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A micromechanically motivated diffusion-based transient network model and its incorporation into finite rubber viscoelasticity

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ABSTRACT

This paper presents the development of a physical-based constitutive model for the representation of viscous effects in rubber-like materials. The proposed model originates from micromechanically motivated diffusion processes of the highly mobile polymer chains described within the formalism of Brownian motion. Following the basic assumption of accounting for the elastic and the viscous effects in rubber viscoelasticity by their representation through a separate elastic ground network and several viscous subnetworks, respectively, the kinetic theory of rubber elasticity is followed and extended to represent also the viscous contribution in this work. It is assumed that the stretch probability of certain chain segments within an individual viscous subnetwork evolves based on the movement of the chain endpoints described by the Smoluchowski equation extended in this work from non-interacting point particles in a viscous surrounding to flexible polymer chains. An equivalent tensorial representation for this evolution is chosen which allows for the closed form solution of the macroscopic free energy and the macroscopic viscous overstress based on a homogenization over the probability space of the introduced micro-objects. The resulting model of the viscous subnetwork is subsequently combined with the non-affine micro-sphere model and applied in homogeneous and non-homogeneous tests. Finally, the model capacity is outlined based on a comparison with in the literature available experimental data sets.

1. Introduction

Polymers are characterized by remarkable properties making them qualified for applications in all areas of engineering. They can appear in liquid or amorphous solid form, behave ductile in the case of glassy polymers or rubber-like for elastomers. The latter, to be considered in this work, can in particular be characterized by the large deformations they can sustain as well as the rate and history dependence of the resulting stresses in the material. This response is attributed to their peculiar microstructure including a network of highly mobile and flexible polymer chains formed by their three-dimensional cross-linking. From a constitutive modeling point of view the challenge lies in the development of physical-based models to depict this behavior. In that regard one distinguishes *static network theories* for the modeling of elastic effects and *transient network theories* for the modeling of time-dependent effects in rubber-like materials. A brief review of those is provided in Sections 1.1 and 1.2, respectively, before in Section 1.3 the scope of the current work is discussed which lies within the development of a new transient network theory for rubber-like materials. Its incorporation into finite

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viscoelastic constitutive models, as well as the resulting implementation and application to realistic experiments and its qualitative comparison with existing experimental data sets are the main contributions of this work.

1.1. Static network theories

Early experimental results in Treloar (1944) indicate the characteristic *S*-shaped load versus stretch curve for the elastic nature of rubber materials in uniaxial tensile tests in the form of an initially decreasing stiffness of the material and a rapid increase thereafter. The reported deformation range, up to an eightfold extension of the material with an almost full recovery of its initial shape upon unloading, outlines one of their main mechanical characteristics and reason for their applicability in various areas of engineering and material science. Further experimental results are given in Rivlin and Saunders (1951), James et al. (1975), and James and Green (1975), among others. The latter introduced a graphical presentation of the results which allowed for a more convenient fit of the material data of constitutive models in terms of their strain energy function. Inspired by the form of such a function for an isotropic, incompressible, hyperelastic material various strain-invariant based phenomenological expressions are proposed to capture the characteristic response of rubber (Mooney, 1940; Rivlin, 1948; Ogden, 1972; Yeoh, 1993). These empirical theories lack a direct physical justification of the parameters appearing in the proposed expressions of the strain energy function.

On the contrary, the kinetic theory of elasticity (Meyer et al., 1932) accounts for the underlying physics by assuming that the material consists of a large number of polymer chains which do form a static network by being permanently cross-linked at junction points. A chain segment, considered as part of a polymer molecule approximated as an idealized chain of freely rotating links, between two such junction points possesses a large number of possible conformations in terms of translational and rotational degrees of freedom which are driven by the influence of the thermal motion of the chain endpoints. Since the angles between adjacent bonds are considered to be random with equally distributed probability, the bond orientations do not correlate resulting in a Gaussian distribution of the end-to-end vector of an unrestrained chain segment. This probability can then be linked through the Boltzmann relation to the entropy and the free energy of a single chain (Kuhn, 1934, 1936; Guth and Mark, 1934). This, as *Gaussian statistics* denoted background for the single entropic chain segments, is used for the derivation of the *Gaussian network models* (Wall, 1943; Flory and Rehner Jr., 1943; James and Guth, 1943; Troloar, 1943a,b; Flory, 1944) consisting of a highly cross-linked network of such Gaussian chains providing a link of the micromechanical polymer model to macroscopic scales. The agreement of those models with the experimental results are acceptable up to stretch regions where the individual chain segments are far from being fully extended.

Such limitation is overcome in the *non-Gaussian statistics* of Kuhn and Grün (1942) and later by Flory (1953) based on their account of the finiteness of the chain extensibility where the modified probability density function of a chain with a certain length and its resulting entropy is expressed in closed form in terms of the inverse Langevin function. An account for such a finite extensibility of the individual chain segments in network models results in so called *non-Gaussian network models*. Examples within that frameworks are the *three-chain model* considered in James and Guth (1943) and Wang and Guth (1952), the *four-chain model* by Treloar (1946) as an extension of the model in Flory and Rehner Jr. (1943), or the more recently developed *eight-chain model* by Arruda and Boyce (1993a) which successfully is able to represent the response of these materials in uniaxial extension and compression, biaxial extension, plane strain compression, and pure shear problems. A *full network theory* is proposed in Treloar (1954) and Treloar and Riding (1979) for uniaxial extension and biaxial tensile deformation, respectively, and extended in Wu and van der Giessen (1993) to fully three-dimensional deformation processes. It is noted that, whereas the three-chain model and the full network theory result in *affine* network formulations, meaning that they preserve the affinity of the network deformation with regard to the macroscopically applied deformation, the remaining *non-affine* network models do come along without such restriction. Chains oriented in the direction of loading display a higher resistance to the stretch when approaching their limiting value compared to other chains in the network. Hence, the internal structure of the polymer becomes heterogeneous which leads to a deviation of chain stretches when compared to those resulting from the macrostrain. Only the non-affine models allow for such adjustment of the polymer microstructure.

Even though the underlying mechanisms of the individual chain segments in these theories account for their finite extensibility, the possible chain conformations in between two junction points is not influenced by the surrounding polymer chain segments. This is on the contrary done within *constrained junction theories* (Ronca and Allegra, 1975; Flory et al., 1976; Flory, 1977; Erman and Flory, 1978; Flory and Erman, 1982) and within *constrained segment theories* (Deam and Edwards, 1976; Heinrich and Straube, 1983, 1984; Edwards and Vilgis, 1988; Heinrich and Kaliske, 1997; Kaliske and Heinrich, 1999). In Miehe et al. (2004) a micromechanically motivated network model, including a micro-tube constraint based on Edwards (1967) to account for the surrounding polymer chains, together with a non-affine micro-to-macro transition based on a homogenization procedure defined on a micro-sphere of space orientations is developed. The resulting framework, called the *non-affine micro-sphere model*, yields an excellent performance in homogeneous and non-homogeneous tests. Further references on the elastic behavior of rubber-like materials can be found in Treloar (1975) and the review articles by Boyce and Arruda (2000) or Marckmann and Verron (2006).

1.2. Transient network theories

Besides the elastic ground response of rubber-like materials, captured by the above outlined static network theories, their behavior is characterized by a finite viscoelastic overstress which governs rate-dependent effects such as relaxation