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Two-scale model for the effect of physical aging in elastomers filled with hard nanoparticles

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ABSTRACT

A two-scale model is developed, and solved numerically, to describe the mechanical behavior of elastomers filled with hard nanoparticles. Of particular interest is the slow recovery of the elastic modulus after large-amplitude oscillatory deformation. To account for this effect, the physical aging of the glassy bridges between the filler particles is captured with two thermal degrees of freedom for the matrix material, namely a kinetic and a configurational one. Formulating the two-scale model enriched with aging in a nonequilibrium thermodynamics context, first results in a constitutive relation for the Cauchy stress tensor. Second, the dynamics of physical aging is described, which eventually results in the slow recovery of the elastic modulus with waiting time. The proposed model is investigated numerically under large amplitude oscillatory shear deformation. Of particular interest in this respect is the coupling of the micro-scale dynamics with the physical aging on the macroscopic scale. This coupling is examined in detail, both in an approximate way using a Gaussian approximation, as well as numerically, under specific conditions. It turns out that the CONNFFESSIT approach (Laso and Öttinger 1993 [46]) can not be employed for the numerical solution of the model under arbitrary loading conditions because of the novel structure of the two-level coupling term. While a procedure for solving the model numerically for the case of strong applied deformation is presented in this paper, other solution methodologies need to be sought for the cases of weak and no applied deformation.

1. Introduction

Composite materials, being widely used in different practical applications due to their remarkable properties, are of great interest to researchers concerned with fundamental modeling. This is because the behavior of entire system is the result of an intricate combination and coupling of dynamics on different length- as well as time-scales. The particular interest of this paper is the analytical modeling and numerical simulation of the mechanical behavior of composites that consist of an elastomer matrix filled with hard particles of nanometers size.

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Filling an elastomer with nanoparticles adds significant rate-dependence to its mechanical behavior, and thus results in increased dissipation, as compared to the unfilled elastomer [1]. A possible explanation, that is used in this paper as a basis for the model formulation, for these significant changes in the material behavior is the following. If the matrix material adheres well to the filler particle surface, the mobility in the matrix is slowed down close to these surfaces. More specifically, the mobility in a matrix material element is decreased gradually the closer this element is located to the filler particle surface. Effectively, this can be captured by an increase in the local glass transition temperature of matrix material as the distance to the filler particle surface decreases. If, in close enough vicinity to the particle surface, the local glass transition temperature is higher than the actual (laboratory) temperature, an effective glassy layer is present around the filler particle. At high enough volume fraction of filler particles and in a certain temperature regime, these glassy layers may then overlap, thereby creating so-called glassy bridges between the filler particles. Therefore, such composites consist essentially of a rubbery-state elastomer matrix that is permeated by a glassy network with filler particles, leading in mechanical reinforcements of up to about 100 times. The existence of glassy layers around filler particles is supported by the literature, e.g. by NMR studies [2] or more recently by a mechanical analysis of model systems [3,4]. For more details on this issue, the reader is referred to, e.g., [5] and references therein.

Once the glassy bridges are formed between the particles, the interparticle dynamics can be analyzed in terms of the knowledge about the thermo-mechanics of bulk polymer glasses [6,7]. Specific features of bulk polymer glasses that are relevant also for the glassy-bridge induced effects are the viscoplastic yielding behavior and strain softening, as well as the effect of physical aging on the mechanical behavior. For example, when making use of bulk yielding kinetics in the nanocomposite context, one can rationalize the highly nonlinear rate-dependent mechanical response of such nanocomposites, including the prominent Payne effect [5,8–10].

In an earlier publication, a thermodynamically-inspired concurrent two-scale model has been developed to describe the mechanical behavior of elastomers filled with hard nanoparticles [5]. While that model takes the yielding kinetics of the glassy bridges into account, the physical aging of the glassy bridges is neglected. However, it is assumed that the physical aging of the glassy bridges may be related to the so-called Mullins effect in cyclic deformation [11–13]. This effect consists in a softening due to mechanical deformation, however, that softening is only present at strains smaller than the maximal previously applied strain. If the material is loaded beyond the maximal previously applied strain, initially no softening is present at these previously unvisited strains, while after repeated loading to these higher strains there is again softening. It has been found that the softening is not permanent, but that e.g. the permanent set or the complete stress-strain response can recover (partly) at a rate that is temperature-dependent, which is also sometimes called 'healing' [11–14]. Modeling the Mullins effect in terms of an extended two-scale model is beyond the scope of this paper. However, in order to embark towards this long-term goal, this paper aims at studying the effect of physical aging of the interparticle matrix material on the mechanical response of the entire composite. Specifically, the deformation protocol of [8,9] is employed, that consists of a specific combination of mechanical rejuvenation (softening) and physical aging. Since the proper description of physical aging is rather involved and a topic of current research activities in the literature, the modeling effort for the case of nanocomposites can be split into two steps. First, the physical aging and mechanical rejuvenation can be studied from a thermodynamic perspective for bulk glassy polymers, e.g. as done in [15–18]. Second, the lessons learned from that latter work can be built into the two-scale nanocomposite model developed in [5], which is the topic of this paper.

The manuscript is organized as follows. In Sec. 2, the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) framework of nonequilibrium thermodynamics is introduced, followed by its application to the model developed for nanoparticle-filled elastomers in Sec. 3. The general concurrent two-scale model is summarized in Sec. 3.5. In Sec. 4, this model is made material-specific, whereafter it is analyzed numerically for illustration purposes by means of CONNFFESSIT-type simulations in Sec. 5. Finally, conclusions are drawn in Sec. 6.

Before we start, let us comment about the notation used throughout the entire paper. Greek indices α, β, γ, ... are used for the Cartesian components of vectors and tensors, and Einstein's summation convention is used for indices that occur twice. Furthermore, with respect to operators, subscripts α and (α,β) imply contraction with any vector A_α and any tensor $A_{\alpha\beta}$ multiplied from the left, respectively, while subscripts γ and (γ,ε) imply contraction with the vector A_γ and tensor $A_{\gamma\varepsilon}$ multiplied from the right, respectively. An analogous notation is used for continuous indices. Specifically, let $\boldsymbol{\xi}$ denote the position in the space of (micro-)states. If a generalized field depends on $\boldsymbol{\xi}$, this implies continuous contraction (i.e. integration) over $\boldsymbol{\xi}$ with what is multiplied from the left, while a dependence on $\boldsymbol{\xi}'$ implies continuous contraction (i.e. integration) over $\boldsymbol{\xi}'$ with what is multiplied from the right. Finally, it is mentioned that boundary terms are neglected entirely, because the main goal of this paper is the modeling of bulk material behavior. In contrast, the case where boundaries and interaction with the surrounding are of interest has been studied, e.g. in [19,20].

2. GENERIC framework

The framework used in this paper to formulate the dynamics of the system is the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [21–23], which has also been used in our preceding work [5,17,18]. It is a formal thermodynamic procedure to set up evolution equations for a set of variables $\boldsymbol{\mathcal{X}}$. In this section, we recapitulate the explanation of the methodology given in [17]. Specifically, in the GENERIC framework, the reversible ("rev") and irreversible ("irr") contributions are clearly distinguished,

$$\partial_t \boldsymbol{\mathcal{X}} = \partial_t \boldsymbol{\mathcal{X}}|_{\text{rev}} + \partial_t \boldsymbol{\mathcal{X}}|_{\text{irr}} , \tag{1}$$