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A micro-continuum-mechanical material model for failure of rubber-like materials: Application to ageing-induced fracturing

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ABSTRACT

Rubbery polymers are subjected to severe environmental conditions under service. As a consequence of various ageing mechanisms, the outer surface of rubber components hardens in time and cracking occurs as a result of combined mechanical and chemical processes. Conventional phenomenological hyperelastic constitutive models do not account for material softening. Consequently, the stored energy and stresses tend to infinity as stretch increases. In this contribution, a network alteration for the ageing mechanism of rubber-like materials is introduced along with a micromolecular description of material failure. The proposed micro-continuum material model is based on a serial construction of a Langevin-type spring representing the energy storage owing to conformational changes induced by deformation, to a bond potential representing the energy stored in the polymer chain due to the interatomic displacement. For the representation of the micro–macro transition, the non-affine kinematics of the micro-sphere model is used. The Morse potential is utilized for the interatomic bond, which describes the energetic contribution to rubber-like materials and governs the failure of the polymer chain in terms of bond rupture. A novel numerical scheme for the FE implementation of the proposed model is demonstrated. The hardening phenomenon as a result of diffusion limited oxidation of rubber is explained by the principle of mass conservation which dictates simultaneous modulus hardening along with decrease in ultimate stretch observed in aged rubbery polymers.

1. Introduction

Elastomeric materials are utilized thanks to their distinct properties. Large extensibility and energy absorption associated with highly viscoelastic response make rubber an attractive material in industrial use. It owes its large extensibility to long chain molecules forming the polymer network, which makes the rubbery polymers act quite dissimilar to crystalline solids possessing regular lattice structure and to amorphous glasses. The energy storage in crystalline solids and amorphous glasses is primarily due to interatomic distortion where the configurational changes in the lattice are small and, hence, entropic contributions to the overall behaviour are neglected. On the other hand, rubbery polymers well above the glass transition temperature T_g possess no intermolecular attractions and the amount of energetic distortions of the intra-molecular bonds is commonly omitted. This notion is known as ideal or strictly entropic elasticity and was based on the stress-temperature experiments of Meyer and Ferri (1935) by which they concluded that internal energy is solely a function of absolute temperature. Although the idealization of rubber elasticity and models based on Gaussian and

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non-Gaussian statistical mechanics proved successful results, it was later shown by Chadwick and Creasy (1984) that this idealization is too restrictive and ideally entropic elasticity excludes thermal expansion about the reference state. Alternatively, they have proposed the so-called *modified entropic elasticity* concept by which the internal energy is split into $e = e_1(\theta) + e_2(J)$ thermal and distortional parts where J denotes the volume change. The existence of energetic contributions to the deformation is demonstrated by Shen and Blatz (1968) and Shen and Croucher (1975). They have found out that energy contribution f_e to the uniaxial load f is around 20% under uniaxial tension (UT).

Another drawback of entropic elasticity is that material behaviour cannot be described beyond the locking stretch $\lambda_{lock} = \sqrt{N}$. Let us consider a single chain consisting of N monomer segments each having a length l. According to the Langevin statistics proposed by Kuhn and Grün (1942), the total length is bounded by $L_{max} = Nl$. The elastic force carried by the polymer chain is then attributed to the reduction of entropy upon deformation as a result of molecular alignment. In the limiting case, as the stretch approaches the locking stretch $\lambda \to \lambda_{lock}$, the force and the free energy tend to infinity. In reality, as the stretch approaches λ_{lock}, the force in the chain attains a maximum as soon as the stored energy overcomes the energy barrier of the bond and chain breaks either at cross-link point or elsewhere throughout chain. At this stage of non-Gaussian region, it is expected that the energetic contribution to the overall behaviour cannot be neglected anymore.

Gao and Klein (1998) proposed the *virtual internal bond* (*VIB*) model which directly integrates the atomic bond potential into the constitutive model for amorphous brittle materials. The continuum-atomistic link is provided by the Cauchy–Born rule and the macroscopic stresses and moduli are obtained by integrating the partial derivatives of the energy density function over a unit sphere. Volokh (2007a, b) introduced the concept of softening hyperelasticity as an alternative to the VIB model at larger length scales. Energy storage tends to infinity in traditional hyperelastic laws. The model of Volokh incorporates a saturation type exponential free energy $\Psi = \Phi\{1 - \exp(-W/\Phi)\}$ bounded by the failure energy Φ. W denotes any conventional phenomenological hyperelastic free energy function. Then, the additional parameter Φ acts as an energy limiter to the hyperelastic law enforcing material softening.

Although, the softening hyperelasticity and the VIB model, both approach the fracture problem similar to the strength of material approach to fracture for which the material is characterized by yield or fracture stress, it proves helpful as the structure is modelled with defects or inhomogeneities which act as stress raisers. It was later shown by Gao and Ji (2003) that the Griffith approach to fracture is not applicable since the fracture strength is not bounded by the theoretical strength of the solid, whereas the VIB model has proved that the stress in an infinite nanostrip approaches the theoretical strength as the strip height approaches a critical threshold and remains constant beyond this value.

Cavity growth and void coalescence plays a crucial role at the onset of crack initiation and growth at crack tip (see Le Cam et al., 2004). For the modelling of low-density porous hyperelastic materials and cavitation, compressible constitutive models are utilized. Gent and Lindley (1958) showed that, under highly triaxial stress state, the load displacement diagram of flat cylindrical rubber sheets exhibit a break point corresponding to the creation of cavities. Three broad categories of material models can be distinguished for porous hyperelastic materials and cavitation. In the first group, a separable strain energy density function is introduced by a hyperelastic incompressible part accompanied by a volumetric term. For incompressible behaviour, the second term is generally utilized as a penalty term. For compressible hyperelastic materials with fixed porosities, various phenomenological models were proposed (see Blatz and Ko, 1962; Ogden, 1972, 1976; among others). The second group of models deals with a macroscopic continuum consisting of a void and an incompressible matrix and dates back to Ball (1982). In his work, he described nucleation of cavity in a finite elastic spherical body under radially distributed tension. He found that at a critical stress level, which is not a priori given material parameter, the solution bifurcates, corresponding to cavity nucleation. Hence, cavity formation is shown to be an intrinsic material instability. Attempts to extend this approach to general three-dimensional framework have been made by Horgan and Abeyaratne (1986), Hou and Abeyaratne (1992). Hou and Abeyaratne (1992) proposed a solution for an arbitrary triaxial stress state of a sphere containing central cavity. They prescribed a kinematically admissible deformation field. The strain field proposed was utilized by Danielsson et al. (2004) and applied for the analytical solution for compressible Neo-Hookean materials. Based on the kinematics of Hou and Abeyaratne, Li et al. (2007a, b) have proposed a new model for cavitation and cavity growth and proposed a cavity growth criterion in the context of damage mechanics. Third group of models is based on modelling incompressible matrix with a given void fraction in terms of homogenization schemes. For a more extensive review on the homogenization based approaches, we refer to Castaneda (2007a, b) and references therein.

1.1. A new modified entropic elasticity model for rubber-like materials

A controversy remains between rubber elasticity models based on the statistical mechanics approach and fracture mechanical investigations on rubber. Fracture mechanical investigations on rubber date back to the successive contributions of Rivlin and Thomas (1953), Thomas (1955, 1958), Greensmith and Thomas (1955), and Greensmith (1956). In this set of contributions, the Griffith criterion was proved to be valid for rubber and the testing methodology which is still under use in rubber industry was firstly introduced. Griffith criteria state that *a cut of length c will spread by an amount dc at a certain deformation if and only if the energy stored W elastically in the test piece of thickness t is thereby decreased by an amount dW greater than the increase of surface energy due to formation of new surfaces*,

$$-\frac{\partial W}{\partial A} = T_c \quad \text{where } dA = tdc. \tag{1}$$