Models for the Investigation of the Structure of Vulcanizates

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Summary: For the investigation of vulcanizates structure, new models have been developed relating the modulus of vulcanizates and the volume fraction of filler. The parameters of the models are the filler distribution and the properties of the shell surrounding the filler particles. Three functions of filler distribution have been assumed. Dynamic mechanical properties of a series of vulcanizates were tested and the parameters of the models were computed. The obtained data allows estimating the properties of the shell formed around filler particles in vulcanizates and to distinguish the functions of filler distribution.

Keywords: carbon black; elastomers; fillers; modeling; reinforcement

Introduction

Carbon black added to a polymer system causes a considerable change in its properties, particularly in the dynamic properties of vulcanisates. Understanding of the mechanism of reinforcement of elastomers by carbon black is one of the most important problems faced by rubber science and technology. It is known that the polymer - filler interaction leads to the formation of rubber shells around the filler particles. The modulus of the shells formed around carbon black particles in vulcanizates is higher than the modulus of the rubber matrix.

The properties of this shell have a great influence on the properties of rubber (e.g. dynamic modulus) [1-3] and can be a clue towards explaining the phenomenon of reinforcement. One of the possible ways of looking for an explanation of this phenomenon and the behaviour of filled vulcanizates is to develop models assuming the existence of particular structures producing the changes in the properties. If a good agreement between the experimental and the theoretical data is obtained then an analysis of parameters of a model describing the structures can be performed.

The effects of fillers on dynamic mechanical properties of rubber give some important information about the structure of vulcanizates. Therefore, this paper will discuss the models derived to describe the dynamic mechanical properties of rubber in order to investigate the structure of vulcanizates.

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Theory

It is well known, that the time of a mixing a rubber compound has a great influence on the level of dispersion of carbon black and on the dynamic modulus of the rubber [4-5]. Even from such a simple experiment it is obvious that the dispersion of filler is an important factor. However, the importance of how it relates to others parameters can be examined by models.

Rubber - filler interaction is represented in this model by the value of the modulus and dimension of the shells existing around particles of carbon black.

A multiphase cuboid system is divided into equal cubes containing different amounts of filler placed at corners (Figure 1) [6].

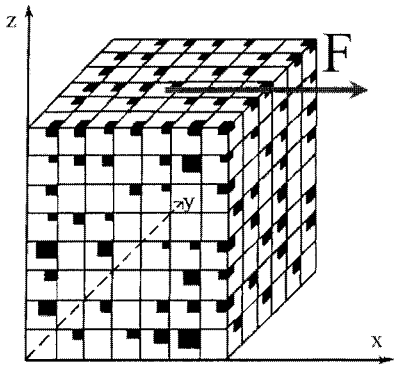

Figure 1. Three dimensional model with random distribution of carbon black.

Each of the cubes can be represented by the models described earlier [7]. Good adhesion and incompressibility of each phase have been assumed. A simple shear force has been applied to the cuboid but the forces and deformation of the individual cubes are not known a priori.

The forces carried by the planes parallel to X-Y have the same value:

$$F = \sum_{i=l}^{i=l} \sum_{j=1}^{j=n} F_{i,j,k} \qquad (1)$$

where: $F_{i,j,k}$ is the force acting on the cube with the coordinates i,j,k and l and n are the number of cubes on the axes x and y.

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Displacement d of the upper surface relative to the lower is equal to the displacement of a column for which the indices i and j are fixed, leading to:

$$d = \sum_{k=1}^{k=m} d_{i,j,k} \tag{2}$$

Using the definition of modulus (G=τ/γ) and counting the sums of cubes in the model, the following formula is obtained:

$$G = \frac{mF}{D\sum_{i=1}^{i=l}\sum_{j=1}^{j=m}\sum_{k=1}^{k=n} d_{i,j,k}} = \frac{mF}{D\sum_{j=1}^{j=N} d_j} \tag{3}$$

where: D is the dimension of the elementary cube, and N the number of all cubes in the model (N=l*m*k) .

As the result of the calculation with some simplification and grouping of expressions, the following expression has been obtained:

$$G = \frac{1}{\sum_{j=1}^{j=k}\left(\frac{a_j n_j}{G_j N}\right)} \tag{4}$$

Where: G-modulus of system; a_j - factor characterizing the stress concentration, n_j – number of the cubes containing the filler concentration in the ranged c,c+dc; G_j-modulus of "j" cube and N number of the cubes in the model.

The expression n_i/N is the probability of appearance of a cube with a volume fraction of filler between c and c+dc. It is also the probability of the occurrence of a_j and G_j, if they are monotonous functions of c.

Going up to an infinite number of cubes, the sum is replaced by integration:

$$G = \frac{1}{\int_0^1 \frac{a(c)}{G(c)} f(c)dc} \tag{5}$$

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Three functions of the model are unknown and should be fixed:

- G(c) –modulus of the elementary cube,
- f(c) - function of probability of the density of filler distribution,
- a(c) -stress concentration function.

Based on existing works it is difficult to propose a density function of the probability of filler distribution in rubber. Therefore, three types of distribution were considered:

- parabolic distribution (approximation of Gaussian function)
- uniform distribution
- inverted parabolic distribution

There are two parameters describing the function of filler distribution, namely: **a** and **b** (parameters of functions, which are the lowest and the highest possible values of filler amount) or $\bar{y}$ and $\sigma = s^2$ (estimators of functions which are the average value of the filler fraction and the standard deviation of filler distribution).

The function of stress concentration indicates the ratio of the force acting on an elementary cube to the average value of the force. The preliminary calculation showed that a sensible function is a certain power of volume fraction of filler, e.g. $(\mathbf{a(y)=C(a,b)y^3}$ where $\mathbf{y=c^{1/3}})$.
The moduli of elementary cubes are calculated from assuming the appearance of a shell of rubber matrix on the filler surface. The shell is a result of rubber-filler interaction because the adsorption of polymer molecule chains on the filler surface may reduce their mobility)[2,7].
Each of the cubes can be represented by the models described earlier (model B)[7]. The properties of the shell (thickness and modulus) are the parameters of the model.

In order to become a general problem solving tool, the model should be dimensionless and the parameters should have a relative meaning.
The whole model has three parameters viz. dimension, r (ratio of the thickness of the shell to the side of the elementary cube D) and relative value of the modulus of the shell, m (ratio of the modulus of the rubber matrix, G_o, to the shell modulus, G_{shell}) and the parameter of the distribution of filler[7].

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Application of the Theory

The tested samples were sulphur vulcanizates of NR and Cl-IIR as well as blends of both rubbers with N990 and N220 carbon black. For the vulcanizates of NR filled with N220 carbon black, different times of mixing of these compounds were applied to obtain different dispersions of the fillers. The concentration of carbon black for both types of compounds ranged from 0 to 80phr. The dynamic properties of the vulcanizates were determined using a D-8 apparatus produced by H.W. Wallace of Croydon. Simple shear forces with the frequency of 0.25Hz were applied. The test results were obtained in a range of amplitudes of deformation from $\gamma = 0.004$ to $\gamma = 0.35$.

The model parameters were calculated until good agreement between theoretical and experimental data was obtained. The goodness of fit was checked by the χ^2 test.

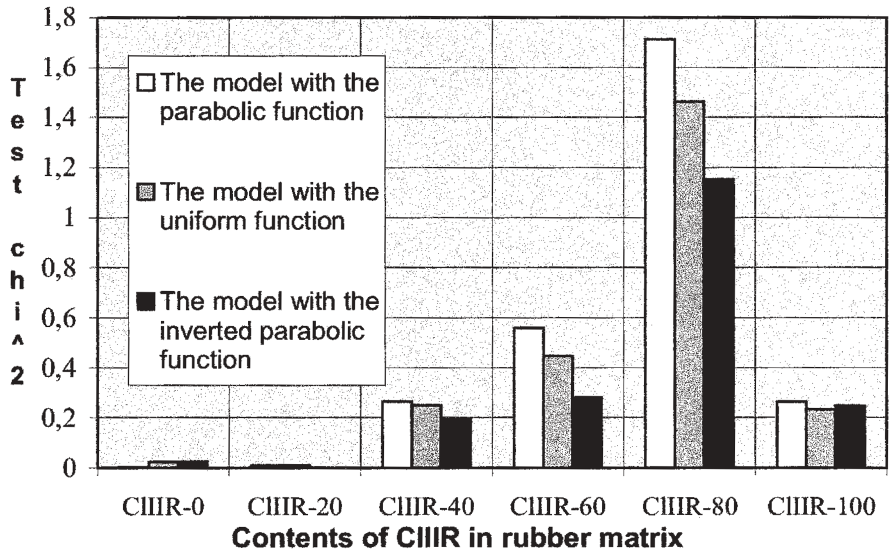

Figure 2. Test of goodness of fit of model-to-experiments data for NR+Cl-IIR +N990 carbon black vulcanizates at the amplitude of shear deformation $\gamma = 0.004$.

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The results show good agreement with the experimental data. The values of the test of fitness in most cases are much better than the critical value for the level of confidence of 0.9. These good values of agreement confirm the reasonability of the model and allow discussion of the structure parameters. The analysis of values of the χ^2 test leads to the suggestion that the inverted parabolic function of the filler distribution is the best for the tested vulcanizates (Figure 2-3). The average values of the test χ^2 for the vulcanizates with N990 carbon black are 0.242, 0.209, and 0.166 for parabolic, uniform and inverted parabolic function of the density of probability, respectively.

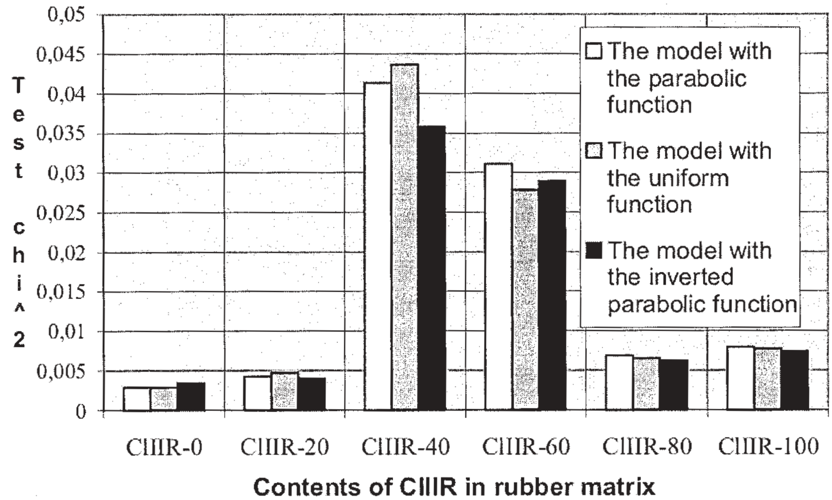

Figure 3. Test of goodness of fit of model-to-experiments data for NR+Cl-IIR +N990 carbon black vulcanizates at the amplitude of shear deformation $\gamma = 0.35$

The average values of the χ^2 test for the vulcanizates of NR compounds/N220 carbon black with different times of mixing are on a similar level, namely: 0.825, 0.711, and 0.438 for the three functions of filler distribution respectively as shown in Table 1.

The parameters s^2 (the percentage of maximum variance[7] of the probability functions of the filler distribution) become smaller when the amplitude of deformation increases for vulcanizates filled with N990 and N220. This can be explained as a result of breaking out the large filler aggregates or agglomerates (probably temporarily) and destruction of the filler-filler network [4].

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The value of s^2 for the smallest amplitude of deformation is very high. The tendency to reach such a high value indicates the existence of large aggregates of filler, which carry over the force from one cube to another. Unfortunately, such phenomenon is not directly considered in the proposed models.

The parameter of the shell thickness allows to calculate the volume fraction of the shell. The calculated values strongly depend on the type of the functions of the density of probability and range thus:

- parabolic function, from 1,5 to 25.9%,
- uniform function, from 2.2 to 27.5%,
- inverted parabolic function, from 1 to 3.7%,

when vulcanizates are filled with 80phr of N990 carbon black.

As can be seen in Figures 2 and 3 for the low structure carbon black (N990), the data for the inverted parabolic function seems to be more accurate; the same is true for high structure carbon black (N220). The parameters of modulus of the shell should be higher than modulus of the rubber matrix. However for the vulcanizates filled with non-reinforcing black N990 (and the large deformation) in the majority of cases (except 60 and 80 % of chlorobutyl rubber in the rubber matrix) the value of the modulus of the shell is lower than for the rubber matrix. This phenomenon has been pointed out before (called eye-ball shape separation) and has been explained as a result of voids produced by the separation of carbon black particles from rubber matrix [7-8]. The separation is due to the deformation of the material and indicates low adhesion between filler particles and rubber.

In the vulcanizates with 60 and 80% of Cl-IIR presumably unequal distribution of carbon black in both rubbers lead to formation of quite strong filler network which behave very similar to networks of active fillers.

The moduli of the shells (the m parameters) calculated for the vulcanizates with N220 carbon black are much higher than the modulus of the rubber matrix (Table 1). Therefore, in this case separation of the rubber matrix from the surface of carbon black is not observed. As can be expected, if the time of mixing of rubber compounds is longer then the parameter of distribution is lower, which shows better dispersion of the filler. Also the parameter r (thickness of the shell)

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becomes lower when the time of mixing is longer. A better dispersion of the filler and a greater surface accessible to an interaction with the rubber matrix can give this result.

Table 1. Models with parabolic, uniform and inverted parabolic functions of filler distribution, results for NR + N220 compounds with different times of mixing.

Parabolic

Sample	Deformation amplitude	Parameters of models			Test of goodness of fit; χ^2
		s^2	r	$m(G_o/G_{shell})$ $*10^{-6}$	
A (2min)	0.004 0.35	27 2.9	0.215 0.093	12 80	1.577 0.141
B(5min)	0.004 0.35	27 0.1	0.211 0.092	14 63	2.271 0.0376
C(10min	0.004 0.35	27 0.1	0.209 0.095	15 44	1.866 0.824
D (15min)	0.004 0.35	27 0.1	0.210 0.091	16 47	1.685 0.0474
E (20min)	0.004 0.35	27 0.2	0.189 0.087	18 39	1.429 0.0235

Uniform

A (2min)	0.004 0.35	25.5 0.1	0.174 0.102	10.7 48	1.390 0.131
B(5min)	0.004 0.35	27 0.1	0.164 0.091	10.6 52	1.961 0.037
C(10min	0.004 0.35	26.9 0.1	0.162 0.093	10 54	1.402 0.81
D (15min)	0.004 0.35	26.8 0.1	0.161 0.090	10.1 8	1.51 0.047
E (20min)	0.004 0.35	27 0.2	0.152 0.095	10.2 43	1.217 0.023

Inverted parabolic

A (2min)	0.004 0.35	27 9.8	0.081 0.0065	200 2100	0.923 0.195
B(5min)	0.004 0.35	27 8.4	0.077 0.0085	480 1300	1.284 0.0547
C(10min	0.004 0.35	26.9 8.3	0.065 0.0109	240 750	0.755 0.0547
D (15min)	0.004 0.35	26.8 7.8	0.075 0.0125	190 590	1.026 0.060
E (20min)	0.004 0.35	27 8.4	0.076 0.0140	190 250	0.8182 0.0314

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For all distribution functions of filler (the three functions mentioned above) the higher values of modulus were obtained for the smallest amplitude of deformation. The most sensible value of the modulus of the shell for the inverted function of filler distribution, ranged from 100 to 1000 times higher than the modulus of the rubber matrix. These results are in good agreement with the published results [8, 9]. The values of r parameters obtained for the inverted function have the lowest value compare to other functions; they are also the most reasonable values.

The modulus parameters calculated for different functions of filler distribution do not vary significantly and all of them change in the same way with the content of chlorobutyl rubber in the rubber matrix. For example, it was found that all functions give the smallest modulus of the shell at the same composition of the rubber matrix.

From the comparison of the results obtained for the models assuming variability of the shape factor of filler particles[7] with the model considered here, it seems obvious that the meaning of these elements of structure is similar. In both cases, similar values of test of goodness of fit were obtained (Figure 4).

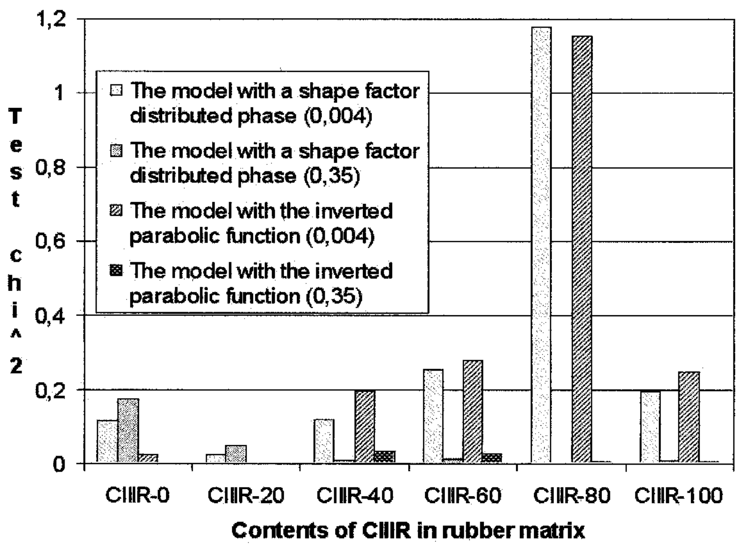

Figure 4. Comparison of data (NR+Cl-IIR +N990) of the model with the inverted parabolic function of filler distribution, with the model assuming a shape factor of filler particles.

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Conclusions

All agree that the filler as one of the main component of the filled vulcanizates has a very important role in improving the dynamic performances of the rubber products. Many new ideas, theories, models and observations about how and why the filler alters the properties of vulcanizates have been presented. This suggests that multiple mechanisms of these phenomena may be involved. The properties of the shell formed on the filler surface as a result of polymer-filler interaction play an important role in the explanation of the modulus change of the rubber systems and other reinforcing effects [2,3,7,8].

The search for better understanding of the structure of vulcanizates and description of the properties vulcanizates called for the examination of the influence of the filler distribution in the rubber matrix. The distribution seems to be an important factor in the structure of vulcanizates. The presented results confirm this view. After investigating the models, it is quite clear that by substituting different functions of filler distribution to the model, it is possible to obtain various influence of volume fraction of filler in the modulus of a rubber system. The data obtained indicates that the influence of filler distribution on the dynamic modulus of vulcanizates is on a similar level as the shape factor of filler particles.

Three simple functions of density of the probability of filler distribution were proposed. The function of inverted parabolic seems to be the most interesting. If this function is really more common, therefore it would indicate that it is more probable to find spaces with huge concentration of filler and the spaces with very low concentration than the spaces with average concentration of filler.

The values of the test of goodness of fit are much better in most cases than the critical value (1,61) for the level of confidence of 0.9, meaning that the agreement of model to experimental data is quite good.

The data obtained (presented here and in [6]) makes it possible to draw a number of conclusions, some of them are indicated below:

- The distribution of filler seems to be an important factor in vulcanizates' structure and can help to explain the reinforcing effects.

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- The parameters „S^2 (percentage of the maximum variance) become smaller when the amplitude of deformation increases, it can indicate that during large deformation the filler-filler network or the agglomerates of carbon black may break down.
- The most probable distribution of filler is the inverted parabolic function. The modulus of the shell formed around filler particles is smaller (except for 60 and 80% of CI-IR) than the calculated modulus for the rubber matrix for vulcanisates with N990 carbon black; for N220 the moduli of the shell are approximately 500 times higher than modulus of matrix.
- The thicknesses of the shell (parameter r) become lower as the time of mixing of the rubber compounds are longer.
- The parameter r allows calculating the volume fraction of immobilised shell, ranging from 1% to 26% of the rubber matrix.

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