constant g could be determined from the G_r of blacks having negligible structure in the range of modern furnace blacks. Then $g = (G_r - G_{r_0})/C$ for $\beta C = 0$ in eq. (22). For G_{r_0} a rough estimate of 0.9 was given in earlier articles.^{11,12} Preferably, taking negligible structure $\beta = 0$ in eq. (22) and graphing G_r for low structure blacks against volume concentration C , both G_{r_0} and g could together be obtained from the intercept G_{r_0} and slope g of the graph. This has the advantage that some synthetic rubbers are too weak to determine

G_r without a little reinforcing black. Equation (22) predicts that the graph will have upward (C^2) curvature at high concentrations if the black does not have negligible structure $\beta = 0$. For accurate calculation of g this procedure should use the present test prescription and a standard rubber compound. Moreover, the standard compound should be chosen for applying eq. (22) to determine β from G_r values for the range of modern furnace blacks. With G_r and G_{r_0} from eq. (17), β could be calculated by transposing eq. (22),

$$\beta C = \frac{G_r - G_{r_0} - gC}{G_r - G_{r_0} + gC} \quad (23)$$

The aggregate structure of carbon blacks is usually compared by measurements of oil absorption. This involves adding dibutyl phthallate while working the oil and black with a spatula until round pellets are formed. The disadvantages of this measurement are that it includes surplus oil in fortuitous structures, and it includes oil in some primary structure that will not survive shear mixing into rubber. I suggest that the surplus oil might be floated off by shearing the oil and black pellets in water followed by centrifuging to deposit all black and relevantly associated oil and black. This proposal might be refined by selecting a shear rate sufficient to produce a 1 : 1 relation with the above β from the G_r of rubber mixes.

DISCUSSION

Bueche³³ and Kraus³⁴ considered that the Blanchard–Parkinson approach did not provide an adequate basis for quantitative treatment of reinforcement. They argued that prestretch softening is due to short chains at the limit of their elongation. Taking this into account, Blanchard suggested²¹ that Blanchard–Parkinson linkage strengths partly reflect vulnerability to overall stress, not just the intrinsic strength of macromolecular bonds. But emphasis on the part played by short chains is not justified by the evidence of the experiment. After prestretching, the stress–strain shape indicates that highly extended short chains contribute substantially to modulus only at extensions approaching the prestretch. My view is that prestretching detaches some normal chains and detaches most of a relatively small number of short chains. At extensions near the prestretch, the stress contribution of the few remaining short chains is disproportionate, just as

in rubber composites a minor fraction of textile fibers eliminates rubbery extensibility. After prestretching, the modulus G at much lower strains is determined by the majority of normally stretched chains in accordance with basic elasticity theory [i.e., eq. (2)].

Bueche³³ pointed out that some of the energy involved in breaking bonds is lost in friction as broken chains retract. Therefore, Blanchard¹¹ was wrong to estimate energies of the broken bonds; he should have claimed only that linkage strength factors X were correlated to the energy dissipated in breaking them. Bueche³³ argued that G_r in part reflects a slow return to equilibrium of displaced particles, entanglements, and network junctions, hence, the importance of having a test prescription for G_r that minimizes C_2 , and of adopting a standard compound when using G_r to evaluate the structure parameter β .

Erman and Mark³⁵ and Medalia and Kraus³⁶ asserted that the basic elasticity theory is not quantitatively applicable to reinforced systems. However, the primary modulus G^* is obtained by large prestretches, and in that case the basic eq. (2) applies over a very wide range of stretches from 100% up to near the prestretch. Moreover, this study has shown that derivation of apparent crosslinking from G^* is in good agreement with that from equilibrium swelling. How to measure and compare the crosslinking of vulcanizates is of great interest to rubber technologists.

Temporary chain entanglements are a factor in causing errors of applying the basic theory. Theoretical treatments of entanglements have been given by Deam and Edwards,³⁷ Ball and colleagues,³⁸ and Edwards and Vilgis.³⁹ These approaches are referred to as the “slip link” model. There are also the “constrained-junction” models of Ronca and Allegra⁴⁰ and Flory and Erman.⁴¹ However, the temporary entanglement modulus $2C_2$ can be made negligible by measuring the modulus at 100% and by using much greater prestretches. Moreover, Berry et al.¹³ showed that there is close agreement between G^* and $2C_1$ for highly prestretched vulcanizates. Therefore, temporary entanglements do not preclude quantitative application of basic elasticity theory.

For many technological comparisons, trapped chain entanglements can be regarded as an adjunct of crosslinking, that is, without allowance for their number. But the basic equations may require establishment of front factors to make comparisons between some polymers and conditions of vulcanization.³⁵

The theoretical hydrodynamic factor ($1 + 2.5C$)

for particle concentrations C was not used, because the underlying assumptions do not apply to equilibrium swelling or to tension modulus at high stretches. However, dynamic modulus is obtained in very different conditions from tension modulus, and it is determined by several different properties of carbon black. Hence, $(1 + 2.5C)$ may have a base role for dynamic modulus, as envisioned by some authors. Recently, Heinrich and Vilgis⁴² investigated the dependence on dynamic strain of the viscoelastic properties of eight carbon blacks in two different rubbers. Their approach is based on the Kraus model for the strain-dependent agglomeration–deagglomeration rates of fillers. By choosing tension modulus at 100%, I avoided the low strain moduli for which filler deagglomeration occurs.^{15,29} Dynamic modulus at these low strains is of great technological importance, but is beyond the scope of this article.

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