A thermodynamical framework for the thermo-chemo-mechanical couplings in soft materials at finite strain

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ABSTRACT

This paper focuses on the modeling of thermo-chemo-mechanical behaviors of soft materials (polymer, rubber, etc.) at large strains within a rigorous thermodynamical framework. We consider thermo-viscoelastic materials involving chemical reactions that are described by a kinetic approach. Preliminary numerical tests are considered to prove the capability of this framework to take into account strong thermo-chemo-mechanical couplings.

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1. Introduction

The behavior of soft materials (polymers, rubbers, etc.) is complex due to their micro-structures but also due to the multiphysics phenomena that can occur in these materials. For instance the numerical simulation of material curing (vulcanization/reticulation) implies to take into account of thermo-chemo-mechanical couplings and therefore requires specific coupled behavior models. For the simulation of industrial parts in operating conditions, it can also be useful to develop thermo-chemo-mechanical models to simulate some process, for instance to predict the aging of industrial parts undergoing severe operating conditions (in aeronautics or spatial applications). In this kind of applications, thermal and chemical aging can be coupled with mechanical damage phenomena. Material processing and aging may involve completely different phenomena and therefore completely different models but require a rigorous thermodynamical framework.

The thermodynamics of irreversible processes is the main basic tool to build behavior models. The pioneer work of Prigogine and co-authors is fundamental as it interprets and models chemical reactions in the context of irreversible processes (see for instance Prigogine, 1968). Prigogine considered that a thermodynamical system can be described by classical state variables (temperature, volume, etc.) and by additional ones for reactive systems. Thus, the thermodynamical energy potential (Gibbs or Helmholtz free energy) is dependent on these new thermodynamic variables. Following this framework it is possible to define thermodynamic fluxes and forces related to chemistry. Thermodynamic chemical forces are defined from the first variations of the chemical free energy potential with respect to chemical internal variables. Prigogine and coworkers, therefore proposed a general definition of chemical affinities (chemical thermodynamic forces) which can be found in the earlier work of De Donder (1928). The generalization of these fundamental concepts to continuum mechanics can be done straightforwardly by considering the concept of local state and introducing internal variables (see Germain et al., 1983 and reference therein).

The evolution equations for chemistry and mechanical irreversible processes can be established from the definition of a thermodynamic potential of energy or eventually from a pseudo potential of dissipation by applying either the Onsager reciprocity concept (see Onsager, 1931) or using the convex framework of generalized standard materials (see Halphen and Nguyen, 1975). The concept of local states and internal variables has been used by many authors in the literature in the context of soft materials inside which chemical reactions occur. Gigliotti and Grandidier (2010) and Gigliotti et al. (2011) proposed a chemo-mechanical coupled model in the context of elastic behavior involving thermo-oxidation reactions in a polymer matrix. They also consider the diffusion of species in the material to predict aging. Lion and Höfer (2007) and Mahnken (2013) proposed specific material models for the thermo-chemo-mechanical curing models for polymers. These thermo-viscoelastic models take into account mechanical, thermal and chemical deformations (dilatation and shrinkage). The chemistry is phenomenologically described by a kinetic approach. André and Wriggers (2005) proposed a small strains thermo-chemo-mechanical model to simulate the vulcanization of rubber materials. Thermomechanical behavior is assumed to be elasto-visco-plastic and two phenomenological chemical reactions are considered to describe the vulcanization process. In the work of Kannan and Rajagopal (2011), the authors developed a finite strains framework to model the vulcanization process of rubber assuming a viscoelastic behavior involving chemical reactions. Chester and Anand (2011) and Loeffel and Anand (2011) also achieved very interesting work for different applications in which complex mechanical behavior models at finite strains are coupled with thermo-chemical phenomena that involve diffusion processes.

In this paper, we propose a rigorous and generic thermodynamical framework based on the thermodynamics of irreversible processes and the local state hypothesis that can be used to develop thermo-chemo-mechanical models. As already proposed by some authors, we assume that the volume variation is decomposed into a thermal part (dilation), a chemical part (shrinkage) and a mechanical part (compressibility). Thus, the hydrostatic pressure is coupled to the chemical, mechanical and thermal states. This decomposition also implies that the heat capacity and the chemical evolution depend on pressure and volume variations. A kinetic (phenomenological) description of the chemical reactions is adopted. The thermodynamic chemical force is directly linked to the mechanical state, because the mechanical parameters and the volume variation depend on the chemical state. The hydrostatic pressure and the deviatoric strain can have a positive or a negative influence on the chemical evolution. The main originality of this paper lies in two points. First, we propose a new form of chemical potential of energy. This potential takes into account an initiation process depending on temperature. Below a given temperature, no reaction occurs and the energy is stored as heat. This potential is defined to allow a clear definition and admissible form of the heat capacity. Second, the chemical evolution that is associated to this potential naturally takes into account the influence of the mechanical state. We propose a new evolution law

for chemical processes that is directly inspired from visco-plasticity modeling: the chemical evolution rate is assumed to be zero whenever the thermodynamical force becomes negative (no chemical reversion is allowed) and a chemical viscosity parameter is introduced. This parameter enables a control of mechanical influence on chemical evolution.

The paper is organized as follows: in Section 2, the thermodynamical framework is discussed, fundamental hypothesis and conservation equations are presented. In Section 4, this thermodynamical framework is applied to formulate a phenomenological thermo-chemo-visco-elastic model. In Section 5, some simple numerical examples are provided. They illustrate both the genericity of the proposed model and the consequence of some fundamental hypothesis on the model response for simple and homogeneous tests.

2. Thermodynamical framework

2.1. Definition of a chemical internal variable

In this work, we consider a solid body subjected to thermo-mechanical loadings. This body is viewed as a closed[1] thermodynamical continuum system that exchanges no mass outside the system. Furthermore, as classically assumed, neither creation nor destruction of mass is allowed. Let us assume that the initial configuration (at $t = 0$) is defined by a stress free and heat flux free state. In this configuration, the chemical species are balanced: the reaction rates are zero in this state. Based on the classical continuum mechanics, the body is considered at the initial position $\boldsymbol{X}$ and at a current position $\boldsymbol{x}$ in an Euclidean space. The material point can be viewed as an infinitesimal element of volume of density $\rho(\boldsymbol{x}, t)$ (the initial density is denoted ρ_0). The closed system hypothesis leads to:

$$\dot{\rho} + \rho \text{div}(\boldsymbol{v}) = 0 \tag{1}$$

where $\text{div}(\boldsymbol{v})$ is the Eulerian divergence of the velocity of the material point and $\dot{\rho}$ is the total time derivative of the density (so called material time derivative[2]). Assuming that this infinitesimal element of volume is a mixture of all chemical species that compose the material, one can define the current mass concentration of the ith chemical species relative to the current infinitesimal volume (of the mixture), denoted $\rho_i(\boldsymbol{x}, t)$. Assuming that no diffusion of chemical species occurs, the mass conservation can also be defined:

$$\begin{cases} \dot{\rho}_i + \rho_i \text{div}(\boldsymbol{v}) = m_i & i = 1, 2, \ldots, n \\ \sum_{i=1}^{n} m_i = 0 \end{cases} \tag{2}$$

where $m_i(\boldsymbol{x}, t)$ is the production rate of mass of the ith chemical species at point $\boldsymbol{x}$ per unit of current volume due to local reactions.[3] Given the molar mass of each

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[1] Chemical reactions in soft material often involve matter (gas) diffusion and therefore the problem should be considered as an open thermodynamical system; however we neglected this effect in this work.

[2] Derivative of quantity upon time holding initial position constant: $\dot{\rho} = (\partial \rho(\boldsymbol{x}, t)/\partial t)_{\boldsymbol{X}}$.

[3] In the case of reactive diffusive system one should take into account the mass flux φ_i (defined by unite of surface) of the ith species, such as