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Stiffening Effect of Carbon Black: Its Interpretation by a Modified Guth-Gold Equation

ALIAS BIN OTHMAN* AND M.J. GREGORY**

Increasing the volume fraction of carbon black in natural rubber vulcanisates results in a non-linear increase in the modulus. This stiffening effect is usually explained in terms of the Guth-Gold type of equation which relates the modulus to the shape factor, occluded volume and the hydrodynamic effects of the filler. However, work with natural rubber crosslinked using different vulcanising systems shows that the Guth-Gold type of equation, which has hitherto been used, is inadequate for predicting the modulus of filled rubbers. The discrepancy between different vulcanising systems could be attributed to the effect of carbon black on crosslinking efficiency. A modification of the equation which takes this into account has been found to give a better description of the experimental results.

The use of fillers in rubber ranks as one of the two most important processes in rubber technology — only vulcanisation can be considered to surpass it in its universal application.

Carbon black is the principal filler used in rubbers. Generally, the incorporation of carbon black alters the properties of rubber; some show an improvement while others deteriorate[1]. This paper discusses the stiffening effect of carbon black.

The Hydrodynamic Theory

The stiffening effect of carbon black has been a subject of considerable investigation since the early twentieth century, but the phenomena involved in the stiffening effect still remain the subject of considerable controversy. At present, the hydrodynamic theory, which is appropriate to large strains, has been the most cited theory explaining the stiffening effect.

In the hydrodynamic theory, the rubber is regarded as a continuum and attention is focussed on the effect of carbon black without concern for the behaviour of the rubber at the molecular level. The mechanism proposed was derived mainly from the formally identical problem of the increase in viscosity of a liquid caused by a suspension of solid particles. For rigid particles at concentrations sufficiently small for interaction between particles to be neglected, the viscosity of the suspension is given by the Einstein equation[2]:

$$\eta = \eta_o (1 + 2.5C) \qquad ...1$$

where η and η_o are the viscosities of the suspension and liquid respectively and C is the volume concentration of particles.

Use of the viscosity relationship given by *Equation 1* was proposed for the analogous elastic problem of rubber containing fillers, with the viscosity η replaced by Young's modulus E. Smallwood[3] showed that the stress-strain data of several large particle size fillers at low concentration fitted the relationship:

$$E = E_o (1 + 2.5\ \phi) \qquad ...2$$

where E and E_o are the Young's Moduli of filled and unfilled rubbers respectively and ϕ is the volume fraction of filler. To take into account higher concentrations of filler by considering the hydrodynamic interactions between pairs of particles, Guth and Gold[4] added an

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

**Deceased. Formerly with Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8 NL, United Kingdom

extra term involving the square of the concentration of the fillers to the Smallwood equation:

$$E = E_o (1 + 2.5 \phi + 14.1 \phi^2) \quad ...3$$

Guth[5] found that *Equation 3* fitted the data for rubber filled with fine thermal black up to a volume fraction of 0.3. *Equation 3* however could not be used to predict the modulus of rubber containing fillers which exist as a cluster of particles forming asymmetric aggregates. To take into account the asymmetric nature of carbon black aggregates, Guth proposed a modified equation:

$$E = E_o (1 + 0.67 f\phi + 1.62 f^2 \phi^2) \quad ...4$$

where f is the ratio of the length to diameter of the aggregate (or the shape factor). With a proper choice of the value of f, *Equation 4* was able to account for the variation of modulus E for several rubber-filler systems. For systems containing up to about 30% volume concentration of N330 black, a shape factor of 6.5 was required[6]. However, later studies of the shape of carbon black particles and aggregates using the electron microscope[7] indicated that the shape factors of most blacks are less than 6.5; they are usually in the range of about 2 to 3. Thus, if the value of the shape factor f, is taken as between 2 and 3, the predicted value of E will be much lower than the experimental values given by Mullins and Tobin[6].

With rubbers filled with carbon black, the void spaces which are present within carbon black aggregates/agglomerates are filled with rubber. The rubber is occluded within the interstices of the carbon black structures. When subjected to stress, this occluded rubber is shielded to a significant extent from deformation which the bulk of the rubber undergoes and it thus acts as part of the filler rather than as part of the rubber matrix[8,9,10].

Sambrook[11] proposed that the effective volume fraction of carbon black, ϕ', *i.e.* the volume fraction of carbon black plus the volume fraction of occluded rubber, should be used in *Equation 3* instead of the volume fraction of filler, ϕ. The value of ϕ' could be calculated from the value of ϕ and the DBPA value using the relationship given by Medalia[8]:

$$\frac{\phi'}{\phi} = \frac{46.75 + \text{DBPA}}{68.26} \quad ...5$$

where DBPA is the amount of dibutyl phthalate absorbed per 100 g carbon black. Using the values of ϕ', Sambrook observed that the values of Youngs' modulus obtained were about 20% higher than experimental values, suggesting that the use of *Equation 5* in conjunction with *Equation 3* does not adequately describe the stiffening effects of carbon black.

Later, Medalia[12] observed that the effective volume fraction of carbon black (ϕ') was equal to the volume fraction of carbon black (ϕ) plus about half of the occluded volume of rubber, *i.e.*

$$\phi' = \phi + 0.5\phi_{occ} \quad ...6$$

where ϕ_{occ} is the volume fraction of the occluded rubber. This signifies that only about half of the total occluded rubber (as calculated from the DBPA values) is shielded from deformation and acts as filler. Using the new effectiveness factor, Medalia[13] showed that the experimental and calculated values of shear modulus at 10% strain amplitude for several filled rubbers were in reasonably good agreement.

EXPERIMENTAL

Sample Preparation

All vulcanisates were based on natural rubber having the formulation shown in *Table 1*. Four different types of carbon black were used; they were: N110, N347, N550 and N762, and their relevant properties are as listed in *Table 2*.

The vulcanising systems used were the conventional, semi-EV and EV sulphur systems *(Table 1)* having CBS:S ratios of 0.6:3, 1:1.8 and 6:0.3 p.p.h.r. respectively and the peroxide system with dicumyl peroxide of 1-4 p.p.h.r.

Vulcanisates were prepared from masterbatches which were mixed in a 1-litre capacity laboratory internal mixer. Vulcanising agents

TABLE 1. NATURAL RUBBER FORMULATION

Compound	Formulation (p.p.h.r.)	
	Sulphur system	Peroxide system
Natural rubber (SMR L)	100	100
Carbon black[a]	0–80	0–80
Zinc oxide	5	
Stearic acid[c]	1.5	
Antioxidant, TMQ[d]	1	1
Process oil[e]	0–8	0–8
Sulphur[c]	0.3–3	
CBS[f]	0.6–6	
Dicumyl peroxide[g]		1–4

p.p.h.r. = parts per hundred parts of rubber by weight
[a]Cabot Corporation
[b]Durham Chemical Ltd.; 99.9% pure (dry basis)
[c]Anchor Chemical Company Ltd., England
[d]Monsanto Ltd., London; poly 2,2,4-trimethyl 1,2-dihydroquinoline, 98.3% active
[e]Shell UK; Dutrex 729
[f]Monsanto Ltd.; N-cyclohexyl benzothiazole-2-sulphenamide
[g]Hercules Powder Company Ltd.; Dicup R, 99% pure

TABLE 2. GRADES OF CARBON BLACK USED

Type of carbon black (ASTM designation)	Particle diameter (nm)	E.M. surface area (m^2/g)
N110	11–19	125–155
N347	26–30	80–100
N550	40–48	36–52
N762	61–100	17–33

were incorporated into 300 g portions of masterbatches using an open two-roll mill having rollers 330 mm length and 152 mm diameter. The temperature of the mill was thermostatically maintained at about 60°C and the friction ratio of the front to back roller was 1:1.25.

Rubber sheets were cured in a square frame mould, of dimensions 228 × 228 × 1.5 mm in steam-heated presses at 150°C one day after the addition of vulcanising agents. Sulphur-based vulcanisates were cured for the time required to develop maximum torque on a Monsanto rheometer at 150°C, while for the peroxide-based system, the vulcanisation time was 90 min. All tensile test-pieces of 3.8 mm width and 100 mm test length were die-stamped from moulded sheets using the appropriate dies.

Stress-strain Measurements

All measurements were carried out on samples which were conditioned for 24 h at room temperature (23°C) after vulcanisation. The measurements of force and deflection were carried out using a tensile testing machine on previously undeformed samples. The samples were held using a spring-loaded pad grip and extended at a rate of 20% extension per minute.

The recorder chart speed was 200 mm per minute and zero deflection was taken as the zero load position.

The extension ratio, λ, was taken as the ratio of the deformed length to the original undeformed length of the sample and the nominal stress was obtained by dividing the applied load by cross-section of the sample. The modulus A was taken from the slope of the linear portion of the plot of nominal stress (σ) against $\lambda-\lambda^{-2}$ *(Figure 1)*.

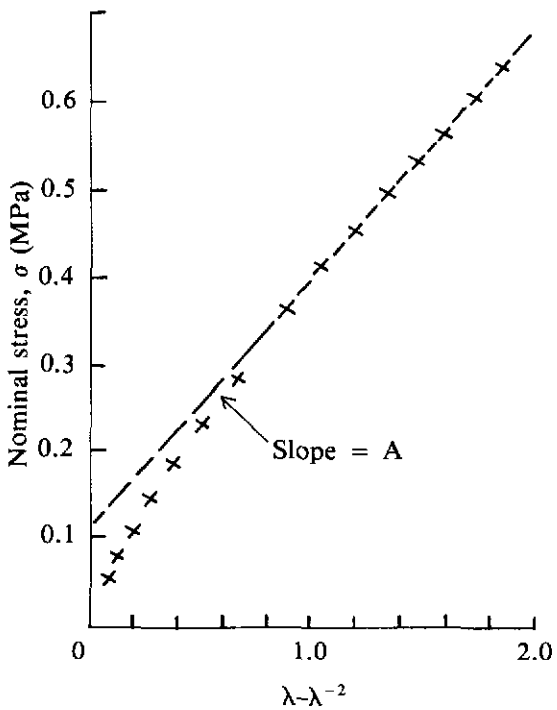

Figure 1. Stress-strain behaviour of rubber filled with 20 p.p.h.r. carbon black (N347).

Equilibrium Swelling Measurements

Swelling measurements were carried out on 25 mm-square samples, cut from 1 mm-thick moulded sheet. The pre-weighed samples were swollen in n-decane contained in a covered container placed in the dark for one week, during which the weights of the samples were regularly monitored. The swollen samples were subsequently transferred into fresh solvent (*i.e.* n-decane) and left to stand for several more days. At equilibrium swelling (*i.e.* when the swollen weight remained constant) the weights of the swollen samples were recorded. The samples were subsequently deswollen in an oven at 60°C. The difference between the weight of swollen and deswollen samples was taken as the true weight of the solvent imbibed.

During swelling, a small proportion of non-rubbers leached out, since they are soluble in the swelling agent[14]. The amount of non-rubbers leaching out was very small (about 1%) and no significant effect on the results was expected.

RESULTS AND DISCUSSION

The Volume Filling Effect

Typical values of modulus A are given in *Table 3*. As expected, the presence of carbon black gives a non-linear increase in the values of modulus A. The increase in modulus with increasing concentration of carbon black is usually described by the use of the Guth-Gold[4] *type of hydrodynamic equation. When the* same principle is applied to the increase in values of A for filled rubber relative to that of the unfilled rubber (A_o), the Guth-Gold type of equation takes the form:

$$A = A_o (1 + \alpha\phi + \beta\phi^2) \qquad ...7$$

where α and β are constants associated with the shape factor and occluded volume effects. Rearranging *Equation 7* gives:

$$\frac{\left(\frac{A}{A_o} - 1\right)}{\phi} = \alpha + \beta\phi \qquad ...8$$

If *Equation 8* is valid, plots of $(A/A_o - 1)/\phi$ *versus* ϕ should be a straight line of slope β and intercept α, the constants of which should be the same for rubbers filled with the same type of carbon black since the constants are functions of occluded volume and shape factor. However, as *Figure 2* shows, the values of α and β were independent of the types of carbon black but

TABLE 3. TYPICAL VALUES OF MODULUS A

CBS/S ratio (p.p.h.r.)	Type of black	Modulus A at different black loadings (MPa)		
		20 p.p.h.r.	40 p.p.h.r.	60 p.p.h.r.
0.5/0.9	N550	0.26	0.41	0.59
1.0/1.8		0.56	0.79	1.10
1.5/2.7		0.79	1.13	1.51
0.5/0.9	N347	0.28	0.36	0.62
1.0/1.8		0.52	0.76	1.35
1.5/2.7		0.80	1.13	2.05

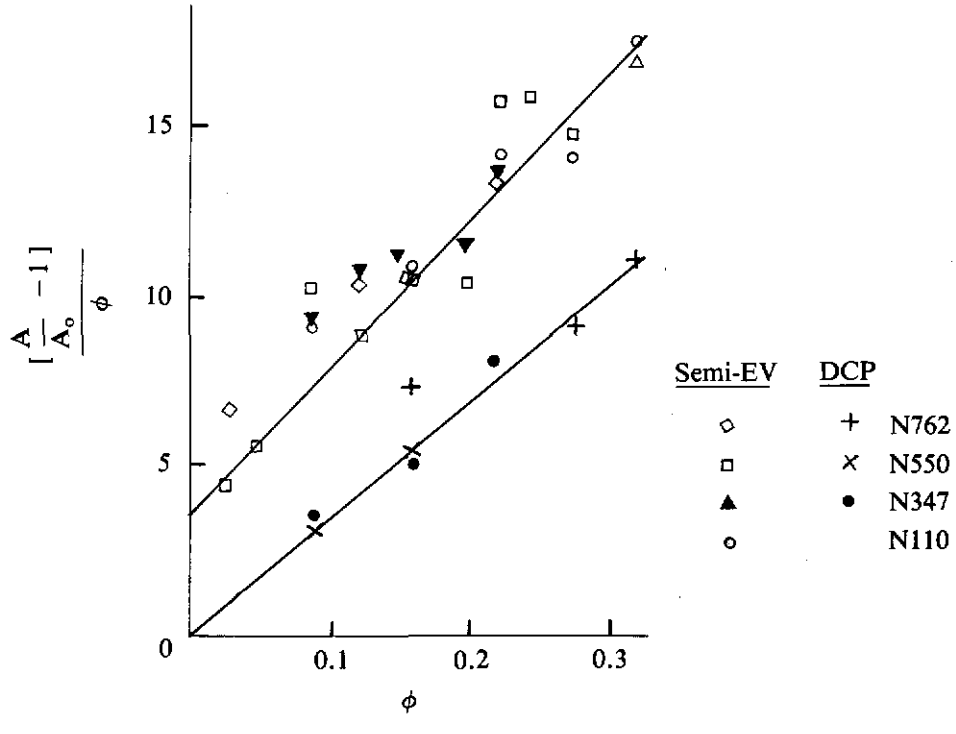

Figure 2. Influence of vulcanising systems and types of black on $[(A/A_o)-1]/\phi$ values.

depended on the two vulcanising systems used. This suggests that the difference in shape factor and occluded volume of carbon black gives no significant change in the values of the slope and intercept of the $(A/A_o-1)/\phi$ *versus* ϕ plots. Hence it must be assumed that other factors, in addition to the volume filling effects, determined the stiffening effects of carbon black.

The Enhancement of Crosslink Density

Several authors[15,16,17] have reported that there were differences between the cure efficiency

of black-filled peroxide and sulphur-cured rubbers. Kraus[15] for instance stated that the incorporation of 50 p.h.r. N330 black resulted in a 40% increase in the crosslinking efficiency for the sulphur-cured rubbers, while for the corresponding peroxide-cured rubbers, he obtained a maximum apparent 'black contribution' of about 20%. Porter[17] reported that the presence of carbon black in the conventional N-cyclohexyl benzothiazole-2-sulphenamide (CBS)-accelerated sulphur vulcanising system increased the crosslinking efficiency of rubber, but with the peroxide vulcanising system, particularly at higher crosslink density, it tended to suppress it. Based on these reports, it is likely that the differences observed between the results for rubbers crosslinked using the peroxide- and sulphur-based vulcanising systems shown in *Figure 2* were due to the differences in their cure efficiencies.

If the presence of carbon black alters the crosslink density of the sulphur- and peroxide-cured rubbers, *Equation 7* does not adequately describe the stiffening effects of carbon black. To take into account the changes in the rubber matrix, it is proposed that *Equation 7* takes the form:

$$A = A_o F(\phi) [1 + \alpha\phi + \beta\phi^2] \quad ...9$$

where $F(\phi)$ is a function which is associated with the change in modulus of the rubber matrix due to the presence of carbon black, which may be different for different vulcanising systems. If $F(\phi)$ and $F'(\phi)$ are the functions for peroxide- and sulphur-cured rubbers respectively,

$$\left[\frac{A}{A_o}\right]_{CBS/S} = \frac{F'(\phi)}{F(\phi)} \left[\frac{A}{A_o}\right]_{DCP} \quad ...10$$

where the ratios $\left[\frac{A}{A_o}\right]_{CBS/S}$ and $\left[\frac{A}{A_o}\right]_{DCP}$ are those for rubbers crosslinked using sulphur and peroxide vulcanising systems respectively.

There is no evidence to indicate whether the differences in the crosslinking efficiencies between the peroxide- and sulphur-based vulcanising systems are due to an enhancement of the crosslinking efficiency for the latter or the suppression of the crosslinking efficiency of the former or both. However, since we are interested in the differences between the crosslinking efficiencies of the two vulcanising systems, for simplicity, it is assumed that the crosslink density of the peroxide-cured rubbers is independent of filler loading. The modulus of filled rubbers crosslinked using dicumyl peroxide is then given by:

$$A = A_o (1 + \alpha\phi + \beta\phi^2) \quad ...11$$

For the corresponding sulphur vulcanising system, we may therefore write:

$$\frac{\left[\frac{A}{A_o}\right]_{CBS/S}}{F'(\phi)} = 1 + \alpha\phi + \beta\phi^2 \quad ...12$$

where $(1 + \alpha\phi + \beta\phi^2)$ is the scaling factor due to the volume filling effects of the black. Using *Equation 12,* values of $F'(\phi)$ for rubbers crosslinked using sulphur vulcanising systems may be estimated using the experimental values of A and A_o and the values of α and β for the corresponding rubbers crosslinked using the peroxide vulcanising system.

For rubbers crosslinked using the sulphur vulcanising system (*i.e.* semi-EV, CBS/S), results *(Table 4)* show that $F'(\phi)$ increases with black loading up to about 20 p.p.h.r., after which it remains fairly constant. At black loadings of more than 10 p.p.h.r., about 40%–50% increase in the $F'(\phi)$ value over that of the unfilled rubber was observed. The function $F'(\phi)$ appears to be independent of crosslink density and the type of black used.

Determination of the crosslink density of filled rubbers and hence the term $F(\phi)$ could not be made directly because no direct technique is available. For unfilled rubbers, the number of crosslinks present can be determined from equilibrium swelling data using the Flory-Rehner equation[18], relating the volume fraction of rubber (V_r) and the molecular weight between crosslinks (M_c) namely:

$$M_c = \frac{-\rho V V^{1/3} r}{[ln(1 - V_r) + V_r + \chi V_r^2]} \quad ...13$$

TABLE 4. VALUES OF F'(ϕ) FOR SULPHUR-CURED RUBBERS

CBS/S ratio (p.p.h.r.)	Type of black	Value of F'(ϕ) at different black loadings				
		5 p.p.h.r.	10 p.p.h.r.	20 p.p.h.r.	40 p.p.h.r.	60 p.p.h.r.
0.5/0.9	N550	0.98	1.25	1.38	1.45	1.35
1.0/1.8		1.13	1.32	1.65	1.56	1.53
1.5/2.7		0.98	1.16	1.40	1.34	1.26
0.5/0.9	N347	1.11	0.93	1.43	1.28	1.54
1.0/1.8		1.09	1.21	1.62	1.55	1.87
1.5/2.7		1.07	1.10	1.35	1.34	1.71

where ρ is the density of rubber, V is the molar volume of the solvent and χ is the solvent-rubber interaction parameter. In the presence of fillers, *Equation 13* fails because swelling is also restricted by the fillers and the value of V_r will not represent that of the rubber matrix. However if the equivalent value of V_r for the rubber matrix is known, the value of M_c and hence the crosslink density ($\nu = \rho/2M_c$) can be calculated.

Crosslink Density of Filled Rubbers

The dependence of degree of restriction of swelling on the volume fraction of filler has been quantitatively investigated by Kraus[15], Lorenz and Parks[16], and Porter[17]. Kraus' investigations were based on a model which assumed that the rubber molecules covering the surfaces of filler particles were not displaced by swelling agents, and were not able to swell at all. Away from these layers, restriction to swelling was assumed to decrease with distance from the filler surfaces, until at a certain distance, the rubber matrix swelled normally, that is, to the extent of the corresponding unfilled rubber. Using different polymers, several sulphur vulcanising systems and solvents and different crosslink densities, Kraus obtained the relation:

$$\frac{V_{r_o}}{V_r} = 1-[3c(1-V_{r_o}^{1/3})+V_{r_o}-1]\left[\frac{\phi}{1-\phi}\right] \quad ...14$$

where V_{r_o} and V_r are the volume fractions of rubber matrix for unfilled and filled rubbers respectively and c is a constant for a given filler. Lorenz and Parks[16] on the other hand considered restricted swelling of the rubber matrix in the neighbourhood of filler particles. The zones nearest to filler particles were considered to exhibit the smallest swelling and zones sufficiently far from filler particles exhibited the same swelling as the unfilled rubber. For N330 black-filled natural rubber, Lorenz and Parks found that their results followed an empirical relationship:

$$\frac{Q}{Q_o} = ae^{-z} + b \quad ...15$$

where Q and Q_o refer to the weights of the swelling agent imbibed per unit weight of rubber matrix in filled and unfilled rubbers, z is the weight of filler per unit weight of rubber matrix and a and b are constants. A similar observation was also made by Porter[17].

Equations 14 and *15* were derived assuming that the presence of carbon black did not influence the crosslink density of the rubber. If, however, the presence of filler influences the crosslink density of rubber, the restriction of swelling will be due to one or more of the following three causes:

(a) The filler may cause an increase in crosslinking efficiency of the vulcanising agents, thus giving additional chemical crosslinks.

(b) The filler may restrict swelling of rubber because of adhesion of rubber to filler

surfaces either by physical absorption or through the formation of rubber to filler bonds.

(c) The filler may alter the affinity of swelling agent for rubber.

If the same types of carbon black and swelling agent are used, the contributions to swelling from factors (b) and (c) for rubber crosslinked using different vulcanising agents will be about the same. Any difference in swelling will be only due to factor (a).

The results obtained from the swelling tests were analysed in accordance with the treatment put forward by Kraus and Lorenz and Parks. The equation due to Kraus *(Equation 14)* predicts a linear dependence of $[1-(V_{r_o}/V_r)]$ on $[\phi/(1-\phi)]$ but the results obtained did not conform to *Equation 14*. Similar observations were made by Porter[17].

When the results were analysed in accordance with the relation due to Lorenz and Parks, they conformed with *Equation 15* in that a linear dependence of Q/Q_o on e^{-z} was obtained *(Figure 3)*. The values of Q/Q_o at equal e^{-z} were different for rubbers crosslinked using different crosslinking systems; the values for rubber crosslinked using the EV and peroxide systems were approximately the same, but both were higher than for the corresponding rubbers crosslinked using the semi-EV and conventional systems, which were also approximately the same. The two linear equations representing rubbers crosslinked using the EV or the peroxide systems and the semi-EV or the conventional systems are, respectively:

$$\left[\frac{Q}{Q_o}\right]_{\text{DCP,EV}} = 0.41e^{-z} + 0.59 \quad \ldots 16$$

$$\left[\frac{Q}{Q_o}\right]_{\text{Semi-EV, conv.}} = 0.56e^{-z} + 0.44 \quad \ldots 17$$

The difference in the slopes between *Equations 16* and *17* was about 38%, being due to the differences in restriction to swelling. These

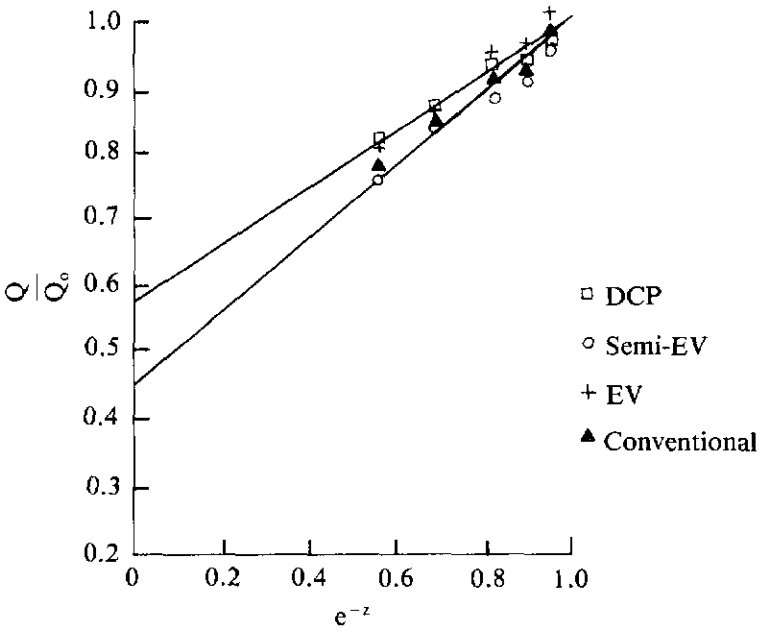

Figure 3. The swelling behaviour of carbon black (N347) filled rubbers crosslinked using different vulcanising systems.

differences were consistent with the results obtained earlier, where the values of $F'(\phi)$ for the sulphur-cured rubbers were about 40% higher than for the corresponding peroxide-cured rubbers.

To accommodate the changes in the rubber matrix, it is proposed that the Lorenz and Parks equation be modified to:

$$Q = Q_m (ae^{-z} + b) \qquad ...18$$

where Q_m replaces Q_o and a and b are constants. Q_o is the weight of swelling agent imbibed per unit weight of unfilled rubber while Q_m is the corresponding value for the rubber matrix of filled rubber. The parameter Q_m is defined as:

$$Q_m = \text{Weight of solvent imbibed/Weight of rubber matrix}$$

$$= \frac{\rho_s}{\rho} \left(\frac{1}{V_r} - 1 \right) \qquad ...19$$

where ρ_s is the density of solvent and V_r is the volume fraction of the rubber matrix.

For rubbers crosslinked using the peroxide vulcanising system, if the presence of carbon black is assumed to have no influence on the crosslink density of the rubber matrix, (from *Equation 16*):

$$Q_m = Q/(0.41e^{-z} + 0.59) \qquad ...20$$

Using the experimental values of Q, values of Q_m were calculated. For the peroxide-cured rubbers used, values of Q_m of filled rubbers were observed to be approximately the same as the equivalent unfilled rubber, in accordance with the assumption made *(Table 5)*.

The values of Q_m for the corresponding rubbers crosslinked using sulphur systems were calculated based on the values of a and b (of *Equation 18*) for that of the peroxide-cured rubbers. Using the calculated values of Q_m, values of V_r were obtained using *Equation 19*. These values of V_r which were for the rubber matrix of filled rubbers, were used for the calculations of M_c (and ν) using *Equation 13* by taking $\chi = 0.41$[17,19,20]. For rubbers crosslinked using an EV (CBS/S) system, the calculated values of M_c and crosslink density were observed to be independent of black loading *(Table 5)*. This indicates that the crosslinking efficiency of an EV system is not affected by

TABLE 5. INFLUENCE OF CARBON BLACK (N347) ON CROSSLINK DENSITY

System	Calculated value	Black loading (p.p.h.r.)					
		Unfilled	5	10	20	40	60
Dicup (3.0 p.h.r.)	Q_m	1.54	1.52	1.52	1.57	1.54	1.55
	$M_c \times 10^{-3}$ (g/mole)	4.98	4.87	4.87	5.12	4.97	5.10
EV CBS/S(6/0.3)	Q_m	1.97	1.99	1.97	2.0	1.95	1.95
	$M_c \times 10^{-3}$ (g/mole)	7.55	7.71	7.60	7.78	7.42	7.43
Semi-EV CBS/S(1.0/1.8)	Q_m	1.85	1.82	1.77	1.79	1.77	1.71
	$M_c \times 10^{-3}$ (g/mole)	6.81	6.62	6.32	6.42	6.31	5.91
Conventional CBS/S(0.6/3.0)	Q_m	1.72	1.72	1.68	1.69	1.65	1.65
	$M_c \times 10^{-3}$ (g/mole)	5.98	5.97	5.75	5.82	5.56	5.43

the presence of carbon black and is consistent with the findings of Porter[17].

For rubbers crosslinked using the conventional and semi-EV systems, M_c was observed to vary with carbon black loading. Assuming that the crosslink density of the unfilled rubber (ν_o) represents the crosslink density of the rubber matrix unaffected by the presence of carbon black, then for rubber crosslinked using the semi-EV or conventional systems, a 60 p.h.r. N347 black gave rise to about 10% to 15% higher crosslinking efficiency compared to the corresponding rubber crosslinked using an EV or peroxide system. For the four different types of vulcanising systems used, the variations in crosslink density of rubbers, plotted as ν/ν_o *versus* ϕ are shown in *Figure 4*. Some scatter of results was observed, but essentially the values of ν/ν_o for rubbers crosslinked using the semi-EV and conventional systems were linearly related to the volume fraction of carbon black (ϕ).

Modification of Guth-Gold Equation

The Guth-Gold equation which is used to predict the modulus of filled rubber relative to that of the unfilled rubber was derived based on the assumption that the presence of fillers does not enhance the crosslink density of the rubber matrix. To take into account the change in the crosslink density of rubber, it is proposed that the equation be modified to:

$$A = A_m (1 + \alpha\phi + \beta\phi^2) \qquad ...21$$

where A_m is the modulus of the rubber matrix. Using the values of M_c given in *Table 5*, values of A_m were calculated *(Table 6)*.

Contrary to that observed earlier *(Figure 2)*, when these values of A_m were used in the Guth-Gold equation instead of A_o, values of $(\frac{A}{A_m} - 1)/\phi$ at equal values of ϕ for the four different vulcanising systems used were approximately the same *(Figure 5)*. This suggests the

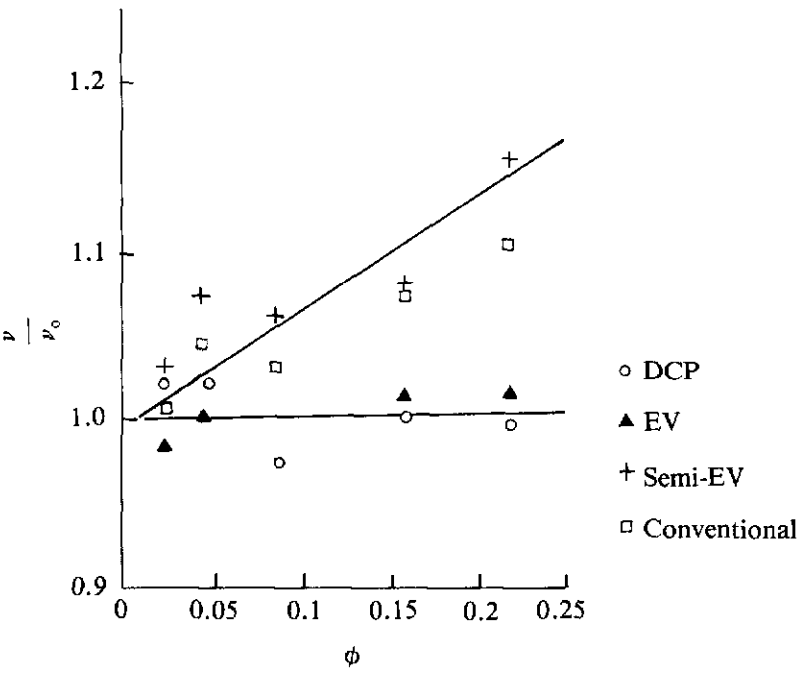

Figure 4. Variation of crosslink density with volume fraction of carbon black (N347).

TABLE 6. INFLUENCE OF CARBON BLACK ON THE EXPERIMENTAL VALUES OF A AND A_m

System	Experimental value	Black loading (p.p.h.r. N347) Unfilled	5	10	20	40	60
Peroxide	A_{expt}	0.51	0.61	0.68	0.79	1.15	1.82
	A_m	0.48	0.49	0.49	0.46	0.48	0.47
EV	A_{expt}	0.29	0.34	0.37	0.47	0.76	1.14
	A_m	0.31	0.31	0.31	0.30	0.32	0.32
Conventional	A_{expt}	0.40	0.45	0.55	0.71	1.16	1.76
	A_m	0.39	0.40	0.41	0.41	0.43	0.44

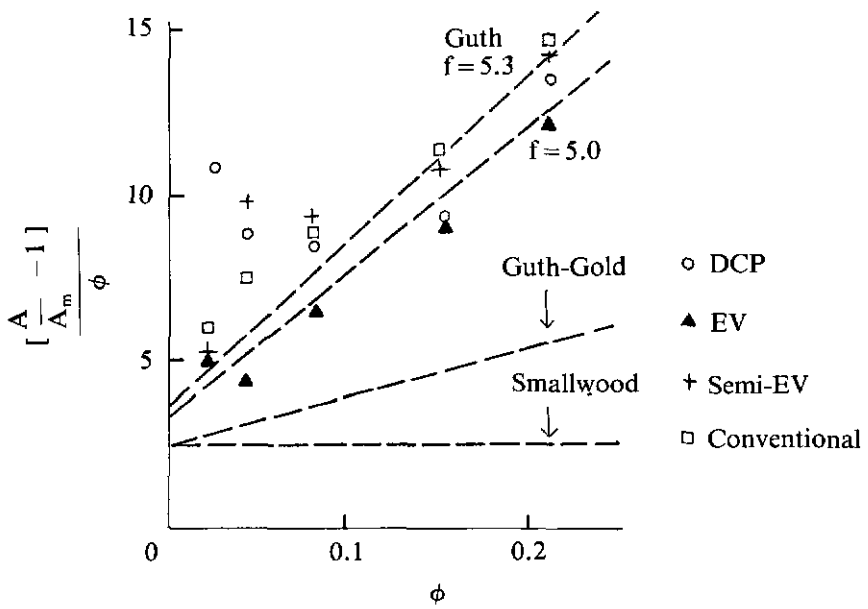

Figure 5. Comparison between the experimental $[(A/A_m)-1]/\phi$ values with the theoretical predictions for rubber filled with carbon black (N347).

proposed *Equation 21* is valid and A_m should be used in place of A_o in order to account for any change in the crosslink density of the rubber matrix.

Even though the modulus A could satisfactorily be described using *Equation 21*, the coefficients α and β did not appear to conform to the Guth-Gold equation; *Equation 3* predicts much lower moduli than the experimental values *(Figure 5)*. The use of the Guth equation *(Equation 4)* with $f = 5.3$ may be able to fit the experimental data, but such a value for f is rather high for most blacks[8], and consequently it is not favourable.

Lately[8-12] a concept of effective volume of carbon black was introduced where the total volume of 'filler' was assumed to comprise the volume fraction of filler, ϕ, and a proportion

of rubber occluded within the black structure which is shielded from deformation. The shielded rubber acts as part of filler rather than part of rubber when subjected to stress. Medalia[12] showed that about half of the occluded rubber acts as a filler and the effective volume of filler/carbon black (ϕ') was given by *(Equation 6)*:

$$\phi' = \phi + 0.5\phi_{occ} \qquad ...22$$

where ϕ_{occ} is the volume fraction of occluded rubber, which can be calculated using *Equation 5*. When the values of ϕ' were used in *Equation 21* in place of ϕ, the results obtained *(Figure 6)* were observed to conform with the Guth-Gold equation *(Equation 3)*, with a slope (β) of about 14 and an intercept (α) of 2.5. This suggests two possibilities:

- The shape factor f of the Guth equation[4] plays an insignificant part in the hydrodynamic equation used for predicting the modulus of filled rubbers
- The occluded volume causes the difference between the experimental values and those calculated using Guth-Gold/Guth type of equation shown in *Figure 5*.

From the preceding discussion, it is clear that, in order to describe the modulus of carbon black-filled rubbers over that of the unfilled rubbers, three factors have to be considered:

- The effects of enhancement of crosslink density due to the presence of carbon black
- The effective volume fraction of filler/carbon black
- The hydrodynamic effects of the fillers/carbon black.

When these factors are taken into consideration, the modulus of filled rubber *(A)* was found to conform to the equation:

$$A = A_m (1 + 2.5\phi' + 14.1\phi') \qquad ...23$$

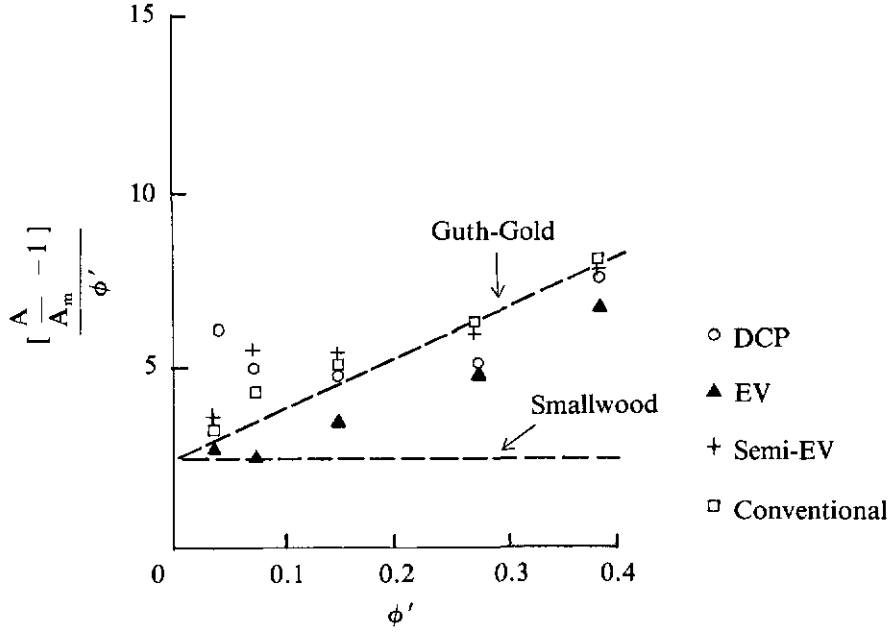

Figure 6. Modified representation of the 'Guth-Gold' plots for the results obtained using carbon black filled rubbers.

where A_m is the modulus of the rubber matrix and ϕ' is the effective volume fraction of filler/carbon black. For rubbers crosslinked using the peroxide and EV vulcanising systems, results showed that A_m is equal to that of unfilled rubber (A_o), and for rubbers crosslinked using the semi-EV and conventional systems, values of A_m were essentially linearly related to the volume fraction of carbon black.

CONCLUSIONS

The presence of carbon black has been observed to enhance the crosslinking efficiency of the semi-EV and conventional sulphur vulcanising systems, without affecting that of the corresponding EV sulphur and peroxide vulcanising systems. These differences make the Guth-Gold equation, which has hitherto been used for predicting the modulus of filled rubber, to be inadequate. A modification of the Guth-Gold equation, which takes into account the changes in the rubber matrix due to the presence of carbon black has been found to give a better description of the results. The proposed equation suggests that the effect of the shape factor of carbon black on the stiffness of the vulcanisate is insignificant, and the effective volume fraction, which is the volume fraction of carbon black plus half that of the occluded rubber should be taken as the true volume fraction of 'filler'.

The increase in the crosslink density of rubber due to the presence of carbon black could present a problem when predicting the modulus of filled rubber since carbon black or other fillers which undergo different preparation techniques may have different catalytic effects on the rubber. However, knowing that the stiffening effect of carbon black also changes with vulcanising systems, this factor could be taken into consideration.

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