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MECHANICAL PROPERTIES OF VULCANIZATES WITH FILLERS

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Abstract—New models have been developed relating the modulus of vulcanizates and volume fraction of filler. The models take into account the shape of filler particles and the modulus of the interphase. The usefulness of these models has been verified by determination of dynamic modulus for a series of vulcanizates. The new models have been compared with the well known models of Guth, Takayanagi, Sato and Furukawa.

INTRODUCTION

The rubber products manufacturing industry consumes a large number of different fillers. The properties of vulcanizates containing fillers differ very much from those of the pure-gum rubber; the difference is especially evident in mechanical properties. The complexity of filler particles, their aggregations as well as the large range of particle dimensions are the reasons for the different interactions within the filler particles and between filler and rubber. Effects of these interactions are the presence of "bound rubber" and other phenomena.

The prediction of the mechanical properties of heterogeneous materials by using mathematical models has been known for a long time; the investigations of Einstein [1], Guth [2], Smallwood [3] and Kerner [4] are of prime importance. However, none of these formulae can be used for the satisfactory description of the properties of rubber vulcanizates. This is due to neglect of the shape factor of the filler particles and the adhesion between the filler and the rubber matrix. Therefore, further works have regarded the manifold properties and structure of a heterogenous system of vulcanized rubber. Sato and Furukawa [5] assume a chain structure for the rubber matrix and the possibility of different adhesion between filler and rubber, while Medalia [6] sees the importance of "bound rubber" and has applied the factor of an unfolded structure of filler particles in his model. Similar dependences have been published by Krause [7]. The models of Takayanagi [8], Pakuła and Kryszewski [9] include the coefficient of filler particle size. However, for the most part, the phenomenon of rubber viscoelasticity has been omitted although Christensen [10], Roscoe [11] and Hashin [12] have taken this problem into account in their models.

Most of these formulas do not fit satisfactorily to the results of the heterogeneous system of rubber with filler [13, 14, 15]. These disadvantages stimulated construction of other simpler models which could include factors approaching the theoretical equations and be fitted to the experimental data. Coran and Patel [16] developed such a model, which after recalculation can be used for the more general representation of rubber experimental results [17]. This formula, however, is of no recognised physical value, because of difficulties involved in the interpretation of the coefficients. For this reason the application of Coran and Patel's model is limited.

However, models are designed not only for the prediction of material properties but also to explain the structure producing the property changes.

NEW MODELS

The complex models developed from rigorous theoretical considerations have no advantages over simple ones according to experimental results. Hence, simple models which respect the structure of the material are preferred. The Zorll model [18] meets these requirements. This model can be developed to allow for the complexity of filler particles as well as to the presence of the interphase between filler particles and rubber matrix representing "bound rubber" in the system. This consideration is supported by many morphological results [19, 20] which give evidence for the irregular shape of filler particles. The differentiation of rubber-filler interactions involving such wide modification of the properties of rubber vulcanizates is represented in the model by the incorporation of the value of the modulus and dimensions of the interphase existing between rubber matrix and filler. With the assumption of uniform distribution of filler particles in rubber, the heterogeneous material can be divided into equal cubes. Each cube always includes the same corner representing the filler. It can be easily shown that the properties of the whole material can be identified by the properties of the elementary cube.

Three types of models are developed as follows:

(A) Two-phase system model with a perpendicular form of the distributed phase;

(B) Three-phase system model with a cubic form of the distributed phase;

(C) Three-phase system model with a perpendicular form of the distributed phase.

Good adhesion between the viscoelastic phases and incompressibility of each phase have been assumed.

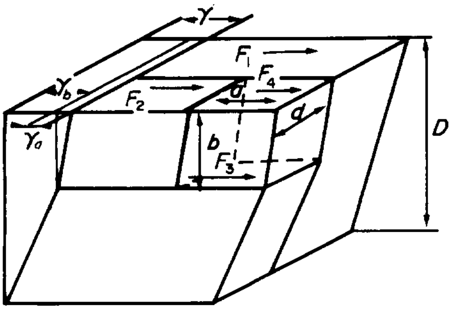

Fig. 1. Model A after a deformation with the forces and deformation distribution.

Comparatively little is known about the nature of the bonds between filler particles and the rubber matrix. Although even a chemical bond is conceivable, physical forces prevail in most cases. Therefore upon deformation of filled rubber, the segments of its macromolecules can slide along the surface of the filler. These models were solved under conditions of simple shear deformation. Models A and B comprise two parameters while model C has four parameters describing the shape of the interphase.

Model A

The structure of this model after deformation with the force and deformation distribution is shown in Fig. 1. The size of the distributed phase is prescribed by sides a, b, d of the perpendicular and the elementary cube has sides of dimension D. Since only two of three sides are independent variables, the third reflecting the volume fraction of the distributed phase, these expressions

$$k = \frac{b}{a} \quad \text{and} \quad m = \frac{d}{a}$$

are used for convenience.

In an experiment of simple shear upper and lower surfaces of the sample are strongly bonded to the metal plate, so the shear deformation at all points attached to the plate is uniform. The different modulus value of some part of the testing material creates the proportional force acting on it. Therefore, the elementary cube is divided into four regions. Three of them belong to elastomer and the fourth represents the filler. On each region different forces act during a deformation and they can be calculated separately. The effect of non-uniformity of stress, which can arise on the phase border is neglected in this consideration (as by Zorll [18]).

The deformation of the model consists of two components: one for the upper part of the model (containing filler) and the other for the lower part of the model (pure elastomer). Forces acting upon the model can be connected with sizes, moduli and deformations of the model by the equations:

$$F_1 = G_0 D(D - ma)\frac{\gamma}{D} \tag{1}$$

$$F_2 = G_0 ma(D - a)\frac{\gamma_a}{ka} \tag{2}$$

$$F_3 = G_0 Dma\frac{\gamma_b}{D - ka} \tag{3}$$

$$F_4 = G_F a^2 m\frac{\gamma_a}{ka} \tag{4}$$

where

G_0 = modulus of matrix
G_F = modulus of filler

The total force and deformation of the model can be written thus:

$$F = F_1 + F_2 + F_4 \tag{5}$$

$$\gamma = \gamma_a + \gamma_b \tag{6}$$

The modulus of model, G, can be calculated using Eqns 1 to 6 from:

$$G = \frac{\dfrac{F}{D^2}}{\dfrac{\gamma}{D}} = \frac{F}{D\gamma} \tag{7}$$

With the assumption that $G_F \gg G_0$

$$\frac{G}{G_0} = 1 + \frac{mx\left[\dfrac{G_0}{G_F}(1 - k) - xk(1 - xk) + x\right]}{k\left[\dfrac{G_0}{G_F} + x(1 - xk)\right]} \tag{8}$$

where

$$x = \frac{a}{D}$$

The volume fraction of filler can be expressed:

$$c = \frac{abd}{D^3} = \frac{kma^3}{D^3} = kmx^3$$

and with the assumption $G_0/G_F \rightarrow 0$, eqn (8) can be transformed into:

$$\frac{G}{G_0} = 1 + \frac{yB^2(yA^5 + B - A^3B)}{A^4(B - yA^2)} \tag{9}$$

where

$y = c^{1/3}$
c = volume fraction of filler
$A = k^{1/3}$
$B = m^{1/3}$

Equation (9) is written in the form of $G/G_0 = f(c)$, which can be easily compared with experimental data.

Model B

In this model it is assumed that an adhesive layer exists around the filler particles. The adhesive layer is mainly responsible for the physical interaction between filler and rubber macromolecules. This can contribute to form a secondary structure because the filler particles interact with each other only through these layers. It is also assumed that the distributed phase and surrounding filler interphase have a cubic form, with sides a and a_1 respectively. The thickness of

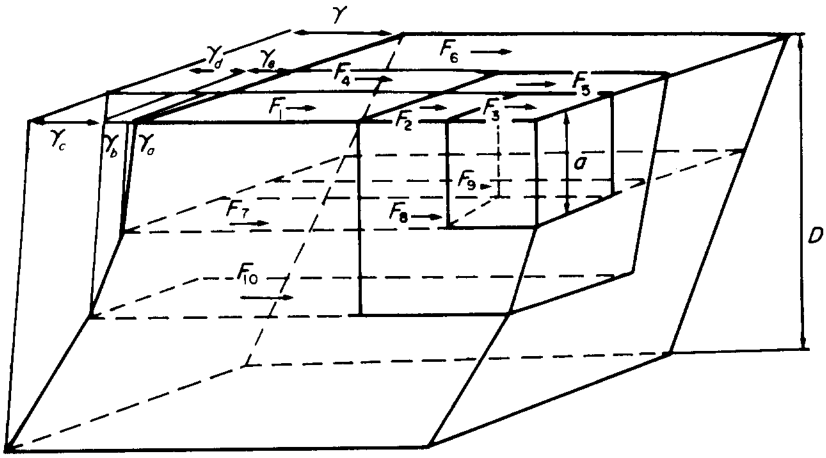

Fig. 2. Model B after a deformation with the forces and deformations distribution.

the adhesive interphase is $a_1 - a$. The distribution of the forces acting upon the model and model deformations are shown in Fig. 2. Terms $x = a/D$ and $t = a_1/D$ are used for convenience.

The same method of calculation as for model A was used. If it is assumed that G_F (modulus of filler) is much greater than G_1 (the modulus of interphase) then:

$$\frac{G}{G_0} = 1 + \frac{t^2(t^2 - xt + x^2)}{(t^2 - xt + x^2)(1 - t) + \vartheta(t - x)} \tag{10}$$

where

$$\vartheta = G_0/G_1$$

For simplicity $r = a_1/a = t/x$ and $y = c^{1/3}$ can be substituted and Eqn (10) is transformed into:

$$\frac{G}{G_0} = 1 + \frac{r^2 y^3(r^2 - r + 1)}{y(r^2 - r + 1)(1 - yr) + \vartheta(r - 1)} \tag{11}$$

Model C

The results of models A and B have shown the importance of the shape of filler particles as well as the presence of the layer of interphase. It was reasonable to combine all these elements in one model (Fig. 3).

The expressions $k = b/a$, $m = d/a$ and $x = a/D$ are similar to those used in model A. The dimensions of the adhesive interphase layer are proportional to the respective perpendiculars representing the distributed phase. Therefore, further expressions can be used, namely $k = b_1/a_1$ and $m = d_1/a_1$. The final form of the equation for this model, obtained in a similar way as the previous cases, is:

$$\frac{G}{G_0} = 1 + \frac{\begin{array}{r} rB^2y[AB^2\vartheta(1 - A^3)(r - 1) \\ + y(B + ryA^5 - A^3B)W] \end{array}}{A^4[AB^2\vartheta(r - 1) + y(B - ryA^2)W]} \tag{12}$$

where

$W = r^2 - r + 1$
$r = a_1/a$
$y = c^{1/3}$
c = volume fraction of filler)
$A = k^{1/3}$
$B = m^{1/3}$
$\vartheta = G_0/G_1$

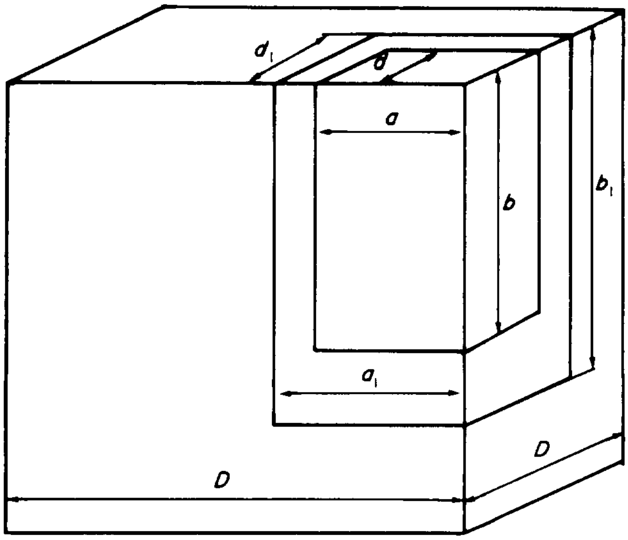

Fig. 3. Model C—the combination all the elements of models A and B.

Table 1. Value of parameters A, B and χ^2 for the model A (Eqn 9)

Sample number	Deformation amplitude	Parameters for Eqn 9		Test of goodness of fit
		A	B	
0-A	0.004	1.18	1.38	0.1165
	0.35	1.12	1.24	0.1741
0-B	0.004	—	—	—
	0.35	1.04	0.84	0.0546
20-A	0.004	1.12	1.24	0.0255
	0.35	1.14	1.38	0.0509
20-B	0.004	1.08	0.78	1.6500
	0.35	1.07	0.89	0.0062
40-A	0.004	1.21	1.12	0.0214
	0.35	1.18	1.38	0.0103
40-B	0.004	—	—	—
	0.35	1.10	1.00	0.0027
60-A	0.004	1.00	0.70	0.0558
	0.35	1.13	1.15	0.0128
60-B	0.004	—	—	—
	0.35	0.98	0.77	0.0028
80-A	0.004	1.12	0.85	0.1788
	0.35	1.02	0.90	0.0035
80-B	0.004	—	—	—
	0.35	0.90	0.60	0.1408
100-A	0.004	1.14	0.96	0.0094
	0.35	1.08	1.20	0.0091
100-B	0.004	1.09	0.79	1.7361
	0.35	0.92	0.60	0.0065

* Figures show the amount of chlorobutyl rubber in the blend and letter shows type of carbon black (A is MT-FF, B is ISAF-LS).

Table 2. Value of parameters r, ϑ and χ^2 test for the model B (Eqn 11)

Sample number*	Deformation amplitude	Parameters for Eqn 11		Test of goodness of fit
		r	ϑ	
0-A	0.004	1.12	1.12	0.5893
	0.35	1.12	1.18	0.4111
0-B	0.004	1.56	0.16	1.3214
	0.35	1.54	1.18	0.0322
20-A	0.004	1.12	1.18	0.1560
	0.35	1.12	1.18	0.2902
20-B	0.004	1.62	0.28	0.8632
	0.35	1.42	0.99	0.0648
40-A	0.004	1.48	1.18	0.2397
	0.35	1.12	1.18	0.2830
40-B	0.004	1.60	0.24	0.4691
	0.35	1.12	1.18	0.2830
60-A	0.004	1.64	0.70	0.2293
	0.35	1.14	1.18	0.0511
60-B	0.004	—	—	—
	0.35	1.48	0.85	0.0398
80-A	0.004	1.36	1.18	0.0062
	0.35	1.26	0.99	0.0071
80-B	0.004	1.48	0.02	1.7698
	0.35	1.22	0.07	0.0268
100-A	0.004	1.62	1.11	0.1964
	0.35	1.12	1.18	0.0384
100-B	0.004	1.62	0.24	0.5896
	0.35	1.48	0.83	0.0257

* Sample indication as in Table 1.

Table 3. Value of parameters A, B, r, ϑ and χ^2 test for the model C (Eqn 12)

Sample number*	Deformation amplitude	Parameters for Eqn 12				Test of goodness of fit
		A	B	r	ϑ	
0-A	0.004	1.18	1.27	1.16	1.25	0.0087
	0.35	1.17	1.27	1.08	1.25	0.0286
0-B	0.004	1.17	1.27	1.64	0.30	0.6204
	0.35	1.07	1.17	1.68	0.95	0.0284
20-A	0.004	1.06	1.27	1.12	1.15	0.0018
	0.35	1.07	1.28	1.16	1.25	0.0249
20-B	0.004	1.17	1.27	1.68	0.35	0.1958
	0.35	1.07	0.87	1.04	1.15	0.0060
40-A	0.004	1.17	0.97	1.12	1.10	0.0151
	0.35	1.18	1.27	1.04	1.25	0.0081
40-B	0.004	1.07	1.17	1.64	0.20	0.3446
	0.35	1.09	0.97	1.16	0.90	0.0033
60-A	0.004	1.07	0.97	1.64	0.95	0.0056
	0.35	1.07	0.98	1.20	1.25	0.0117
60-B	0.004	0.97	1.07	1.68	0.05	1.2247
	0.35	1.07	0.97	1.12	0.20	0.0021
80-A	0.004	1.07	0.87	1.60	1.10	0.0012
	0.35	1.02	0.90	1.00	1.00	0.0035
80-B	0.004	0.97	1.07	1.64	0.00	0.2979
	0.35	0.87	0.67	1.12	0.05	0.0201
100-A	0.004	1.14	0.96	1.04	1.05	0.0088
	0.35	1.07	1.17	1.04	1.05	0.0091
100-B	0.004	1.07	0.97	1.44	0.35	0.0628
	0.35	0.97	0.76	1.08	0.35	0.0051

* Sample indication as in Table 1.

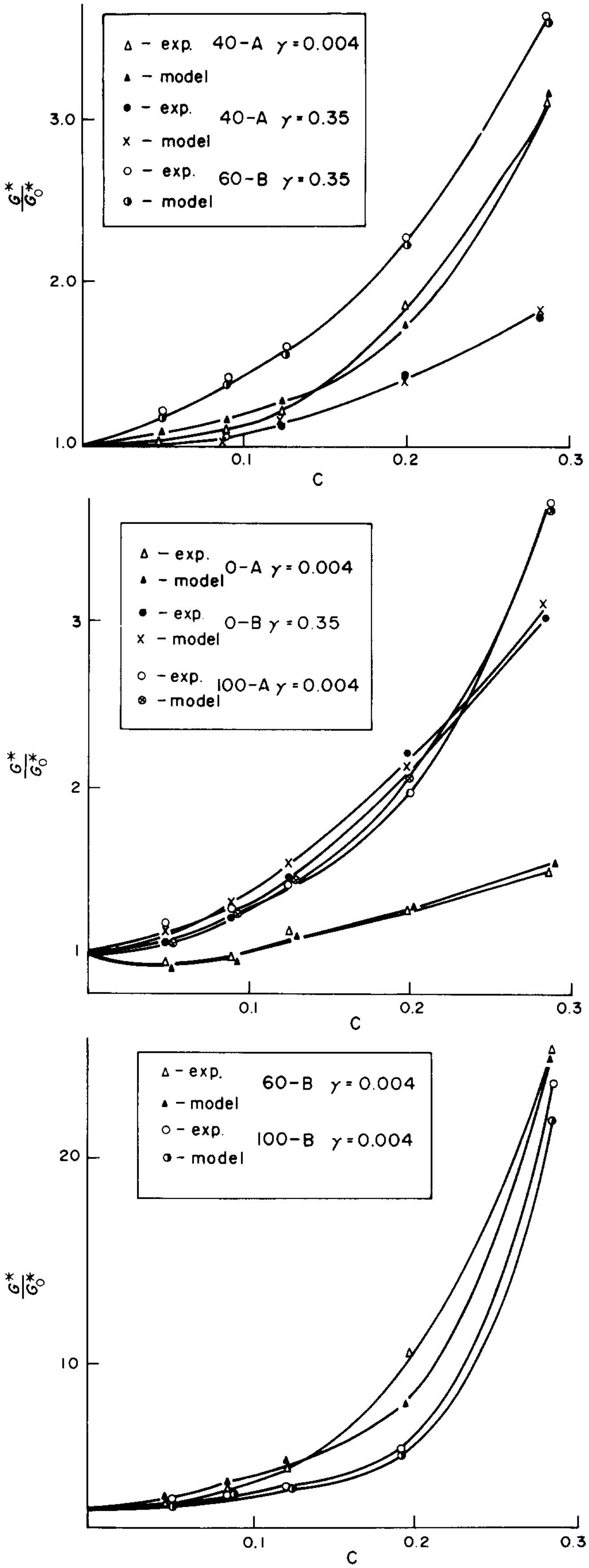

Fig. 4. Examples of the model C application.

The general equation of model C can be simplified to Eqns (11) or (9). If $A = 1$ and $B = 1$ then Eqn (12) takes form of Eqn (11), and when additionally $r = 1$ the Zorll formula [18] is obtained.

MODELS-TO-EXPERIMENTS CORRELATION

The prediction of moduli is very important for the practical material which must undergo dynamic conditions of working. For this reason the developed models have been checked under dynamic conditions.

For the experiments the D-8 apparatus produced by Wallace of Croydon was used. It has been described already (15). The simple shear forces were applied at various deformation amplitudes and a frequency of 0.25 Hz. For comparison, the testing results obtained at amplitudes of $\gamma = 0.004$ and $\gamma = 0.35$ are considered here.

The samples were sulphur vulcanizates of natural rubber (SMR-5), chlorobutyl rubber (HT 10-66 from Esso Chemicals) as well as blends of both rubbers. As fillers N-990 (MT-FF) and N-219 (ISAF-LS) carbon blacks produced by Cabot Comp. were used. The concentration of carbon black ranged from 0 to 80 phr. For the correlation of models with experimental results, the values of parameters A, B, r and ϑ were selected by means of a computer until good agreement was obtained.

Goodness of fit was checked by χ^2 test. In cases when the χ^2 value exceeded those tabulated for the level of the four parameters mentioned above, then conformity was considered not to have been found, i.e. a lack of correlation. Both groups of values (A, B, r, ϑ) and χ^2 test are shown in Tables 1 and 2 for models A and B respectively. The results show good accordance, especially for the experiments at high deformation amplitude. For four cases only significant deviation of model A from the experimental data was found. Each of these deviations appears in the tested samples of vulcanizates with ISAF carbon black at the smallest amplitude used. In these vulcanizates a secondary network exists connected with filler-to-filler and filler-to-rubber interactions. At higher amplitude of deformation, the secondary network is destroyed and in these circumstances agreement of the model A with experimental results is achieved. This is due to the destruction of bonds between filler and the adhesion layer, as well as the breaking of the secondary network, because it leads to the separation of the filler from the sur-

Table 4. Value of parameters φ and $\alpha = E_B/E_A$ for Takayanagi models*

Sample	Deformation amplitude	Parameters for Eqn *a* φ	Parameters for Eqn *a* α	Test of goodness of fit	Parameters for Eqn *b* φ	Parameters for Eqn *b* α	Test of goodness of fit
0-A	0.004	0.5	3.0	0.057	0.60	3.8	0.037
	0.35	0.8	3.0	0.015	0.70	4.5	0.011
0-B	0.004	—	—	—	—	—	—
	0.35	1.0	7.0	0.191	0.86	39.0	0.192
20-A	0.004	0.7	5.0	0.052	0.90	4.5	0.016
	0.35	1.0	3.0	0.001	1.0	3.0	0.001
20-B	0.004	—	—	—	—	—	—
	0.35	1.0	7.0	0.202	0.95	4.9	0.804
40-A	0.004	0.5	33.0	1.509	—	—	—
	0.35	1.0	3.0	0.079	0.85	4.41	0.063
40-B	0.004	—	—	—	—	—	—
	0.35	1.0	5.0	0.148	0.82	29.0	0.115
60-A	0.004	1.0	10.0	1.382	0.98	17.0	1.381
	0.35	0.96	5.0	0.079	0.82	11.0	0.069
60-B	0.004	—	—	—	—	—	—
	0.35	1.0	9.0	0.247	0.88	59.0	0.219
80-A	0.004	—	—	—	—	—	—
	0.35	0.86	7.0	0.069	0.80	99.0	0.034
80-B	0.004		—	—	—	—	—
	0.35	0.98	11.0	0.162	0.92	33.0	0.126
100-A	0.004	1.0	7.0	0.535	0.88	4.3	0.476
	0.35	0.86	5.0	0.034	0.95	4.9	0.021
100-B	0.004	—	—	—	-	—	—
	0.35	1.0	9.0	0.188	0.88	71.0	0.171

* Equations of the models:

$$\text{(a)}\quad \frac{E_a}{E_A} = \left[\frac{\varphi}{(1-\lambda)+\alpha\lambda} + 1 - \varphi\right]^{-1}$$

$$\text{(b)}\quad \frac{E_b}{E_A} = \lambda\left(\frac{\varphi}{\alpha} + 1 - \varphi\right)^{-1} + 1 - \lambda$$

where

E_A = modulus of matrix; E_B = modulus of filler; $\alpha = E_B/E_A$; φ = shape factor ($c = \varphi\lambda$); c = volume fraction of filler.

Table 5. Value of parameter for Guth model*

Samplex number**	Deformation amplitude	Parameter f	Test of goodness of fit
0-A	0.004	1.3	0.023
	0.35	1.5	0.004
0-B	0.004	—	—
	0.35	3.3	0.032
20-A	0.004	1.9	0.001
	0.35	1.5	0.013
20-B	0.004		—
	0.35	3.3	0.045
40-A	0.004		
	0.35	1.7	0.028
40-B	0.004	—	
	0.35	2.7	0.030
60-A	0.004	4.9	0.392
	0.35	2.3	0.014
60-B	0.004		
	0.35	3.7	0.016
80-A	0.004	—	
	0.35	2.7	0.016
80-B	0.004	—	
	0.35	4.1	0.096
100-A	0.004	3.5	0.129
	0.35	2.3	0.014
100-B	0.004		—
	0.35	3.7	0.030

* Equation of Guth model:

$$\frac{E}{E_0} = 1 + 0.67fc + 1.62f^2c^2$$

where

E_0 = modulus of matrix; f = shape factor;
c = volume fraction of filler.

** Figures show the amount of chlorobutyl rubber in the blend and letter shows the type of carbon black (A is MT-FF, B is ISAF-LS).

Table 6. Value of parameters for Sato and Furukawa model

Sample number**	Deformation amplitude	Parameters for Eqn* β	Parameters for Eqn* ξ	Test of goodness of fit
0-A	0.004	2.6	0.85	0.010
	0.35	0.3	0.40	0.034
0-B	0.004	—		
	0.35	3.7	0.65	0.036
20-A	0.004	0.5	0.35	0.001
	0.35	0.0	0.05	0.003
20-B	0.004			
	0.35	3.5	0.65	0.012
40-A	0.004			
	0.35	3.9	0.85	0.015
40-B	0.004			
	0.35	1.6	0.46	0.003
60A	0.004	7.8	0.66	0.191
	0.35	1.8	0.60	0.009
60-B	0.004	—		
	0.35	3.8	0.60	0.003
80-A	0.004	7.9	0.48	1.606
	0.35	0.6	0.00	0.072
80-B	0.004	3.6	0.60	0.079
	0.35	1.5	0.00	0.062
100-A	0.004	3.6	0.60	0.079
	0.35	0.3	0.05	0.045
100-B	0.004	—		
	0.35	1.5	0.15	0.016

* Equation of Sato and Furukawa model:

$$\frac{E}{E_0} = 1 + \frac{y^2}{2-2y} + \beta(1+\xi)\frac{y^3(1-y/2)}{1-y^2} - \left[y^3\left(1+\frac{y^2}{2-2y}\right)+\frac{y^2}{1-y}\right]\frac{(1+y-y^2)\xi}{3(1-y+y^2)}$$

where

E_0 = modulus of matrix; c = volume of fraction of filler; $y = c^{1/3}$; ξ = parameter of adhesion ($\xi = 0$ perfect adhesion, $\xi = 1$ absence of adhesion); β = macromolecular parameter.

** Sample indication as in Table 5.

rounding layer. It has been also found that the value of parameters A and B for most vulcanizates become closer to 1 at higher amplitude of deformation. This confirms a more regular form of the filler particles. It is interesting that for model B the value of coefficient ϑ exceeds 1 for the vulcanizates with MT-FF carbon black. This means that the modulus of the interphase is lower than the modulus of the rubber matrix. This phenomenon can be explained by the appearance of vacuoli (empty spaces) in the interphase produced by separation of the carbon black particles from the rubber. This separation is due to the deformation of the tested material and indicates low adhesion between the distributed phase and the matrix. Model C is suitable for the simultaneous investigation of the influence of the interphase as well as the shape coefficient of the filler particles (Table 3). For this model good correlation has been found at the adopted level of confidence for all tested vulcanizates even for tests at the smallest amplitude used. Apart from one case (sample 60-B) the accordance is very good. Examples are shown in Fig. 4.

All the suggestions for the parameter change concerning model A and B are also valid for model C. This is true for the change of the shape factors A and B and also for the modulus factors when the amplitude of deformation arise. Fortunately the value of all parameters in model C describes more regular structure and in this way is more realistic. For comparison, the agreement between some of the literature models and the experimental results was examined. The same selection method of model parameters was used (i.e. fitting by computer) for Takayanagi [8], Guth [2] and Sato and Furukawa [3] models.

The results of fitting are summarized in Tables 4, 5 and 6. The values of test of goodness of fit show that The models agree poorly with the experimental data. This is particularly evident for vulcanizates containing ISAF-LS carbon black when tested at the smallest deformation amplitude. In the cases where successful fit of the experimental data was observed, some of parameter values have no physical meaning. High values of the parameter φ and small χ for Takayanagi models (Table 4) are contradictory to the vulcanizate structure.

Guth's model agreed with the experimental data measured by $\gamma = 0.004$ for vulcanizates containing MT-FF carbon black (Table 5), if the shape factor realized a high value (60-A, 100-A). Such values of the shape factor seem rather unlikely for this kind of vulcanizate. Also some parameter values obtained from computer fitting the Sato and Furukawa equation (Table 6) lack physical meaning (for example perfect adhesion of MT-FF carbon black to matrix containing 80% CI-IIR and 20% NR).

Contrary to Guth, Takayanagi and Sato and Furukawa models, the values of the parameters of the new models are reasonable (especially shape factor) and agree with data from Electron Micrographs [19, 20]. From the data shown in Table 3, one can see that the shape coefficients in model C are no higher than 2. The value of these coefficients computed for Guth's model (see Table 5) are higher although even the date for the vulcanizates containing ISAF carbon black tested at the smallest amplitude deformation have not been found. The high values of shape factor can be expected.

SUMMARY AND CONCLUSIONS

Three models A, B and C have been developed for the evaluation of structure and prediction of the modulus of vulcanizates with different amounts of filler. Model C appears especially valuable, if one notes the high accordance of its data with experiment. The structure can be evaluated e.g. the adhesive interphase properties from the dynamic mechanical properties of the vulcanized rubber.

Of course, the obtained structure must be confirmed by an independent method. For the prediction of the dependence of the dynamic mechanical properties on the amount of filler, the experiments can be limited to the few tests necessary for the calculation of equation parameters.

One can see from Table 4 to Table 6 that the models do not predict values of modulus for the small amplitude of deformation. This is also true for the vulcanizates containing active filler. No really satisfactory parameters for Guth and Takayanagi and Sato–Furukawa models can be selected. On the other hand, the new models (particulary model C) display good correlation between theoretical and empirical data.

Consideration of the results of the model formulae suggests practical applications of the new model for the prediction of moduli of vulcanizates containing different concentration of reinforcing filler. The advantage of these models is their value even for mechanical characteristics rubber at small amplitude of deformation.

Further development of the models may lead to prediction of the values of the model parameters. Even now, one can see the influence of activity of fillers on the parameters r and ϑ. Also the values of parameters A and B can probably be predicted. Their values seem to be more dependent on the rubber matrix than on the type of carbon black. However, a satisfactory relationship between the model parameters and the composition of a vulcanizate can be achieved by means of a large number of tests of different heterogeneous materials. The range of the applicability of the presented models must also be evaluated. The results of this work show the potential for practical application of these models.

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