A rubber elasticity and softening model based on chain length statistics

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Abstract

The classical statistical theory of polymerization predicts a random distribution of polymer chain lengths. This distribution has long ago been known in the polymerization theory but, to the best of our knowledge, has not so far been utilized in mechanics of polymers. In the present paper, we incorporate this chain length statistics into full network rubber models which are based on continuous directional distributions of polymer chains. The free energy of the full network results as an integral of single chain energies over the unit sphere. In the case of an initially isotropic spatial arrangement of chains and ideally elastic behavior an analytical solution in terms of micro-structural parameters of the network is obtained. Introducing a softening criterion formulated in terms of the minimal number of chain segments available in the distribution we can describe not only elastic behavior but also inelastic phenomena especially pronounced in filled rubbers. These are, for example, the Mullins effect, permanent set and strain induced anisotropy. In this case, numerical integration over the unit sphere is applied. Predictions of the model demonstrate good agreement with experimental data with respect to the above mentioned phenomena.

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1 Introduction

According to the classical statistical theory of polymerization the probability that a linear polymer molecule is composed of exactly $k$ segments is given by the expression

$$P(k) = p^{k-1}(1-p), \quad k = 1, 2, \ldots,$$

known as the geometric probability density function, where $0 < p < 1$ denotes the probability of the chain propagation while $1 - p$ represents the probability of the chain termination. These are exactly the events that the polymer chain connects to a monomer with either two or one "live" end, respectively (see Fig. 1). Representation (1) is based on the assumption of the classical polymerization theory that $p$ remains constant over the whole polymerization process.

Figure 1: Simplified illustration of the polymerization process

Higgs & Ball [17] demonstrated how arbitrary chain length distributions including (1) can be taken into account in order to evaluate the elasticity modulus of cross-linked polymer networks. Such networks were considered as a circuit of polymer chain trees with different connectivities. Every polymer chain strand between cross-links was represented as a resistor and the stiffness of the system was expressed in analogy to the electric resistance of the circuit.

However, to the best of our knowledge the above mentioned chain length statistics has not so far been applied to large strain rubber elasticity or softening models. For ex-
ample, it appears to be very advantageous for full network rubber models which turned out to be very effective in modeling both elastic and inelastic behavior of polymers and rubbers. The full network models (also called micro-plane models) consider a set of chains continuously distributed in all spatial directions. Within this concept, three-dimensional models result from the integration of single polymer chain energies over the unit sphere. By this means, both isotropic and anisotropic directional distributions of chains can be taken into account (see, e.g. [31]). In the isotropic case the integration can be carried out analytically provided the entropic energy of a single polymer chain can be expanded in the Taylor series of the stretch square [19]. Alternatively, various numerical integration schemes can be applied. For example, James-Guth 3-chain [21] and Arruda-Boyce 8-chain models [1] are based on a 3 and 8-point integration scheme, respectively (see also [3]).

On the basis of the Arruda-Boyce model Smeulders & Govindjee [27] considered molecular weight distributions which are directly related to chain length distributions. The authors consider an evolution of this distribution due to a cluster fragmentation and depolarization as proposed by Ziff & McGrady [32]. The evolution is based on a kinetic equation whose kernel depends on the current chain length but does not explicitly depend on the mechanical deformation. This shortage is improved in [27] by means of a phenomenological damage function depending on the strain history.

If the free energy of a single polymer chain includes internal variables the model resulting from the integration over the unit sphere can describe several inelastic phenomena peculiar to filled rubbers like for example the Mullins effect (see, e.g., [24]), permanent set and strain induced anisotropy. Using the average number of chain segments $N$ in the network as such an internal variable and applying the above mentioned 8-chain model Marckmann et al. [23] and latter Chagnon et al. [5] described the isotropic Mullins effect. An anisotropic generalization of this model based on a phenomenological evolution equation for $N$ and a 21-point integration scheme by Bažant & Oh [2] was further proposed by Diani et al. [10]. Göktepe & Miche [14] presented an anisotropic model of the Mullins effect based on a phenomenological evolution equation for a damage variable and the 21-point integration scheme. By means of a phenomeno-
logical Mullins effect evolution function and 42-point numerical quadrature [2] Rebouah & Changnon [26] recently described induced anisotropy and permanent set in a silicone rubber and a biological soft tissue.

In order to describe elastic and inelastic behavior of polymers and rubbers the classical Gaussian or non-Gaussian chain statistics can be applied within a network model. According to the non-Gaussian chain statistics the entropic energy and force developed by a freely jointed chain are expressed in terms of the inverse Langevin function [22]. In turn, the Gaussian statistics describes end-to-end distances $r$ of a polymer chain with a fixed number of segments even in better agreement with the exact distribution [28]. However, both statistics applied to polymer molecules are related to the random walk theory and have nothing in common with the geometric distribution (1) resulting from the polymerization process.

Applying the latter statistics Govindjee & Simo [15] proposed a three-dimensional model of the chain network evolution based on the consequent chain debonding from carbon black aggregates. The model is formulated in terms of the principal stretches and is isotropic. Dargazany & Itskov [8] further developed this concept and used the 21-point integration scheme [2] for the three-dimensional generalization. The resulting model describes the Mullins effect including deformation induced anisotropy and permanent set in accord with various experimental data (see also [9]). Both these models consider filler particles as rigid bodies and take their contribution into account by means of the strain amplification concept. Accordingly, the (micro) deformation on polymer chains is not affine with the (macro) deformation of the body.

As we can see, the chain statistics has so far been used mostly in the form of the above mentioned inverse Langevin function describing the chain force or as the probability distribution of chain end-to-end distances or at least as the average number of chain segments. To the best of our knowledge, the distribution of chain lengths or segment numbers as it results from the polymerization process illustrated above has not yet been applied in the constitutive modeling but can play an important role. In the present paper, we are thus going to implement this distribution to a full network rubber elasticity and softening model. Applying an analytical integration over the unit
an analytical full network rubber elasticity model is formulated for the case of initially isotropic spatial distribution of chains. A softening model is based on an assumption that the minimal number of chain segments available in the distribution increases with the maximal stretch. This assumption is motivated by the fact that the end-to-end distance of the chain depending on the stretch cannot exceed its contour length depending on the number of segments. The model does not explicitly consider filler particles mostly responsible for inelastic effects in filled rubbers. The influence of the reinforcement is taken into account indirectly by the chain length distribution depending on the cross-linking density and by this means on the filler concentration.

The full network softening model requires the numerical integration over the unit sphere. The so obtain model includes very few physically interpretable material constants and is able to describe the Mullins effect, strain induced anisotropy and permanent set in excellent agreement with experimental data.

The paper is organized as follows. In Chap. 2 we recall the classical probability density function of polymer chain lengths and express it both in a continuous and discontinuous form in terms of the minimal and average number of chain segments. The discontinuous form of this probability density function is further implemented in Chap. 3 into the analytical full network rubber elasticity model. In turn, the continuous form is applied for the anisotropic softening model in Chap. 4. The influence of few model parameters on the stress-stretch response is further studied. Finally, predictions of the model are compared to experimental data.

2 Chain length statistics

2.1 Discontinuous probability density function

The above chain length probability density function (1) can be generalized to an arbitrary minimal number of chain segments \( n \) available in the network as follows

\[
P(k) = p^{k-n} (1 - p), \quad k = n, n+1, \ldots
\]
It a priori satisfies the normalization condition

$$\sum_{k=n}^{\infty} P(k) = 1 \quad (3)$$

for any $n$. The most of the network models operate with the average (mean) number of chain segments $N$. Thus, it is convenient to express $P(k)$ in terms of $N$. To this end, we first obtain

$$N = E[k] = \sum_{k=n}^{\infty} P(k) k = \sum_{k=n}^{\infty} p^{k-n} (1-p) k = n - \frac{p}{p-1}, \quad (4)$$

where $E[k]$ denotes the mean value of a random variable $k$. By means of the definition

$$\Delta = N - n \quad (5)$$

we can thus write

$$p = \frac{\Delta}{\Delta + 1} \quad (6)$$

The probability density function (2) takes thus the form

$$P(k) = \frac{1}{\Delta + 1} \left(1 + \frac{1}{\Delta}\right)^{n-k}. \quad (7)$$

### 2.2 Continuous probability density function

It is useful to generalize this probability density function to a continuous form. In this case we set

$$P(u) = ap^{u-n} (1-p), \quad (8)$$

where $u$ is a real valued number of segments and $a$ is a normalization factor. The latter one results from the normalization condition

$$1 = \int_{n}^{\infty} P(u) du = a \frac{p - \frac{1}{\ln p}}{\ln p} \quad (9)$$
as \( a = \frac{\ln p}{p - 1} \). By this means, the continuous probability density function (8) can be given in the following exponential form (cf. [29, 30]).

\[
P(u) = \frac{1}{\Delta} e^{-\frac{a - u}{\Delta}},
\]

(10)

where instead of (6)

\[
\Delta = -\frac{1}{\ln p}.
\]

(11)

In view of the identity

\[
N = E[u] = \int_{n}^{\infty} P(u) \, du = n + \Delta
\]

(12)

relation (5) is valid for this continuous distribution as well.

Both discrete and continuous probability density functions (7) and (10) are illustrated in Figs. 2 and 3 for \( n = 1 \) and different values of \( \Delta \). Accordingly, all the functions are strongly monotone decreasing and flatten with the increasing \( \Delta \). One can also observe that the discrete and continuous probability density functions with the same values of \( \Delta \) are very close to each other.

![Figure 2: Discontinuous probability density function (7) of the number of chain segments for \( n = 1 \) and various values of the parameter \( \Delta \)](image-url)
Figure 3: Continuous probability density function \( P(u) \) of the number of chain segments for \( n = 1 \) and various values of the parameter \( \Delta \)

3 An analytical full network rubber elasticity model

A full network model describes a set of chains continuously distributed in all spatial directions. In the following we assume an initially homogeneous directional distribution of chains which implies an isotropic response of the network. Let \( w(\Lambda) \) be a strain energy function of chains with the same end-to-end direction per unit referential volume. \( \Lambda = \lambda^2 \) denotes square of the chain stretch \( \lambda \) related to the end-to-end direction of the chain in the reference configuration. Then, the strain energy of the whole network per unit referential volume can be obtained by integrating over the unit sphere as

\[
W = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi w(\Lambda) \sin \theta d\theta d\phi, \tag{13}
\]

where \( \theta \) and \( \phi \) denote spherical angles of the referential chain end-to-end direction. We further assume that the function \( w(\Lambda) \) is analytic and can thus be expanded in the

\[
W = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi w(\Lambda) \sin \theta d\theta d\phi, \tag{13}
\]
Taylor power series around some point $\Lambda_0$

$$w(\Lambda) = \sum_{i=0}^{\infty} w_i (\Lambda - \Lambda_0)^i, \quad w_i = \frac{1}{i!} \left. \frac{d^i w}{d\Lambda^i} \right|_{\Lambda=\Lambda_0}, \quad i = 0, 1, \ldots \quad (14)$$

as proposed by Puso [25] (see also [4]). In the following we set

$$\Lambda_0 = \frac{1}{3} \text{tr} C, \quad (15)$$

where $C = F^T F$ denotes the right Cauchy-Green tensor defined in terms of the deformation gradient $F$. In this case, the series (14) can be integrated analytically over the unit sphere according to (13), which leads to

$$W = \sum_{i=0}^{\infty} w_i W_i, \quad W_i = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} (\Lambda - \Lambda_0)^i \sin \theta d\theta d\phi, \quad i = 0, 1, \ldots, \quad (16)$$
where \[25 \|19\]

\[
\begin{align*}
W_0 &= 1, \\
W_1 &= 0, \\
W_2 &= \frac{4}{45} A, \\
W_3 &= \frac{16}{945} B, \\
W_4 &= \frac{16}{945} A^2, \\
W_5 &= \frac{128}{18711} AB, \\
W_6 &= \frac{320}{81081} A^3 + \frac{512}{729729} B^2, \\
W_7 &= \frac{256}{104247} A^2 B, \\
W_8 &= \frac{1792}{1772199} A^4 + \frac{8192}{15949791} AB^2, \\
W_9 &= \frac{28672}{33671781} A^3 B + \frac{32678}{909138087} B^3, \\
W_{10} &= \frac{81920}{303046029} A^2 B^2 + \frac{1024}{3741309} A^5, \ldots
\end{align*}
\]

(17)

The first three terms \(W_1, W_2\) and \(W_3\) were reported by Puso \[25\], while further terms can easily be obtained by a mathematical software (as for example MAPLE) and are given in \[19\]. In (17), \(A\) and \(B\) denote strain invariants expressed in terms of the principal invariants of the right Cauchy-Green tensor

\[
I_C = \text{tr}C, \quad \Pi_C = \frac{1}{2} \left[ (\text{tr}C)^2 - \text{tr}C^2 \right], \quad \Pi \Pi_C = \det C
\]

(18)

by

\[
A = I_C^3 - 3 \Pi_C, \quad B = I_C^3 - \frac{9}{2} I_C \Pi_C + \frac{27}{2} \Pi \Pi_C.
\]

(19)

According to the non-Gaussian statistical theory of rubber elasticity \[22\] the force developed by polymer chains with the same end-to-end direction per unit referential
area (nominal stress) can be expressed by

\[ f(\lambda) = C \sqrt{k} \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{k}} \right), \]  

(20)

where \( k \) again denotes the number of chain segments and \( C \) is a constant. \( \mathcal{L}^{-1} \) represents the inverse of the Langevin function \( \mathcal{L} \) defined by

\[ \mathcal{L}(x) = \coth(x) - \frac{1}{x}. \]  

(21)

The inverse Langevin function can directly be expanded into the Taylor power series around the zero point as follows [18, 7] (the first four terms are due to Kunh and Grün [22])

\[ \mathcal{L}^{-1}(y) = \sum_{i=1}^{\infty} c_i y^{2i-1} = 3y + \frac{9}{5}y^3 + \frac{297}{175}y^5 + \frac{1539}{875}y^7 + \frac{126117}{67375}y^9 + \frac{43733439}{21896875}y^{11} + \frac{231321177}{109484375}y^{13} + \frac{20495009043}{9306171875}y^{15} + \frac{1073585186448381}{476522530859375}y^{17} + \frac{4387445039583}{1944989921875}y^{19} \ldots \]  

(22)

Inserting this representation into (20) and integrating over \( \lambda \) we obtain

\[ w(\Lambda) = \int_0^{\sqrt{\Lambda}} f(\lambda) d\lambda = Ck \sum_{i=1}^{\infty} c_i \frac{(\Lambda)}{k^i}. \]  

(23)

Substituting \( \Lambda \) by \((\Lambda - \Lambda_0) + \Lambda_0\) and using the binomial formula we further write

\[ w(\Lambda) = \frac{1}{2} Ck \sum_{i=1}^{m} \left( \frac{\Lambda - \Lambda_0}{k} \right)^i \sum_{j=0}^{m-i} \binom{i+j}{i} \left( \frac{\Lambda_0}{k} \right)^j, \]  

(24)

where the infinite series is truncated after \( m \) terms. This series has exactly the form of (14) and can be used for the integration over the unit sphere. Thus, according to (16)

\[ W(k) = \frac{1}{2} C \sum_{i=0}^{m} W_i \sum_{j=0}^{m-i} \binom{i+j}{i} \Lambda_0^i k^{1-i-j}. \]  

(25)
The strain energy is represented here as a function of the number of chain segments \( k \) which has so far been considered as a constant and only its average value has been used \[18\]. Now, we are in a position to implement the above discussed distribution of chain lengths. For example, for the discrete probability density function \((7)\) the strain energy function of the network takes the form

\[
\Psi = \sum_{k=n}^{\infty} W(k) P(k) = \frac{1}{2} C \sum_{i=1}^{m} W_i \sum_{j=0}^{m-i} \frac{c_{i+j}}{i+j} \binom{i+j}{i} \Lambda_j^{k-i-j}, \quad (26)
\]

where \( E[k^0] = 1 \) while

\[
E[k^{-i}] = \sum_{k=n}^{\infty} P(k) k^{-i}, \quad i = 1, 2, \ldots \quad (27)
\]

represent negative moments of \( P \).

In the following numerical example the above presented model is compared against experimental data by Arruda and Boyce \[1\] for silicone rubber and against the full monodisperse network model with the constant number of chain segments \( k \). The latter result was obtained for \( C = 0.435 \) MPa and \( k = 7.9 \) \[31\] by the numerical integration over the unit sphere according to \[13\]. To this end, a high-order numerical cubature with 900 integration points \[12\] was applied. The model predictions are obtained for the following values of the material constants \( C = 0.51, n = 10 \) and \( \Delta = 3 \). The nominal stress versus stretch diagrams are plotted in Figs. 4 and 5 for uniaxial tension (with principal stretches \( \lambda_1 = \lambda, \lambda_2 = \lambda_3 = \lambda^{-1/2} \)) and plane strain compression \((\lambda_1 = \lambda, \lambda_2 = 1, \lambda_3 = 1/\lambda)\), respectively. First of all, one can observe very fast convergence of the series \(26\) and generally good agreement with the experimental data. In the case of uniaxial tension the model predictions are as good as the results of the monodisperse model. In the case of plane strain compression, our model is even much closer to the experimental data than the full monodisperse network model.
Figure 4: Uniaxial compression of silicone rubber: comparison of model predictions against experiential data [1] and the full monodisperse network model with the constant number of chain segments

4 An anisotropic softening model

According to (20) the chain force tends to infinity as the chain length tends to its maximal value at the fully stretch straight state with $\lambda = \sqrt{k}$. Thus, for any material direction the above analytical model is restricted by the condition

$$\lambda_{\text{max}} < \sqrt{n},$$

(28)

where $\lambda_{\text{max}}$ denotes the maximal stretch ever reached in the loading history. Now, we assume that in the virgin state of the rubber network $n = 1$. In this case, for every material direction we have to adopt a deformation driven evolution of the minimal number of chain segments such that the condition (28) is always satisfied. This evolution can be expressed by

$$n(d) = \nu^2 \lambda_{\text{max}}^2(d),$$

(29)
Figure 5: Plane strain compression (pure shear) of a silicone rubber: comparison of model predictions against experiential data [1] and the full monodisperse network model with the constant number of chain segments

where $\mathbf{d}$ denotes a unit vector specifying a material direction. $\nu > 1$ is a material constant which can be referred to as sliding ratio. It expresses the ratio of the chain contour length $k_l$ to the length at break or debonding from the filler aggregate. In [8] it is expressed in terms of the debonding chain force $F_d$ as

$$\nu = \frac{1}{\mathcal{L} \left( \frac{F_d}{RT} \right)}, \quad (30)$$

where $K$ denotes the Boltzmann constant and $T$ is the absolute temperature. Following [23] and [8] we assume that the broken/debonded segments still contribute to the entropic energy of the network. The softening is only due to the evolution of the chain length distribution. In order to describe the softening as a continuous process we further apply the continuous probability density function [10] and assume that $\Delta = \text{const}$ although $n(\mathbf{d})$ increases with the increasing $\lambda_{\text{max}}(\mathbf{d})$ according to [29]. This means that the form of the probability density function remains unchanged, it only shifts parallel the $u$-axis to higher values of $u$. 

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The free energy of all chains in a direction specified by a unit vector $d$ can thus be given by

$$
\psi(d) = \int_{\nu^2 \lambda_{\text{max}}^2(d)}^{\infty} \tilde{w}(\lambda, u) P(u) \, du = \frac{1}{\Delta} \int_{\nu^2 \lambda_{\text{max}}^2(d)}^{\infty} \tilde{w}(\lambda, u) e^{\nu^2 \lambda_{\text{max}}^2(d)/\Delta - u} \, du,
$$

where $\lambda$ denotes the stretch in this direction. Note that in comparison to [15] (31) implies the evolution of not only the integration domain but also of the probability density function itself. The entropic energy $\tilde{w}(\lambda, u)$ of a chain with $u$ segments results from (20) as follows

$$
\tilde{w}(\lambda, u) = \int_{1}^{\lambda} f(\bar{\lambda}) \, d\bar{\lambda} = Cu \left[ \frac{\lambda}{\sqrt{u}} \xi^{-1} \left( \frac{\lambda}{\sqrt{u}} \right) + \ln \frac{\xi^{-1} \left( \frac{\lambda}{\sqrt{u}} \right)}{\sinh \xi^{-1} \left( \frac{\lambda}{\sqrt{u}} \right)} \right].
$$

For the evaluation of the inverse Langevin function we used a simple and accurate Padé approximation

$$
\xi^{-1}(y) \approx y \frac{y^2 - 3y + 3}{1 - y}
$$

recently proposed in [6]. The integration over the unit sphere requires now a numerical procedure as

$$
\Psi = \sum_{i=1}^{s} \omega_i \psi(d_i) = \frac{1}{\Delta} \sum_{i=1}^{s} \omega_i \int_{\nu^2 \lambda_{\text{max}}^2(d_i)}^{\infty} \tilde{w}(\lambda_i, u) e^{\nu^2 \lambda_{\text{max}}^2(d_i)/\Delta - u} \, du,
$$

where $d_i$ specifies the direction of an integration point on the unit sphere, $\lambda_i$ is the stretch in this direction and $\omega_i (i = 1, 2, \ldots, s)$ stands for the corresponding weight factor.

The first Piola-Kirchhoff (nominal) stress resulting from this free energy function

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can be expressed by

\[ t = \frac{\partial \Psi}{\partial \lambda} = \frac{1}{\Delta} \sum_{i=1}^{s} \omega_i \frac{\partial \lambda_i}{\partial \lambda} \int_{0}^{\infty} \frac{\partial \tilde{w}(\lambda_i, u)}{\partial \lambda_i} e^{\frac{\nu^2 \lambda_i^2}{\Delta} (d_i)} du \]

\[ = \frac{C}{\Delta} \sum_{i=1}^{s} \omega_i \frac{\partial \sqrt{d_i} C d_i}{\partial \lambda} \int_{0}^{\infty} \mathcal{L}^{-1} \left( \frac{\lambda_i}{\sqrt{u}} \right) \sqrt{u} e^{\frac{\nu^2 \lambda_i^2}{\Delta} (d_i)} du. \]  \hspace{1cm} (35)

Here, \( \lambda_{\text{max}}(d_i), (i = 1, 2, \ldots, s) \) are considered as internal variables. In this case, one can set

\[ -\sum_{i=1}^{s} \frac{\partial \Psi}{\partial \lambda_{\text{max}}(d_i)} \dot{\lambda}_{\text{max}}(d_i) = D, \]  \hspace{1cm} (36)

where \( D \) denotes dissipation. It is seen that \( D = 0 \) in the case of elastic process where \( \dot{\lambda}_{\text{max}}(d_i) = 0, (i = 1, 2, \ldots, s) \).

According to the second law of thermodynamics written in the form of the reduced dissipation inequality

\[ D \geq 0. \]  \hspace{1cm} (37)

It is shown in Appendix that our model satisfies this condition and is thus thermodynamically consistent.

For the numerical integration in (34) and (35) we applied a numerical procedure by Heo & Xu [16] with \( s = 45 \) points on a half-sphere. In a comparative study [11] it was shown that this cubature provides the best compromise between the amount of anisotropy artificially induced by the integration and computational efforts. The defined integrals in (34) and (35) were evaluated by a mathematical software (MAPLE).

The so-obtained model includes only three material constants \( C, \Delta \) and \( \nu \). Setting \( C = 1 \) we studied the influence of \( \Delta \) and \( \nu \) on the material response to uniaxial tension cycles. After a loading cycle in one \( (x) \) direction uniaxial tension in an orthogonal direction \( (y) \) was simulated. The results of the parameter study are illustrated in Fig. 6. It is seen that the model is able to describe stress softening, permanent set and deformation induced anisotropy.

In the following numerical example the model is validated against experimental data [8, 9] on the anisotropic Mullins effect. In these experiments cross-shape spec-
Figure 6: Uniaxial tension cycles in two orthogonal directions: predictions of the model for $C = 1$ and different values of $\Delta$ and $\nu$. 

- $\Delta = 1, \nu = 1.001$, $x$-direction
- $\Delta = 1, \nu = 1.001$, $y$-direction
- $\Delta = 0.6, \nu = 1.001$, $x$-direction
- $\Delta = 0.6, \nu = 1.001$, $y$-direction
- $\Delta = 0.8, \nu = 1.001$, $x$-direction
- $\Delta = 0.8, \nu = 1.001$, $y$-direction
- $\Delta = 1, \nu = 1.01$, $x$-direction
- $\Delta = 1, \nu = 1.01$, $y$-direction
- $\Delta = 3, \nu = 1.001$, $x$-direction
- $\Delta = 3, \nu = 1.001$, $y$-direction
- $\Delta = 10, \nu = 1.001$, $x$-direction
- $\Delta = 10, \nu = 1.001$, $y$-direction
imens made of 50 phr carbon black filled polychloroprene rubber were subjected to subsequential uniaxial tension cycles in two orthogonal directions. First, the virgin specimen was subject to loading-unloading cycles of uniaxial tension (x-direction) with the stepwise increasing stretch amplitudes 1.30, 1.45, 1.60 and 1.75. After unloading to the stress-free state, the sample was unclamped and clamped again for the consequent loading in the orthogonal direction (y-direction). In Figs. 7 and 8 the first Piola-Kirchhoff (nominal) stress in the loading direction (respectively, x and y) is plotted versus stretch. The experimental data are compared there against model predictions obtained for the following values of the material constants: \( C = 0.82 \text{Mpa}, \Delta = 3.2 \) and \( \nu = 1.0015 \).

One observes that the stress softening appears only below the maximal stretch previously reached in the loading history. This phenomenon is specific for filled rubbers and referred to as Mullins effect [24], mentioned before. The permanent set and strain induced anisotropy are also well pronounced. The latter effect is apparent as the material response in y-direction becomes softer after the loading and unloading in x-direction. The model predictions demonstrate very good agreement with the experimental data in respect of all aforementioned phenomena.

5 Conclusion

The classical non-Gaussian chain statistics describes the distribution of chain end-to-end distances \( r \) for a fixed number of chain segments \( k \). In the present paper, we applied the distribution of chain lengths (segment numbers) independent of the end-to-end distance as it results from the polymerization process [13]. This distribution has long ago been known in the polymerization theory (see, e.g., [29, 30]) but, to the best of our knowledge, has not so far been utilized in mechanics of polymers. The probability density function has an exponential form and has been specified for arbitrary minimal number of chain segments \( n \). We presented both discontinuous and continuous forms of this function expressed in terms of the mean number of segments \( N \). Further, we incorporated this probability density function into an analytical full network rubber
Figure 7: Cyclic uniaxial tension with stepwise increasing amplitude in $x$-direction: model predictions for $C = 0.82\text{Mpa}$, $\Delta = 3.2$ and $\nu = 1.0015$ vs. experimental data on 50 phr carbon black filled polychloroprene rubber (see [8, 9]).

Further, we applied the continuous form of the chain length probability density function to the numerical full network model. The resulting model includes only three physically based material constants and is able to describe many important inelastic effects of filled rubbers like for example the Mullins effect, permanent set and deformation induced anisotropy. The basic concept of the model is evolution of the minimal chain segment number $n$ in every spatial direction with the maximal stretch ever reached in the loading history in this direction. The model demonstrates excellent agreement with experimental data of uniaxial cyclic tension tests in two orthogonal directions. All the above mentioned inelastic effects peculiar to filled rubbers are well predicted.
Figure 8: Cyclic uniaxial tension with stepwise increasing amplitude in \( y \)-direction: model predictions for \( C = 0.82 \text{Mpa} \), \( \Delta = 3.2 \) and \( \nu = 1.0015 \) vs. experimental data on 50 phr carbon black filled polychloroprene rubber (see [8, 9]).

References


Appendix

In order to prove the inequality (37) where $D$ is expressed by (36) it suffices to show that

$$\frac{\partial \Psi}{\partial \lambda_{\text{max}}(d)} \leq 0,$$

(38)

since $\lambda_{\text{max}}(d) \geq 0$ for any direction $d$. With the abbreviation $a = \nu^2 \lambda_{\text{max}}^2(d)$ we can write

$$\frac{\partial \Psi}{\partial \lambda_{\text{max}}(d)} = 2\nu^2 \lambda_{\text{max}}(d) \frac{\partial \Psi}{\partial a}.$$  

(39)
By \((31)\) the derivative on the right hand side can be expressed by

\[
\frac{\partial \Psi}{\partial a} = -\frac{1}{\Delta} \left. \tilde{w}(\lambda, u) \, e^{\frac{a-u}{\Delta}} \right|_{u=a} + \frac{1}{\Delta} \int_{a}^{\infty} \tilde{w}(\lambda, u) \frac{\partial}{\partial a} e^{\frac{a-u}{\Delta}} \, du
\]

\[
= -\frac{1}{\Delta} \tilde{w}(\lambda, a) - \frac{1}{\Delta} \int_{a}^{\infty} \tilde{w}(\lambda, u) \frac{\partial}{\partial a} e^{\frac{a-u}{\Delta}} \, du.
\]

Integration by parts further yields

\[
\frac{\partial \Psi}{\partial a} = \frac{1}{\Delta} \left[ -\tilde{w}(\lambda, a) + \tilde{w}(\lambda, u) \, e^{\frac{a-u}{\Delta}} \right|_{u=a} - \lim_{u \to \infty} \tilde{w}(\lambda, u) \, e^{\frac{a-u}{\Delta}} + \int_{a}^{\infty} \frac{\partial \tilde{w}(\lambda, u)}{\partial u} \, e^{\frac{a-u}{\Delta}} \, du \right]
\]

and consequently

\[
\frac{\partial \Psi}{\partial a} = \frac{1}{\Delta} \int_{a}^{\infty} \frac{\partial \tilde{w}(\lambda, u)}{\partial u} \, e^{\frac{a-u}{\Delta}} \, du.
\] (40)

Thus, in view of \((39)\) the sufficient condition for \((38)\) is that

\[
\frac{\partial \tilde{w}(\lambda, u)}{\partial u} \leq 0.
\] (41)
Taking (32) into account we further obtain

\[
\frac{\partial \tilde{w}(\lambda, u)}{\partial u} = C \left[ \frac{1}{2} \frac{\lambda}{\sqrt{u}} \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{u}} \right) + \ln \frac{\mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{u}} \right)}{\sinh \mathcal{L}^{-1} \left( \frac{\lambda}{\sqrt{u}} \right)} \right] = CA \left( \frac{\lambda}{\sqrt{u}} \right), \tag{42}
\]

where the function \( A(y) \) is given by

\[
A(y) = \left[ \frac{1}{2} y \mathcal{L}^{-1}(y) + \ln \frac{\mathcal{L}^{-1}(y)}{\sinh \mathcal{L}^{-1}(y)} \right]. \tag{43}
\]

The behavior of this function is shown in Fig. 9. It is seen that this function is non-positive on the relevant interval \( y \in [0, 1] \), which guarantees that the condition (38) is satisfied.