The double network, a model describing filled elastomers

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The model presented here to describe the deformation behaviour of filled elastomers is based on the observation that deformation occurs inhomogeneously. As a result of extending a filled rubber, the filler particles become aligned in rows parallel to the stretching direction. The rows are connected to each other by strands emanating from the filler particles, forming a second network that is superimposed on the molecular network. The stress–strain behaviour can be described by writing the stress as a superposition of stresses of the individual networks, $\sigma = (1-\Phi)\sigma_1 + \Phi\sigma_2$. The parameter Φ gives the volume fraction of strands between the filler particles. Macroscopic properties such as stress–strain behaviour or stress-induced crystallization of filled elastomers are described well by this model.

(Keywords: network model; elastomers; reinforcement; filler; fully extended chains; stress–strain behaviour; stress-induced crystallization)

INTRODUCTION

The classical statistical theory of rubber elasticity attributes elastic stresses entirely to changes in the conformational entropy of the individual network chains[1–3]. Since the basic behaviour of polymer networks is predicted correctly, i.e. the dependence of elastic moduli on crosslink density and temperature, there have been numerous attempts to carry over the statistical theory of rubber elasticity to filled elastomers (see, for example, the review article of Kraus[4]). The increase in modulus of a filled system is generally attributed to two factors: first, hydrodynamic interactions caused by the filler particles; and secondly, the non-Gaussian distribution of chains between the filler particles[5–8,19]. In all these descriptions, a homogeneous deformation of the matrix is assumed. On the other hand, if one considers a filled elastomer as a series of strands with alternating sections of rubber and filler, then the average local strain of the matrix is greater than the applied macroscopic strain of the sample. This consideration, which has been formulated by Bueche[9] as the strain amplification concept, leads to a fundamentally inhomogeneous deformation behaviour of filled elastomers. This behaviour has been shown by Hess using electron microscopy[10].

Using the inhomogeneous deformation of filled elastomers as a starting point, we have developed in this work a mathematical description of the load–extension behaviour, based on the superposition of two networks. One network is formed by the chemically crosslinked matrix; the second arises due to the adhesion of the matrix to the filler particles, which act as network points. When the sample is deformed, strands form between the filler particles. The strands are mathematically described as subchains in the supernetwork. Neither network is treated as being ideally Gaussian, but a description is used in which some of the subchains are fully stretched.

THEORY

Preliminary development

Ortmann, Dietrich and Bonart[11,12] developed a model describing the influence of the finite extensibility of network chains on the orientation behaviour of a polymer network. The model is based on the following assumptions:

(i) The network is considered as a so-called 'phantom network', consisting of non-interacting chains. Each chain consists of N statistical segments of length l.

(ii) The density distribution of the chain vectors where $r < r_{\max} = Nl$ is approximated by an affinely deforming Gaussian distribution.

(iii) A fully extended chain behaves like a rod and it continues to orientate in a pseudo-affine manner.

(iv) The deformation takes place at constant volume.

The density distribution $p_G(r_0)$ of the end-to-end vector of a random walk is as follows:

$$p_G(r_0) = \frac{b^3}{\pi^{2/3}} \exp(-b^2 r_0^2) \tag{1}$$

where $b = [3/2\pi l^2)]^{1/2}$.

A deformed network is assumed to consist of chains that are fully extended, and chains that are coiled and can be deformed further in an affine manner. The density distribution of a deformed network is as follows:

$$p(\mu, \mathbf{r}) = [1 - \Psi(\mu)] p_{<}(\mu, \mathbf{r}) + \Psi(\mu) p_{=}(\mu, \mathbf{r}) \tag{2}$$

where $\Psi(\mu)$ expresses the portion of fully extended chains as a function of the strain rate μ; $p_{<}(\mu, \mathbf{r})$ represents the probability density of the end-to-end vectors that are

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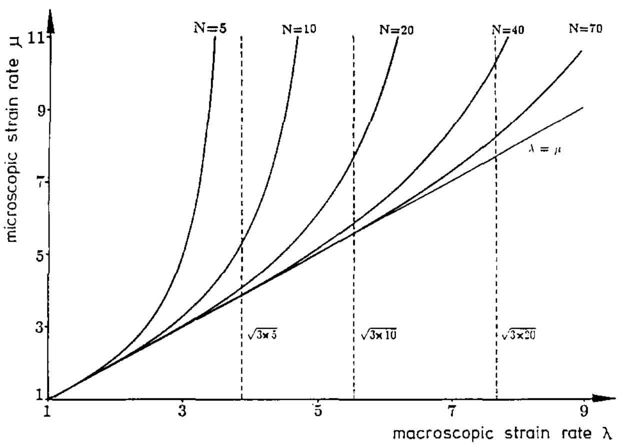

Figure 1 Model strain ratio μ as a function of the macroscopic strain ratio. For small strains $\mu=\lambda$ (affine deformation). On reaching the extensibility limit $(3N)^{1/2}$ (------), μ diverges

more or less randomly coiled and can displace affinely; and that $p_{=}(\mu, \boldsymbol{r})$ is the probability density of the network chains that are fully extended. By integrating the affine deformed Gaussian function, $p(\mu, \boldsymbol{r})$:

$$p(\mu, \boldsymbol{r})=\frac{b^3}{\pi^{3/2}}\exp\left[-b^2r^2\left(\frac{\mu^3-(\mu^3-1)\cos^2\vartheta}{\mu^2}\right)\right] \tag{3}$$

from $r_{\max}=Nl$ up to ∞, one will obtain $\Psi(\mu)$:

$$\Psi(\mu)=2\pi\int_0^{\pi}\mathrm{d}\vartheta\sin\vartheta\int_L^{\infty}\mathrm{d}r\, r^2p(\mu, \boldsymbol{r}) \tag{4}$$

A good analytical expression for the above integral is given, for $\mu>1.1$ and $N>5$, by:

$$\Psi(\mu)=\frac{\mu^3}{\mu^3-1}\left\{1-\mathrm{erf}\left[\frac{1}{\mu}\left(\frac{3N}{2}\right)^{1/2}\right]\right\} \tag{5}$$

Comparing macroscopic measurable parameters with the model, it is necessary to establish a relationship between the macroscopic strain ratio λ and the microscopic strain ratio μ. The macroscopic strain ratio λ must possess a limit if $\Psi(\mu)$ reaches 1, i.e. when only fully extended chains are present. At this point the network cannot be stretched further.

Let us consider a random walk of the end-to-end vectors through the network. By increasing the number, M, of individual chain vectors $\boldsymbol{r}_j$, the specimen vector $\boldsymbol{R}$ will reach macroscopic dimensions and will displace in an affine manner. From this one obtains the following relation between the microscopic and the macroscopic strain ratios:

$$\langle z^2\rangle_{p(\mu,r)}=\langle z^2\rangle_0\lambda^2 \tag{6}$$

where $\langle z^2\rangle_{p(\mu,r)}$ is the variance of the deformed Gaussian distribution and $\langle z^2\rangle_0$ is the variance of the z component of the macroscopic specimen vector. Calculating the left-hand side of equation (6) one obtains a functional relation between μ and λ:

$$\lambda^2=\mu^2-\frac{\mu^5}{\mu^2-1}[1-\mathrm{erf}(\eta)+\eta\,\mathrm{erf}'(\eta)]+3N\Psi(\mu) \tag{7}$$

where $\eta=(3N/2)^{1/2}/\mu$, $\mathrm{erf}(\eta)$ is the error function, and $\mathrm{erf}'(\eta)$ is the first derivative of the error function.

The function $\mu(\lambda)$ is shown in *Figure 1*. As long as the portion of fully extended chains is small, the model strain ratio is equal to the macroscopic strain ratio λ. When a significant amount of fully extended chains is reached (see *Figure 1*), μ becomes larger than λ, and increases rapidly.

The model for a filled elastomer

Active fillers, such as carbon black or surface-modified silica, possess the capability to adsorb or bind polymer chains. Therefore multi- or polyfunctional crosslinks exist in addition to the tetrafunctional crosslinks of the rubber matrix.

TEM investigations of unstretched and stretched carbon-black-filled samples[13] give an insight into the micromorphology. Undeformed samples (*Figure 2*) at the microscopic level reflect an inhomogeneous filler distribution. One can see areas of densely packed fillers and others completely free from filler particles. This fact implies different mechanical properties at the microscopic level.

As shown in *Figure 3* a uniaxial deformed sample undergoes a change in morphology. As a result of a uniaxial deformation, bands are formed that run from one end of the sample to the other, and the filler particles are linked by these bands.

According to the TEM results a filled sample consists

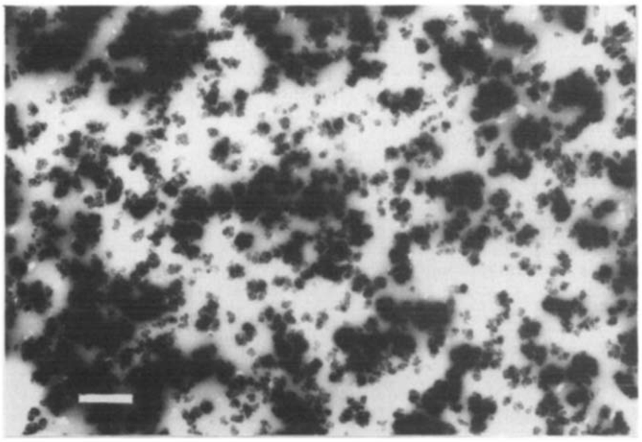

Figure 2 Unstretched, carbon-black-filled (40 phr, Corax N 765) sample viewed in the transmission electron microscope. The white bar marks 600 nm

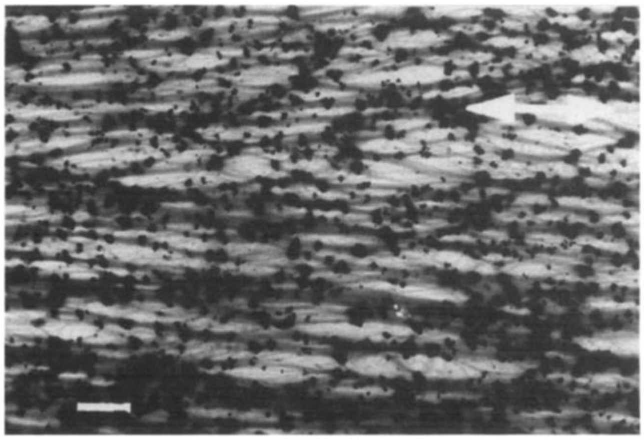

Figure 3 Stretched, carbon-black-filled (40 phr, Corax N 765) sample viewed in the transmission electron microscope. The white bar marks 1100 nm and the arrow indicates the direction of stress

of two different networks, a 'matrix network' and a 'super network'. The filler-free areas form the matrix network (*Figure 2*) caused by chemical crosslinking of the elastomer chains. So the mechanical properties of this network are determined by the statistical parameters of an unfilled, but crosslinked, elastomer matrix.

In the case of the supernetwork, the polyfunctional filler particles are regarded as the crosslinks in this network. The bands connecting the filler particles are only visible in the deformed state (*Figure 3*). These bands represent the network chains of the supernetwork. To describe the double network model mathematically, we use the assumptions and the formalism shown above (preliminary development).

The probability density of the end-to-end vector in each network is represented by a Gaussian function. Their sum is the total probability density, i.e.

$$p_{\text{total}}(r_0) = (1-\Phi)p_1(r_0) + \Phi p_2(r_0) \tag{8}$$

where Φ is the volume fraction of the supernetwork in a filled system, and $p_1(r_0)$ and $p_2(r_0)$ are the probability densities of the matrix and the supernetwork respectively, such that:

$$p_1(r_0) = \frac{b_1^3}{\pi^{3/2}} \exp(-b_1^2 r_0^2) \qquad p_2(r_0) = \frac{b_2^3}{\pi^{3/2}} \exp(-b_2^2 r_0^2)$$

where b_1 and b_2 are functions of the statistical parameters N_1 or N_2 and l_1 or l_2 of each network. N_1 and N_2 are average numbers of statistical segments forming a network chain; l_1 and l_2 are the lengths of the statistical segments in the different networks.

The probability density of a deformed and filled system is:

$$\begin{aligned} p_{\text{total}}(\mu, r) = (1-\Phi)\{[1-\Psi_1(\mu)]p_{1<}(\mu, r) + \Psi_1(\mu)p_{1=}(\mu, r)\} \\ + \Phi\{[1-\Psi_2(\mu)]p_{2<}(\mu, r) + \Psi_2(\mu)p_{2=}(\mu, r)\} \end{aligned} \tag{9}$$

where $\Psi_1(\mu)$ and $\Psi_2(\mu)$ determine the amount of fully extended chains in each network. The total amount of fully extended chains can be evaluated using:

$$\Psi_{\text{total}}(\mu) = (1-\Phi)\Psi_1(\mu) + \Phi\Psi_2(\mu) \tag{10}$$

MACROSCOPIC PROPERTIES OF THE DOUBLE NETWORK

Strain rate λ

The fundamental assumption is that both networks are independent of each other. Therefore we can calculate the macroscopic strains λ_1 and λ_2 in each network. The total macroscopic strain λ is a mathematical combination of λ_1 and λ_2. As shown in equation (6) the macroscopic strain ratios λ_1 and λ_2 are functions of the model strain ratio μ:

$$\langle z_1^2 \rangle_{p_1(\mu, r)} = \langle z_1^2 \rangle_0 \lambda_1^2 \tag{11}$$

$$\langle z_2^2 \rangle_{p_2(\mu, r)} = \langle z_2^2 \rangle_0 \lambda_2^2 \tag{12}$$

where $\langle z_1^2 \rangle_0 = 1/(2b_1^2)$ and $\langle z_2^2 \rangle_0 = 1/(2b_2^2)$.

The expressions for $\langle z_1^2 \rangle_{p_1(\mu, r)}$ and $\langle z_2^2 \rangle_{p_2(\mu, r)}$ from equation (7) are:

$$\langle z_{1,2}^2 \rangle_{p_{1,2}(\mu, r)} = \frac{1}{2b_{1,2}^2}\left(\mu^2 - \frac{\mu^5}{\mu^3 - 1} D_{1,2}\right) + N_{1,2} l_{1,2}^2 \Psi_{1,2}(\mu) \tag{13}$$

$$D_{1,2} = 1 - \operatorname{erf}(\eta_{1,2}) + \eta_{1,2} \operatorname{erf}'(\eta_{1,2}) \tag{14}$$

The variance of the z component of the overall macroscopic specimen vector is the sum of the variances in each single network, and:

$$\langle z_{\text{total}}^2 \rangle_0 \lambda^2 = (1-\Phi)\langle z_1^2 \rangle_0 \lambda_1^2 + \Phi\langle z_2^2 \rangle_0 \lambda_1^2 \tag{15}$$

and

$$\langle z_{\text{total}}^2 \rangle_0 = \frac{(1-\Phi)b_2^2 + \Phi b_1^2}{2b_1^2 b_2^2} \tag{16}$$

Combining equations (15) and (16) and substituting for $\langle z_1^2 \rangle_0$ and $\langle z_2^2 \rangle_0$, we obtain the functional relation between the microscopic strain ratio μ and the macroscopic strain ratio λ:

$$\lambda = \left[\frac{2b_1^2 b_2^2}{(1-\Phi)b_2^2 + \Phi b_1^2}\left((1-\Phi)\frac{1}{2b_1^2}\lambda_1^2 + \Phi\frac{1}{2b_2^2}\lambda_2^2\right)\right]^{1/2} \tag{17}$$

λ is a function of the macroscopic strain rate and it enables us to describe macroscopic measurable properties of filled samples in terms of the double network.

Stress

The macroscopic stress σ_{total}, applied to a filled system, is described by the sum of the individual stresses, and they are added according to the volume fraction Φ of the supernetwork, such that:

$$\sigma_{\text{total}} = (1-\Phi)\sigma_1 + \Phi\sigma_2 \tag{18}$$

$$\sigma_1 = G_1\left(\lambda_1 - \frac{1}{\lambda_1^2}\right)\frac{1}{1-\Psi_1(\lambda_1)} \tag{19a}$$

$$\sigma_2 = G_2\left(\lambda_2 - \frac{1}{\lambda_2^2}\right)\frac{1}{1-\Psi_2(\lambda_2)} \tag{19b}$$

σ_1 and σ_2 can be calculated with the Gaussian deformation functions. Therefore the retractive force is purely entropic. In particular, we consider that our model describes the mechanical behaviour at high deformations and show that it is determined by fully extended chains. We do not consider elastic energy contributions to the retractive force, which provide a constant portion to the total stress at high deformations. Elastic energy effects are more significant at small deformations. Here, 50% or more of the retractive force can be due to elastic energy effects (see Grassler[14]). Furthermore, we do not take into account stress softening, caused by relaxation processes, or detachment of rubber chains from the filler particles.

Equations (19a) and (19b) contain the empirical factors $1/(1-\Psi_1)$ and $1/(1-\Psi_2)$, which take the high force contributed by fully extended chains into account. At high deformations, when a certain amount of fully extended chains is present, the empirical factors diverge and the stress will rise rapidly.

Influence of the network parameter on the shape of the stress–strain curve

To describe a filled system the model requires five parameters, N_1, N_2, l_1, l_2 and Φ. In the following we will show how the parameters change the shape of the stress–strain curve.

(i) First, N_2 alone was changed and the other parameters remained constant, i.e. $N_1 = 30$, $l_1 = 3 \times 10^{-9}$ m, $l_2 = 3 \times 10^{-9}$ m and $\Phi = 0.50$. *Figure 4* shows that, the smaller the number of statistical segments in the supernetwork, the steeper the upswing of the stress–strain

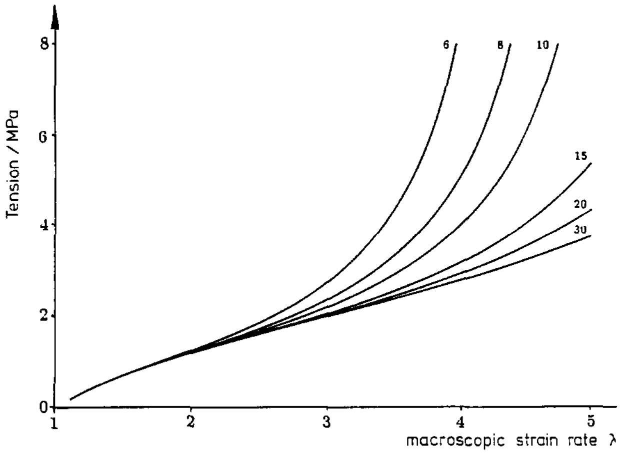

Figure 4 Stress–strain curves for different N_2. The values of N_2 are shown on each curve

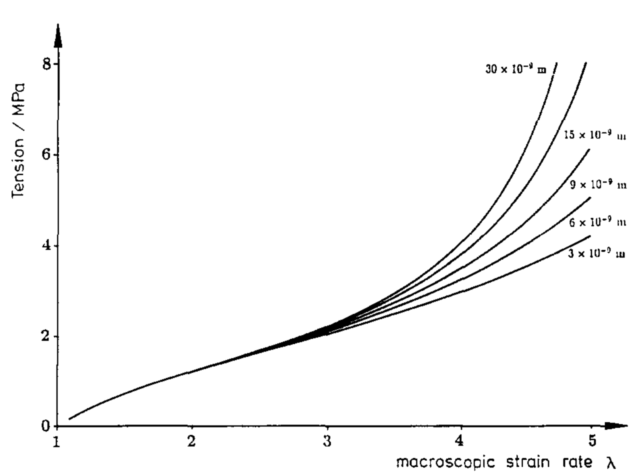

Figure 5 Stress–strain curves where the length of the statistical segment l_2 is varied. The values of l_2 are shown on each curve

curve. Additionally the beginning of the upswing is shifted to a lower macroscopic strain.

(ii) Secondly, the effect of the segment length l_2 was tested. The values of the constant parameters were: $N_1=30$, $N_2=10$, $l_1=3\times10^{-9}$ m and $\Phi=0.50$. A longer statistical segment in the supernetwork resulted in a greater slope of the stress–strain curve (*Figure 5*), but the beginning of the upswing was not changed very much.

(iii) Thirdly, the volume fraction of the supernetwork was changed and the other parameters kept constant. An increase of the volume fraction of the supernetwork caused a shift of the stress upswing to a smaller macroscopic strain. In addition the stress level rises at small deformations. It is obvious that the shape of the stress–strain curve is affected more and more by the statistical parameters of the supernetwork, while Φ is increasing.

According to the points mentioned above, one can draw the conclusion that the shape of the computed stress–strain curves was mostly affected by the number of statistical segments in the supernetwork. The parameters l_2 and Φ do not have such serious consequences on the shape of the curves. The beginning of the upswing is essentially stipulated by N_2.

Stress-induced crystallization

In a strained natural rubber the entropy S of the network chains is reduced. According to $T_M=\Delta H/\Delta S$, the melting temperature T_M of the crystals is shifted to higher temperatures. Consequently it is possible to obtain crystals in a stretched specimen at temperatures above the isotropic melting point.

In this case we assume that the volume fraction of fully extended chains $\Psi_{\text{total}}(\mu)$ is proportional to the portion of stress-induced crystals C_{cr}. Equation (20) gives the functional relation between $\Psi_{\text{total}}(\mu)$ and C_{cr}:

$$C_{\text{cr}}=f\Psi_{\text{total}}(\mu) \qquad (20)$$

f is a proportionality factor, which indicates the amount of fully extended chains that are transformed into stress-induced crystals.

(i) Some fully extended chains or chain segments exist and are joined by adjacent and preoriented chains to form a crystal. Here $f>1$ because not all the chains in a crystal are mechanically fully extended ones (*Figure 6a*).

(ii) For $f=1$, a stress-induced crystal is only built by fully extended chains and each of these chains is part of a crystal (*Figure 6b*).

(iii) For $f<1$, not every fully extended chain takes part in a stress-induced crystal (*Figure 6c*).

MODEL AND EXPERIMENT

Stress–strain curve

The stress–strain data of filled polydimethylsiloxane (PDMS) networks were taken from Mark[15]. He and his coworkers[16] prepared samples by mixing tetraethyl orthosilicate (TEOS) with vinyl-terminated PDMS, which can be hydrolysed to give an SiO_2-filled polymer. These filled elastomers can be regarded as model systems because the elastomer chains are attached with their ends to the filler particles.

Stress–strain curves of these systems are compared with our double network model in *Figure 7*, from which it can be seen that the experimental data are well described by the double network model. Owing to the preparation technique, ideal conditions exist; complete attachment of the chain ends to the filler surfaces, almost spherical shape of the filler particles and no filler aggregation. According to these circumstances there has to be a correlation between the filler surface in each sample and the volume fraction of the supernetwork, which is gained by fitting the experimental data. The surface area able to attach

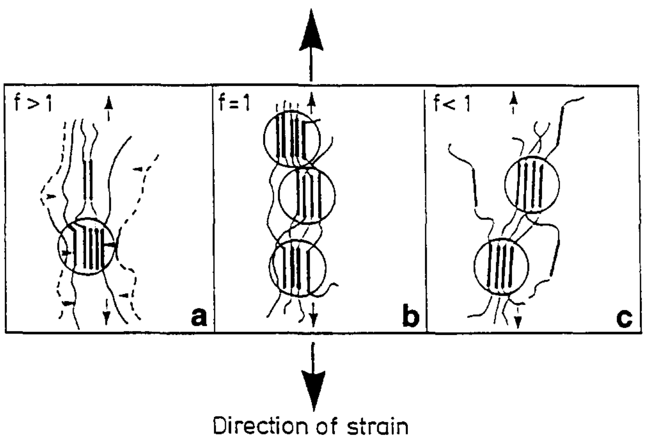

Figure 6 Schematic description of stress-induced crystallization. The straight thick lines, pointing in the direction of stress, mark the fully extended chains. The stress-induced crystals are accentuated with circles

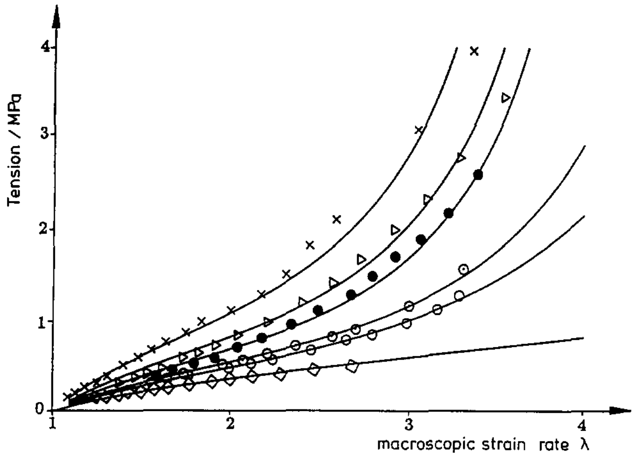

Figure 7 Stress–strain curves of filled PDMS networks: (◇) unfilled, (○) 2.3 vol%, (⊙) 4.5 vol%, (●) 9 vol%, (△) 10.8 vol% and (×) 14.5 vol% silica. The full curves are computed according to the double network model

Table 1

Sample (i)	a	b	c	d	e	f
$V_F(i)$ (vol%)	0.0	2.3	4.5	9.0	10.8	14.5
$\Phi(i)$ (vol%)	0.0	25.0	34.0	48.0	57.0	70.0
$\left(\frac{V_F(i)}{V_F(f)}\right)^{2/3}$	-	0.29	0.46	0.73	0.82	1.00
$\frac{\Phi(i)}{\Phi(f)}$	-	0.33	0.48	0.70	0.81	1.00

polymer chains is proportional to the experimental volume fraction of the filler particles raised to the two-thirds power:

$$\left(\frac{V_F(i)}{V_F(f)}\right)^{2/3}=\frac{\Phi(i)}{\Phi(f)} \tag{21}$$

The left-hand side of equation (21) represents the surface ratio of the filler particles, and the right-hand side the volume fraction of the supernetwork. Both ratios are standardized for the sample with the highest filler content (sample number f). The index for each sample (i) is shown in *Table 1*. Additionally we added the numerical values of both sides of equation (21).

As one can see, there is indeed a correlation between the parameters $V_F(i)$ and $\Phi(i)$. The volume fraction Φ of the supernetwork is proportional to the filler surface available to attach polymer chains.

In addition to this, the validity of the double network model has been tested by fitting stress–strain curves of carbon-black-filled rubbers. Before recording the stress–strain data, the samples had been prestretched to avoid stress softening or the so-called Mullins effect[17]. The Gaussian deformation functions of the model can only describe completely reversible deformations.

Nevertheless natural rubber possesses the property of forming stress-induced crystals, which act as additional crosslinks in the deformed system. To avoid the influence of the stress-induced crystals, the measurements have been carried out at 343 K. Stress–strain data have been recorded from samples with different carbon black contents, and the double network model has been fitted to the experimental data (*Figure 8*). The best-fit parameters can be seen in *Table 2*.

Stress-induced crystallization

The parameters resulting from the fit of the experimental data (*Table 2*) were used to calculate the volume fraction of the stress-induced crystals. Experimental data have been taken from calorimetry measurements[18]. As *Figure 9* shows, we are able to calculate the volume fraction of stress-induced crystals as a function of the macroscopic strain rate λ. In this case when the proportionality factor is set to 1 in equation (20), we achieved a good conformity between model and experiment. The proportion of stress-induced crystals

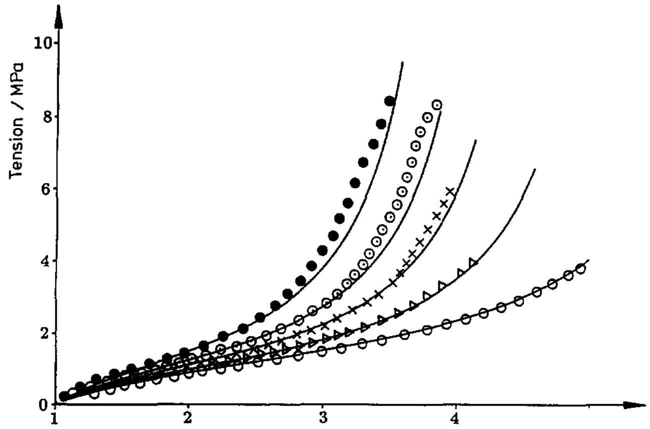

Figure 8 Mechanical stress as a function of the macroscopic strain ratio λ. The symbols represent the experimental data of every filler content: (○) 10 phr, (△) 20 phr, (×) 30 phr, (⊙) 40 phr and (●) 50 phr. The full curves are calculated according to equation (18)

Table 2

Carbon black content (phr)	Number of segments N_1	Number of segments N_2	Segment length (nm) l_1	Segment length (nm) l_2	Volume fraction of supernetwork, Φ
10	40	14	1.6	30	0.25
20	40	9	1.6	30	0.45
30	40	8	1.6	30	0.50
40	40	6	1.6	30	0.56
50	40	6	1.6	30	0.70

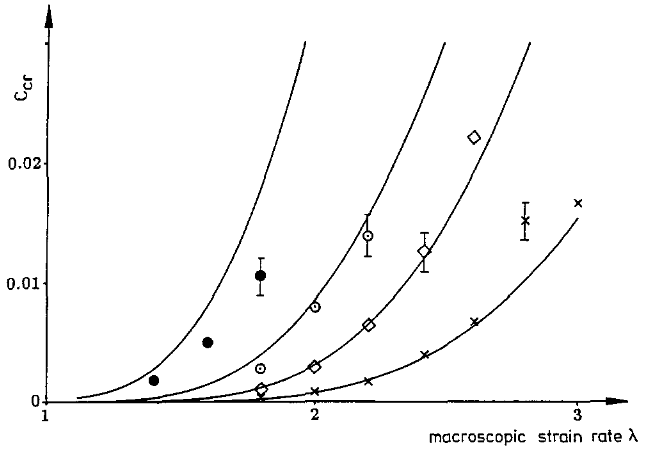

Figure 9 Volume fraction of the stress-induced crystals as a function of the macroscopic strain ratio. The experimental data (×) 10 phr, (◇) 20 phr, (⊙) 30 phr and (●) 50 phr are compared with the theoretical data (full curves)

only is overestimated for the sample with 50 phr carbon black.

Here a proportionality factor, $f < 1$, will provide a better fit of the experimental data. According to *Figure 9*, we concede that not every fully extended chain is part of a strain-induced crystal, if the filler load is fairly high. The number of chains attached to the filler surface is increasing with increasing filler content, and consequently the chain mobility is reduced. There is no doubt that numerous fully extended chains exist in a deformed and highly filled elastomer. Thus, owing to the reduced mobility, not every fully extended chain is part of a stress-induced crystal.

CONCLUSIONS

In this paper a model has been developed to describe the mechanical properties of uniaxial deformed filled elastomers. The double network model separates the filled elastomer into two components: one reflects the statistical properties of the unfilled and crosslinked rubber matrix; in the other one, the filler particles act as crosslinks and the connecting rubber molecules are the network chains.

The limited extensibility of the network chains has been taken into account and it becomes clear that the supernetwork controls the mechanical properties at high deformations. A small number of statistical segments N_2 in the supernetwork causes a remarkable number of fully extended chains at small deformations. N_2 is a function of the filler content. An increasing filler content decreases the average distance between the fillers, which are the crosslinks of the supernetwork.

The parameter l_2 (length of the statistical segments in the supernetwork) reflects the restrictions caused by active fillers:

(i) Polymer chains are adsorbed by the filler surfaces and their segmental mobility decreases in these regions. On the filler surface the polymer chains possess a two-dimensional mobility[4]. The chains are preoriented around the filler particles.

(ii) The average diameter of the filler particle is 10 or more times greater than the monomer length of the elastomers. Therefore the molecules are bound with several segments to the filler surface and have restricted mobility.

It is apparent from the fit of the model to the experimental data of filled PDMS networks that the volume fraction of the supernetwork is a function of the filler surface provided for attachment in filled systems. In carbon-black-filled elastomers, the surface activity of the fillers determines the volume fraction of the supernetwork. Highly active fillers cause a greater volume fraction of the supernetwork than less-active fillers. The parameter Φ is sensitive to the filler surface and the filler surface activity.

Additionally the double network model describes the stress-induced crystallization without changing the parameters obtained, describing the experimental stress–strain curve of filled natural rubber (see *Table 2*). The theoretical description of stress-induced crystallization allows statements about the process of crystal formation under deformation. At least the double network model reveals that deformation is completely inhomogeneous. In a deformed sample the supernetwork is highly stressed. Bands are connecting the filler particles whereas the matrix network is less stressed. These bands consist of rubber molecules, which are well oriented in the direction of deformation. The molecules of the supernetwork carry the major load applied to a filled system.

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