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A sigmoid function to characterise the mechanical behaviour of rubber materials

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ABSTRACT

A new phenomenological hybrid chain network model for polymer based materials has been developed. At the microscopic scale, the "beta function for growth rate", as introduced by Yin et al. [30,29] for describing growth, has been taken to describe the sigmoidal shape of the stiffness rise to the breaking point at high strains of a single chain molecule. In this paper the model is redefined and used to model an entropy-elastic (rubber elastic) behaviour in relatively small strain regimes. In order to capture large strain regimes while maintaining the overall sigmoidal shape of the stiffness rise the model is extended by an energy-elastic term. On the macroscopic scale, the network of polymer chains are represented by isotropic three-chain and eight-chain network models that are linked together by a weighting function for describing the transition between them.

The proposed model has been calibrated for different polymers simultaneously in the extensional range. It successfully predicted the experimental findings from literature, Treloar [21,22], other material data for Spider silk reported by Denny [4] and data of natural rubber compounds of different hardnesses reported by Koshal [12].

1. Introduction

The realistic description of rubberlike materials still represents a challenge. Many of these materials are presumed to exhibit purely J-shaped stress–strain behaviour, which results from a progressive recruitment and alignment of polymer chains stress. Measurements, however, show that stress–strain curves and corresponding stiffness rise of single chains and multi-chain polymer networks are sigmoidal in shape (S-shaped). As the load rises, a chain with an initial stiffness unfolds and approaches first its yield point before strain hardening to a maximum stiffness. Further increase in load will take it to its breaking point that is linked to a gradual reduction of its stiffness. Examples of materials with a sigmoidal stress–strain curve are textile materials such as synthetic felt composed of entangled polyester filaments [10] or natural fibres such as spider silk and other polyamide fibres [11].

The outline of the paper is the following. A review of some basic material models for polymers is presented in Section 2. Two growth models are then presented that will be used for the derivation of the new model presented in Section 3. The results of the model evaluations are presented in Section 4 and conclusions are given in Section 5.

2. Material models

Subsection 2.1 starts with the description of a general model that can be used to describe nonlinear mechanical behaviour of incompressible isotropic elastic materials. This is followed by a discussion of the characteristics of the classical wormlike chain model in the context of the micromechanics of single polymer chains and its implementation in network models. Details of the development of a new wormlike chain model that produces asymmetrical uni-modal curves and the implementation of this model into network models are presented. These network models will finally be combined into a hybrid model. Two growth models are then presented that will be used for the derivation of the new polymer model presented in Section 3.

2.1. Modelling incompressible isotropic elastic materials

An incompressible and isotropic material in the virgin state can be described with the nonlinear material law from Refs. [19,20].

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$$\sigma + p\mathbf{I} = \varphi_1\mathbf{B} + \varphi_2\mathbf{B}^2 \tag{1}$$

where $\boldsymbol{\sigma}$ is the Cauchy stress tensor, p is an undetermined pressure, $\mathbf{I}$ is the identity tensor, and $\mathbf{B}$ stands for the left Cauchy–Green deformation tensor. The scalar material response functions φ_1 and φ_2

$$\varphi_1 = 2\frac{\partial\Psi}{\partial\Im_1} \quad \text{and} \quad \varphi_2 = 4\frac{\partial\Psi}{\partial\Im_2} \tag{2}$$

can be determined by an *Helmholtz free-energy density function* per unit reference volume Ψ. They have to satisfy the integrability condition

$$\frac{\partial\varphi_1}{\partial\Im_2} = \frac{1}{2}\frac{\partial\varphi_2}{\partial\Im_1} \tag{3}$$

that is always satisfied, if φ_1 is only a function of $\Im_1$, and if φ_2 is only a function of $\Im_2$. The alternative invariants are defined as the trace of the left Cauchy–Green deformation tensor $\mathbf{B} = \mathbf{F}\mathbf{F}^{\mathrm{T}}$ with $\mathbf{F}$ being the deformation gradient

$$\Im_1 = I_1 = \mathrm{tr}\mathbf{B} \quad \text{and} \quad \Im_2 = I_1^2 - 2I_2 = \mathrm{tr}\mathbf{B}^2 \tag{4}$$

and depend themselves on the first and second principal stretch invariants I_1 and I_2. Due to the incompressibility condition the third principal stretch invariant is $I_3 = \det\mathbf{B} = 1$ and can therefore be neglected. Furthermore, the strain energy density Ψ has been assumed to be a separable function in terms of the invariants $\Im_1$ and $\Im_2$

$$\Psi = \underbrace{\Psi_1(\Im_1)}_{\text{entropy–elastic term}} + \underbrace{\Psi_2(\Im_2)}_{\text{energy–elastic term}} \tag{5}$$

The first term can be associated with a very soft material behaviour (entropy-elastic term) and the second term with the stiffening of the material that occurs at higher deformations (energy-elastic term). In order to describe different deformation modes, new invariants $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$ have been introduced that are the solutions of the cubic equations

$$\tilde{\lambda}_1^3 - \Im_1\tilde{\lambda}_1 + 2 = 0; \quad \tilde{\lambda}_2^6 - \Im_2\tilde{\lambda}_2^2 + 2 = 0 \tag{6}$$

derived from the from the invariants $\Im_1$ and $\Im_2$ in the uniaxial deformation. The relations for $\tilde{\lambda}_1 = \tilde{\lambda}_1(\Im_1)$ and $\tilde{\lambda}_2 = \tilde{\lambda}_2(\Im_2)$ always have a real value and can be expressed in the tensile range with Cardano's formula. For the simple tension $\tilde{\lambda}_1 = \tilde{\lambda}_2 = \lambda$.

$$\begin{aligned}\tilde{\lambda}_1 &= 2\sqrt{\frac{\Im_1}{3}}\cos\left(\frac{1}{3}\left(\pi - \arccos\left(\left(\frac{3}{\Im_1}\right)^{\frac{3}{2}}\right)\right)\right)\\ \tilde{\lambda}_2 &= \sqrt{2\sqrt{\frac{\Im_2}{3}}\cos\left(\frac{1}{3}\left(\pi - \arccos\left(\left(\frac{3}{\Im_2}\right)^{\frac{3}{2}}\right)\right)\right)}\end{aligned} \tag{7}$$

This model has been originally developed for predicting the mechanical behaviour of materials for tensile experiments. It can easily be extended to incorporate the complete range of a deformation process that is needed in order to characterize both tensile and compressive behaviour of materials made from polymers. Next section will describe the micromechanics of a single polymer chain. This is important for understanding the terminology and the implementations of chain models into network environments in order to describe multi-axial stress states.

2.2. Micromechanics of a single polymer chain

A single polymer chain with an actual end-to-end length r_{ch} is assumed to consist of N independently oriented links of equal segment size ℓ, the so-called *Kuhn statistical segment length*, so that $L = N\ell$. Therein, L is the *contour length* that is the maximum possible end-to-end distance of a fully extended chain, by which $0 < r_{ch} \leq L$. When N is large enough, the average root-mean-square end-to-end length for an undeformed chain is $r_0 = \sqrt{N}\ell = \sqrt{L\ell}$ [14–16]. The deformation of the chain can be described either by the *chain stretch* $\lambda_{ch} = r_{ch}/r_0$ or the *relative chain stretch* $\lambda_{r_{ch}} = r_{ch}/L = \lambda_{ch}/\sqrt{N}$, with $\lambda_{r_{ch}} \in [N^{-1/2},\ 1]$.

2.2.1. The wormlike chain model

The Kratky–Porod or discrete wormlike chain (WLC) model [13] treats DNA as a semi-flexible polymer chain that is smoothly curved due to thermal fluctuations. Since a direct analytical solution for the force-extension relationship is not available, Marko and Siggia [3,18] introduced an approximation formula

$$F_{ch} = \frac{k_B\mathscr{T}}{A_p}\left(\frac{r_{ch}}{L} + \frac{1}{4\left(1 - \frac{r_{ch}}{L}\right)^2} - \frac{1}{4}\right) \tag{8}$$

where $F_c = k_B\mathscr{T}/A_p$ is the *characteristic force*, $k_B = 1.381\times10^{-23}$(J/K) Boltzmann's constant, $\mathscr{T}$ the absolute temperature and A_p the *bending persistence length*, with $\ell \leq A_p \leq L$, this is why the WLC model is also called the persistent chain model. For the WLC, the end-to-end mean-squared length is $r_0 = \sqrt{2AL}$, and thus $\ell = 2A_p$ [7,18]. The disadvantage of the classical WLC model is that as r_{ch} approaches L, the axial force tends to grow to infinity.

The WLC model is a one-dimensional model based on statistical mechanics able to describe the entropy-elastic behaviour of biomaterials. Unfortunately, this model produces purely J-shaped stress–strain curves that do not correspond with experimental results. The stress–strain curves of single chains are sigmoidal in shape.

2.3. Network models

The following sub-sections give a brief overview of widely used entropy elastic network models, namely, the three-chain model and the eight-chain model in which the WLC is used as a building block. They have been proposed in the literature for modelling rubber elasticity. These models will be used to develop the sigmoidal function model that is proposed in the next section.

2.3.1. The three-chain network model

The three-chain model, originally proposed in Refs. [9,24] is a separable and symmetric function assuming a network that can be replaced by three independent sets of non-Gaussian chains, which are according to Fig. 1 (a) parallel to the three principal axes of deformation x, y and z. This model only captures the principle strain directions. In Refs. [5,6] a three-chain approximation has been introduced for the strain energy ψ of a Gaussian chain. They proposed to express ψ as a separable function in terms of principle stretches λ_i $(i = 1, 2, 3)$

$$\psi = \sum_{i=1}^{3}\psi_i = \psi(\lambda_1) + \psi(\lambda_2) + \psi(\lambda_3). \tag{9}$$

The separable form of Eq. (9) illustrates the close relationship between the three-chain approximation and the hypothesis by Valanis and Landel [23]. However, the three-chain model is not capable of picking up strain hardening effects. In order to increase