A network evolution model for the anisotropic Mullins effect in carbon black filled rubbers

Roozbeh Dargazany, Mikhail Itskov*

Department of Continuum Mechanics, RWTH Aachen University, Elfschornsteinstr. 18, 52062 Aachen, Germany

A R T I C L E   I N F O

Article history:
Received 25 November 2008
Received in revised form 3 March 2009
Available online 5 April 2009

Keywords:
Microstructure
Anisotropy
Filled elastomers
Rubber network
Permanent set
Stress softening

A B S T R A C T

To the best of our knowledge, there are no constitutive models that properly describe experimental data on anisotropy of the Mullins effect. In this paper, such a micro-mechanical model is proposed for carbon black filled rubbers. The model describes the deformation induced anisotropy and permanent set as well. Damage of the polymer-filler network is considered as a consequence of chain sliding on or debonding from aggregates. In contrast to previous works on anisotropy of the Mullins effect we do not introduce any phenomenological damage function. Damage in different directions is governed by a network evolution concept which describes the changes in the inter-aggregate distribution of polymer chains. The model includes a few number of physically motivated material constants and demonstrates good agreement with own experimental data on subsequent uniaxial tensions in two orthogonal directions.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Regarding considerable economic potential and vast technical application of rubber-like elastomers, their mechanical properties have become a subject of intensive studies during the last century. One of the important mechanical characteristics of rubber is stress softening after the first loading cycle which is referred to as the Mullins effect. It was experimentally observed and reported (see, e.g., Mullins, 1948) along with deformation induced anisotropy and time-independent residual strains generally known as permanent set.

In the last few decades, numerous constitutive models have been developed in order to describe different aspects of mechanical behavior of rubber-like materials and in particular the Mullins effect. The proposed concepts can generally be classified as phenomenological and micro-mechanically motivated models. Among several phenomenological approaches Dorfmann and Ogden (2004) applied a theory of pseudo-elasticity which along with stress softening is able to take into account permanent set. Although the model is isotropic and does not describe the deformation induced anisotropy, it shows good agreement with experimental results in one loading direction. Another softening model proposed by Ehret and Itskov (2009) for soft biological tissues includes the Mullins effect as a special case and is able to consider permanent set and deformation induced evolution of anisotropy. Generally, phenomenological approaches include a number of material parameters which usually have no physical interpretation and should be defined by a fitting procedure. These procedures can be excessively elaborate and numerically expensive. Furthermore, distinct sets of material parameters can fit to one and the same set of experimental data and the exact contribution of single parameters to the material response is often unclear.

According to experimental results stress softening at the same strain level decisively depends on the filler concentration in the rubber network. In unfilled elastomers softening is negligible but becomes very pronounced in rubbers with a high filler concentration. Nevertheless, stress softening in rubber-like materials was initially attributed solely to the rubber network. Thus, on the basis of an experimental study Harwood et al. (1965) proposed several possible sources of damage including debonding and recreation of cross-links, chains residual stretch and chain breakage. Expanding the above assumption, Marckmann et al. (2002) proposed a model considering damage as a result of link breakages and matrix alteration. They incorporated the old network alteration theory into the eight chain model (Arruda and Boyce, 1993). As a consequence, their model is able to consider stress softening both in unfilled and filled rubbers but does not describe induced anisotropy and permanent set and shows an unrealistic stress upturn in the primary loading. Chagnon et al. (2006) further optimized the network alteration theory by relaxing some basic assumptions. Thus, the final theory showed better agreement with experiments although it still suffers from an unrealistic stress upturn in the primary loading.

Although slight stress softening does occur in unfilled rubbers as well, its mechanism differs fundamentally from that one
underlying softening in filled rubbers (Harwood et al., 1965). This motivated another class of theories in which damage is considered as an effect of filler contribution. Bueche (1960) developed a physically based model considering consequent debonding of chains from fillers during the primary loading. He supposed that chains with different lengths are distributed within the rubber network and employed statistical mechanics in order to describe the Mullins effect. Further developing his basic assumption of chain breakage, Dannenberg (1974), Rigbi (1980) attributed softening to the surface mobility and slippage of bonded segments of polymer chains over the aggregate surface. Govindjee and Simo (1991) proposed a three-dimensional model of the chain network evolution which included three new features. First, polymer chain distribution inside the rubber matrix was implemented. Second, consequent debonding as a direct result of network elongation was taken into account and, finally, the concept of network decomposition was applied in which the rubber network is decomposed into elastic rubber (CC) and polymer-filler (PP) networks.

Although the resulting three-dimensional model was obtained by summation over principal strain directions, its numerical implementation was solely applied to the one-dimensional case. In order to improve the model, the same authors (Govindjee and Simo, 1992) further proposed a phenomenological concept based on the previous assumptions. This concept was easily implemented into a finite element code and showed good agreement with experimental data. Like the previous formulations this model was isotropic and did not describe permanent set. Drozdov and Dorfmann (2001) further proposed another kind of the network evolution theory. They classified polymer bonds into two groups: flexed and extended bonds. The number of bonds in these groups evolves as a consequence of network deformation. With this assumption, their model was able to consider isotropic stress softening and permanent set.

Quite recently, Göktepe and Miehe (2005) proposed an anisotropic extension of the theory by Govindjee and Simo (1992). The CC network is considered to be purely elastic and its strain energy is formulated by applying a concept of non-affine micro–macro transition to a tube model by Kaliske and Heinrich (1999). Damage is attributed to the PP-network and described by an approach proposed by Govindjee and Simo (1992). The model was able to take into account permanent set and deformation induced anisotropy which represents a clear advantage in comparison to previous models. However, the model was not compared to experimental data on anisotropy of the Mullins effect while softening was simulated by means of a phenomenological damage function.

Another model by Diani et al. (2006) was obtained as an extension of the network alteration theory. In order to predict induced anisotropy and permanent set the model utilizes a phenomenological damage function. It demonstrates good agreement with experiments for the unloading in the first direction but suffers from an unrealistic stress upturn in the prediction of the loading branches.

In the present paper, we pursue the concept of network decomposition by Govindjee and Simo (1991) and propose a new micromechanical model for the polymer-filler network where softening of the equilibrium stress–stretch behavior is based on an evolution of the polymer chain network suspended between carbon black aggregates. Finally, the model is compared with own experimental data on subsequent uniaxial tensions in two orthogonal directions. It is referred to as end-to-end distance. Using the abbreviation

$$\alpha = \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right)^2,$$

where $\theta$ denotes the supplement of the valence angle and following the lead of Bueche (1960), Govindjee and Simo (1991), the probability density function for a FRC is obtained as

$$p(r) \, dr = \frac{3\alpha}{2\pi l^2} \frac{\omega^2}{m^2} \frac{1}{r^3} dr.$$

The above function shows a better agreement with the exact chain distribution than a non-Gaussian one (see, e.g., Treloar, 1975), although the latter one is still advantageous in application to the calculation of the entropy and the resulting free energy. For this reason, the non-Gaussian distribution will be used in the next chapter for the derivation of the free energy of the FRC.

### 2.2. Probability distribution function of polymer chains between aggregate surfaces

Within the rubber matrix, filler particles are joined together and form aggregates representing the smallest colony of fillers. In turn, aggregates are connected to polymer molecules at different places on their surfaces. The aggregate surface is not homogeneous. It consists of a low-energy background with some chemically highly energetic sites. The latter ones called active adsorption sites are responsible for binding with polymer segments. The hierarchical structure of filler reinforcement is schematically shown in Fig. 1.

Let $A$ be the total area of active adsorption sites inside the rubber matrix and $N$ be the number of bonded segments of polymer chains per unit volume. Then, one defines the average area of active adsorption sites available for the formation of a bond with one structural segment of a polymer chain as $\kappa = A/N$ (see, e.g., Bueche, 1961).

We consider further a set of chains in a particular direction $d = R/r$ both ends of which are connected to two aggregate surfaces. In order to evaluate the end-to-end distance of polymer chains between the aggregates, the rough fractal surface of the aggregates is simplified as a non-penetrable, flat surface. Accordingly, in the following we assume that the aggregate surfaces are separated by an average distance $r$ (Fig. 1).

A chain segment is assumed to be bonded to the active adsorption site if its end is placed within a certain distance $\Delta r$ from the
aggregate surface. The probability that exactly the $n$th segment of this chain is also bonded to active sites of the opposite aggregate is 

$$p(r) = \sqrt{\frac{3\pi}{2\pi n l^2 \exp(-\frac{\kappa r}{l})}},$$

where $\kappa \Delta r$ represents the volume where the bonding of segments to aggregate surface can take place. The assumption that $\Delta r = l$ gives a good estimation for the probability function (see, e.g., Bueche, 1961).

Thereby, we assume that none of segments between the number 1 and $n$ is joined to an aggregate surface in the sense of the above concept of the polymer-aggregate bond. Considering $r = \frac{r}{l}$ as relative distance, the probability of this state is expressed as (cf. Govindjee and Simo, 1991)

$$P(n, r) = \sqrt{\frac{3\pi \kappa^2}{2\pi n l^2 \exp(\frac{\kappa r}{l})}},$$

where

$$B = -G - \frac{\kappa}{\sqrt{\pi l}} \left[ \sqrt{6\pi n e^{-G}} + 3\kappa \sqrt{\pi \text{erf}(\sqrt{G})} - \sqrt{6\pi e^{-Gn}} - 3\kappa \sqrt{\pi \text{erf}(\sqrt{Gn})} \right], \quad G = \frac{3\pi r^2}{2n}.$$
In Fig. 2 the effect of the parameter $\kappa$ on the probability (4) as a function of $n$ is studied. All curves are normalized to render their integral to unity. It is seen, for example, that with increasing $\kappa$ the mean value of $n$ decreases, which can be explained from the micro-mechanical point of view. Indeed, the increasing filler concentration $\kappa$ leads to a shortening of the average distance between aggregates so that the probability of longer chains between them decreases.

The probability function (4) includes the additional parameter $\beta$ which solely depends on the molecular structure of chains. Thus, the representations of Bueche (1961), Govindjee and Simo (1991) result from (4) as special cases by setting there $\kappa = \frac{\rho_0}{\rho_{pp}}, \beta = 1$ and $\kappa = 2, \beta = 1$, respectively.

2.3. Chains substitution

The number $n$ and length $l$ of segments of a FRC are related to those of the so-called freely jointed chain, $n_i$ and $l_i$, respectively by Kuhn (1934)

$$l_i = al, \quad n_i = bn,$$  \hspace{1cm} (6)

where the coefficients $a$ and $b$ are calculated by Treloar (1975)

$$a = \frac{1}{\cos \left( \frac{\pi}{4} \sqrt{\alpha} \right)}, \quad b = \cos^2 \left( \frac{\pi}{2} \sqrt{\beta} \right) \sqrt{\alpha}. \hspace{1cm} (7)$$

The free energy of the FRC can be obtained on the basis of the chain substitution concept [Flory, 1989; Treloar, 1975]. By this means, the valence angle is taken into account. Accordingly, the non-Gaussian strain energy of the FRC can be written by

$$\psi_c(n, \bar{r}) = bnKT \left( \frac{\bar{r}}{abn} + \frac{\beta}{\ln \frac{\beta}{\sinh \beta}} \right), \hspace{1cm} (8)$$

where $\beta = g^{-1}(\frac{1}{abn})$ and $g^{-1}$ denotes the inverse Langevin function. Finally, $T$ stands for the temperature (isothermal condition is assumed) and $K$ is Boltzmann’s constant. The free energy function (8) resulting from the FRC concept will further be implemented for all polymeric chains in the rubber matrix.

A good approximation of the inverse Langevin function can be achieved, for example, by the following approximation (Puso, 2003)

$$g^{-1}(x) \approx \frac{3x}{1 - x^2}. \hspace{1cm} (9)$$

The chain force can further be calculated as

$$F(n, \bar{r}) = \frac{\partial \psi_c}{\partial \bar{r}} = \frac{\partial \psi_c}{\partial \bar{r}} = \frac{KT}{al} g^{-1} \left( \frac{\bar{r}}{abn} \right), \hspace{1cm} (10)$$

3. Network decomposition

Our model is based on the network decomposition concept which was widely used in order to describe the microstructure of filled rubber-like materials (see, e.g., Klüppel, 2003). According to Govindjee and Simo (1991), the rubber matrix is decomposed into a pure rubber network and a polymer-filler network which act parallel to each other. In line with this assumption, the free energy of the rubber matrix $\Psi_M$ can be represented by

$$\Psi_M = \Psi_{ec} + \Psi_{pp}, \hspace{1cm} (11)$$

where $\Psi_{ec}$ and $\Psi_{pp}$ denote the free energies of chains in pure rubber network and chains distributed between filler aggregates, respectively. By this means, one assumes that there is no interaction between both networks. The network decomposition concept is illustrated in Fig. 3.
3.2. Polymer-filler network

The evolution of the polymer-filler network is assumed to be responsible for the already mentioned stress softening. In order to calculate the contribution of the polymer-filler network to the free energy \( W_{pp} \), we consider a particular direction \( d \). Let \( N(n, \bar{r}) \) be the number of chains with the number of segments (relative length) \( n \), the relative end-to-end distance \( \bar{r} \) and the end-to-end direction \( d \).

Now, by considering filler aggregates as rigid bodies, the free energy of the corresponding polymer-filler network is expressed by

\[
N(n, \bar{r})\psi_c(n, \bar{r}),
\]

where \( \psi_c \) is given by Eq. (8). Integration over the whole set \( D_\delta \) of relative chain lengths \( n \) available in the direction \( d \) further yields the free energy of chains in this direction as

\[
W_d = \int_{D_\delta} N(n, \bar{r})\psi_c(n, \bar{r})dn,
\]

which will further be discussed in the context of network evolution.

4. Network evolution

In the previous section the model of the virgin (undeformed, undamaged) filler-reinforced rubber has been presented. Deformation of the material leads to the evolution of the polymer-filler network which, in turn, results in many important deformation induced phenomena like stress softening, anisotropy or permanent set.

In the following, the network evolution is understood to be an interaction of two simultaneous processes referred to as aggregate-polymer debonding and network rearrangement. In this section, each of these processes and their contributions to the above mentioned deformation induced effects will be discussed in detail.

4.1. Aggregate-polymer debonding

Consider a set of polymer chains placed between two aggregates and bounded to their active sites (see Fig. 4). Recall that these polymer chains generally represent a part of longer molecular chains. Let us denote the averaged inter-aggregate distance in the virgin and elongated network by \( r_0 \) and \( k_1r_0 \) (\( k_2r_0 \)), respectively, where \( k_1 < k_2 \) represent micro-stretches in the inter-aggregate direction \( d \). In the course of deformation, the polymer chains begin to slide on or debond from the aggregates. This debonding starts with the shortest chain and gradually involves longer and longer chains.

The strength of monomer bonds within polymer chains is far higher than that of polymer-filler bonds. Thus, even at large strains polymer chains do not break but rather slide from their bonding sites on the aggregate surface. During consequent unloading, the distance between aggregates again decreases. However, the debonded chains do not reattach back to the aggregates surface. Thus, the maximal micro-stretch \( \lambda_m \) previously reached in the loading history is crucial for the description of the polymer-filler debonding.

In order to formalize the sliding process, we consider Fig. 5, in which the distribution profile of polymer chains with initial relative distance \( r_0 = r_0/l \) is plotted versus the number of segments \( n \). The below diagram illustrates the chain force versus the number of segments. Clearly, this force tends to infinity as the end-to-end distance of the chains tends to its inextensibility limit.

The debonding or the sliding takes place if the force magnitude exceeds the effective interaction strength of polymer-filler bonds denoted by \( F_{eff}^{c-f} \). This force is achieved when a chain reaches its maximal length which is expressed as \( \nu\lambda_m r_0 \), where \( \nu > 1 \) denotes a sliding ratio. Thus, the chains with the contour length \( L < \nu\lambda_m r_0 \) are already debonded. By means of (7), this condition can alternatively be written as (see Fig. 5)

\[
n < \frac{\nu\lambda_m r_0}{ab}.
\]

Thus, the sliding ratio results from the equation

\[
F(n, r_0, \lambda_m r_0) = F_{eff}^{c-f}.
\]
where \( n_{c-f} \) denotes the number of chain segments in the case of debonding. Taking (10) into account we get

\[
 n_{c-f} = \frac{\tilde{r}}{\mathcal{F}(\frac{\tilde{r}}{a})/ab} .
\]  

(18)

On the other hand, one can write according to (16)

\[
 n_{c-f} = \frac{\nu_0 \tilde{r} a \bar{\theta}}{ab} .
\]  

(19)

Comparison of these two expressions yields

\[
 v = \frac{1}{\mathcal{F}(\frac{\tilde{r}}{a})/ab} .
\]  

(20)

where we keep in mind that \( \tilde{r} = \lambda_m f_0 \) is true just in the case of primary loading, at which the debonding can occur.

According to Huber and Vilgis (1998) the value of \( F^\text{eff}_{c-f} \) does not depend on the length of the chain, although several other parameters (e.g., the aggregate surface geometry, chain geometrical position with respect to the aggregate surface, etc.) effect it. For this reason, \( F^\text{eff}_{c-f} \) averaged over all active aggregate surfaces can and will be considered as a material parameter. In view of (20), this is true for the sliding ratio \( v \) as well, since it is uniquely expressed in terms of \( F^\text{eff}_{c-f} \) and other material constants.

It is seen that the relative length of a chain connecting two adjacent aggregates is bounded below by \( n_{c-f} \). Looking at Fig. 6 one can see that it can also be bounded above. Indeed, chains whose length exceeds some upper limit could not be placed between the aggregates even from the purely geometrical point of view. First, the Gaussian distribution function of chains between two aggregates does not take into account the finite volume of the molecules which becomes relevant for long chains. Second, the probability to a long chain between two aggregates without intermediate bounds to their active sides is considerably less than the predicted value. Third, aggregates represent rigid geometrical obstacles for chains paths which are not considered by the Gaussian distribution but, considerably reduce the probability of long chain paths. Furthermore, long chains will probably intersect themselves and build internal cross-links whose contribution is taken into account by the rubber network contribution. This justifies the assumption of the relative length upper limit \( n_{\text{max}} \) of chains connecting two aggregates.

Accordingly, the set of available relative lengths of chains bounded to aggregates in the direction \( \mathbf{d} \) can be expressed by

\[
 D_\Lambda(\lambda_m) = \left\{ n \left| \frac{\lambda_m f_0}{ab} \leq n \leq n_{\text{max}} \right. \right\} ,
\]  

(21)

where \( \lambda_m \) denotes the maximal micro-stretch reached in this direction. By means of this value the loading history influences the material behavior in the direction \( \mathbf{d} \).

Note that the set (21) is defined for freely rotating chains and is direction dependent. Thus, it can be considered as a three-dimensional extension of the one-dimensional domain proposed by Govindjee and Simo (1991) for freely jointed chains. Besides, Eq. (21) includes the upperbound parameter \( n_{\text{max}} \) which restricts the number of active segments to a finite number.

4.2. Network rearrangement

The concept of chain rearrangement in rubber network as a result of deformation has recently been explored (see, e.g., Govindjee and Simo, 1991; Diani et al., 2006). It is usually assumed that after debonding chains do not contribute to the network entropic energy any more and their energy is thus lost. This concept considers molecular chains bonded to aggregates only at two points which might be, indeed, well justified for relatively short chains. However, longer molecular chains are usually bonded at different places to aggregates and have numerous cross-linkages with other chains.

During polymerization, molecular chains with a high number of segments (often known as degree of polymerization) normally appear. Several micro-mechanical methods have been developed in order to determine the distribution of the molecular chain lengths in rubber network in the steady state after the polymerization (see, e.g., Ito, 1969; Smeulders and Govindjee, 1999). According to some studies on this subject the mean value of the chain length is relatively high. For example, for polystyrene this value is more than \( 10^9 \) (see, e.g., De Gennes, 1979). For this reason, the actual status of a polymer molecule with many linkages to aggregates and other chains should be taken into account in the network modeling. Debonding of chains from the aggregate surface does not necessarily result in the complete loss of their role in the network entropic energy. Vice versa, the debonding can even lead to the recruiting of some new active segments. Indeed, we can imagine three simultaneously happening competitive processes accompanying debonding (see Fig. 7):

1. Deactivation of some segments.
2. Activation of some segments.
3. No effect on number of active segments.

Note also that with increasing inter-aggregate distance one of these processes triggers another one and so on. All in all, one can
assume that the total number of active segments remains constant (see, e.g., Markcmaan et al., 2002). The debonding is also considered as an irreversible process such that no new bonds can appear during the further loading or after unloading.

As discussed before, we assume the Gaussian pattern for the chains distribution \( P(n, r_0) \) between aggregates both in the reference and deformed configuration. Since the integration will be carried out only over the set available chains \( D_k \)

\[
\int_{D_k} P(n, r_0) d n < 1. \tag{22}
\]

In order to satisfy the normalization condition, a normalization function \( g(\lambda_m) \) is introduced such that

\[
\int_{D_k} P(n, r_0) g \left( \frac{d_m}{\lambda_m} \right) d n = 1. \tag{23}
\]

The amplification of the probability distribution caused by the function \( g \left( \frac{d_m}{\lambda_m} \right) \) is illustrated in Fig. 8.

Multiplying then the term \( P(n, r_0) g \left( \frac{d_m}{\lambda_m} \right) \) by the total number of active chains \( N_c(r) \) with the relative end-to-end distance \( r \) per unit referential volume, we obtain the distribution function

\[
N(n, r) = N_c(r) g \left( \frac{d_m}{\lambda_m} \right) P(n, r_0). \tag{24}
\]

Taking further into account that this distribution may change only during primary loading, where \( \lambda = \lambda_m \), yields

\[
N(n, r) = N_c(\lambda_m r_0) g \left( \frac{d_m}{\lambda_m} \right) P(n, r_0) = N_p(\lambda_m P(n), \tag{25}
\]

where the abbreviations \( N_p(\lambda_m) = N_c(\lambda_m r_0) g(\lambda_m) \) and \( P(n) = P(n, r_0) \) are used. The earlier assumption of a constant number of active segments leads to the condition

\[
\int_{D_k(\lambda_m)} N_p(\lambda_m P(n)) d n = \int_{D_k(\lambda_m)} N_p(\lambda_m \frac{d_m}{\lambda_m}) P(n) d n d n. \tag{26}
\]

Since \( N_p(\lambda_m) \) does not depend on \( n \), (26) simplifies to

\[
N_p(1) \int_{D_k(\lambda_m)} P(n) d n d n = N_p(\lambda_m \frac{d_m}{\lambda_m}) \int_{D_k(\lambda_m)} P(n) d n. \tag{27}
\]

By means of the abbreviations

\[
N_0 = N_p(1), \quad \phi \left( \frac{d_m}{\lambda_m} \right) = \frac{\int_{D_k(\lambda_m)} P(n) d n d n}{\int_{D_k(\lambda_m)} P(n) d n}. \tag{28}
\]

one thus receives

\[
\hat{N}_p \left( \frac{d_m}{\lambda_m} \right) = N_0 \phi \left( \frac{d_m}{\lambda_m} \right). \tag{29}
\]

The variable \( N_0 \) represents the number of active chains per unit undeformed volume. It depends on the molecular mass of segments and density of the polymer network. For this reason, \( N_0 \) can and will be considered in the following as a material parameter.

Finally, considering (29) and (29) in (15), we obtain

\[
\Psi = \int_{D_k(\lambda_m)} N_0 \phi \left( \frac{d_m}{\lambda_m} \right) P(n) \psi (n, \lambda_m) d n. \tag{30}
\]

5. Transition to the macro-model

5.1. 3D generalization

Now, we are going to formulate the macroscopic energy of the three-dimensional network. It is generally assumed that the virgin rubber network is initially homogeneous and isotropic and the macroscopic free energy is regarded as the sum of microscopic strain energies of all active chains available within the network which can be calculated by integration over the unit sphere. Applying the isotropic space distribution (chains are spread equally in all directions), we can write

\[
\Psi_{cc} = \frac{1}{4\pi} \int_S N_c \psi (n, \lambda_m) d u, \quad \Psi_{pp} = \frac{1}{4\pi} \int_S \Psi d u, \tag{31}
\]

where \( S \) represents the unit sphere. The integration is carried out numerically by

\[
\Psi_{cc} \equiv \sum_{i=1}^k w_i N_c(\lambda_i \frac{d_i}{\lambda_i}) , \quad \Psi_{pp} \equiv \sum_{i=1}^k \Psi \frac{d_i}{\lambda_i} w_i, \tag{32}
\]

where \( w_i \) are weight factors corresponding to the collocation directions \( \frac{d_i}{\lambda_i} (i = 1, 2, \ldots, k) \). The numerical scheme with 21 integration points by Bažant and Oh (1986) is used.

Substitution of (30) into (32) results in:

\[
\Psi_{cc} = \sum_{i=1}^k \frac{w_i N_c(n, \lambda_i)}{\psi(n, \lambda_i)}, \quad \Psi_{pp} = \sum_{i=1}^k \frac{\Psi \frac{d_i}{\lambda_i}}{w_i}, \tag{33}
\]

5.2. Strain amplification

In filler-reinforced rubber networks, the stretch of the polymer chains between aggregates (micro-stretch) generally exceeds the stretch applied to the rubber matrix (macro-stretch). This phenomenon is referred to as strain amplification. The strain amplification concept is based on the fact that the filler aggregates are considerably stiffer than polymer chains connecting them. This inhomogeneity of the material leads to the inhomogeneity in the micro-stretch distribution. The strain amplification theory goes back to Harwood et al. (1965).

In order to quantify the strain amplification, a concept of hydrodynamic reinforcement can be used. Accordingly, the amplification function \( X \) establishing a relationship between the micro-stretch \( \lambda_m \) and the macro-stretch \( \lambda \) in the direction \( \frac{d_m}{\lambda_m} \) is defined by

\[
\lambda = X \left( \frac{d_m}{\lambda_m} \right) \frac{\lambda - C}{1 - C}, \tag{35}
\]
where $C \in (0, 1)$ represents the volume fraction of filler ($C < 0.3$ in most studies). The exponent $x$ depends on the structure of the filler network. For example, Bueche (1961) showed that $x = 1/3$ in the case of statistically homogeneous distribution of spherical particles (see also Govindjee, 1997; Bergström and Boyce, 1999). For the realistic distribution of aggregates the above value can and will be used as a rough approximation. This concept was verified experimentally by Rault et al. (2006) and is based on the following reasonable assumptions:

1. Filler aggregates are distributed randomly and even colonized randomly in three dimensions.
2. The stiffness of rubber matrix is negligible in comparison to that of one of filler aggregates which can thus be considered as rigid inclusions.

From the micro-mechanical point of view, strain amplification as a result of the hydrodynamic reinforcement strongly depends on the particle properties and the aggregation process. Thus, considering deformation of aggregates, more accurate models of strain amplification can be developed, which is not a subject of the present study.

Note that the strain amplification concept applies to micro-stretches and does not contradict the incompressibility constraint discussed in the next section. Indeed, this constraint is a purely phenomenological, macroscopic phenomenon and does not necessarily hold for microscopic deformations.

### 5.3. Final formulation

Now, the total strain energy of the network can be obtained by inserting (34) into (11). Taking the incompressibility condition\[ \det \mathbf{F} = 1 \] into account the constitutive equation for the first Piola-Kirchhoff stress tensor $\mathbf{T}$ can be written by\[ \mathbf{T} = \frac{\partial \Psi_M}{\partial \mathbf{F}} - p \mathbf{F}^{-T} = \frac{\partial \Psi_{cc}}{\partial \mathbf{F}} + \frac{\partial \Psi_{pp}}{\partial \mathbf{F}} - p \mathbf{F}^{-T}, \] where $\mathbf{F}$ denotes the deformation gradient and $p$ stands for an arbitrary scalar parameter which can be defined according to a particular boundary value problem. In view of (13) and 35, we thus obtain:\[ \mathbf{T} = \sum_{i=1}^{k} \lambda_i \mathbf{F}^{-1} \left( n_i - \frac{\partial}{\partial \mathbf{F}} \right) \frac{\partial}{\partial \mathbf{F}} \mathbf{F} + \sum_{i=1}^{k} \lambda_i \mathbf{F}^{-1} \left( n_i - \frac{\partial}{\partial \mathbf{F}} \right) \frac{\partial}{\partial \mathbf{F}} \mathbf{F} \right) + \mathbf{N_0} \left( \frac{\partial}{\partial \mathbf{F}} \right) \frac{\partial}{\partial \mathbf{F}} \mathbf{F}, \] where $n_i$ and $N_0$ denote the average number of segments within one chain and the whole number of chains in the pure rubber network, respectively. Note also that micro-stretches $\lambda_i$ are calculated according to (35).

### 6. Parameter study

The model presented above includes at all seven material parameters: $\kappa, \nu, f_0, n_{\text{max}}, N, N_0K_T$ and $N\sqrt{\kappa}$. The effect of the latter two parameters is linear since they appear in the free energy functions of the pure rubber and polymer-filler networks as proportionality factors. Further, $n_i$ governs the response of the pure elastic network which does not influence the stress softening and anisotropic material behavior being the main subject of the present study. For this reason, we focus in the following on the first four parameters and examine their effect on the overall response of the proposed model and in particular on the induced anisotropy and permanent set.

To this end, the behavior of the model is studied in subsequential uniaxial tension cycles in two orthogonal directions. The response to the variation of material constants $\kappa, \nu, f_0$ and $n_{\text{max}}$ is then compared to the reference solution obtained with the material parameters given in Table 1. The results are presented in Fig. 9, where every diagram corresponds to the change in only one of the above parameters with respect to the reference set.

<table>
<thead>
<tr>
<th>$\kappa$</th>
<th>$\nu$</th>
<th>$f_0$</th>
<th>$n_{\text{max}}$</th>
<th>$n_i$</th>
<th>$N_0K_T$</th>
<th>$N\sqrt{\kappa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>1.001383</td>
<td>8.216</td>
<td>100</td>
<td>100</td>
<td>0.80 MPa</td>
<td>0.87 MPa</td>
</tr>
</tbody>
</table>

### 7. Comparison with own experimental data

The objective of this section is to assess predictive capabilities of the proposed constitutive model by comparison to a new set of experimental data on subsequential uniaxial loading–unloading.
cycles in two orthogonal directions. The experiment is performed at room temperature with the strain rate of 40 \% \text{min}\^{-1}. In this experimental study, a cross-shaped specimen made from 50 phr carbon black filled polychloroprene rubber (CR) was used (see Fig. 10). Thus, the filler concentration was 33\% in mass and 20\% in volume (C = 0.2). The four arms of cruciform specimens were multiply slit-parallel to the sides, in order to obtain a nearly homogenous state of uniaxial tension in the measurement (see, e.g., Pawelski, 2001).

The experimental procedure was as follows. First, the virgin specimen was subject to loading–unloading cycles of uniaxial tension (x-direction) with the increasing stretch amplitudes 1.15, 1.30, 1.45, 1.60 and 1.75. At each stretch amplitude, five cycles were applied. After unloading to the stress-free state, the sample was unclamped.

---

**Fig. 9.** Sensitivity analysis of the material parameters included in the model. Solid lines denote reference set of parameters ($\kappa = 4.1$, $v = 1.0013$, $\nu = 0.22$, $n_{\text{max}} = 100$, $n_c = 100$, $N_{K_T} = 0.80$ MPa, $N_{K_T} = 0.87$ MPa). Circle-line and square-line depict model predictions due to modified values.
and clamped again for the consequent loading in the orthogonal direction (y-direction). Thus, residual strains accumulated in the specimen are included in the new reference configuration. Then, the above described loading procedure was repeated in y-direction.

The results of this experiment are shown in Fig. 11 in form of nominal stress $T$ versus stretch $\chi$ diagrams. In the case of elongation in x-direction, the classical Mullins effect and permanent set are observed after the first loading cycle. In y-direction, stress-
stretch diagrams reveal the Mullins effect as a strongly anisotropic phenomenon and also show considerable permanent set.

By means of the seven material parameters the model was fitted to the above presented experimental data. To this end, the least square error function was minimized with the aid of the Levenberg–Marquardt algorithm. The so-obtained values of the material parameters are given in Table 1 while the predicted stress–stretch curves are plotted in Fig. 12 against the experimental diagrams for every direction. For the fitting we used the unloading curve corresponding to the stretch amplitude 1.6 in x-direction. For the fitting we used the unloading curve corresponding to the maximal stretch set. To this end, the material parameters were evaluated by fitting only to the unloading curve corresponding to the maximal stretch amplitude. Good agreement with other loading-unloading curves in x-direction and all loading-unloading curves in y-direction is obtained automatically.

8. Conclusion

Recent experimental studies (see, e.g., Diani et al., 2006; Itskov et al., 2006) revealed that stress softening in filled rubber-like materials is a strongly anisotropic phenomenon, which has not been studied in details yet. The motivating key for this work was the absence of micro-mechanical models that can describe experimental data on the anisotropic Mullins effect of filled rubber-like materials without using empirical damage functions. Thus, we have proposed in the present paper a purely micro-mechanical network evolution theory granting a new insight into the damage mechanism which takes place inside the rubber network. Without using a damage function, the constitutive formulation is obtained based on partial energy dissipation of debonded chains and orientational changes in inter-aggregate chain distribution. These orientational changes of microstructure automatically result in the permanent set and induced anisotropy as macroscopic phenomenon. The model includes seven material parameters which all have a clear physical interpretation.

A simple structure combined with the low number of material parameters makes the model suitable for a finite element implementation. The excellent performance of the model was illustrated by comparing to a new set of own experimental data particularly designed to reveal the anisotropic Mullins effect and permanent set. To this end, the material parameters were evaluated by fitting only to the unloading curve corresponding to the maximal stretch amplitude. Good agreement with all other experimental curves is obtained automatically.

Acknowledgements

The authors thank the German Research Foundation (DFG) for the financial support of this work. The experimental part of this study is a result of a cooperation with Professor E. Haberstroh (Institute of Rubber Technology, RWTH Aachen University) whose contribution is also gratefully acknowledged.

References


