Hyperelasticity of Rubbery Materials with Chains’ volume, Nonaffine Deformation, and Topological Constraint

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Abstract. Rubbery materials play a significant role in industrial field for the reason of better excellent elasticity. A hyperelastic model is proposed, into which chains’ volume, nonaffine deformation, and topological constraint are introduced. After obtained the model, it is naturally transformed to investigate homogeneous deformations for isotropic and incompressible rubbery materials and verified by Treloar’s experiments. The results show that the present model has ability to express the hyperelasticity of rubbery materials, and the highly predictive accuracy with only simple computation makes the novel model adequate for engineering applications.

1. Introduction
Rubbery materials are able to undergo large, reversible deformations and they have been widely used in industrial applications [1], such as structural bearing [2][3], tires [4], medical devices [5][6], and so on due to their particular mechanical properties. Rubbery materials exhibit a complicated nonlinear behaviour including viscoelasticity [7], Mullins effect [8][9][10], and hyperelasticity [10] etc.. The mechanical response of rubbery materials is usually investigated by numerical simulations, one of them is the finite element method. However, it is still difficult to get the relevant material constants to make them work. So it should be necessary to establish a reliable hyperelastic model for rubbery materials which could be able to express the complex deformations.

The hyperelasticity of rubbery materials can be described by a strain energy density function (SEDF). Once the SEDF is obtained, the stress-stretch relationship can be deduced according to the elastic theory. Two approaches exist to find such a function: one is statistical mechanics and the other is phenomenological theory [10].

In the last few decades, many phenomenological constitutive models, such as Mooney-Rivlin model [11], Gent model [12], Yeoh model [13], Nunes model [14], and Exp-Ln model [15] etc., were proposed or applied by the authors [16][17]. A detailed review for phenomenological models was given by Beta [18]. Although some of the phenomenological models could predict the mechanical properties of rubbery materials well, the coefficients of them lack of physical meanings which are related to the microstructures of polymers. The non-entropic theory of rubbery elasticity for a flexible chain was also detailedly stated by Drozdov [19]. In addition, based on the statistical theory, some micro-mechanical models were also developed. James and Guth [20] proposed a 3-chain model which assumed that the polymer network could be presented by three chains that were oriented in three
principle directions. Then, the 3-chain model was improved by Elias-Zuniga in 2006 [21]. Describing the polymer network by means of using four polymer chains, a 4-chain model was presented in [22]. Based on the analysis of the 3-chain and 4-chain models, Arruda and Boyce [23] proposed an 8-chain model (sketched in figure 1). In the 8-chain model, the eight polymer chains are attached to the eight corners of a cube and a center junction. The 8-chain model shows good ability to characterize the behaviour of rubbery materials and it has been widely employed by many authors to express their materials. In recent years, Lopez-Manchado et al. [24] developed a network model with the tube constraints and Kroon [25][26] improved the 8-chain model by considering the topological constraints to account for the non-affine deformation of a polymer chain. However, most of the previous models for rubbery elasticity are unable to essentially explain the deformation mechanism. Few of them have taken the chains’ volume [27], the non-affine deformation, and the topological constraint into account simultaneously. A major objective of our present work is to develop a realistic hyperelastic model to predict the mechanical response of rubbery materials under simple or complex deformations. Introducing the chains’ volume, the non-affine deformation, and the topological constraint into the 8-chain model, a novel hyperelastic model is given. Finally, the new model is verified by Treloar’s experiments [28] and shows broad prospects in its engineering applications.

2. Network model

We start by considering a cube cell containing eight polymer chains first (see figure 1), which was proposed by Arruda and Boyce [23]. The side length of the undeformed cube is $a_0$, and $e_1$, $e_2$, and $e_3$ are the principal directions of deformation. The eight polymer chains are OA, OB, OC, OD, OE, OF, OG, and OH, respectively. After deformation, point O is assumed still at the center of the cube, and the side lengths of the three principal directions separately become $\lambda_i a_0 (i=1,2,3)$.

![Figure 1. 8-chain model introduced by Arruda and Boyce](image)

A simple chain in figure 1 is taken consisting of $N$ segments of equal length $l$. The vector between the end points of a chain is $r$, and the maximum magnitude of $r$ is $|r|_{max}=Nl$. It is well-known that the Gaussian distribution theory of rubber elasticity fails to describe the mechanical response of rubbery materials. Thus, the non-Gaussian statistics theory leads to a more realistic molecular distribution function that is valid over the whole range of $r$ up to ultimate or fully extended length. The non-Gaussian probability density function expressed by inverse Langevin is written as follows

$$p_{\text{chain}} (r) = C_{\text{chain}} \exp \left[ -N \left( \frac{r}{Nl} + \ln \frac{\beta}{\sinh \beta} \right) \right]$$

(1)

where $C_{\text{chain}}$ is the normalization constant, $r=|r|$, and $\beta$ is defined by Langevin function

$$\coth \beta - 1/\beta = r / Nl \pm L(\beta)$$

(2)

According to random walk theory, the root-mean-square value of $r$ for an unstrained chain is $r_0=\sqrt{Nl}$. This equation has been employed by many authors to get the chain stretch by $\lambda = r/r_0$, such as Elias-Zuniga [21], Kroon [26], and so on. However, the random walk theory ignores the volume and size of the chain, which may be not in accordance with a real polymer chain. In this paper, we take the volume and size of a flexible chain into account. Then the root-mean-square value of $r$ is assumed as [27]

$$\lambda = \frac{r}{r_0} = \frac{Nl}{r_0}$$
where \( v \) describes the effect of the volume and size of the chain. When \( v = 0.5 \), equation (3) degrades to the result of the random walk theory. If the volume and size of a chain are taken into account, we should easily have that \( v > 0.5 \), i.e. \( r_0 > \sqrt{N}l \). Therefore, the stretch of a molecular chain is calculated by \( \lambda_c = r_0 / N^{1/3} \). Then, the probability density function expressed by equation (1) is rewritten as

\[
p_{\text{chain}} (\lambda_c) = C_{\text{chain}} \exp \left\{ -N \left( \frac{\lambda_c}{N^{1/3}} \beta + \ln \frac{\beta}{\sinh \beta} \right) \right\}
\]

(4)

where \( \beta = L^{-1}(\lambda_c / N^{1/3}) \).

In addition, the topological network constraint of the polymer network around the cube cell (see figure 1) is also considered in the present model. The constraint probability density function of one side in ei direction is employed as follows in the present work, it is just empirical:

\[
p_{\text{con}} (\lambda_i) = C_{\text{con}} \exp \left( -\frac{h}{\alpha^i \lambda_i^i} \right), \quad i = 1, 2, 3
\]

(5)

where \( C_{\text{con}} \) is the normalization constant, \( h \) and \( \alpha \) are the parameters used to control the topological network constraint. Here, we let \( C_{\text{con}}^{1} = C_{\text{con}}^{2} = C_{\text{con}}^{3} = C_{\text{con}}^{4} = C_{\text{con}}^{5} \) for simplicity. Using equation (4) and (5), the probability density function of the cube cell (shown in figure 1) could be calculated by

\[
p_{\text{cube}} = p_{\text{chain}} \left( \lambda_c \right) \prod_{i=1}^{3} p_{\text{con}} \left( \lambda_i \right)
\]

(6)

According to Boltzmann’s equation, the configuration entropy of the cube cell can be computed by

\[
S_{\text{cube}} = k_B \ln p_{\text{cube}} = 8k_B \ln p_{\text{chain}} (\lambda_c) + 2 \sum_{i=1}^{3} \ln p_{\text{con}} (\lambda_i)
\]

(7)

where \( k_B \) is Boltzmann’s constant. In order to accord with the kinetic theory, we make an assumption that there is no change of the internal energy when the chain deforms. Then, the Helmholtz free energy of the cube cell is given by [35]

\[
w_{\text{cube}} = -T S_{\text{cube}}
\]

(8)

Submitting equation (4), (5), (6) and (7) into equation (8), we have

\[
w_{\text{cube}} = 8T k_B N \left( \frac{\lambda_c}{N^{1/3}} \beta + \ln \frac{\beta}{\sinh \beta} \right) + 2T k_B \sum_{i=1}^{3} \left( \frac{h}{\alpha^i \lambda_i^i} \right) + w_0
\]

(9)

where \( T \) is the absolute temperature and \( w = 8k_B T \ln C_{\text{chain}} + 6k_B T \ln C_{\text{con}} \). If we introduce the chain density \( n \), the strain-energy density function is provided by

\[
W = \mu N \left( \frac{\lambda_c}{N^{1/3}} \beta + \ln \frac{\beta}{\sinh \beta} \right) + 2G_{\text{con}} \sum_{i=1}^{3} \left( 1 / \lambda_i^i \right) + W_0 + \lambda \lambda_c + W_{\text{con}} + W_0
\]

(10)

where \( \mu = n k_B T \) is the shear modulus and \( G_{\text{con}} = \mu \eta / 8 \). In equation (10), \( W_t \) is the strain-energy density function of the free network considering equation (3), and \( W_{\text{con}} \) is the strain-energy density function caused by the topological constraint for the cube cell. To correlate the microscopic scale deformation to the macroscopic, the homogenization method is put into use here. In this paper, we assume that the stretch of the chain \( \lambda_c \) is non-affine whereas the principal stretch \( \lambda_i (i=1, 2, 3) \) affine. Thus, the micro-macro transformation of \( \lambda_c \) is given by [20]

\[
\lambda_c = K (\lambda_m - 1) + 1
\]

(11)

where \( K \) is the non-affine coefficient and \( \lambda_m \) is the macroscopic scale of \( \lambda_c \). For 8-chain model, \( \lambda_m \) is expressed by

\[
\lambda_m = \sqrt[3]{\sum_{i=1}^{8} \lambda_i^i / 3}
\]

(12)

When \( K = 1 \), the transformation of the chain stretch is affine. According to the theory of continuum mechanics, the principal Cauchy stress \( \sigma_i \) of an incompressible material could be calculated from the strain energy density function as [10]

\[
\sigma_i = \lambda_i \frac{\partial W}{\partial \lambda_i} - p = \lambda_i \frac{\partial W_{\text{chain}}}{\partial \lambda_i} \frac{\partial \lambda_m}{\partial \lambda_i} \frac{\partial \lambda_m}{\partial \lambda_c} + \lambda_c \frac{\partial W_{\text{chain}}}{\partial \lambda_c} \frac{\partial \lambda_m}{\partial \lambda_m} - p = \mu KN^2 \beta \frac{\lambda_i^2}{3 \lambda_m} - \frac{2G_{\text{con}}}{\alpha \lambda_m^3} - p
\]

(13)
in which \( \lambda_i \) are the principal stretches which meet the incompressibility constraint \( \lambda_1 \lambda_2 \lambda_3 = 1 \), and the pressure \( p \) is an arbitrary hydrostatic stress that should be determined by the boundary conditions. In order to determine the parameters expediently, the inverse Langevin function can be evaluated by a Pade approximant

\[
\beta = \frac{\lambda_+ - \lambda_-}{N^{1/2} - N^{-1/2}}
\]

Applying equation (14) to (13), the Cauchy stress \( \sigma_i \) is rewritten as

\[
\sigma_i = \frac{K}{\lambda_m} \frac{3N-2N^{2v-1} \lambda_i^2 - 2G_{\text{con}}}{N^{2v-2} - 3 \lambda_i^2} \lambda_i - \frac{2G_{\text{con}}}{\alpha \lambda_i^2} - p
\]

For the purpose of eliminating \( p \), the following equation is obtained

\[
\sigma_i = \sigma_j = \frac{K}{\lambda_m} \frac{3N-N^{2v-1} \lambda_i^2 - 2G_{\text{con}}}{N^{2v-2} - 3 \lambda_i^2} \lambda_i + \frac{2G_{\text{con}}}{\alpha \lambda_i^2} \left( \frac{1}{\lambda_i^2} - 1 \right)
\]

From equation (16), we can see that the new model degrades to 8-chain model when \( K=1 \), \( v=0.5 \) and \( G_{\text{con}}=0 \). This new model owns six parameters, i.e., \( \mu, K, N, v, G_{\text{con}}, \alpha \). Among them, \( \mu, K \) and \( N \) have definite physical meanings, while \( v, G_{\text{con}} \) and \( \alpha \) are empirical and applied to describing the effect of the volume and size of the chain and the topological constraint empirically, respectively. Before the identification of parameters, it is to be noted that (i) \( v \) is larger than 0.5 but smaller than 1, (ii) \( K \) varies around 1, and (iii) \( \alpha \) is usually close to 1.

### 3. Parameter identification and model validation

Equation (16) is developed for homogeneous deformations and the nominal stress-stretch relations are provided for simple tension (ST), pure shear (PS), and biaxial tension (BT). This present model is compared with 8-chain model as well as predicting the mechanical response of Treloar’s material [28].

#### 3.1 Simple tension

Let us consider a material particle at the position \( \mathbf{X} = [x_1, x_2, x_3]^T \) in the undeformed reference framework \( \mathbf{e}_i (i=1,2,3) \). After deformation, it has a new place \( \mathbf{x} = [x_1, x_2, x_3]^T \) in the deformed reference framework. Then, a pure homogeneous deformation could be described by

\[
\begin{bmatrix}
  x_1 \\
  x_2 \\
  x_3 
\end{bmatrix}
= \begin{bmatrix}
  \lambda_1 & 0 & 0 \\
  0 & \lambda_2 & 0 \\
  0 & 0 & \lambda_3 
\end{bmatrix}
\begin{bmatrix}
  x_1 \\
  x_2 \\
  x_3 
\end{bmatrix}
\]

where \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) are constant principal stretches. Then, the deformation gradient tensor \( \mathbf{F} \) is given by

\[
\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}
\]

For an incompressible material, we require that \( \text{det} \mathbf{F} = \lambda_1 \lambda_2 \lambda_3 = 1 \). In the initial state, \( \mathbf{F} = \mathbf{I} \), the unit tensor. Simple tension leads to

\[
\lambda_1 = \lambda_2 = \lambda_3 = 1 / \sqrt{\lambda}
\]

\[
\sigma = \sigma_{\text{ST}}, \sigma_2 = \sigma_3 = 0
\]

By means of introducing equation (19) and (20) into (16), we obtain the nominal stress-stretch constitutive relationship

\[
f_{\text{ST}} = \frac{K}{\lambda_m} \frac{3N-N^{2v-1} \lambda_i^2 - 2G_{\text{con}}}{N^{2v-2} - 3 \lambda_i^2} \lambda_i + \frac{2G_{\text{con}}}{\alpha \lambda_i^2} \left( \frac{1}{\lambda_i^2} - 1 \right)
\]

\[
\lambda_m = \left( \frac{\lambda^2 + 2/ \lambda}{3} \right)^{1/3}
\]

The expression of \( f_{\text{con}} \) in equation (21) was also utilized by Lopez-Manchado et al. [20] to investigate the polymer network of elastomer nanocomposites. Letting \( v=0.5, K=1, \) and \( G_{\text{con}}=0 \) in equation (21), the nominal stress expression of 8-chain model is written as

\[
f_{8\text{-chain}} = \mu_{8\text{-chain}} \left( 3N_{8\text{-chain}} - \lambda_m^2 \right) \left( \lambda - 1 / \lambda^2 \right) / \left( 3N_{8\text{-chain}} - 3 \lambda_m^2 \right)
\]
3.2 Pure shear

A pure shear of homogeneous deformation is described as follows

\[ \lambda_1 = \lambda, \lambda_2 = 1, \lambda_3 = \lambda^{-1} \] (24)

\[ \sigma_i = \sigma_{PS}, \sigma_2 = \sigma_3 = 0 \] (25)

Thus, the nominal stress associated to the stretch is

\[ f_{PS}^{fr} = f_{PS}^{fr} + f_{con}^{fr} \] (26)

\[ \lambda_n = \sqrt{\left( \lambda^2 + 1 + 1/\lambda^2 \right)/3} \] (27)

Setting \( \nu=0.5, K=1, \) and \( G_{con}=0 \) in equation (21), the nominal stress related to 8-chain model is supplied with

\[ f_{8-chain}^{fr} = 3N_{8-chain} - \mu_{8-chain} \left( \lambda - 1/\lambda^3 \right) \] (28)

3.3 Biaxial tension

A homogeneous biaxial tension is given by

\[ \lambda_1 = \lambda_2 = \lambda, \lambda_3 = \lambda^{-2} \] (29)

\[ \sigma_1 = \sigma_2 = \sigma_{PS}, \sigma_3 = 0 \] (30)

This leads to the following expression of the nominal stress as

\[ f_{BT}^{fr} = f_{BT}^{fr} + f_{con}^{fr} \] (31)

\[ \lambda_n = \sqrt{2\lambda^4 + 1 + 1/\lambda^4}/3 \] (32)

If we make \( \nu=0.5, K=1, \) and \( G_{con}=0 \) in equation (21), the nominal stress-stretch relationship of 8-chain model could be described by

\[ f_{8-chain}^{fr} = 3N_{8-chain} - \mu_{8-chain} \left( \lambda - 1/\lambda^3 \right) \] (33)

Hereto, we have got the nominal stress-stretch equations of the new model and 8-chain model. In the following subsection, we utilize the well-known standard experimental data which is published by Treloar [28] for the cases of simple tension, pure shear, and biaxial tension deformations. These results have been widely accepted as representative benchmarks of rubbery materials’ response and chosen by many authors to verify their models, such as Arruda and Boyce [23].

Figure 2. The fitted numerical values of the material parameters in 8-chain model and the new model are identified from the experimental simple tension data by Treloar: \( \mu_{8-chain}=0.255 \text{ MPa}, N_{8-chain}=26.12, \mu=0.2445 \text{ MPa}, \nu=0.502, N=27.9, G_{con}=0.04 \text{ MPa}, K=1.023. \)
Figure 3. The predicted results of 8-chain model and the new model for pure shear are compared with the experimental pure shear data by Treloar with the parameters identified from the simple tension data alone.

Figure 4. The predicted results of 8-chain model and the new model for biaxial tension are compared with the experimental biaxial tension data by Treloar with the parameters identified from the simple tension data alone.

3.4 Identification of coefficients

The present model has six model parameters and most of them have physical signification which enables to evaluate them from physical measure or bibliographic information. Nathelss, all microscopic structural effects are not expressed accurately and numerical values of the model coefficients must be fitted. We use the nonlinear least square method for the identification of the six parameters ($\mu$, $K$, $N$, $\nu$, $G_{\text{con}}$, $\alpha$). This method is implemented in the commercial package Matlab\textsuperscript{TM}. Treloar’s experimental data [28] is adopted to verify the present model. We choose the simple tension data to fit the parameters in 8-chain model and the new model. The fitted coefficients are illustrated as $\mu_{8\text{-chain}}=0.255$ MPa, $N_{8\text{-chain}}=26.12$, $\mu=0.2445$ MPa, $\nu=0.502$, $N=27.9$, $G_{\text{con}}=0.04$ MPa, $\alpha=0.8602$, and $K=1.023$. In figure 2, we compare the fitted results of 8-chain model reported by Arruda and Boyce [23] and the new model with the experimental simple tension data by Treloar [28]. It is shown that each of the two models describes the experimental data of simple tension very well. In addition, $\nu=0.502$, $K=1.023$ and $G_{\text{con}}=0.04$ MPa mean that the volume and size of the chain, the non-affine transformation of the chain stretch, and the topological network constraint for the cube cell in Treloar’s material maybe exist and should not be ignored in order to obtain an accurate network model. The new model is validated using the pure shear and biaxial tension data. The predicted results of 8-chain model and the new model for pure shear and biaxial tension are displayed in figure 3 and 4, respectively. In figure 3 and 4, we can find out that (i) the new model of equation (16) and 8-chain model both are in well agreement with the experimental data for the pure shear, (ii) 8-chain model underestimates the biaxial tension data which has been discussed in the original paper by Arruda and Boyce [23]. Compared with 8-chain model, the new model provides a better prediction for biaxial tension as well as simple tension and pure shear. The effects of the volume and size of the polymer chain, the non-affine transformation of the chain stretch, and the topological network constraint for the
cube cell have improved the predictions of the new model, especially for the biaxial tension. When the volume and size of the polymer chain are considered, the initial end points distance $r_0$ is larger than $\sqrt[N]{N}$. The maximum of extensibility of molecular chains is not the same as the one in ideal free networks. The molecular chains reach their extension limit earlier in uniaxial deformation, which was also found out by Bechir, Chevalier, and Idjeri [1].

4. Conclusion

Combining the network model concepts proposed by Arruda and Boyce [23], Lopez-Manchado [24], Doi and Edwards [28] et al., we proposed a new network model to describe the multiaxial elastic response of rubbery materials. In the present model, the volume and size of the polymer chain, the non-affine transformation of the chain stretch, and the topological network constraint in the polymer network are taken into account. The new model uses six parameters ($\mu$, $K$, $N$, $v$, $G_{\text{con}}$, $\alpha$) that are determined from the only experimental data of simple tension loading. We demonstrate this new model by the experimental data from Treloar [28]. The same model parameters identified from simple tension are applied to predict the response of pure shear and biaxial tension correctly. These parameters are shown to be independent on the state of deformation. The results show that the present model provides an excellent fit to the nominal stress-stretch response of rubbery materials. This new model has the ability to model the elasticity of rubbery materials and could be adapted to engineering applications. The strong predictive abilities with simple computation make it suitable for engineering applications.

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